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UNIVERSITY OF AUCKLAND

SCHOOL OF ENGINEERING

THE MECHANICAL PROPERTIES OF
GLASSY POLY (METHYL METHACRYLATE)

A Thesis submitted as part of the requirements for the
Degree of Ph.D. (Engineering)

J. B. Meikle M.E.
April, 1970

==================================
praetera nisi erit minimum, parvissima quaque corpora constabunt ex partibus infinitis, quippe ubi dimidiae partis pars semper habebit dimidiam partem nec res praefiniet ulla. ergo rerum inter summan minimamque quid escit? nihil erit ut distet; nam quamvis funditus omnis summa sit infinita, tamen, parvissima quae sunt, ex infinitis constabunt partibus aeque. quod quoniam ratio reclamat uera negatque credere posse animum, victus fateare necesset esse ea quae nullis iam praedita partibus extent et minima constant natura.

Lucrertius Carus Titus
De Rerum Natura
Book 1, line 615

The old adage should be stood on its head:
of applied science it can reasonably be said
"If a thing is worth doing, it is worth doing
even badly....."

J. M. Ziman
the Rutherford Memorial Lecture
Royal Society of London, 1968
1. **ABSTRACT**

The mechanical properties of glassy poly (methyl methacrylate) have been examined by means of constant strain-rate tests at differing strain-rates and temperatures. Both fast-cooled and slow-cooled samples have been examined in order to determine the effect the rate of cooling has upon the mechanical properties. The $\beta$ and $\alpha'$ relaxations were revealed in the experimental results. The difference in mechanical properties of fast- and slow-cooled samples could not be satisfactorily explained by the theory of Rusch.
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4. **INTRODUCTION**

The basic aim of this work was to examine the influence of time and temperature upon the mechanical properties of a simple polymer. The polymer chosen — conventional poly (methyl methacrylate) is an amorphous polymer about which much is already known in detail. The material was also readily available. The effect of time on the mechanical properties of the polymer was investigated by performing (nominally) constant-rate-of-strain tests in uniaxial compression because this was a convenient technique for which equipment was already available. The tests were performed in the glassy temperature regime for the polymer. There were two main objectives. The first of these was to see if there was some kind of equivalence between time and temperature (with respect to their influence on mechanical properties) which could be established for the glassy polymer. As the polymer is both greatly stiffer and stronger in the glassy state than in the rubbery state, it finds its structural uses more often in this temperature regime. Such an equivalence is not well established at the moment. In particular the proposition of Rusch\(^{(13)}\) was examined. The second objective was to see in detail how some of the sub-glass transitions were reflected in the constant-strain-rate mechanical properties — this has not been a common testing technique for polymers.
The $\beta$ and $\alpha'$ transitions were found to appear in the observed data. The $\alpha'$ transition did not appear for samples which were quickly cooled. A second major area of work which was complementary to the two just mentioned followed some early work by Tobolsky and McLoughlin (131). They found that the stress-relaxation properties of poly (methyl methacrylate) depended markedly upon the rate at which the samples were cooled through the glass transition temperature. The constant strain-rate tests were therefore conducted on samples cooled both quickly and slowly. An attempt was made to relate the differences in the observed properties for the two kinds of samples to the theory of Rusch, and to the relaxation occurring. The theory of Rusch was found not to agree with the present observations.
5. MOLECULAR RELAXATIONS REFLECTED IN PROPERTIES OF POLY (METHYL METHACRYLATE)

5.1 General Nature of Poly (Methyl Methacrylate)

Poly (methyl methacrylate), first commercially produced in 1931, is the first member of a homologous series - the poly (α-alkyl methacrylates). The monomer molecule is

\[
\begin{array}{c}
\text{H} \\
\text{-C-C-} \\
\text{H} \\
\text{-O-C=O} \\
\text{CH}_3
\end{array}
\]

The polymer is the product of an addition polymerization of the vinyl type (molecular unit \( \text{CH}_2 = \text{CHX} \)). The methyl-acrylate polymers are di-substituted - a methyl group rather than a hydrogen atom is bonded to the backbone α carbon atom (\( \text{CH}_2 = \text{CCH}_3 \)). This group is normally referred to as the α-methyl group.

The group X is an α-alkyl acrylate (-COOR) in which R is an α-alkyl, in poly (methyl methacrylate) a methyl group -(CH₃).

5.2 Stereoisomers of Poly (Methyl Methacrylate)

Because the substituted carbon atoms in vinyl polymers take asymmetric positions it is possible to produce stereoisomers by controlling the polymerization (sect. 5.5b). The backbone carbon atoms (●) form a planar zig-zag and the arrangement of the X-groups (●) then determines the steric nature. There are two stereoregular arrangements (syndio- and isotactic) and the irregular arrangement (atactic). (see fig 5.1 and fig 5.2).
FIG 5.1 SYNDIOTACTIC POLY(METHYL METHACRYLATE)

FIG 5.2 - TACTICITY
Groups added to the polymer may take d or l configurations with respect to the molecule to which they are adding. The syndiotactic arrangement then becomes ...dlldldl..., the isotactic arrangement ...ddddd...(or ...lllll...), the atactic arrangement shows no regular sequences of great length.

The degree of tacticity of poly (methyl methacrylate) is normally measured by a nuclear magnetic resonance method (151) in which the absorption bands caused by resonance with the protons in the \( \alpha \)-methyl group are measured. The deuterated chloroform \((\text{CDCl}_3)\) used as a solvent has no proton absorptions. Three absorption bands are found, each corresponds to a different configuration of three adjacent \( \alpha \)-methyl groups. The bands correspond to ddd or lll triads (isotactic), ldl or dld triads (syndiotactic), and ddl, dll, lld and ldd triads (heterotactic).

Havriliak and Roman (116) have shown that in a poly (methyl methacrylate) having a high degree of syndiotacticity the ester \((-\text{COOCH}_3\)) groups are in a planar configuration perpendicular to the plane of the main chain carbon zig-zag. This (shown in fig 5.1) is the structure also proposed by Tsvetkov and Verkhotina (153).

5.3 Molecular Relaxations: Theories

These attempt to explain for polymers in general the relaxation properties which are reflected as transitions in various measured parameters in terms of proposed mechanisms. If more than one transition appears in the
properties, then usually more than one theory is required to explain this.

Deustch Hoff and Reddish suggested that the observed relaxation be named \( \alpha, \beta, \gamma \) etc. according as they occur at the highest, next highest, etc. temperature (at fixed observation frequency) or lowest, next lowest frequency (at constant observation temperature). If the relaxations are separated sufficiently in time (at constant temperature) or temperature (at constant time) then each is characterised by a short-time (unrelaxed) modulus (say \( G_U \)) and long-time (relaxed) modulus (say \( G_R \)). The relaxed modulus for one relaxation (say \( \beta \)) \( G_R^{\beta} \) becomes the unrelaxed modulus for the next relaxation: \( G_R^{\beta} = G_U^{\alpha} \). This, if it is observed, is usually seen in properties measured over a very wide time scale. If the relaxations shift in time differently with a change in temperature (i.e. have different apparent activation energies \( \Delta H_a(T) \)) the transitions may overlap in time scale at some temperatures but are resolved at other temperatures.

The \( \alpha \) transition is normally the most dramatic and is usually referred to as the primary transition. It is associated with the large fall in (say) the shear modulus of the polymer (from about \( 10^9.5 \) to \( 10^6 \) MNm\(^{-2}\)) occurring between the glassy and rubbery states. A typical apparent activation energy \( (\Delta H_a^\alpha) \) is a few hundred Kcal/mol. The other relaxations mostly occur in the glassy state although some relaxations may occur at higher temperatures (especially in crystalline polymers). The apparent activation energies of these
secondary transitions are typically a few tens of Kcal/mol.
The theories of the primary ($\alpha$) transition appropriate to a discussion of mechanical properties may be grouped according to type.

(i) **Normal mode based on Gaussian sub-molecular model**
The polymer chain is supposed to consist of segments of perhaps 20 or 50 monomer units. These units then individually can take part in rearrangements of configuration (while the whole macromolecule remains an entity). The molecular motion involved is a coupled micro-Brownian one, transition of segments from one local configuration to another being achieved by internal rotations about skeletal C-C bonds. The theories of Rouse, Bueche, Gotlib and Volkenstein, Nakada, Zimm, Pao and Kästner are of this class. Originally intended as a model of macromolecules in dilute solution in a solvent of given viscosity, the concept has been extended to treat the motion of macromolecular segments in an "artificial" viscous medium - the adjacent macromolecules.

(ii) **Free volume theories**
Extension from the "hole theory" of liquids having viscosity has in a similar fashion lead to the theories of Glasstone Laidler
and Eyring (60), Fowler and Guggenheim (61),
Doolittle (62)(63), Williams Landel and
Ferry (64), Bueche (65)(66) and Turnbull
and Cohen (67)(68).

(iii) Barrier theories
If the energies of configuration of a
macromolecule resulting from interaction
with adjacent molecules can be represented
by means of some energy/configuration
relation then appropriate statistical ideas
can be applied to the probabilities of various
configurations. This leads to the barrier
theories of Fröhlich (69), Hoffmann (70)(71)(72),
Hoffmann and Pwieffer (73) and Hoffmann and
Axilrod (74).

(4) Secondary transitions
Where it is thought that a specific mechanism
provides a valid explanation for observed
secondary transitions a theory of some
generality may be proposed. Those commonly
recognised are -
(a) Crankshaft theory
of Schatzki (75)(76) and Boyer (77). This
supposes that a short segment of a polymer
backbone or side-group can rotate as a
crankshaft about two co-linear C-C bonds
at the segment ends. The proposed geometries
of Schatzki and of Boyer differ.
(b) **Local mode theories**

of Yamafuji and Ishida\(^{(59)}\), Saito et al.\(^{(14)}\), and Takayanagi\(^{(78)}\). These theories are similar to the normal mode theories for the primary transition except that the segments are envisaged to be only a few molecules long.

(c) **Side-chain relaxations**

Below the temperature of the primary transition \(T_g\) the micro-Brownian motion of chain segments is not possible. If a second relaxation exists it is usually attributed to a side-chain relaxation. If there is no side-chain, it is usually attributed to a local mode motion (as in poly (vinyl chloride) \(^{(14)(146)}\).

In poly (methyl methacrylate) the larger side group inhibits local mode motion of the main chain. In polystyrene\(^{(16)(17)}\) there are two subsidiary relaxations below \(T_g\) (373°K), one at 323°K and one at 173°K (10 Hz). It is usual to attribute one of these to a side-chain motion and one to a main chain local mode motion\(^{(14)}\).

Some side-chain motions are only possible if there is a co-operative main chain local mode motion, for example, that in poly (butene 1)\(^{(18)}\). There are several salient features usually observed for side-chain relaxations\(^{(14)}\).
a) the apparent activation energy
\( \Delta H_a \) is usually about 10-20 Kcal/mol

b) the relaxation spectrum is much less broad than that of the primary transition, and nearly symmetric

c) local mode transitions vanish in the region of the primary relaxation but side-chain relaxations still persist

d) a transition (\( \gamma \) relaxation) will occur in poly (\( n \)-alkyl methacrylates) (having side-chain sequence \( -(CH_2)_n-1 CH_3 \)) if \( n \geq 3 \).

This is known as Willbourne's rule

**Relaxations Shown in Dielectric Studies**

Molecular motions may be observed by their influence on dielectric properties. In this case the investigative force acts directly on polar groups in the polymer. In the case of poly (methyl methacrylate) the dielectric properties are dominated by a strong electric dipole in the ester side group (\(-COOCH_3\)). Dielectric studies may thus be a useful adjunct to mechanical property studies. The appropriate theories of the primary transition (dipole-elastic motions: Mikhailov\(^{(33)}\)) are those of Zimm\(^{(48)}\), Kastner\(^{(53)}\)\(^{(54)}\)\(^{(55)}\), Stockmayer and Baur\(^{(56)}\), Kirkwood and Fuoss\(^{(57)}\), Hammerle and Kirkwood\(^{(58)}\) and Yamafuji and Ishida\(^{(59)}\). The barrier theories discussed above also pertain to the dielectric properties at the primary transition. The secondary transitions may also be evinced by changes in the dielectric properties. These are termed dipole-radical processes by Mikhailov\(^{(33)}\).
5.4a The $\alpha$-Relaxation in Poly (Methyl Methacrylate)

This relaxation has been studied many times by means of many different techniques. For the conventional polymer (type IV, see 5.5b) dilatometric techniques place the glass transition temperature at 376 to 378°C (see table 5.2). If observed by dynamic mechanical or dielectric techniques at a few Hz, the temperature appears about 10 to 20°C higher (see table 5.1). If observed by NMR at about $5 \times 10^{-7}$ Hz the transition appears at about 473°C (table 5.1). The isotactic polymer (type II, see 5.5b) has a dilatometric transition at 320°C while the syndiotactic polymer (type I) transition is at 390°C.

Ferry (37) has noted that the glass transition shifts about 3°C for a decade change in the measuring rate. Heydemann and Guicking (3) observed a decrease of 3°C in the dilatometric transition for a change in cooling rate from $7 \times 10^{-3}$ to $2 \times 10^{-3}$ °Ks$^{-1}$. Wittman and Kovacs (6) give the variation as \( \Delta T / \Delta \log t = -0.62°C \).

Heijboer (86) has noted that the difference in \( T_g \) for dynamic mechanical measurements made at 1 Hz and dilatometric measurements made at $1.7 \times 10^{-2}$ °Ks$^{-1}$ is about 20°C.

The first observations of the $\alpha$ transition seem to have been made by Alekandrov and Lazurkin (147). The transition appeared to start at 383°C (for \( f = 1.67 \times 10^{-2} \) Hz) or 404°C (for \( f = 16.7 \) Hz). Plastication lowered the transition temperature to 343°C for 10% plasticizer and to 303°C for 30% plasticizer.

Heydemann and Guicking (3) observed an upward shift of 0.018°C/atm. in \( T_g \) for dilatometric measurements under pressure.
McLoughlin and Tobolsky (122), when making relaxation measurements between 313 and 428°K found the time-temperature superposition principle (64) to hold in this temperature range. The master curve was the same for molecular weights ($\overline{M}_n$) of $1.5 \times 10^5$ and $3.6 \times 10^6$. The polymer was plasticized by water for temperatures near $T_g$, this was observed as a decrease in the temperature to reach a certain modulus at a certain time.

Bueche (130) measured creep in the range 313 to 433°K and determined a master curve (64). The activation energy for creep was 50 Kcal/mol at 423° and increased to a maximum of 250 Kcal/mol at 383°K. The shift factor $\dot{\alpha}$ followed the WLF law (64) within this range. The activation energy fell again below 383° indicating a change in the mode of molecular motion. The observed activation energies for creep near $T_g$ depended markedly on the rate of cooling of the specimens.

Read (108) has documented the change in dynamic modulus, dynamic stress- and strain-optical coefficients and the appropriate loss moduli in the range of the $\alpha$-transition.

Shindo et. al. (1) (table 5.1) found that $\Delta H_\alpha$ measured near $T_g$ increased as the isotactic content of the polymer decreased. The isotactic segments have a greater degree of freedom and thus greater internal chain mobility. This is borne out by solution (125) and solid-state studies (32)(104)(100)(126) on polymers of various molecular weights in dielectric and NMR studies.
Studies of higher poly (n-alkyl methacrylates) have revealed that $T_g$ decreases with increased side-chain length\(^{(8)}\). This is attributed to an "internal plastication" effect. There is a systematic decrease in density and inter-chain interactions as the side-chain length is increased. This may be interpreted as a lower monomeric friction coefficient and therefore higher free volume\(^{(37)}\). Intermolecular forces thus play a large part in the primary transition. Many other investigations of the transition are noted in table 5.1. The effects of various material parameters on the transition are discussed further in 5.5.

5.4b The $\alpha'$ Relaxation

The $\alpha'$ relaxation is observed only in experiments of relatively long time scale\(^{(120)}\). It has been observed to occur at temperatures from 328 to 341°K in dilatometric experiments: at 335°, 333°, 330°, 341°K\(^{(6)}\), 341°K\(^{(7)}\), 323°\(^{(8)}\), 340°\(^{(9)}\), 335°\(^{(3)}\); in dielectric experiments at 333°K\(^{(154)}\)\(^{(88)}\); in dynamic mechanical experiments at 333°K\(^{(88)}\); in creep experiments at 340°K\(^{(10)}\); in yield experiments at 333°K\(^{(145)}\) (see table 5.2). Thompson\(^{(120)}\) performed shear and tensile creep experiments in order to derive the retardation spectra $L$ ($\log t$) and $M$ ($\log t$) and observed an inflexion in these functions from $10^6 - 10^{11}$ s (298°K) which he attributed to the $\alpha'$ relaxation. He commented that there was as yet no satisfactory molecular explanation.
Heydemann and Guicking\(^{(3)}\) found that the transition as observed in dilatometric experiments was not influenced by pressure. Kopplemann\(^{(8)}\) found an inflexion in a plot of the half-widths of the dynamic mechanical and dielectric $\beta$ loss peaks plotted against temperature at 333°K. This temperature was found to be an (unspecified) function of the thermal treatment. He attributed the inflexion to a transition in the glassy state. Three inflexions were seen in the loss modulus/frequency plot at 293°K, at $10^{-3}$ at $3 \times 10^0$ and at $10^3$Hz. These were attributed to three different loss mechanisms. It seems that the $10^{-3}$ Hz relaxation reported could be the $\alpha'$ relaxation.

Wittman and Kovacs\(^{(6)}\) performed dilatometric measurements on a series of polymers of differing tacticities (see table 5.2). They found that an isotactic (type II) polymer - (their sample A) - showed no transition. Their sample B (type II), however, ($i = .59$, $s = .11$, $h = .30$) did show a transition at 334°K, somewhat above the glass transition temperature for this sample (321°K). All other samples (see table 5.2) exhibited an $\alpha'$ transition. The transition appeared only in polymers containing syndio- and hetero-tactic sequences and they concluded that the relaxation was associated with the concurrence of these sequences. They stated that the relaxation appeared to have only a small effect on the rheological parameters.
5.4c The Beta Relaxation

The beta relaxation has been investigated many times by means of many different techniques. The data from some of these investigations is summarized in tables 5.1 and 5.2. The relaxation has an activation energy of about 18 Kcal/mol, and appears at about 280–290°C in dilatometric experiments and at about 293°C (1 Hz) and 350°C (10^3 Hz) in dynamic mechanical experiments. The relaxation was first observed in dielectric experiments at 323°C (60 Hz) (29) and has subsequently been observed in mechanical measurements (10)(20)(23-26)(30-31)(80-90), in dielectric measurements (29-34)(85)(91-94), and in NMR measurements (21)(35) to mention a few.

The relaxation is most commonly supposed to arise from the rotation of the polar ester side groups (-COOCH₃) (24-28), this motion being strongly hindered by the α-methyl groups (30).

Heijboer (86) has stated that because the β-maximum in G'' for poly (methyl methacrylate), poly (ethyl methacrylate), poly (propyl methacrylate) and poly (butyl methacrylate) all occur at about 283°C while the α-transition temperatures for these polymers differ by up to 80°C it is to be concluded that the molecular mechanism for the β-relaxation differs greatly from that responsible for the α-relaxation (see text figure 1).
The storage shear modulus for methyl-, ethyl-, propyl- and butyl-methacrylates is shown after Heijboer in text figure 2.
Ferry (37) conjectured that the rotation of the carbonyl groups involved some local motion of the main chain although its major convolutional rearrangements are frozen in the glassy state. Heijboer states that it is this co-operative nature which results in the retardation (or relaxation) spectra of the $\beta$-relaxation being so broad. Koppelmann (87) found a peak in $\tan \delta_{\text{mech}}$ at a frequency of $10^{0.5}$ Hz at a temperature of 298 K and inflexions in both $E'$ and $G'$ as a function of frequency at the same temperature. The inflexion in $G'$ appeared one decade lower in frequency than that in $E'$. A consequence of this is that Poisson's ratio $\nu$ goes through a minimum (0.12) at the transition (10 Hz) being higher at both higher and lower frequencies - 0.32 ($10^{-2}$ Hz) and 0.30 ($10^{3}$ Hz). Thurn and Wolf (103) found $E''$ and $\epsilon''$, the loss moduli in dynamic mechanical and dielectric experiments to peak at the same frequency, thus indicating a close correlation in the respective relaxations. Read (108) performed optical-mechanical measurements at 8 Hz. Various peaks due to the $\beta$-relaxation were found. $\delta$, the mechanical damping lag angle peaked at 323 K; $E''$, the dynamic storage modulus at 298 K; $D''$, the dynamic compliance at 343 K; $\delta - \delta'$, the angle by which the birefringence leads the strain at 283 K; $K''$, the dynamic storage strain-optic coefficient at 278 K; $\delta'$, the angle by which the stress leads the birefringence at 346 K; and $C''$, the dynamic storage stress-optic
coefficient at 353°K.

The wide spread in temperatures was attributed to the broad spectrum of mechanical relaxation times and the differing contributions of various parts of the spectrum to different properties.

Shindo et al. (1) found that a stereo-block sample (type III) of poly (methyl methacrylate) showed fine structure in the dielectric β loss peak. Two inflexions were seen: at 298.1°K (at \( \log f = 0.8 \) and 2.0), at 307.4°K (1.1, 2.0) and at 317.8°K (1.1, 2.0).

E. V. Thompson (120) conducted creep experiments and produced a master creep curve at 298°K by the method of reduced variables (37). The shear (L(\( \log t \)) ) and tensile (M(\( \log t \)) ) creep spectra showed a broad peak from \( 10^{-4} \) to \( 10^{4} \) s. The activation energies for non-normalized data were 29.2 and 26.3 Kcal/mol, respectively and for normalized data (109) 17.9 and 17.7 Kcal/mol, respectively. Thompson commented that the activation energies thus determined over a wide temperature range reflect all the processes operative in that range and may, in fact, be influenced by the temperature dependence of processes operative at higher and lower temperatures. This is further discussed here under 10.13.

Wittman and Kovacs (6) investigated a series of polymers of widely different tacticities. In all they found a (dilatometric) transition in the range 263-283°K. They conclude this to be a transition common to all poly (methyl methacrylates). Since the triad analysis (151) varies within wide limits the transition is probably due to the chemical nature of the polymers, in fact
the pendant ester side-group.

Heijboer (86) has summarised some important factors influencing the $\beta$-transition: 1) Inherent main chain flexibility lowers the magnitude and temperature of the relaxation. 2) Inter-chain forces of steric origin do not have much influence on the damping maximum. 3) Substitution of groups of increased polarity in the side-chain shifts the $\beta$ loss-maximum to higher temperatures.

A. J. Curtis (111) has commented on the methods for determining the activation energy of the $\beta$-relaxation. Often the activation energy has been determined from plots of tan$\delta$ at constant frequency as a function of temperature rather than from tan$\delta$ at constant temperature as a function of frequency. The calculation of $\Delta H$ in the first case then implies that the distribution of relaxation times is not a function of temperature, this is not always true (109).

Heijboer (86) has discussed the influence of stereoregularity on the $\beta$-transition in terms of an isotactic ($i = 0.95$) (151) and an syndiotactic ($s = 0.85$) (151) polymer. The chain flexibility is considerably greater for the isotactic polymer than for the syndiotactic polymer, as a consequence $T_g$ is $70^0K$ lower. The $\beta$-transition is, however, only $20^0K$ lower. See text figure 3.

Fewer side-groups are thought to be mobile in the isotactic polymer. These observations are supported by the dielectric measurements of Mikhailov and Borisova (104).
The dielectric increment $\Delta \varepsilon_\beta = (\varepsilon_\nu - \varepsilon_\alpha)$ is little dependent upon temperature below the glass transition temperature \(^{(1)}\). That this increment is maximum for a polymer having $i = 0.7$ has been explained by Yamafuji and Ishida \(^{(127)}\). Shindo et al. \(^{(1)}\) conclude that the dependence of the $\beta$-relaxation on tacticity seems to be related to the length of the stereosequences in the polymer \(^{(127)}\).

Ferry \(^{(37)}\) has shown that the method of reduced variables leads to anomalous shift factors for all poly (n-alkyl methacrylates) (up to poly (n-hexyl methacrylate)) because the $\alpha$ and $\beta$ transitions may overlap. When they are separated the shift factor for the $\beta$-transitions usually follows an Arrhenius equation the activation
energy decreasing with increased side-group length. McCrum et al.\textsuperscript{(11)} have shown that the $\alpha$ and $\beta$ relaxations normally merge when the measuring frequency is as high as $10^4$ Hz. Heijboer\textsuperscript{(86)} has noted that the time-temperature superposition (method of reduced variables) works well for the $\beta$-relaxation if $\alpha$ and $\beta$ relaxations are well resolved. This can normally only be achieved for measurements over a wide range of frequencies at several close temperatures which is inconvenient for mechanical property experiments. The advantage of measuring over a wide frequency range at a single temperature is that the temperature and thus the molecular environment is not changed. Heijboer\textsuperscript{(30)} has shown that the $\beta$-transition temperatures of all the poly (n-alkyl methacrylates) are close to $298^oK$ (1 Hz) if the $\alpha$ and $\beta$ transitions are well resolved. (see text figure 2). He further states that the activation energies for the series are all nearly the same. This is contrary to the statement of Ferry\textsuperscript{(37)}.

Sasabe and Saito\textsuperscript{(121)} have shown that the $\alpha$ and $\beta$ relaxations are well resolved if the measurement temperature is low or if the measurements are made at high pressures. Shindo et al.\textsuperscript{(1)} have shown that in an isotactic (type II) polymer the $\beta$-relaxation becomes masked by the $\alpha$-relaxation as the temperature is increased. At high temperatures the single absorption observed is largely due to the $\alpha$-relaxation. For a syndiotactic polymer (type I) by contrast they state that the $\alpha$-relaxation becomes masked by the $\beta$-relaxation and at high temperatures the absorption
is largely due to the $\beta$ process. This must be a consequence of the relative magnitudes of the $\alpha$ and $\beta$-relaxations in the two stereotypes or the change in magnitudes with temperature. Saito et al. (14) have investigated time-temperature superposition for the $\beta$-relaxation in terms of their creep and relaxation data. The spectrum of relaxation (or retardation) times is very broad. Superposition was achieved for data taken from 215-348$^\circ$K. This implies that when the $\beta$-relaxation is well resolved, the width of the spectra are either independent of temperature or change only slowly with temperature. They state that the spectra derived at temperatures above and below $T_g$ should always be distinguished because there may be interaction of the $\alpha$ and $\beta$ relaxations. The spectrum derived by the second approximation method (37) is of "wedge and box" form (225) and agrees well with that derived from reduced creep data (38). The first approximation method of Ferry and Ninomiya (39) is not adequate. The shift factors from creep and relaxation experiments agree well and closely fit an Arrhenius relationship. The normalised spectra of Ferry (40) for poly (methyl methacrylate) and poly ($\alpha$-propyl methacrylate) and that for poly ($\alpha$-butyl methacrylate) (14) superpose well showing that the mechanism of the $\beta$-relaxation is the same in all of these polymers. The height of
The retardation spectrum \( L(\log t) \) is approximately proportional to the number of carbon atoms in the side-chain.

Heijboer \(^{(86)}\) has listed references \(^{(20)(31)(82)(85)(136)}\) in which the \( \beta \)-relaxation has been attributed to rotation of the side-chain methoxy-carbonyl groups of poly (methyl methacrylate) about the carbon-carbon bond. He supposes that at temperatures below the glass transition only a small fraction of the side-chains take part. In so far as they are free to do so, they all do equally freely. Above the glass transition temperature all side-chains are free and the motion is coupled with that of the main chain thus augmenting the \( \alpha \)-relaxation. If the \( \tan \delta \) curves for poly (ethyl methacrylate) and poly (t-butyl methacrylate) are compared, it is found that in the second case the \( \beta \) maximum is greater in height but at the same temperature, while the \( \alpha \) maximum is of greater height and appears at a higher temperature. (see text figure 4).

Heijboer has explained that by supposing that fewer t-butyl side-chains participate in the \( \beta \) relaxation than do ethyl side-chains. Those not free to move in the glassy state will contribute to the \( \alpha \)-relaxation when not hindered. This is confirmed by his dielectric measurements. For the groups free to move the relaxation time is the same (the \( \beta \)-peak remains at the same temperature). The side-chain motion is thus either relatively free or completely hindered \(^{(85)}\). Heijboer
concludes that the bulkiness of the side group determines whether it can move or not whereas the local environment of the group will determine the activation energy. Deutsch et al. (31) showed that substitution of Cl for the \( \alpha \)-CH\(_3\) (i.e., a chloro-acrylate) did not affect the \( \beta \)-relaxation thus leading to the conclusion that the relaxation occurs in the side-chain. McCrum et al. (11) have stated that the \( \beta \)-relaxation is caused by a hindered rotation of the ester group about the carbon-carbon bond the hindrance arising from the \( \alpha \)-methyl groups of the two adjacent molecules.
Ishida and Yamafuji\(^{(32)}\) consider the motion to be an oscillatory rotation below \(T_g\), but a hindered rotation only above \(T_g\). Saito et al.\(^{(14)}\) have noted that the relaxation times of the \(\beta\)-relaxation for poly (n-alkyl methacrylates) do not seem greatly affected by the side-chain length. (Presumably this means that the hindrance is not greatly affected by the side-chain length). The spectra of relaxation times do, however, sharpen and increase in height as the side-chains are lengthened\(^{(14)}\). Saito et al. also note that spectra derived below \(T_g\) are considerably broader than those derived above. Heijboer\(^{(86)}\) has investigated the question of hindered motions systematically. Poly (methyl acrylate) has hydrogen atoms rather than methyl groups in the \(\alpha\)-position. The glass transition temperature is \(100^\circ\)K lower than that of poly (methyl methacrylate) as a result (see text figure 5). If the relaxations present in co-polymers of methyl acrylate and methyl methacrylate are plotted (for constant frequency) on a composition-temperature diagram, it is seen that the \(\beta\)-relaxation disappears for 66 mol.% or more methyl acrylate (see text figure 6). The \(\gamma\)-relaxation of poly (methyl acrylate) at \(153^\circ\)K (1 Hz) is shown neither to occur in or be identical with the \(\beta\)-relaxation of poly (methyl methacrylate). Replacement of the \(\alpha\)-methyl groups by hydrogen results first in a decrease in the \(\beta\)-relaxation temperature as hindrance to ester group motion is reduced and finally
a complete disappearance of the relaxation altogether as the hindrance is removed. Further evidence is obtained by examining the behaviour of the $\beta$-relaxation in co-polymers of methyl methacrylate with styrene and with $\alpha$-methyl styrene.

\[
\begin{align*}
\text{STYRENE} & \quad & \text{CH}_3 \\
\text{H} & - C - \text{CH}_2 & - C - \text{CH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{\textit{\alpha}-METHYL STYRENE} & \quad & \text{CH}_3 \\
\text{H} & - C - \text{CH}_2 & - C - \text{CH}_2 \\
\end{align*}
\]

In the case of the styrene co-polymer the $\beta$-relaxation shifts to a lower temperature as the styrene content of the co-polymer increases as happens with the methyl acrylate co-polymer. (see text figures 7 and 8). Dielectric evidence\(^{(137)}\) also leads to the conclusion that the ester group motion is hindered. Co-polymerization with $\alpha$-methyl styrene does not result in a shift of the $\beta$-relaxation temperature. This is regarded by Heijboer\(^{(86)}\) as strong evidence that the $\beta$-relaxation results from a motion of the ester side-groups which is hindered by the $\alpha$-methyl groups and which disappears when the hindrance is removed.
Sasabe and Saito\(^{(121)}\) suggest that when the relaxation times of two molecular relaxations are similar there may be coupling between the two relaxations. (Coupling here should be distinguished from mere overlapping). (This situation does not often occur, but it does happen for the \(\alpha\) and \(\beta\) relaxations in poly (methyl methacrylate) ). They concluded that there was coupling in the case of poly (methyl methacrylate) because their plots of the log (dielectric relaxation time) for the \(\beta\)-transition vs. 1,000/T showed a break near \(T_g\). They then referred to the coupled relaxation as \(\alpha\beta\). Kopplemann\(^{(88)}\) has investigated the question of interaction between the relaxation of the ester side groups and the relaxation of main chain segments. In the glassy state the segmental motion of the backbone is negligible and there can be no interaction. As the ester groups are coupled by a direct chemical link to the backbone an interaction might be expected when and if the relaxation times become comparable. It is not expected that mechanical and dielectric properties will be similar even if there is such interaction as the external investigative forces act at different points on the macromolecules. Text figures 9 and 10 show the storage modulus after Kopplemann. The mechanical \(\beta\)-relaxation is observed as a peak in \(\tan\delta\) at 293\(^o\)K (1 Hz) which shifts to 373\(^o\)K (10\(^3\) Hz). The peak shifts again to a lower frequency as the temperature is increased through the glass transition
Real part of the dynamic Young's modulus of PMMA plotted against frequency. The parameter denotes the temperature in °C.

(PMMA mechanical measurements). Real part of the dynamic Young's modulus of PMMA plotted against frequency. The parameter denotes the temperature in °C.
(PMMA mechanical measurements). Imaginary part of the dynamic Young's modulus of PMMA plotted against frequency. The parameter denotes the temperature in °C.

Loss factor of the dynamic Young's modulus of PMMA plotted against frequency. The parameter denotes the temperature in °C.
temperature. (see text figures 11 and 12). (The same effect has been observed for dielectric properties by Shindo et al.\(^{(1)}\)). In dielectric experiments Kopplemann found the \(\alpha\)-relaxation much smaller in magnitude because the force on the backbone acts not directly but through the carbon-carbon bond from the polar ester group. The dielectric \(\beta\)-transition could be investigated above \(T_g\) at very high frequencies. The dielectric and mechanical \(\beta\) peaks approach each other at low temperatures and are expected to tend to the same limit. The dielectric frequency of maximum loss was shown to be a linear function of temperature through the glass transition temperature (380°K) demonstrating that the \(\beta\) mechanism persists at temperatures above \(T_g\). (see text figure 13).

![Diagram](image)

(PMMA position of relaxation maxima). Temperature-frequency shift of the relaxation maxima of PMMA. Triangles denote mechanical measurements and circles denote dielectric measurements.
The mechanical frequency of maximum loss curves around at 380°K, the maximum loss frequency remaining sensibly constant at $3.10^3$ Hz from 373 to 388°K. This shows the mechanical $\beta$-relaxation to be coupled to the $\alpha$-relaxation at these temperatures. The height of the mechanical and dielectric $\beta$-loss peaks as a function of temperature both rise suddenly at $T_g$. The mechanical peak, however, rises much more sharply above $T_g$. (see text figure 14). This indicates that there is an interaction with the $\alpha$-relaxation and an extra contribution to the $\beta$-loss when the main chain is excited. The steep increase in the $\beta$-loss peak height above $T_g$ cannot be explained by a sudden decrease in the peak half-width which decreases smoothly from 333 to 423°K. (see text figure 15).

(a) Mechanical measurements. (b) Dielectric measurements.
The nature of the interaction is not clear. It probably consists of a co-operative interaction involving several units the extent of the co-operative range probably depending on temperature (138). Koppelmann (88) has further explained how the interaction might be conceived in terms of a simple mechanical model. (see text figure 16). In a first approximation the spring compliances are taken to be independent of temperature, the dashpot viscosity follow an Arrhenius law. The resultant storage modulus behaviour cannot be obtained from a generalized Maxwell model. The model behaviour matches the experimental information for poly (methyl methacrylate). The $\alpha$-relaxation is hindered by the $\beta$-relaxation if the relaxation time of the $\beta$-relaxation is greater than that of the $\alpha$-relaxation. This behaviour will be shown
in the polymer if

1) The external forces act in such a manner that chain segment movements as well as side group movements are strongly excited,

2) In certain temperature ranges the relaxation time spectra of primary and secondary relaxations overlap at least partially,

3) The mobility of chain segments is at least partially hindered by insufficient mobility of the side groups if the primary relaxation spectrum contains times equal or smaller than the times in the secondary spectrum.
Havriliak(12) does not attribute the dielectric loss to a rotation of the ester side-chain group. He has interpreted his dielectric data for syndio- and iso-tactic poly(methyl methacrylate) in terms of a chain structure consistent with his own infra-red absorption experiments. The variation in dipole moment as a function of temperature has been treated as a chain segment of length varying with temperature. The predominantly syndiotactic polymer is shown to have a planar zig-zag backbone, the ester groups taking perpendicular planar positions. (fig. 5.1). The dipole moments in the ester planes can then either be up or down. Adjacent triads can then take six arrangements - viz. ddd, ddu, udu, uuu, uud, dud. The spectroscopic frequencies of uuu-ddd, ddu-udd, and udu-dud are expected to be the same. The dipole moment of these triads on the other hand are quite different, particularly when adjacent triads are coupled. By combining the triads a molecular segment can be constructed which has a dipole moment consistent with the experimental value (the chain is assumed to have a helical form with five monomer units in two turns). Although this does not lead to any unique structure, many side-chain conformations are excluded. The infra-red absorption experiments of Havriliak and Roman(116) showed that ester group rotations could take place above Tg but were frozen below Tg. Both the relative intensities of the ester oxygen absorption peaks corresponding to the triad arrangements discussed above and their sum were found to be constant below Tg. The relative values of
different peaks were a function of temperature above $T_g$, although their sum remained constant. In syndiotactic poly (methyl methacrylate) all of the ester groups are perpendicular to the main chain so that the component of the dipole moment parallel to the chain is zero. The dielectric evidence then leads to the conclusion that the $\beta$-relaxation must be an orientation about an axis parallel to the main chain axis.\(^{(12)}\) The dielectric properties of the poly (methyl methacrylate) have been investigated by Reddish.\(^{(192)}\) He has presented the results as a loss/frequency/temperature map. (fig. 5.3) Miller\(^{(139)}\) has observed that the dielectric $\beta$ peak is normally observed 15-20 K lower than the mechanical peak. This has also been observed by McCrum et al.\(^{(11)}\) Mikhailov and Borisova\(^{(104)}\) have commented that the dielectric $\beta$ loss-peak is smaller and the $\alpha$-peak larger for isotactic (II) poly (methyl methacrylate) than for either syndiotactic (I) or conventional (IV) polymers. In the isotactic polymer the $\alpha$ loss-peak is greater than the $\beta$ peak, while in a conventional polymer the $\beta$-peak is much larger than the $\alpha$-peak. This was also observed by Shindo et al.\(^{(1)}\) Heijboer\(^{(222)}\) has reported work in which the influence of certain co-monomers upon the $\beta$-transition in poly (methyl methacrylate) was examined. These results are summarized below in Table 5.3.
FIGURE 5.3 TAN δ AFTER REDISH
### Table 5.3

**Effects of Co-Polymerization Upon $\beta$-Relaxation**

<table>
<thead>
<tr>
<th>Name and amount of co-monomer</th>
<th>Formula of co-monomer</th>
<th>Feature of co-monomer</th>
<th>Effect on Secondary dispersion region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate</td>
<td>$CH_2=CHCOOCH_3$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glycol dimethacrylate 20%</td>
<td>$CH_2=CHCOOCH_2$</td>
<td>Cross-linking</td>
<td>Somewhat depressed, slightly shifted to lower frequency</td>
</tr>
<tr>
<td>N-methyl methacrylamide 30%</td>
<td>$CH_2=CHCONHCH_3$</td>
<td>Polarity</td>
<td>Depressed, shifted to lower frequency</td>
</tr>
<tr>
<td>Cyclohexyl methacrylate 60%</td>
<td>$CH_2=CHCOOC_6H_{11}$</td>
<td>Bulkiness of side group</td>
<td>Depressed, stays at same frequency</td>
</tr>
<tr>
<td>Methyl acrylate 20, 40, 60 and 80%</td>
<td>$CH_2=CHCOOCH_3$</td>
<td>Flexibility backbone chain</td>
<td>Strongly depressed; shifted to higher frequency</td>
</tr>
<tr>
<td>Acrylic acid 60%</td>
<td>$CH_2=CHCOOH$</td>
<td>Flexibility backbone chain and polarity</td>
<td>Strongly depressed; shifted to higher frequency</td>
</tr>
</tbody>
</table>
There is a considerable body of evidence to support the view that the \( \beta \)-relaxation in poly (methyl methacrylate) is caused by a rotation of the polar ester side groups \((-\text{COOCH}_3\)) about the C-C backbone bond which is hindered by the two adjacent \( \alpha \)-methyl groups. A contrary point of view is taken however by Havriliak who attributes the mechanical and dielectric \( \beta \) relaxations to the same cause - an orientation of dipoles parallel to the main chain axis.

5.4d Water Relaxation in Poly (Methyl Methacrylate)

Poly (methyl methacrylate) contains hydrophilic groups and can absorb up to 2% water by weight in the glassy state. It has been reported (in 5.4a) that the water may plasticise the \( \alpha \)-relaxation \(^{(22)}\). A new low-temperature relaxation arises as a consequence of the presence of water \(^{(23)}\). This relaxation has been investigated several times \(^{(7)(97)(98)(99)(119)(122)(23)}\). (see table 5.1)

The relaxation occurs at about \( 170^0\text{K} \) (1 Hz) or \( 270^0\text{K} \) (\(10^5\) Hz). The loss-peak (1 Hz) appears to be higher for the conventional (IV) polymer (at \(191^0\text{K}\)) than for either syndiotactic (I) or isotactic (II) polymers (both at \(178^0\text{K}\)) \(^{(97)}\).

Janacek and Kolarick \(^{(122)}\) have shown that this relaxation may be caused by the introduction of many low molecular weight substances, greater amounts causing
an increase in the damping and depression of the damping peak to lower temperatures. They attribute the damping to relaxation of the side-chains involving an interaction of the polar \(-\text{COO}^-\) groups with molecules of low weight. Smaller molecules were found to be more effective in causing damping.

5.4e The \(\alpha\)-Methyl Relaxation

This relaxation has been observed by dynamic-mechanical and NMR techniques \(\text{(99)(21)(105)(117)(35)(100)(101)}\). The relaxation does not affect dielectric properties. The relaxation has been attributed to the rotation of the \(\alpha\)-methyl groups, hindered by the adjacent ester groups \(\text{(21)}\). The relaxation appears at about \(100^0\text{K} \ (1 \ \text{Hz})\) or \(253^0\text{K} \ (10^6 \ \text{Hz})\) (see table 5.2). The relaxation appears at a temperature about \(40^0\text{K}\) lower for the isotactic (II) polymer than for conventional or syndiotactic polymers (IV, I) in NMR measurements \(\text{(105)}\).

5.4f The Ester Methyl Group Relaxation

The ester methyl group (\(-\text{CH}_3\)) is able to rotate independently of the carboxy group (\(-\text{COO}^-\)) in poly (methyl methacrylate). This occurs at very low temperatures \(\sim 4^0\text{K} \ (1 \ \text{Hz})\) \(\text{(102)}\) and \(\sim 70^0\text{K} \ (3.10^7 \ \text{Hz})\) \(\text{(21)}\). Other investigations have been \(\text{(119)(101)(117)}\) (see table 5.1).
5.4g The $\gamma$ Relaxation

Willbourne\(^{(20)}\) has shown that if the side-chain is long enough then the alkyl group (\(-R\)) in the ester side-chain (\(-\text{COOR}\)) or poly (\(\text{\(n\)}\)-alkyl methacrylates) can relax independently of the oxycarbonyl group (\(-\text{COO}^-\)). This relaxation which occurs at 70-170$^\circ$K (100 Hz) for poly (ethyl,\(n\)-propyl, etc. methacrylates (20)(82) is known as the $\gamma$-relaxation. It does not occur in poly (methyl methacrylate) because the ester group is too small.

5.4h Relaxation Map for Poly (Methyl Methacrylate)

It is found that when the temperature of maximum loss (at constant frequency) or (better) the frequency of maximum loss (at constant temperature) is plotted on a log (frequency) vs. reciprocal temperature map for a given relaxation that a line or curve relating the two variables (at maximum loss) can be obtained. Measurements obtained at different times and by many different techniques often show good consistency on this type of plot. Some methods of investigation will, however, not detect some types of transitions (see 5.4e). McCrum, Read and Williams\(^{(11)}\) have collected much of the published data for type IV poly (methyl methacrylate) and constructed such a map. This map (minus data points) is shown in fig. 5.4.
5.5 The Glass Transition as Influenced by Molecular Weight, etc.

(i) Molecular weight

Thompson (126) has measured the glass transition temperature of five poly (methyl methacrylate)s by means of differential thermal analysis. The nuclear magnetic resonance (NMR) triad analyses (according to Bovey and Tiers (151) and the parameters
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1) METHOD OF INVESTIGATION
   D - DYNAMIC MECHANICAL
   C - CREEP
   R - RELAXATION
   S - CONSTANT STRAIN-RATE
   Y - COMPRESSIVE YIELD
   E - DIELECTRIC
   M - NUCLEAR MAGNETIC RESONANCE

2) TYPE OF POLYMER
   I - PRIMARILY SYNDIOTACTIC
   II - PRIMARILY RISTACTIC
   III - STEREOSBLIC
   IV - CONVENTIONAL (ATACTIC)

3) EFFECTIVE FREQUENCY
4) TWO PEAKS

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<td>79</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>2(D)</td>
<td>1.112</td>
<td>0.0120</td>
<td>59</td>
<td>83</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>2(E)</td>
<td>1.120</td>
<td>0.0120</td>
<td>59</td>
<td>83</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>3(A)</td>
<td>1.220</td>
<td>0.0212</td>
<td>95</td>
<td>(5)</td>
<td>168</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>3(B)</td>
<td>1.200</td>
<td>0.0202</td>
<td>69</td>
<td>83</td>
<td>19.5</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>3(C)</td>
<td>1.183</td>
<td>0.0182</td>
<td>59</td>
<td>79</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>3(D)</td>
<td>1.112</td>
<td>0.0120</td>
<td>59</td>
<td>83</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
<tr>
<td>3(E)</td>
<td>1.120</td>
<td>0.0120</td>
<td>59</td>
<td>83</td>
<td>19.4</td>
<td>0.99</td>
<td>III</td>
</tr>
</tbody>
</table>

1) Sample name in reference in parentheses.
2) From density and expansivity given.
3) Following Berry and Tiers (55), isotropic, syndiotactic, heterotactic.
4) As given (or estimated if?
5) Expansivities 1 and 2 before transition 1 and so on.
6) Subscripts m=number average, q=viscosity.
7) From creep measurements.
8) Cooling rate \( 7 \times 10^{-5} \) °C/s.
9) Cooling rate \( 5.2 \times 10^{-4} \) °C/s.
10) Dynamic mechanical and dielectric.
in the equation
\[ T_g = T_g^\infty \frac{-K}{\bar{M}_\eta} \]
fitted by least squares to the data obtained are given below. \( \bar{M}_\eta \) is the viscosity-average molecular weight.

Table 5.4.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample</th>
<th>( T_g^\infty ) ( ^\circ \text{K} )</th>
<th>( (E_2 - E_1) / h ) ( ^\circ \text{K} )</th>
<th>( i )</th>
<th>( h )</th>
<th>( s )</th>
<th>( \bar{M}_\eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>1</td>
<td>321.5</td>
<td>720.4</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>822000</td>
</tr>
<tr>
<td>II</td>
<td>2</td>
<td>327.5</td>
<td>749.3</td>
<td>73</td>
<td>16</td>
<td>11</td>
<td>93000</td>
</tr>
<tr>
<td>III</td>
<td>3</td>
<td>334.8</td>
<td>758.0</td>
<td>62</td>
<td>20</td>
<td>18</td>
<td>57000</td>
</tr>
<tr>
<td>IV</td>
<td>4</td>
<td>387.4</td>
<td>853.4</td>
<td>10</td>
<td>31</td>
<td>59</td>
<td>1070000</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>398.8</td>
<td>874.3</td>
<td>0</td>
<td>36</td>
<td>64</td>
<td>958000</td>
</tr>
</tbody>
</table>

\( (E_2 - E_1) \) is a measure of the flex energy of the polymer chain \(^{148}\). It may be seen that a difference in \( T_g \) of 1\(^\circ\)K or 3.4\(^\circ\)K from \( T_g^\infty \) is attained for type II and type I polymers respectively when \( \bar{M}_\eta = 10^5 \). The difference is even smaller for higher molecular weights.

The glass transition temperature of the syndiotactic polymer (I) and the conventional polymer (IV) are more sensitive to molecular weight than the isotactic (I) polymer. The equation for a completely syndiotactic polymer \((s = 100, h = i = 0)\) is estimated by Thompson to be

\[ T_g = 433 - 4.35 \times 10^5 / \bar{M}_\eta \]
Krause and Roman\textsuperscript{(150)} found a dilatometric transition at 433\,K for a mixture of 25\% isotactic and 75\% syndiotactic polymers. Beevers and White\textsuperscript{(149)} found for a conventional (IV) poly (methyl methacrylate) that
\begin{equation}
T_g = 387^{\pm 1} - (2.1^{+0.2}) 10^5 / \bar{M}_n,
\end{equation}
which held over the range of molecular weights 2740 to 76600. The specific volumes of the polymers were within 0.837\,0.003 cm\,g\,^{-1} at 290\,K and the expansivities $(1.65^{+0.22}) 10^{-4}$ cm\,g\,^{-1} K\,^{-1} ($\alpha_g$) and $(4.38^{+0.33}) 10^{-4}$ cm\,g\,^{-1} K\,^{-1} ($\alpha_1$).

(ii) **Tacticity**

There are four common methods of polymerizing methyl methacrylate which lead to polymers having notably different tacticity characteristics. These four polymer types have been called I, II, III, IV here.

**Type I**

This polymer is predominantly syndiotactic in nature as revealed by the NMR triad analysis\textsuperscript{(151)} and is prepared by free-radical initiation at low temperatures. As
discussed under 5.4a the glass temperature is about 390°K.

Type II

The polymer is predominantly or solely isotactic in nature and is prepared by initiation with a stereospecific catalyst such as phenylmagnesium bromide at about 270°K. The glass temperature is about 320°K.

Type III

This polymer has a stereoblock form and is prepared by an anionic polymerization at low temperatures. Glass temperatures are 333 to 368°K.

Type IV

This is the 'conventional' polymer of commerce and is prepared by free-radical initiation at elevated temperature (usually above 323°K\(^{(139)}\)), typical catalysts being azobisisobutyronitrile or benzoyl peroxide. The polymer typically has a triad analysis of i (isotactic) 6, h (heterotactic) 38, s (syndiotactic) 56\(^{(139)}\) and thus has a high degree of syndiotactic character. Normally polymerization at low temperatures (\(\sim 320°K\)) produces a high molecular weight but incomplete polymerization\(^{(124)}\). The
usual commercial process involves polymerization at both low and high temperatures and polymerization is thus usually complete. The glass temperature is 376-378°K (sect. 5.4a). The relative mobility of the backbone segments of isotactic and syndiotactic polymers has been mentioned under 5.4a already, this is reflected in the flex energies given above (table 5.4). Shindo et al. (1) have determined the activation energy at the glass transition temperature by means of dielectric measurements for a series of polymers of different tactic character. These are presented in table 5.1; it is seen that the activation energy is least for the type II polymer and greatest for the type I polymer. The expected sequence length (most probable) for a type IV polymer involves isotactic segments of two molecules, syndiotactic segments of five molecules (141). The full distribution of probabilities is shown in fig. 5.5.

![Graph](image-url)

**Fig 5.5** Distribution of isotactic and syndiotactic sequence lengths in poly(methyl methacrylates).

**Sample A** (s = 0.75), **Sample B** (s = 0.81) after (14).
The tacticity has a strong influence on the extent of polar interaction between pendant ester side-groups. This depends upon the configuration of the main chain which is greatly different for type I and type II polymers as evinced by the flex energies (720 and 874 ergs). This is because of the effect of configuration of the main chain upon ester group rotation. The average value of the optical anisotropy of a single monomer unit in isotactic (II) poly (methyl methacrylate) is fourteen times the typical anisotropy for an atactic (IV) polymer (142). The melting point of isotactic poly (methyl methacrylate) is 433°K while that of atactic (IV) polymer is greater than 473°K (143).

Wittman and Kovacs (6) have noted that although the glass transition temperature is obviously strongly dependent upon tacticity, there is no apparent good correlation with the triad analysis and they suggest that longer sequences must be investigated in order to determine the dependence.

Karasz and MacKnight (152) found that for polymers of the type \(( \text{CH}_2\text{CXV})_n\) that \(T_g\) varies with tacticity only if \(X \neq Y\) and \(X \neq H \neq Y\). This follows from the theory of Gibbs and di Marzio (148) if it is assumed a) that the effect
of configuration in di-substituted polymers is intramolecular and brought about by changes in the flex energy of the steric isomers and b) that changes in $T_g$ due to side-chain modifications are strictly intermolecular (see sect.5.4a).

(iii) **Plastication**

Mikhailov\(^{(33)}\) found that dibutyl phthalate lowered the primary transition temperature while having no effect on the $\beta$ transition temperature.

Dudek and Lohr\(^{(124)}\) studied the effect of diethyl phthalate as a plasticiser in poly (methyl methacrylate); 3.6% lowered $T_g$ from $381^\circ$ to $372^\circ K$, 8.0% to $357^\circ$ and 16% to $338^\circ K$. Unpolymerized monomer was a more efficient plasticiser; $T_g$ was lowered by 3$^\circ K$ to $378^\circ$, by 0.5$, T_g$ by 1.1%, to 366 by 2.9%, to 353 by 4.6% and to $340^\circ K$ by 8.2% monomer. A small amount of unpolymerized monomer can lower $T_g$ considerably.

(iv) **Crosslinking**

If poly (methyl methacrylate) is cross-linked using ethylene glycol dimethacrylate $10^{20}$ crosslinks per gram (i.e. one cross-link per 60 molecules) will increase the glass temperature by 12$^\circ K$\(^{(140)}\). Crosslinking will decrease the volume expansion coefficients $\alpha_1$ and $\alpha_g$ (but has greater effect on $\alpha_1$) until they are approximately equal\(^{(139)}\).
6. NATURE OF THE GLASS TRANSITION AND THE VITREOUS STATE

6.1 General

In subsequent chapters the mechanical properties of samples of poly (methyl methacrylate) cooled through the glass transition at two different rates will be described and shown to be different. The purpose of this chapter is to examine the question of how differing material 'states' may arise through cooling at different rates. The word 'state' will not be used here in the normal strictly thermodynamic sense (that is to mean a unique description in terms of the thermodynamic state variables) but only in the sense that materials of different 'state' will have different mechanical properties. This definition then, while similar to the thermodynamic one, may not necessarily be so restrictive.

A sufficient description of the state will enable prediction of the deviation of certain of the mechanical properties of materials in different states from some reference properties. As an example it would be possible to predict the mechanical shift-factor\(^{(64)}\) for any attainable material state from an adequate description of that state.

Such a prediction is possible and well established for temperatures above the glass transition (i.e. in the rubbery condition): the Williams-Landel-Ferry (WLF)\(^{(64)}\) principle states an equivalence between mechanical
response times and temperature. The WLF relationship is most useful because it involves only one state variable—temperature. This means that an adequate description of state is afforded by the specification of temperature alone. This simple state description arises from the fact that as far as mechanical properties of sensibly short time scale are concerned, the material is always in configurational equilibrium (in the statistical sense) and further, all other 'variables' of state depend upon the temperature. We have considered here that pressure is not a variable. If pressure may vary then specification of pressure and temperature becomes an adequate description of the material state. The establishment of an equivalence between time and temperature is of theoretical significance and of considerable practical importance. In particular solution of temperature-varying problems is possible and the means for solving problems at one temperature when the mechanical response at another temperature and the equivalence between time and temperature are known are available. Amorphous polymer materials are often practically used in the glassy condition—especially when high strength is a required property. Below the glass transition temperature there is no established principle relating time and temperature nor has been established what is an adequate description of the material state. If above the glass-transition temperature the pressure and temperature are specified then other variables such as volume, enthalpy and entropy of the material are determined. This is not true for
material below the glass transition temperature at least for sensible times. If sufficient time is allowed to expire (for a glassy material) then an equilibrium state characteristic of the temperature and pressure will be reached and again a simple state description may be adequate (193). Because the rate of relaxation of the state variables toward the equilibrium state is very slow however the material may, over a relatively long period, be considered to be in an unchanging or 'frozen' state.

The material above the glass-transition temperature may (as far as sensible time periods are concerned) be considered to be in an equilibrium state - the state is not changing with time. This is to say that if the temperature (or pressure) is changed during some experiment the new state is reached immediately so far as the experiment is affected by the change. Pressures so great as to induce or nearly induce the glass transition must be excepted from the argument (just as temperatures approaching the glass-transition temperature must be). In fact such pressures and temperatures at which the rate of change of configuration becomes apparent in the experiment when incremental changes are made in pressure or temperature may be considered by definition to be glass-transition pressures or temperatures (so far as that particular experiment is concerned).
The glassy material by contrast is not in an equilibrium state so far as the experimental time-scale is concerned. The configurational relaxations accompanying a change in temperature or pressure now occur much more slowly than before. Some state variables may now be observed to be changing with measurable time if one or more of them is changed during or before some experiment. The material cannot now be considered in equilibrium. Any intensive variable may be observed to be changing towards some equilibrium value characteristic of the current values of the extensive variables. Even for sensibly long times equilibrium may not be reached. An adequate description of the mechanical state now will most generally involve specification of the current values of the intensive and extensive state variables and also of their history from some equilibrium state. A most important point now is what restriction may be imposed upon this general specification. If, in the rubbery state, the specification of temperature and pressure alone is a sufficient state description, then there are no other independent state variables. By contrast in the glassy state there may remain a great many specifications of state even when temperature and pressure are specified because there is a lesser degree of dependency amongst the state variables (except for such very long times as when equilibrium is approached). Each different state must be reached from an (equilibrium) rubbery state by a different path in state-variable space.
Some such states may be equivalent so far as the mechanical properties are concerned. This path must necessarily somewhere pass through the region of the glass-transition where large-scale conformational freedom of the polymer main chain is restricted. From the molecular point of view it is this period in the history which is most important in determining the molecular architecture (configuration) and thus the state which subsequently can alter only very slowly. The glass transition itself, whether it is described in terms of the changes in the molecular configurations available or in terms of some state variables, is critical to the change from an easily specified rubbery state to a glassy state. The differing states arising from different cooling programmes are of practical importance since the resulting different states lead to different material mechanical properties.

6.2 Theories of the Glass Transition

6.2a Theory of phase transformations

The glass transition is often considered to be a phase transformation in the conventional sense although there may be some doubt as to whether this is true (see later this section). Gordon(169) has discussed the question of phase transformations in this context. A first-order transformation may normally be observed to occur at a discrete temperature when it is found
that quantities such as the volume $V$ or enthalpy $H$ show a discontinuity in temperature. If the transformation is of second-order then $V$ (say) is continuous through the transformation temperature but the temperature derivative $\partial V/\partial T$ is not. A thermodynamic discussion of such events is more easily made if the system is always in equilibrium (i.e. equilibrium thermodynamics). In thermodynamic equilibrium all physical properties are independent of time. Generally all physical properties and thus the thermodynamic state are fixed if a small number $F$ of the physical properties have fixed values. This may be stated in Gibb's phase rule$^{(170)}$ as

$$F = C - P + 2$$

where $C$ is the number of components and $P$ the number of phases present in the thermodynamic system. The two (2) variables here are temperature and pressure. For a fixed mass of a single polymer $C = P = 1$ and the equilibrium properties are fixed when any two properties are given (say temperature and pressure). Another variable (say the Gibb's free energy $G$) is then a defined function in $(G, P, T)$ space. Similarly the volume $V$ or entropy $S$ are defined functions. The idea of phase transformations may now be defined following Ehrenfest$^{(171)}$. If in the $G$-surface there is a fold then there is by definition a phase transformation of first-order occurring at the temperature and pressure defined by the fold (and $G_{T,P}$ is equal in each phase). $G$ is a continuous function across the fold but $V = (\partial G/\partial P)_T$ and $-S = (\partial G/\partial T)_P$ are not. The first-order
transformation thus shows a discontinuity in first derivatives of G. If the first derivatives of G are continuous but the second derivatives are not, then there is a second-order phase transition according to Ehrenfest. Then V (or S) are continuous functions (of T, P) but their first derivatives are not. Then \( \Delta S = \Delta H = \Delta V = 0 \) and it may be shown (169) that

\[
\Delta \kappa \cdot \Delta c_p / TV \Delta \tilde{\varepsilon} = 1,
\]

which is known as the Ehrenfest equation which is a test for a second-order transformation. Here

\[ \kappa = -1/V(\partial V / \partial P)_T, \quad c_p = (\partial H / \partial T)_P, \quad \alpha = 1/V(\partial V / \partial T)_P. \]

The glass transition is often regarded as being a true second-order phase transformation in the Ehrenfest sense. The question of equilibrium is crucial. Temperley (172) has shown that phase transformations may be considered as a matter of changing structural order (or state) and that a phase transformation involves a change from one type of order to another. The configuration may thus be described by means of one or more ordering parameters. If the behaviour is very simple and equilibrium is maintained all ordering parameters become redundant.

Jones (173) has described the glass transition in the following way. On cooling the liquid there is a progressive increase in the viscosity as the temperature is decreased without any phase separation or crystallization occurring. The transition is arbitrarily
said to have occurred when the viscosity exceeds $10^{13}$ poise. If the temperature of crystallization (a first-order phase transformation) has been passed but the viscosity is less still than $10^{13}$ poise the liquid is supercooled. The supercooled liquid is still then in equilibrium (a metastable one referred to the inherently more stable but non-present crystalline phase) (see text figure 17).

Below the glass transition temperature $T_g$ (defined by the break in the volume-temperature curve) the configuration is not in equilibrium but is largely that frozen out near $T_g$. The volume at temperature $T$
(see text figure 17) will be found to decrease irreversibly and very slowly with time. The material is no longer in equilibrium. The use of the term transformation is then a misnomer. \( T_g \), which should for a true thermodynamic transformation have a fixed value, depends upon the rate of cooling. The configuration frozen-in near \( T_g \) remains approximately unchanged at lower temperatures. We may speak of a 'configurational temperature' or 'fictive temperature' \( T_F \) (Tools 174) at which the actual configuration (at temperature \( T \)) would in fact be an equilibrium one. The use of the term 'second-order phase transformation' to describe the glass transition has come about largely because the variation of the volume or specific heat through the transition resembles that expected for an ideal Ehrenfest second-order transformation. Temperley (172) has discussed the nature of the glass transition. The specific heat \( c_p \) shows a 'smear-out' transition in temperature which is associated with a rapid freezing-in of a particular motional degree of freedom, the time constant changing from a very small value to a very large one as cooling proceeds. It is never possible to associate a definite temperature with this as the interval in which it is observed depends upon the measurement time. The time constant of the freezing-in usually follows a relationship

\[
\tau = A \exp \left( \frac{U}{kt} \right)
\]

where \( U \) is an activation energy. The ordering process
will not take place unless the atomic unit can surmount the energy barrier $U$. The probability of this is proportional to $\exp(-U/kt)$. Here $U$ is usually large compared to $kt$ although the final energy difference on ordering may be small compared to $kt$. During cooling by the time that the overall loss of energy is positive $U/kt$ may be so great that the probability of the event occurring is very small or negligible. The attainment of the thermodynamically most favourable state is thus in practice prevented. Regardless of whether the glass transition is a true Ehrenfest second-order transformation or not several phenomenological theories have been proposed to describe it. The most important of these are the Turnbull-Cohen free volume theory and the Gibbs-diMarzio theory.

6.2b Free-Volume Theories of the Glass-Transition

Turnbull and Cohen(67)(68) have developed a free-volume theory of the glass transition based upon a hard sphere model of a simple fluid. They assume that the major contribution to diffusion comes from molecules jumping into voids having volumes greater than a critical volume $v^*$ and which are formed by redistribution of free volume $v_f$. The redistribution of this free volume requires no energy. The free volume (that part of the specific volume unoccupied by molecules) which requires energy for redistribution $\Delta v_c$ is excepted. The total volume $v$ can then be written
\[ v = v_o + \Delta v_c + v_f. \] The self diffusion constant \( D \) then becomes

\[ D = g u' \int_{v^*}^{\infty} a(v) p(v) dv, \]

here \( g \) is a geometric factor \( 1/6 \), \( u' \) is the gas kinetic velocity, \( a(v) \) is the diffusive displacement, \( p(v) dv \) is the probability that the volume per mole lies between \( v \) and \( v+dv \). It is assumed that

\[ p(v) = \left( \frac{\gamma}{v_f} \right) \exp \left( -\gamma \frac{v}{v_f} \right) \]

where \( \gamma \) is a numerical overlap factor (\( \frac{1}{2} \) to 1) and \( v_f \) is the free volume per mole. If \( a(v) \) is taken as \( a^* \) (the molecular diameter) then

\[ D = g a^* u' \exp \left( -\gamma a^*/v_f \right) \]

which is similar to the Doolittle formula for viscosity (62) if \( D \propto 1/\eta \) where \( \eta \) is the viscosity: the free volume \( v_f \) can be taken as

\[ v_f = \alpha_m \bar{v} m (T-T_m) - \beta_m \bar{v} P, \quad T > T_m \]

and \( v_f = 0 \quad T \leq T_m \]

where \( \alpha_m \) and \( \bar{v} m \) respectively are the mean coefficients of thermal expansion and molar volume from \( T_m \) to \( T \) at zero pressure, \( T_m \) is a reference temperature where \( v_f = 0 \), \( \beta_m \) and \( \bar{v} P \) are respectively the mean compressibility and molar volume from \( P = 0 \) to \( P = P \).

The free volume fraction \( f \) can then be interpreted as
\[ f = \frac{v_f}{Yv^*} \]

If the relaxation time \( \tau \) is assumed inversely proportional to \( D \) then

\[ \tau = \tau_o \exp \left( \frac{B}{T - T_o} \right) \]

and \( \tau \rightarrow \infty \) as \( T \rightarrow T_o \), a temperature at which equilibrium is unattainable at less than infinite time.

It may be shown that at temperatures in the glass transition region all relaxing quantities (volume, for example) become dependent upon cooling rate and will deviate from the equilibrium values.

McCrum et al. (11) have noted that free volume has been given no unique or rigorous definition in the statistical thermodynamic theories of the liquid state. The Doolittle definition (62) (63) is

\[ v_f = v - v_o \]

where \( v_f \) is the free volume, \( v \) the total volume and \( v_o \) the value of \( v \) extrapolated to \( 0^\circ \)K. Thus \( v_f \) is zero at \( T \) zero. The Cohen-Turnbull free volume by contrast is zero at \( T_o \), a temperature above zero.

The free volume however defined is a time-average quantity and is supposed continually redistributed throughout the liquid with random thermal molecular motion. The essence of the free volume theories of the glass transition is that the molecular mobility and thus the relaxation properties at any temperature are dominated by the free volume. The easy redistribution of free volume thus seems to imply a high degree of molecular mobility of some kind.
The Doolittle empirical expression, originally intended to describe the viscosity behaviour of low molecular weight hydrocarbon liquids is

$$\eta = a \exp (b/f),$$

here a and b are constants and $f = v_f/v_o$ the fractional free volume which is a function of temperature and pressure.

The Williams-Landel-Ferry\(^{(64)}\) empirical relation for the temperature dependence of the relaxation times near and above the glass transition temperature is

$$\log \alpha_T = \log \left( \frac{\tau(T)}{\tau(T_o)} \right) = -C_1 \left( T - T_o \right) / \left( C_2^G + (T - T_o) \right),$$

here $T_o$ is an arbitrary reference temperature, $C_1$ and $C_2$ are material constants and $\tau(T)$ is an average relaxation time at temperature $T$. The range of applicability is generally taken to be $T_g < T < T_g + 100^\circ K$.

If the reference temperature $T_o$ is taken to be the (dilatometric) glass transition temperature $T_g$ then $C_1^G$ and $C_2^G$ in

$$\log \alpha_T = -C_1^G (T - T_g) / \left( C_2^G + (T - T_g) \right),$$

take the 'universal' values 17.44 and 51.6$^\circ K$. It is known that these 'universal' values vary somewhat from polymer to polymer. The WLF relation may be derived from the Doolittle relation in the following way:

$$\log \alpha_T = \frac{\log \alpha(T)}{\log \alpha(T_g)} = \log \frac{\eta(T)}{\eta(T_g)} = \frac{b}{2.303} \left( \frac{1}{f(T)} - \frac{1}{f(T_g)} \right)$$
if it is further assumed that

\[ f(T) = f(T_g) + \alpha f(T - T_g) \]

where \( \alpha f \) is a 'thermal coefficient of expansion of free volume' then

\[ \log \alpha_T = \frac{-b/2.303f(T_g)(T - T_g)}{f(T_g)/\alpha f + (T - T_g)} \]

and using the 'universal' values of \( C_1^f \) and \( C_2^f \) and choosing \( b = 1 \)

\[ \alpha f = 4.8 \times 10^{-4} \text{oK}^{-1} \]

and \( f(T_g) = 0.025 \)

This is in accord with the Fox and Flory (176) idea that the glass transition is an iso-free-volume state, that is here occurring for all polymers when \( f(T_g) = 0.025 \).

Bueche (65)(66)(175) has, using arguments similar to those of Turnbull and Cohen, arrived at very similar conclusions about the diffusion constant as related to free volume. He considers in detail the distribution of 'packets' of free volume of different sizes, assuming that they all have a constant specific surface energy and he also considers the possibility of co-operative aggregation of such packets.

Saito et.al. (14) have considered the manner in which free-volume is 'frozen' into a material cooling at a fixed rate from the liquid regime. If the volume is
followed as a function of temperature during such cooling the behaviour may be approximated by two straight lines intersecting at $T_g$ (definition of $T_g$). The volume-temperature relation is really curved in this region and begins to deviate from the liquid line at $T_g^+$ and from the glass line at $T_g^-$. (see text figure 18).

Cooling at differing constant rates of cooling $\sigma = dT/dt$ will result in different values for $T_g$. If cooling is stopped within the glassy region close to $T_g$ a time-dependent isothermal volume contraction occurs which, in a given time, is greater the higher the temperature is. (see text figure 19).
The rate of isothermal volume contraction below the glass transition is normally extremely slow.
Extrapolations of the measurements made on poly (methyl methacrylate) by Rusch(13) would indicate that the equilibrium volume of a sample quenched from $398^\circ$K to $304^\circ$K would be reached in $10^{53}$ s and 80 per cent completed at $10^{42}$ s. At $334^\circ$K these times would be $10^{29}$ and $10^{23}$ s respectively. Even at $363.3^\circ$K ($T_g$ is $378^\circ$K) complete relaxation would take $1.7 \times 10^9$ s or about 56 years. At $363.3^\circ$K 80 per cent of the volume relaxation would be complete in 58 days. The course of volume relaxation for temperatures less than
about 350°K appears to be linear in log (time). The transition as seen in this way is dominated by the volume relaxation. Although it is known that the volume does not relax (for a small temperature decrease) in a simple exponential fashion with time this is a good approximation to the behaviour.

If \( \delta T = T - T_0 \), and \( \delta v = v - v_0 \) are deviations in temperature and volume from some reference state \( (T_0, v_0) \) the course of volume contraction may be written as

\[
\delta T = \left(\frac{1}{\Delta a}\right) \delta v + \left(\frac{\tau}{\Delta a}\right) (d\delta v/dt)
\]

in the manner of a Voigt model with magnitude \( \Delta a \) and relaxation time \( \tau \). Or

\[
d\delta v/dt = (\delta v - \Delta a \delta T/\tau)
\]

If a constant rate of cooling \( \sigma \) is prescribed then

\[
d\delta v/dt = (-\delta v - \Delta a \delta T/\sigma) = d\delta T/dt
\]

The response is in fact non-linear because \( \tau \) (see sect.6.2a) is a strong function of \( T \). \( \Delta a \) may also vary with \( T \). The bend in the volume-temperature curve is a result of this non-linearity in volume contraction.

If a temperature dependence of \( \tau \) upon \( T \) is assumed then a quantitative solution may be found: Spencer\(^{(177)}\) Volkenstein and Pfitsyn\(^{(178)}\). (A spectrum
of relaxation times should in fact be considered). If the specific free volume \( f \) is used then the equations become

\[
\delta f = f - \bar{f}_o
\]

and

\[
\delta T = \left( \frac{1}{\alpha_f} \right) \delta f + \left( \tau/\alpha_f \right) \left( \frac{d\delta f}{dt} \right)
\]

with previous definitions and \( \bar{f}_o \) is the equilibrium (super-bar) value of \( f \) at \( T_o \). In terms of the Turnbull-Cohen theory \( f \) is \( v_f/v^* \). If \( \tau \) is taken as \( \tau = \tau_o e^{1/f} \), the cooling rate \( \sigma \) is constant, and \( \bar{f} = \bar{f}_o + \alpha_f (T-T_o) \)

\[
\frac{df}{d\bar{f}} = -\left( f - \bar{f}_o \right) / \left( \alpha_f \sigma \tau_o e^{1/f} \right)
\]

and a numerical integration may be performed. Saito et al. have performed the integration with \( \alpha_f = 4.8 \times 10^{-4} \), \( \tau_o = 10^{-13} \text{ s} \), and the results for cooling (\( \sigma = 10^{-3}, 10^{-5} \)) and heating (\( \sigma = 10^{-5} \)) are shown in text figure 20.
Similar curves are given by Rusch\(^{179}\) for his effective temperature (see sect. 6.3f) as a function of time during isothermal contraction. These are derived from experimental measurements of \(\log \alpha_T\).

Wherever \(\bar{f} \neq f\) the material is not in equilibrium (this is seen to be true everywhere below \(T_g^+\) as previously defined). There is a marked hysteresis in volume upon reheating. The free volume of \(f(T_g^+)\) at the point of departure \(T_g^+\) is mostly retained for all lower temperatures. The departure of \(f\) from \(\bar{f}\) which defines \(T_g^+\) may be expressed as

\[
f(T_g^+) = 1/(2.303 \log_{10} 10^{13}/\sigma)
\]

\[
T_g^+ = T_o + (\bar{f}(T_g^+) - f(T_o))/(4.8 \times 10^{-4})
\]

and is given in text figure 21,
an arbitrary zero value for \( T_g^+ \) is taken when \( \sigma = 10^{-5} \text{ oKs}^{-1} \). The practically attainable range of cooling rates is seen to be less than that depicted. The range of \( f(T_g^+) \) is also depicted.

At high temperatures

\[
f = \tilde{f} = f_o^- + \alpha_T (T - T_o)
\]

and a WLF type of behaviour will be found for the shift factor. At temperatures below \( T_g^+ \) \( f \) deviates from \( f \) (and \( \tau \) deviates from the equilibrium \( \tau \) ) and the WLF relation is no longer followed. The apparent activation energy \( \Delta H_a = Rd \ln \alpha_T /d (1/T) \) thus rises as temperature is reduced towards \( T_g^+ \), there reaches a maximum and then decreases again as has been observed for poly (methyl methacrylate) in creep studies by Bueche\(^{(130)}\).

Expressions similar to those of Saito et.al., related to the kinetics of the glass transition have been derived by Wunderlich et.al.\(^{(180)}\) on the basis of a 'hole' model of free volume. The specific heat as a function of temperature was derived for programmes of constant rate of change of temperature for various starting points in the (non-equilibrium) glassy and equilibrium (rubbery) states. Experimental measurements on poly (styrene) which supported the theory were reported.
Gibbs and di Marzio\textsuperscript{(148)(181)} have developed a theory of the glass transition which is based upon two fundamental assumptions. They are that the stiffness of the polymer chain backbone to rotation around single chemical bonds and the thermal expansion behaviour at the transition are crucial to any physical model of the transition. The chain stiffness is treated as the energy difference between that of two iso-energy less-favoured orientations (of a carbon atom–carbon atom bond with respect to an immediate neighbour bond in the backbone) and that of one lowest energy favoured orientation. When the stiffness is large the polymer has a high glass transition temperature, when it is not a low glass transition temperature. The thermal expansion behaviour is treated as due to the presence of 'holes' rather as in the free volume theories. The number of 'holes' is a function of temperature. The quasi-lattice model of Flory\textsuperscript{(182)(183)} and Huggins\textsuperscript{(184)} is used. Each molecular unit and each hole is then considered to occupy a single site upon the quasi-lattice. A complete specification of the occupancy then specifies the 'configuration' or whole arrangement of molecules and holes. \( n_x \) chains each of \( x \) molecular units are considered. Each chain then has a finite number of possible spatial conformations on the quasi-lattice. Conformations which include many 'flexed' bonds (i.e. adjacent bonds in the high energy rotational
position) will not be favoured. Moreover there must be a high degree of co-operation in the manner in which different chains occupy the lattice sites. Each site may be occupied only once.

The problem is formulated in statistical mechanical terms in order to find an overall partition function for the chains and holes. An equilibrium configuration may then be sought by allowing the Gibbs free energy to seek a minimum. The constituent \( \times n_x \) molecules and \( n_o \) holes must occupy sites in the \( N_o = \times n_x + n_o \) available on the quasi-lattice. A crucial parameter in the theory is \( \mathbb{P}_T \) the number of possible configurations at temperature \( T \). \( \mathbb{P}_T \) is found to have a minimum value of 1 at a temperature called \( T_2 \) by Gibbs and di Marzio. At this temperature the configurational entropy is zero. The properties of the thermodynamic variables derived from the model show this to be the temperature of a true second-order transition in the Ehrenfest sense.

Some approximations made at this stage for the purposes of numerical evaluation of the theory are that there are only two different energies of orientation of the chemical bonds in the chain backbone - differing by \( \Delta \varepsilon \) (the flex energy) and that there is no co-operation between adjacent chains. The hole energy is taken at \( E_o \), constant with temperature.

As the temperature is decreased towards \( T_2 \), less of the chain bonds take flexed (or high energy) positions and \( n_o \) the number of holes decreases to a small value. Because of the need for co-operative motions of adjacent
chains and the decreasing number of free lattice sites the probability of the configuration being rearranged rapidly decreases as $T_2$ is approached and in fact becomes zero ($\mathcal{P} = 1$) at $T_2$. The expectancy of a rearrangement of configuration in response to external stimuli is very small just above $T_2$, the configuration is, however, effectively 'frozen' whenever the rate of rearrangement cannot accommodate the external stimulus. The observed 'freezing' (or glass transition) as observed may thus occur well above $T_2$. The observed $T_g$ owes its fact to the presence of the underlying $T_2$ and the theory thus has a basis in equilibrium thermodynamics although true quantitative predictions about $T_g$ cannot be made.

The theory has been checked against much experimental data for polystyrene (185). The flex energy $\Delta \varepsilon$ is taken to make $T_g$ coincide with the measured $T_g$ and $E_o$ is chosen so that the difference between glassy and rubbery expansivity agrees with the experimental data. Predictions may then be made about the variation of glass-transition temperature with molecular weight, plastication, and co-polymerization and about the variation of total volume with temperature. Not only do the values of $\Delta \varepsilon$ and $E_o$ seem reasonable but the other predictions agree well with experimental data. The theory thus seems to explain many things well including
some not explained by the free volume theories.

It may be noted that the concept of free volume is, through the inclusion of the 'hole' concept, implicit in this treatment. Further the prediction of a temperature \( T_2 \) at which the configuration is completely 'frozen' is in accord with that of some free volume theories (notably the WLF theory where relaxation times go to infinity (in prediction) at \( (T_g - C_2)^0 K \), normally 550 K below \( T_g \)).

Adam and Gibbs (161) have further extended the theory to explain the temperature dependence of the behaviour of glass-forming liquids in terms of the temperature variation of the size of co-operating regions.

The results for relaxation times practically co-incide with the production of the WLF relation. Another prediction of their extension of the theory is that \( T_g / T_2 = 1.30 \pm 8.4% \) if data for fifteen substances are considered which leads to the prediction that \( T_g / T_2 \) should be constant.

The Gibbs-di Marzio theory does not require that \( T_g \) is found at an iso-free volume state, or that free volume is zero, but only that the configurational rearrangements become catastrophically slow when referred to the experiment period.

6.3 Non-Equilibrium States in Glasses

We now proceed to discuss the literature concerning non-equilibrium glassy states and the possible restrictions upon the general specification of state outlined in 6.1
6.3a Davies and Jones

Davies and Jones (186), Davies (187) and Jones (173) have considered the question of the specification of the thermodynamic state of glasses. Davies (187) treats a system described by $n$ ordering parameter $z^r$ which are added to the $y$ ordinary independent and controllable thermodynamic variables $x^\alpha$. The idea of ordering variables is due to de Donder (188), Frenckel (189), Prigogine and Defay (190) and Meixner (191). The forces conjugate to the thermodynamic co-ordinates are $X^\alpha$ and the affinities conjugate to the ordering parameters $A^r$. For displacements in the co-ordinates and parameters, the change in free energy $G$ is given by

$$-dG = X^\alpha dx^\alpha + A^r dz^r,$$

summation is indicated. In equilibrium $dx^\alpha = 0$ and since $G$ is at a minimum $A^r = 0$. This equilibrium may then be considered a reference state with $X^\alpha$, $x^\alpha$ and $z^r$ zero. For small departures from this equilibrium, it is assumed that linear relationships may be used to relate $X^\alpha$ and $A^r$ to the independent variables:

$$X^\alpha = c_{\alpha \beta} x^\beta + \lambda_{\alpha s} z^S$$

$$A^r = \lambda_{r \beta} x^\beta + \beta_{rs} z^S$$

Here $c_{\alpha \beta}$ are the 'glassy' moduli, $\lambda_{\alpha r}$, the 'reaction coefficients' give the change in 'force' per unit change in the ordering variables. The $\beta_{rs}$, the 'ordering coefficients' give a measure of the forces restoring equilibrium for displacements in the ordering parameters $z$. 

As a first approximation (186) it may be considered that one ordering parameter \( z \) is sufficient. The deviation of this parameter from its equilibrium value for given temperature and pressure then describes the deviation of the state from an equilibrium one. The idea of equilibrium being valid arises from the fact that if the temperature of equilibrium is approached either from above or from below (small displacements), then the volume relaxes towards the same value. The ordering parameter must do likewise and hence \( (\partial G/\partial z)_{P,T} = 0 \) must be an equilibrium condition. The changes in \( z \) and its relationship to Tool's (174) fictive temperature are illustrated by reference to text figure 22.

\[ AB \text{ is the equilibrium volume-temperature curve. At } D, C, W (\text{temperatures } T_1, T_2, T_3) \text{ the degree of order is } z_{T_1}, z_{T_2}, z_{T_3}. \text{ In a cooling experiment of finite time} \]
scale the volume may depart towards N or for a faster time scale towards R. Q, M and W represent glassy states of the system having degrees of order $z_T$, $z_{T_2}$ and $z_{T_3}$ respectively (or fictive temperatures $T_1$, $T_2$, $T_3$) and real temperature $T_r$.

Davies (187) has shown that if one parameter is adequate to describe a liquid-glass system, then it may be shown that the Ehrenfest equation

$$\Delta c_p \Delta \kappa = TV(\Delta \kappa)^2$$

must hold. Davies and Jones (186)(187)(173) show by producing experimental data that it does not. They conclude that a one-parameter description is not adequate.

6.3b Goldstein

Goldstein (192)(193)(194) has discussed the validity of one-parameter theories at length. If, in a linear relaxing system, the relaxation is exponential then the system may be adequately described by one relaxation time. If the relaxation is found to be non-exponential it may always be described by a distribution of (simple) relaxation times. (There are, however, some single relaxation processes which give rise to a non-exponential relaxation). Thus asserting the presence of a spectrum of relaxation times merely means the relaxation is non-exponential, without implying anything about molecular properties. If a spectrum has been found necessary in
order to describe the relaxation and a series of specimens are all brought to a given strain $\varepsilon$ at time zero by means of different stress-time histories, then all will subsequently relax to strain zero differently (if the stress is removed at time zero). The number of parameters needed to describe the subsequent relaxation is equal to the number of relaxation times in the spectrum.

To the extent that the relaxation of the extensive thermodynamic variables volume ($V$) and enthalpy ($H$) to new equilibrium values after a change in pressure ($P$) or temperature ($T$) is linear the same conclusion may be reached. In practice the responses are found to be markedly non-linear and then the concept of the spectrum of relaxation times becomes dubious but the question of whether one parameter will be a sufficient description or not is capable of an operational definition.

In practice where the relaxations are looked at carefully, the description in terms of a distribution of relaxation times is usually found to be necessary. This has been found to be so for polymer glasses, Kovacs (195), zinc chloride, Goldstein and Koneczynj (196), and for silicate glasses, Ritland (197), Spinner and Napolitano (198). The one-parameter theories of Tool (174), Ritland (197) and Kovacs (199) thus cannot generally be valid as they imply exponential relaxation.

The Ehrenfest equation for a second-order transition may be written

$$\frac{dT_2}{dP} = \frac{\Delta a}{\Delta \varepsilon} = TV \frac{\Delta \varepsilon}{\Delta c_p},$$

the experimental evidence shows that it is not generally
obeyed. In fact the inequality

$$\frac{\Delta \beta}{\Delta \alpha} > TV \Delta \omega / \Delta c_p,$$

is usually obeyed showing (186) that a one-parameter
description is inadequate. The thermodynamic variables
V, S, H may be replaced by their excess functions
(that is, the difference of H(T), etc. from the equilibrium
value of H(T), etc.). The excess functions are
$$V_e = V_e(z), S_e = S_e(z), H_e = H_e(z)$$
where z = z(P,T)
is a (possible) single ordering variable. Obviously
z is redundant and,

$$H_e = H_e(V_e), S_e = S_e(V_e), V_e = V_e(P,T).$$

The application of the Ehrenfest equation implies both
that the transition may be described in terms of the
excess thermodynamic function of one parameter and that
the transition occurs when this function takes a
critical value. Goldstein then shows that

$$\frac{dT_g}{dP} = \frac{\Delta \beta}{\Delta \alpha} \text{ if } V_e \text{ determines } T_g,$$
$$\frac{dT_g}{dP} = TV \Delta \omega / \Delta c_p \text{ if } S_e \text{ determines } T_g,$$
$$\frac{dT_g}{dP} = TV \Delta \omega / \Delta c_p \text{ if } H_e \text{ determines } T_g.$$

Since experimentally it is found that
$$\frac{dT_g}{dP} = \frac{\Delta \beta}{\Delta \alpha} \text{ (186)}$$
it is concluded that the free volume theory although
very successful on an empirical basis, is incorrect.
O'Reilly (200) has tabulated $dT_g / dP$ and $T_g V \Delta \omega / \Delta c_p$
for ten glass-forming substances to show good agreement. Thus \( \Delta \beta / \Delta \alpha = T_g V \Delta \omega / \Delta \omega_p \) for few substances but \( dT_g/dP = T_g V \Delta \omega / \Delta \omega_p \) for a larger (but different) group of substances. Only natural rubber is found to obey \( dT_g/dP = \Delta \beta / \Delta \alpha = T_g V \Delta \omega / \Delta \omega_p \). There is thus strong support for an entropy theory such as that of Gibbs\(^{(181)}\) or an enthalpy theory. The volume theories do not explain the influence of pressure upon the glass transition satisfactorily.

Goldstein presents evidence for an enthalpy theory of the glass transition and derives the following equations in the spirit of the Doolittle and WLF relations:

\[
\eta = A \exp \left( \frac{B}{H_e} \right)
\]

\[
H_e = 140 + c_p (T - T_g) - TV \Delta \omega P
\]

\[
B = 5.5 \times 10^3,
\]

which recovers the WLF equation with the same numerical values, and is so just as applicable. The 140 cal/mol is the 'excess enthalpy' corresponding to \( f(T_g) = 0.025 \) in the WLF treatment.

The WLF treatment of free volume has been shown not to be adequate for some inorganic glasses where the viscosity-temperature relation is better described by the Eyring\(^{(201)}\) expression with constant activation energy. In the Eyring treatment the viscosity depends upon temperature in two ways: partly because the number of holes (free volume) increases with temperature and partly because the number of molecules having sufficient energy to
overcome barriers resisting movement into holes increases with temperature. In the WLF treatment, the second of these is neglected. It is apparent that in experiments where the temperature is changed and the liquid is in equilibrium that no separation of the relative importance of free volume and temperature is possible. Only in non-equilibrium regions or experiments where the pressure is changed would the free volume theories show error. Two recent treatments permit the direct role of both a 'structural parameter' and temperature. They are those of Adam and Gibbs (161) (in which the 'structural parameter' is the product of temperature and configurational entropy) and of Macedo and Litovitz (202) (in which an activation energy term is added to the free volume term and which thus derives from Eyring). The question of the adequacy of a specification of state may be posed in various ways: "is the equilibrium state uniquely determined by V or not?"; "in quasi-equilibrium states are changes in H or S uniquely determined by changes in V no matter what the (P,T) history is?". Goldstein points out that "the number of parameters we will need may depend upon the property we are studying". This is a consequence of the practical limitations of both experiment and theory. If a system at fixed pressure is considered specification of temperature alone will define an equilibrium state. We may now ask whether or not all of the variables in a non-equilibrium state reached during a relaxation
process are functions of only one additional thermodynamic variable. It is not assumed that this state can be reached by any reversible process. If now such a volume relaxation requires a spectrum for description then at any instant during the relaxation it is implied that the instantaneous value of the volume is not sufficient to specify its future time dependence. Thus we may say that the instantaneous value of volume will not uniquely determine the instantaneous value of enthalpy. We must ask "for some instantaneous value of the volume does the instantaneous value of the enthalpy reflect the prior thermal history?"

The papers of Goldstein are 'open-ended' in nature. He has re-posed the problem in order that a more indirect answer may be sought.

6.3c O'Reilly

O'Reilly(203) has demonstrated that the existence of densification (as observed to exist for poly (methyl methacrylate by Shiskin(204)) implies that

$$\frac{\partial T}{\partial P} < \frac{\Delta \beta}{\Delta \alpha},$$

which in turn means that a free volume theory is not
suitable (194). Densification means that

\[ V(P_2, T_2) < V(P_1, T_1) \]

where \( V(P_2, T_2) \) and \( V(P_1, T_1) \) are volumes lying on the vitrification line and \( T_2 > T_1, P_2 > P_1 \).

### 6.3d Goldbach and Rehage

Goldbach, Breuer and Rehage (205-209) have examined their data on the behaviour of the volume of poly (styrene) when subjected to step-function programmes of pressure and temperature in order to see whether or not the retardation is linear, and whether or not a single ordering variable may be used to describe the behaviour. In references (205)(206)(208) the data from the experiments is presented. It is stated that a linear region of behaviour exists for the volume changes caused by both temperature and pressure changes. A spectrum of relaxation times is needed to describe the behaviour. This spectrum appears to be different for small pressure changes than for small temperature changes. In (207) and (209) the question of whether the glass transition may be considered as a transition in the formal thermodynamic sense is discussed. The Ehrenfest equation is shown not to hold because the thermodynamic properties frozen in the glassy state depend not only on temperature and pressure but upon their history as well. Thus more than two degrees of freedom exist in the thermodynamic sense. The dependence of the
state upon history could be described using configurational parameters. It was deduced that merely measurement of the variables of state would not enable a decision to be made as to whether the glass transition could be adequately described by one configurational parameter or several. The experimental evidence obtained for poly (styrene) was interpreted to show that in general several independent configurational parameters would have to be used.

6.3e Sharonov and Volkenshtein

Sharonov and Volkenshtein (210)(211) have made calorimetric measurements of the approach of the enthalpy to equilibrium \( (H \rightarrow H_e) \) for step changes in temperature both above and below the glass-transition temperature for poly (styrene) and poly (vinyl acetate). The relaxation time (at constant temperature) is an exponential function of the deviation of enthalpy from equilibrium \( (H - H_e) \). At temperatures below \( T_g \) the relaxation time increases as equilibrium is approached. At temperatures above \( T_g \), the relaxation time decreases as equilibrium is approached. The prior history does not affect the form of dependence of the relaxation time upon \( (H - H_e) \) but does affect the equation parameters. The behaviour could not be accounted for by a spectrum
of relaxation times alone. A single ordering parameter was insufficient, the mean relaxation time was found to depend upon the sample history. It was concluded that at least two internal parameters were needed to describe the behaviour adequately.

6.3f Rusch

K. C. Rusch(13) has proposed that the WLF relation\(^{(64)}\) may be modified to describe behaviour in the glassy region. The temperature \(T\) in the WLF equation is replaced by an 'effective temperature' \(T_e\) which is related to the 'frozen' free volume in the glass. \(T_e = T\) for a glass in equilibrium. The value of \(\log \alpha_T\) calculated from the modified formula (with \(T_e\) obtained from volumetric measurements) for both poly (styrene) and poly (methyl methacrylate) was shown to be in good agreement with measured values of \(\log \alpha_T\) from relaxation experiments.

There is an important disposable parameter in the theory \((\Delta \alpha)\). As it is experimentally impossible to obtain an equilibrium volume further than 15 or 200\(^\circ\)K below \(T_g\), a parameter (here \(T_e\)) must be found to describe adequately the non-equilibrium state of the glass. In this theory it is assumed that relaxation mechanisms are controlled primarily by free volume and the relaxation
times for the non-equilibrium glass are a direct function of the free volume $V_f$. The (specific) free volume $V_f$ is considered to comprise a part $v_f$ which is equilibrium in nature:

$$v_f = (T - T_e) \Delta \alpha_f,$$

here $T_e$ is the temperature (Gibbs-di Marzio transition temperature) at which the equilibrium free volume is zero, and $\Delta \alpha_f$ is the difference in the coefficients of expansion of (equilibrium) liquid and equilibrium glass over the range of temperatures concerned. See text figure 23.
The modified WLF equation may now be written

\[
\log \alpha_T = \frac{-C_1}{C_2} \frac{(T_e - T_0)}{(T_e - T_0)}
\]

(if \(w_f(T_o) = 0\), i.e., \(T_o > T_g\)), here \(T_g\) is the reference temperature, \(C_1, C_2\) are the conventional WLF constants. The effective temperature is then determined by the total free volume:

\[
T_e = T + \frac{w_f(T)}{\Delta \alpha_f} \quad T \geq T_2
\]

\[
T_e = T_2 + \frac{w_f(T)}{\Delta \alpha_f} \quad T \leq T_2
\]

For \(T > T_g\) the effective temperature \(T_e\) equals the actual temperature \(T\) and the conventional WLF equation holds. At any lower temperature, \(T_e\) will depend upon \(w_f\), that is upon the actual volume of the glass. It may be seen then that regardless of whether or not the free volume concept is the correct one to use, the theory amounts to a one-parameter (volume) description of all non-equilibrium glassy states.

It is implied, of course, that temperature (and pressure) are also specified. The effective temperature \(T_e\) has the meaning of a temperature where the equilibrium volume would equal the actual volume at temperature \(T\),

\[
\text{i.e., } w_f(T) + v_f(T) = v_f(T_e).
\]

It is thus inferred that the relaxational behaviour of the non-equilibrium glass at \(T\) is identical to that of a corresponding equilibrium glass at \(T_e\). The definition
of $T_e$ is thus similar to that of Tool$^{(174)}$ for his 'fictive temperature'.

The disposable parameter in the theory is \( \Delta \alpha_T \).

The use of this implies i) that $\nu_f$ is a linear function of temperature above $T_2$ and ii) that there exists a linear equilibrium glass volume-temperature relation for temperatures both above and below $T_2$.

These suppositions cannot really be challenged because measurements cannot be made lower than about $T_g - 15^\circ K$ in order to justify them. It remains that the correct and arbitrary choice of $\Delta \alpha_T$ which causes the experimental and theoretical $\log \alpha_T$ values to fit best seems to be a reasonable one and that the agreement is good and quite sensitive to the value of $\Delta \alpha_T$ chosen. It may be noted that interpretation aside, the choice of an appropriate $T_2$ and $\Delta \alpha_T$ after $T_g$ and $\alpha_1$ the liquid expansivity are determined enables a good if entirely empirical fit to be obtained. This, of course, is the strength of the WLF relation itself.

The WLF equation predicts that $\alpha_T$ approaches infinity as $T$ approaches $T_2 = T_o - C_2$. This is valid only for a system in equilibrium and the parameters $C_1$, $C_2$ determined above $T_o$ may thus be used to estimate $T_2$.

In fact, $\alpha_T$ does not approach infinity as $T_2$ is approached because the glass is never in equilibrium, i.e., $V_f > V_f$. Rusch's equations predict that $\log \alpha_T$ for the equilibrium glass tends to a constant value
for temperatures below $T_2$ and thus avoids this major drawback in the unmodified WLF equation.

**Summary**

For non-equilibrium glasses a sufficient description of 'state' (in the present sense) is lacking. It seems that there is most unlikely to be an adequate single-parameter description. The question of how many of the conventional thermodynamic parameters are related and how many additional parameters would be needed is not resolved. When the single-parameter free volume theories are checked for non-equilibrium cases, or where pressure is a variable, they are found wanting. Apart from theoretical considerations, it may be true that there is some empirical relationship which would enable the WLF equation to be usefully modified for use below $T_2$ and would provide useful qualitative (or possibly quantitative) predictions to be made.
7. TECHNIQUE AND RESULTS OF PRESENT INVESTIGATION

We proceed in this chapter to describe the experimental techniques used (7A) and the results found (7B) in this investigation.

7A. EXPERIMENTAL TECHNIQUES

7.1 Specimen Preparation

The material investigated here is conventional I.C.I. (Imperial Chemical Industries) 'Perspex' (poly (methyl methacrylate)) cast rod stock of nominal diameter 19mm. Specimens of dimensions 0.375 ± 0.001in. length and 0.250 ± 0.001in. diameter were turned axis-on-axis from the centre of the rod. To remove internal stress (caused by machining) and moisture, the specimens were preconditioned by heating for two hours at 413°K while immersed in glycerol. This programme was sufficient to remove the naturally absorbed water (about 1% by weight) quickly without degradation of the polymer. The samples were then subjected to one of two controlled cooling programmes. This involved either quenching from 413°K into ice-water (specimens later designated MR) or cooling naturally in a covered one-quart thermos flask to about 310°K (designated PR). The specimens
were then removed from the bath and stored over phosphorus pentoxide under an air pressure of about $10^{-3}$ atm. until tested this preventing further water pick-up. Initially four cooling programmes were investigated: quenching in ice-water (MR), air-cooling, free-air cooling in glycerol in a 500ml beaker and thermos cooling in glycerol (PR) in each case from $413^\circ$K. The temperature-time profiles recorded by a 32swg copper-constantan thermocouple placed at the centre of a dummy sample for each of these programmes together with the cooling rates near the glass transition temperature are shown in fig 10.4. The cooling rates at the glass-transition temperature of the polymer ($380^\circ$K) for the two cooling rates used were $1.0 \times 10^{-3}$ Ks$^{-1}$ (PR) and $7.4 \times 10^{-1}$ Ks$^{-1}$ (MR).

7.2 Material Characterization

a. Molecular weight-viscosity method

The viscosity-average molecular weight$^{(139)}$ was measured on turnings taken from a pre-conditioned sample in chloroform solution at $298^\circ$K. Fig 10.5 shows the intrinsic viscosity (at zero concentration) $[\eta]$ to be 4.60ml/g (4.25ml/g by the approximate method$^{(155)}$). This leads to the following values for $\bar{M}_\eta$ (table 7.1).
Viscosity Average Molecular Weight

<table>
<thead>
<tr>
<th>Reference</th>
<th>Mark-Houwink Formula</th>
<th>Full Method</th>
<th>Approximate Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chinai et al. (156)</td>
<td>([\eta] = 3.4 \times 10^{-3} M^{-0.83})</td>
<td>1.45 \times 10^6</td>
<td>1.38 \times 10^6</td>
</tr>
<tr>
<td>Bischoff et al. (157)</td>
<td>([\eta] = 4.8 \times 10^{-3} M^{-0.80})</td>
<td>1.62 \times 10^6</td>
<td>1.52 \times 10^6</td>
</tr>
<tr>
<td>Moore et al. (158)</td>
<td>([\eta] = 5.8 \times 10^{-3} M^{-0.79})</td>
<td>1.53 \times 10^6</td>
<td>1.46 \times 10^6</td>
</tr>
</tbody>
</table>

The method is expected to be not more accurate than \(\pm 5\%\) and maybe only \(\pm 20\%\) (155). The value obtained \(\sim 1.5 \times 10^6\) seems in quite reasonable agreement with Thompson (126) and Bueche (130) when the glass transition temperature is considered also. (see table 5.1 and 5.2, sects. 5.5 and 7.2b). Further details are given in 10.9.

b. Glass transition temperature-dilatometric

As part of the results of a linear expansivity experiment (see 7.13), it was found that a sudden softening of the sample (under a stress of 0.14 MNm\(^{-2}\)) occurred at 380\(^0\)K when the rate of sample heating was \(\sim 2.5 \times 10^{-3}\) K s\(^{-1}\). The softening was indicated by a sudden decrease in the length of the sample while sustaining the uniaxial compressive stress. As the sensitivity of the apparatus was equivalent to a strain of about \(2 \times 10^{-5}\) and the observed strain was about \(3 \times 10^{-4}\) the fall constituted a positive indication of the dilatometric transition.
c. Tacticity - nuclear magnetic resonance

The tactility triad analysis by the method of Bovey and Tiers (151) was performed on a Nuclear Magnetic Resonance (NMR) spectrogram run on a Varian A60 spectrometer. About 50mg of polymer taken from a conditioned sample was dissolved in deuterated chloroform (CDCl₃) for this purpose. The appropriate peaks were observed at 8.86τ (isotactic), 9.09τ (syndiotactic) and 8.95τ (heterotactic). The values given by Bovey and Tiers loc. cit. were 8.78, 9.09 and 8.95τ respectively and by Thompson (126) 8.85, 9.15 and 9.00τ. The component peaks were found by fitting three normal curves (having mean values at 8.86, 9.09 and 8.95τ) so that their sum approximated the recorded spectrum. The three peak areas were then found graphically. The resulting analysis was then

- isotactic 12.7%
- heterotactic 37.2%
- syndiotactic 50.1%

which is typical of the conventional free-radical initiated polymer (see table 5.2). Further details are given in 10.8.

d. Anisotropy - X-ray diffraction

In order to determine whether or not the initial rod was
structurally anisotropic, samples were cut both parallel and perpendicular to the rod axis and examined in an X-ray diffractometer. Experimental details are given in 10.7. There was no detectable difference between the two spectra. It is concluded that there is no X-ray evidence supporting structural anisotropy. As the I.C.I. rod material is normally polymerized in moulds and not subsequently processed this is to be expected.

7.3 Mechanical Testing Techniques

The mechanical tests consisted of uniaxially compressing the specimens described in 7.1 at a series of (nominally) constant strain-rates and a series of temperatures and determining the stress-strain curves. Not all combinations of rate and temperature were investigated. Although in both the tests performed in the Instron testing machine and in the hydraulic testing machine (q.v. 7.3a, b) a constant strain-rate is aimed for, it is never achieved. In the case of the Instron machine, although the cross-head speed is maintained constant, there is a significant deflection in the load-cell and fixtures which is a function of the load. Only at the yield-point (where load instantaneously is not varying with strain) is the specimen strain-rate equal to the nominal strain-rate. Similar deflections exist in the hydraulic testing machine, in addition the head speed is not maintained constant especially at high head speeds. Typical strain-rate variations are shown in figs 10.1,
10.2, 10.3 for several cases for both machines. The effect of this is always to make the strain-rate lower than the nominal and in this sense, it is a consistent error. The error is greatest for small strains, for high testing rates and for low test temperatures. As the nominally constant strain-rates are usually separated by about one decade and the rate variations from normal during a test are much smaller than this, they have been neglected here. Had the dependence of mechanical properties on strain-rate been found stonger than it has or had been found non-monotonic these rate variations would perhaps have been serious.

The nominal strain-rates aimed for were $9 \times 10^{-5} \text{s}^{-1}$ (hereafter referred to as $\frac{4}{4}$), $9 \times 10^{-4} \text{s}^{-1}$ ($\frac{3}{3}$), $9 \times 10^{-3} \text{s}^{-1}$ ($\frac{2}{2}$) these tests being performed in the Instron tester and $7 \times 10^{-2} \text{s}^{-1}$ ($\frac{1}{1}$), $7 \times 10^{-1} \text{s}^{-1}$ ($\frac{0}{0}$), $5 \text{s}^{-1}$ ($\frac{1}{1}$), and $3 \times 10^1 \text{s}^{-1}$ ($\frac{2}{2}$) (conducted in the hydraulic machine). The basic test temperatures were 200, 220, 240, 260, 280, 300, 320, 340, 360°C. Other tests were performed at 77, 127, 160, 290, 305, 310, 315, 325, 330, 335, 345, and 350°C. The tests of which results are presented here are indicated in table 7.2. The tests on type PR samples are shown as *, on type MR samples as **.
Table 7.2
Constant Strain-Rate Tests Conducted

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
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<th>1</th>
<th>2</th>
<th>Strain-rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>see p.96</td>
</tr>
<tr>
<td>127</td>
<td>*</td>
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<td>160</td>
<td>*</td>
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<td></td>
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<tr>
<td>200</td>
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<td>*</td>
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<td>220</td>
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<td>240</td>
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<td>260</td>
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<td>****</td>
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<td>305</td>
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<td>325</td>
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<td>360</td>
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Later graphical presentation of this data sometimes shows interpolated points (in parenthesis) for the sake of clarity. Where the plot is of stress/temperature, the interpolation has been made from data at higher and lower rates and vice versa. A preliminary examination of the effects of slenderness-ratio and end lubrication was made. It was found that a slenderness-ratio of six was the best compromise that could be made in order to attempt to avoid both the effects of radial constraint at the ends for short specimens and the effect of buckling for long specimens. The specimen ends were always lubricated with a spray-on suspension of colloidal molybdenum disulphide (Racal MOS2 spray). Further details appear in 10.5. For all tests the area of the specimen as measured at ambient temperature was corrected for change with temperature. For the tests performed in the Instron testing machine, the load-time curve was obtained from the chart-recorder in the normal way. The values of load at various elongations were found by obtaining the elongation from the difference between load-time curves at temperature when a specimen was present and when no specimen was present. This determination of elongation constitutes by far the largest error in the determination of stresses. The error is larger for small strains and may cause an error in the stress of up to 4%. This is further discussed under 10.5. For
tests conducted in the hydraulic machine the load is measured by means of a short stiff load transducer on which are mounted three semiconductor strain gauges. For the rates 1, 0, 1 the relative displacement of the specimen ends is measured directly by means of a duralumin cantilever transducer fitted with one wire strain gauge. For the fastest rate (2) a velocity transducer records the relative velocity of the specimen ends. There is appreciably lower error in the measurement of strain for tests conducted in this machine than for those conducted in the Instron tester.

7.3a The Instron tester

The Instron testing machine used was either a model TT-D (using a GR load cell) or a model TT-C machine (using FR load cell). Conventional Instron accessories were used. Head speeds in excess of 0.2 inches per minute were not used in order that the recorder response time was not exceeded. The temperature enclosure used for these tests was an Instron Environmental Chamber (with Instron controller). The coolant used below ambient temperature was liquid carbon dioxide. With the controller probe close to the specimen the temperature is expected to be within $\pm 1^\circ K$ of that required. At least 30 minutes was allowed for temperature equilibrium to be reached after attaining any new temperature.
7.3b The hydraulic testing machine

This has been described by Briggs (159) and by Dao (160). Since the time of these publications the upper cylinder has been altered to enable various exhaust orifices to be fitted at will. These orifices control the piston speed in the range from $7.5 \times 10^{-4}$ to 19 inches per second. The orifices consist of brass plates 0.125ins thick having central holes ranging from 0.156 to 0.008ins diameter. In 10.11 the attainable strain-rates for specimens of $\frac{3}{8}$ins length is plotted for various drive pressures against the orifice area. The load and displacement are recorded by means of strain gauges affixed to appropriate transducers, a dual strain gauge bridge, a dual-beam Tektronix model 551 oscilloscope and a Dumont type 302 oscilloscope camera using Polaroid type 46L transparency film. For the highest head speed used here a Sanborn model 6LV1 velocity transducer was used to record velocity as the displacement transducer did not have an adequate frequency response (natural frequency about 2KHz). Strain was obtained in this case by enlarging the Polaroid negative, cutting the enlargement of the velocity-time curve into strips of constant time interval and weighing the strips in order to integrate the area beneath the velocity-time curve. The specimen temperatures were achieved for tests in this machine by immersing the specimens for
about five minutes in a hot kerosene bath (for temperatures greater than ambient) or a liquid-nitrogen ethyl-alcohol bath (for temperatures below ambient), removing the specimen and quickly inserting it in the testing machine as the bath temperature drifted slowly through the required value (minus or plus $3^\circ K$ according as the temperature was less or greater than ambient). Both temperatures were measured by a copper-constantan thermocouple using a Honeywell Rubicon potentiometer. The error in temperature measurement is estimated to be $\pm 1^\circ K$. A maximum of six seconds elapsed between the removal of the specimen from the bath and the commencement of the test. The longest testing time (including time for acceleration of the piston and contact with the specimen) was nine seconds. The temperature rise of the outer specimen surface from $200^\circ K$ in six and fifteen seconds are conservatively estimated here at $3.4$ and $8.4^\circ K$ respectively (see 10.4). The temperature of the specimen surface during the test should then vary at worst $5^\circ K$ from that required.

7.5 **Shifting of Stress-Strain Data**

It is possible to shift the stress-strain-rate curves obtained in this work to obtain a 'master-curve' of stress/reduced-strain-rate over a wider scale, but this must be done with caution. If certain corrections to the data are not made, then the conclusions drawn may be seriously in error. This is discussed at length in 10.13.
7B. EXPERIMENTAL DATA

7.6 Stress-Strain Data

a. Stress as a function of strain-rate with temperature as a parameter

Figures 7.2, 7.3 and 7.4 show the data obtained from the constant-strain-rate compression tests presented in the above manner. This data has been normalized as described in 10.13. The PR samples are slowly cooled, MR samples fast-cooled. It may be seen that stress is a function of strain-rate throughout the temperature range investigated. There seems to be evidence for a single transition in mechanical properties. Both the completely unrelaxed and completely relaxed states appear to be outside the range of rate and temperature investigated. At a given strain, strain-rate and temperature the stress for MR material is always considerably lower than that for PR material. The unrelaxed secant moduli appear to be about 705000psi (PR) and 585000psi (MR), the relaxed moduli 310000psi (PR) and 165000psi (MR). There is a considerable difference between the secant moduli of the two materials throughout the transition (amounting to about 130000psi). The data for 4% strain (fig 7.3) shows similar trends. The curves obtained will obviously not superpose perfectly by means of horizontal shifting. It might be conjectured that this is a consequence of some testing machine error (say in the MR data for 280°K) but the same behaviour is observed.
FIG 7.2
for PR and MR samples between 280 and 320°K. This involves many tests performed at different times within the testing sequence and no pattern in the sequence of testing can be found which correlates with these particular tests. As the load transducer for the hydraulic test-machine was calibrated against the Instron load-cell, the possibility of there being a difference here can be discounted. The stress-strain-rate curves for 200° and 360°K show no discontinuity between strain-rates of $\bar{2}$ and $\bar{1}$ which could be attributed to this source. The possibility that heat conducted from the specimens to the semiconductor-gauged hydraulic-test-machine load cell during a test may be discounted for the same reason. Not only are the temperatures in question closer than 200° and 360°K to ambient, but the data in question is for high strain-rates where the contact time is shortest. The possibility that there is some other error must remain, however the curves shown fit the data points well and there is no explanation to be found for this in the testing sequence which is quite random for points at different rates, but the same temperature in this region. There remains the possibility that the behaviour shown is real. It seems improbable, however, that the stresses obtained at lower temperatures are lower than those obtained at higher temperatures for a given strain-rate. The secant moduli at 4% strain and 360°K for both PR
and MR material show a much stronger dependence on strain-rate than do the 4% moduli at 200°C. This is in contrast to the data for 2% strain.

Figure 7.4 shows the stress-strain-rate curves at several temperatures of PR and MR series for comparison. It may be seen that the difference may well be described by a constant difference in stress at any given temperature over the range of strain-rates investigated. This stress difference is seen to be smaller at 300°C (about 2100psi) than at either 240°C (about 3100psi) or 340°C (about 2750psi). The stresses are lower for fast-cooled (MR) material than for slow-cooled (PR) material. Some curves are shown for a preliminary set of tests - the LR series. These samples were 0.500ins diameter and 0.75ins long, moisture was not removed. It can be seen that the moisture present (c. 0.5% by weight) has a similar effect on the mechanical properties to that of fast-cooling the material.

b. **Stress as a function of temperature with strain-rate as a parameter**

Figs 7.5, 7.6 and 7.7 show the stresses presented in this way for PR and MR materials, and the difference between them. Test numbers are also shown. Tests for the strain-rates 4, 3 and 2 were performed on the Instron tester in groups at fixed temperatures. Tests at higher rates were performed on the hydraulic testing machine
in groups at constant strain-rate. Some of the values have been obtained by a linear interpolation as described in 7.5, these are shown in parentheses.

Both PR and MR materials show a transition in mechanical properties in the range 250–270°C (called for the moment the B-transition). The PR material shows in addition a smaller transition at about 330°C (A-transition) which is not shown by the MR material. The A-transition is obscured by the B-transition at high strain-rates (1,2) for the PR material. The existence of the A-transition is shown clearly in fig 7.5 for strain-rate 3 where additional tests have been performed to elucidate this.

The MR curves tend to decrease smoothly in this temperature range. Both A- and B-relaxations are more clearly seen at low strain-rates than at high strain-rates. The relative magnitude of the B-transition as measured by the difference in the limiting stresses \(\sigma_u: unrelaxed, \sigma_R: relaxed\) in the PR data decreases as the strain-rate increases. Although the limiting stresses are not really reached in these experiments, the stress values at 200 and 300°C have been taken as indicative of their behaviour. These values, \(\sigma_{200}\) and \(\sigma_{300}\) are tabulated below. (Table 7.3). The values of \(\Delta\sigma_B = \sigma_{200} - \sigma_{300}\) and \(\Delta\sigma_A = \sigma_{300} - \sigma_{350}\) are also given.
It may be seen that $\Delta \sigma_B$, $\Delta \sigma_B/\sigma_{200}$ and $\Delta \sigma_B/\sigma_{300}$ all decrease smoothly as the strain-rate increases. At the strain-rate of 2 the test time hardly allows any B-relaxation as seen in text figure 24. i) It seems that at strain rates lower than 3, the full transition (as measured by $\Delta \sigma_B$) is seen. ii) It follows that the B-relaxation will not be seen at rates higher than say 2.1. iii) The effective frequency at this rate and 2 percent strain is 1550Hz. iv) The magnitude of the A-relaxation by contrast seems relatively constant when it can be resolved.

<table>
<thead>
<tr>
<th>Strain-rate</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{200}$</td>
<td>12.4</td>
<td>13.1</td>
<td>13.6</td>
<td>13.9</td>
<td>14.2</td>
<td>14.3</td>
<td>14.4</td>
</tr>
<tr>
<td>$\sigma_{300}$</td>
<td>7.7</td>
<td>8.4</td>
<td>9.3</td>
<td>10.0</td>
<td>11.2</td>
<td>12.4</td>
<td>13.3</td>
</tr>
<tr>
<td>$\sigma_{350}$</td>
<td>6.8</td>
<td>7.6</td>
<td>8.2</td>
<td>9.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta \sigma_B$</td>
<td>4.7</td>
<td>4.7</td>
<td>4.3</td>
<td>3.9</td>
<td>3.0</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>$\Delta \sigma_A$</td>
<td>0.9</td>
<td>0.8</td>
<td>1.1</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta \sigma_B/\sigma_{200}$</td>
<td>0.38</td>
<td>0.36</td>
<td>0.32</td>
<td>0.28</td>
<td>0.21</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>$\Delta \sigma_B/\sigma_{300}$</td>
<td>0.61</td>
<td>0.56</td>
<td>0.46</td>
<td>0.39</td>
<td>0.27</td>
<td>0.13</td>
<td>0.08</td>
</tr>
</tbody>
</table>
If the B-relaxation is located crudely by finding the temperature at which the stress is equal to $\sigma_{300} + \frac{1}{2} \Delta \sigma_B$, then the 'relaxation temperatures' (at which this occurs) may be found as given below. (table 7.4). The temperature of maxima and minima in the difference in stress of PR and MR materials is also given.
Table 7.4

B-transition Temperature

<table>
<thead>
<tr>
<th>Rate</th>
<th>B(PR)</th>
<th>B(MR)</th>
<th>A(PR)</th>
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<th>max</th>
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<td>4</td>
<td>258</td>
<td>272</td>
<td>332</td>
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<td>264</td>
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<td>-</td>
<td>279</td>
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<tr>
<td>2</td>
<td>264</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>280</td>
<td>330</td>
<td>276</td>
<td>323</td>
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</tbody>
</table>

This method of locating a 'transition temperature' is rather naive as examination of fig 7.7 reveals that the B(PR)-transition temperature increases with strain-rate, being about 260°K for strain-rate 4 and about 290°K for strain-rate 2. The irregular nature of the curves makes a closer assessment difficult. In the same range of strain-rates, the B(MR) transition temperature changes from about 280°K to about 320°K. In the PR curves, the high temperature (relaxed) end of the B-transition is delineated by a marked plateau; no marked plateau is seen in the MR data. The MR curves also show a large decrease in stress at high temperatures (greater than 350°K). There is always a positive difference between the stresses for PR and MR samples. This difference is maintained.
down to 77\(^{\circ}\)K as seen in fig 7.5. In fig 7.7 (where curves from figs 7.5 and 7.6 are superposed), the anomaly in the MR data for rates of 1 and 0 at high temperatures which was discussed in 7.6a may be seen more clearly. This figure also shows more clearly that although the B-transition temperature varies strongly with strain-rate the A-transition temperature does not appear to vary greatly if at all with strain-rate.

The data for 4\% strain show largely the same behaviour as those for 2\% strain. The increased accuracy of strain determination for the higher strain (and hence of stress determination) results in a set of curves more evenly distributed in stress for different strain-rates. The 4\% data shows that a new transition seems to be occurring at temperatures below 240\(^{\circ}\)K for PR samples (but not for MR samples). This is probably a process characteristic of large strain behaviour as it is not apparent in the 2\% data. The stresses (for rates $\frac{4}{2}$ to 2) in this region are more closely grouped for 4\% strain than for 2\% strain. The B-transition is still apparent for strain-rate $\frac{4}{2}$, but almost non-evident at strain-rate 2. The temperature dependence of the 4\% stress is greater than for the 2\% stress at lower strain-rates, but generally similar for higher strain-rates. The difference in stress (for a given strain-rate and temperature) between PR and MR samples is diminished at 4\% strain when referred to 2\% strain.
The A-relaxation appears only for rates 1, 0, and 1 at 4% strain. This is probably a consequence of the fact that insufficient time for any significant B-relaxation is allowed at high strain-rates and of the fact that for 4% strain the temperature dependence of the stress at low strain-rates is greater. Both of these features would mask the A-transition.

The difference in behaviour between the data for 2% and for 4% strains at 200-240°C are real. The data for the lower three strain-rates arises from tests conducted in a group on the Instron machine, while the upper four strain-rate tests were conducted on the hydraulic machine at different times. This removes the possibility of experimental trends being reflected in the data. In addition, each data point for 4% strain derives from the same experiment which provided the corresponding point for 2% strain and is thus directly related to it.

7.7 Yield Stress Data

Figures 7.8 and 7.9 show the yield stress plotted as a function of temperature. The yield stresses have not been normalized (see 10.13). The investigation was not initially aimed at providing yield stress data and consequently, the information is not as complete as that for smaller strains. At low temperatures and medium to high strain-rates, fracture precedes yield and the yield stress is not available. The yield stress is defined here as the first point in the stress-strain
test where the first derivative of stress in strain becomes instantaneously zero.

Figures 7.8, 7.9 show that the nearly constant stress difference between the PR and MR samples is maintained at the yield strain. At the strain-rate \( \dot{\varepsilon} \) in the temperature range 280-360°K, it may be seen that the yield stress could be approximated as a linear function of temperature. This approximation will not hold for lower temperatures. Data obtained at higher rates may not be so approximated; neither is the yield stress a linear function of reciprocal temperature (fig 7.9).

Figure 7.10 shows the yield stress as a function of strain-rate with temperature as a parameter. It may be seen that the data is well fitted by two straight lines which intersect at a strain-rate which decreases as the temperature decreases. The data for MR material at 340 and 360°K does not permit this conclusion. The stress at which the two lines intersect is shown in text figure 25. Presumably the two different regions represent contributions of different (or sums of different) relaxations or other molecular processes to the yielding.

### 7.8 Typical Stress-Strain Curves

Figure 7.11 shows some typical stress-strain curves. As the test temperature is decreased, the yield strain is seen to increase and then to decrease again. As the strain-rate is increased, the yield strain is seen to take smaller values. The PR material tends to yield at higher strains than the MR material. The initial
moduli are seen to be a function of strain-rate. The initial moduli for MR material at a given temperature and strain-rate are much smaller than for the PR material under the same conditions.

7.9 Master Stress-Strain-Rate Curves and Shift Factors

The stress-log(strain-rate) curves of fig 7.2 each representing data taken at a different temperature may be shifted horizontally until they superpose (as nearly as possible). There is meaning in doing this if there is an equivalence between time and temperature (see sect. 10.13). The curve for one temperature (the reference temperature) remains unshifted. Curves for the two nearest temperatures are shifted horizontally until the best superposition is found. Then the data curves for the next nearest temperatures are shifted to create an extended master curve
and so-on. If there is a real equivalence between time and temperature, the master curve represents the mechanical response for the material at the reference temperature over an increased time scale - more than has been explored experimentally - at the reference temperature. The horizontal shifts made for each temperature then represent the shift factors (sect. 10.13) for each temperature relative to the reference temperature.

In fig 7.12 the master curves so constructed for PR and for MR material at both 2\% and 4\% strain are shown (reference temperature 300\(^\circ\)K). This has been performed for both normalized (right) and non-normalized data (left). Error bars giving the estimated error in shift are shown for different portions of the curves. Fig 7.13 shows the shift factors as a function of temperature.

Fig 7.13 left (centre and lower) shows the shift factors for PR and MR2\% normalized and non-normalized curves with reference temperature 380\(^\circ\)K (i.e. shift factor for 380\(^\circ\)K zero). Fig 7.13 left (upper) shows the PR2\% shift factor for non-normalized data (reference temperature 300\(^\circ\)K) and the shift factor for the corresponding MR data shifted onto the PR2\% curve at 300\(^\circ\)K as datum. Fig 7.13 right shows the shift-factors for 4\% data and the best overall shift-factor curves for all data referred to 380\(^\circ\)K.

7.10 Activation Energies

If the transition being investigated (here the B-transition)
is assumed to be controlled by a relaxation which follows an Arrhenius law then the shift factor should follow the relationship

$$\log_e \alpha_T = \Delta H / R \left(1/T - 1/T_o\right),$$

here $\log_e \alpha_T$ is the natural logarithm of the shift factor (reference temperature $T_o$) for the data at absolute temperature $T$. $R$ is the gas constant and $\Delta H$ the enthalpy of the relaxation controlling the transition. The activation energy may then be obtained from the slope of the straight line fitted to the $\log \alpha_T/(1/T)$ data plot. If the data on this plot may not be well represented by a straight line then the assumption that the transition is controlled by a single Arrhenius-type thermally activated relaxation may not be made.

Figure 7.14 shows such a plot made using the shift factor data presented in 7.9. It may be seen that the data points are fitted quite well by a straight line. The activation energies and estimated errors obtained from these plots are given below in table 7.5.

<table>
<thead>
<tr>
<th>Data</th>
<th>$\Delta H_B$ Kcal/mol</th>
<th>$\Delta H_B$ Kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not-normalized</td>
<td>Normalized</td>
</tr>
<tr>
<td>PR2%</td>
<td>29.6 ±7%</td>
<td>15.2 ±5%</td>
</tr>
<tr>
<td>MR2%</td>
<td>26.9 ±7%</td>
<td>14.7 ±5%</td>
</tr>
<tr>
<td>PR4%</td>
<td>29.4 ±7%</td>
<td>16.7 ±5%</td>
</tr>
<tr>
<td>MR4%</td>
<td>27.1 ±7%</td>
<td>16.7 ±5%</td>
</tr>
</tbody>
</table>

Table 7.5

Activation Energies
It may be seen that there is a considerable difference between the activation energies determined using non-normalized and by using normalized data. There is good agreement between the activation energies determined from the data taken at different strains and those determined for the two different material treatments.

7.11 Dynamic Modulus/Temperature

The dynamic modulus of a rod of poly (methyl methacrylate) treated to PR condition was measured at about 1 KHz in flexural resonance in order to see whether or not an independent assessment of the unrelaxed modulus $E_u(T)$ (and thus of the normalizing factor $c_T$) could be made. A secondary objective was to see the effect of the B-relaxation upon the small strain dynamic properties at this frequency.

The rod, 0.1183ins diameter and 8.485ins long which weighed 1.8197g was suspended 0.224 of the length from each end by fine cotton threads ('Sylko' 40 twist number D141) attached at the other end to the styli of Acos monophonic crystal phonograph pick-ups. One pick-up (the drive unit) was excited by means of a General Radio 1310A oscillator and the output from the other recorded on a Hewlett-Packard 400E AC voltmeter using a Tektronix 1A6 differential preamplifier in a Tektronix 123 amplifier chassis. A 100pF capacitor was used in series with each lead from the signal pick-up to filter out low frequency components. The oscillator frequency was recorded on a Hewlett-Packard 5325B frequency counter. Resonances were found by varying the oscillator frequency
and watching the voltmeter for peaks in the output signal from the signal pick-up.
The modulus may be found from the resonant frequencies of a circular rod by means of the formula (163)

\[ E = 9.19 \times 10^{-6} \left( \frac{l}{d} \right)^4 \left( \frac{m}{l} \right) \left( \frac{f}{F} \right)^2 \]

where
- \( E \) is the dynamic modulus (psi)
- \( l \) is the length of the rod (cm)
- \( d \) is the diameter of the rod (cm)
- \( m \) is the mass of the rod (g)
- \( f \) is the resonant frequency (Hz)
- \( F \) is 1, 2.76, 5.41, 8.95, 13.38, 18.68, etc. for successive resonances.

If \( l/d = 10 \) the correction in resonant frequency resulting from geometric dispersion is less than \( 10^{-3} \).
The fifth harmonic was used here and the formula then becomes

\[ E = 52.159/13.38^2 \left( \frac{1}{T} \right)^2 \text{ psi} \]

where \( T \) is the period. The modulus was measured from 260 to 375\(^{\circ}\)K with the rod suspended in the Instron Environmental Chamber. The accuracy in temperature is estimated at \( \pm 1^{\circ}\)K. These results are shown in fig 7.15.
The resonant frequency varied from 1172 Hz at 260\(^{\circ}\)K to 871 Hz at 375\(^{\circ}\)K. The B-transition is clearly evident in the temperature range from 260 to 330\(^{\circ}\)K as is the onset of the glass transition at 375\(^{\circ}\)K.
The values of \( c_T \) have been estimated from the values of the dynamic modulus at various temperatures obtained above and these values are shown in table 7.6.
These values are in quite fair agreement with those of Wada et al. (9) (see fig 10.7). The measuring frequency here (1KHz) is, however, much lower than that of Wada et al. (33KHz) and the B-relaxation is itself reflected in the values of $c_T$. This agrees with the findings reported under 7.6b.

### 7.12 Volume Measurement

A major measurable difference in the physical properties of the PR and MR samples is that in density (or specific volume). Various methods for measurement of the density

<table>
<thead>
<tr>
<th>Temperature ($^\circ$K)</th>
<th>Modulus (psi)</th>
<th>$1/c_T$</th>
<th>$c_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>398,000</td>
<td>1.174</td>
<td>0.851</td>
</tr>
<tr>
<td>260</td>
<td>391,000</td>
<td>1.153</td>
<td>0.867</td>
</tr>
<tr>
<td>270</td>
<td>381,000</td>
<td>1.123</td>
<td>0.890</td>
</tr>
<tr>
<td>280</td>
<td>378,000</td>
<td>1.117</td>
<td>0.896</td>
</tr>
<tr>
<td>290</td>
<td>356,000</td>
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</tr>
<tr>
<td>300</td>
<td>339,000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>310</td>
<td>320,000</td>
<td>0.945</td>
<td>1.058</td>
</tr>
<tr>
<td>320</td>
<td>300,000</td>
<td>0.885</td>
<td>1.130</td>
</tr>
<tr>
<td>330</td>
<td>277,000</td>
<td>0.817</td>
<td>1.224</td>
</tr>
<tr>
<td>340</td>
<td>256,500</td>
<td>0.755</td>
<td>1.308</td>
</tr>
<tr>
<td>350</td>
<td>250,500</td>
<td>0.739</td>
<td>1.353</td>
</tr>
<tr>
<td>360</td>
<td>247,500</td>
<td>0.730</td>
<td>1.370</td>
</tr>
<tr>
<td>370</td>
<td>243,000</td>
<td>0.716</td>
<td>1.397</td>
</tr>
</tbody>
</table>
of the test-size samples (½ins diameter, 3/8ins long) were tried. These included i) weighing and measuring dimensions ii) Archimedes method using water and air as suspension fluids iii) Archimedes method using air and kerosene as suspension fluids iv) measuring by weighing in air and weighing a pycnometer containing both samples and glycerol of predetermined density. None of these methods was able to give accurate and repeatable results. The method finally adopted was that of measuring the dimensions and weighing samples of ½ins diameter and 3/8ins length. As the source material is expected to be isotropic as received (sect. 7.2d) the material in small and large specimens should be of identical nature. The 'effective' cooling rate of the large specimens at the faster cooling rate will not, of course, be the same as that of the smaller ones, but since the two nominal cooling rates differ by 700 times and the slower rate is only \( 10^{-30} \text{Ks}^{-1} \), the results are not expected to be greatly different for the MR material than those measured on small samples) and not at all different for the PR material. The specimens were weighed to \( \pm 0.0001 \text{g} \) on a Sartorius balance and the dimensions measured (length 3 times, diameter 6 times per density determination) by means of a bench micrometer reading to 0.0001ins. Table 7.7 shows the results obtained expressed in g/ml. at 300\( ^{0} \text{K} \) (specific volumes in ml/g). The specimens
water-quenched from various temperatures show an interesting trend which has not been further explored - the lower temperatures of quench appear to produce densities lower than those obtained from higher quench temperatures. This is unexpected. The mean densities for quench temperatures 413, 403 and 393°K are 1.1786, 1.1755 and 1.1727 g/ml. at 293°K respectively. Statistical 'student's t' tests were performed on the

<table>
<thead>
<tr>
<th>Table 7.7 Density Measurements</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
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<tr>
<td>--------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
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<tr>
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<td>8</td>
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<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Diff%</td>
</tr>
<tr>
<td>Sample</td>
</tr>
</tbody>
</table>
densities obtained for samples 7-12. The results obtained were:-

(i) Water-quenched (MR) samples (from 413-393°K) had a significantly different density than thermos-cooled (PR) samples (99.5% < significance level < 99.95%).

(ii) Water-quenched and water-quenched and subsequently aged (20 hours at 356°K) samples had a significantly different density (99.5 < significance level < 99.95%).

(iii) Water-quenched (from 413°K) and water-quenched (from 403°K) samples had a significantly different density (99% < s.l. < 99.5%).

(iv) Water-quenched (413°K) and water-quenched (393), and water-quenched (403°K) and water-quenched (393°K) samples possibly had different densities (85% < s.l. < 90%) and (80% < s.l. < 85%).

7.13 Dilatometry Measurements

In order that the theory of Rusch\(^{13}\) might be tested, it was necessary that the specific volume of the samples tested in compression be determined at the test temperatures. As the material was isotropic, it was possible to do this by making length measurements only. A 14ins long quartz glass dilatometer consisting of a 19mm diameter outer jacket with
a flame-fuzed flat end and an internal quartz probe rod of 4mm diameter was constructed. A small brass heat-sink 5/8ins o.d. and 5/16ins i.d. of ½ins length located in the bottom of the outer jacket served to contain the ¼ins diameter and 3/8ins long specimen, to align the probe-rod and specimen and also served as the junction of a chromel-alumel thermocouple. The lower end of the dilatometer assembly was lowered about 8ins into a half-gallon (½g) thermos flask containing a 15W heater element and glycerol. The specimen length change was recorded by means of a Hewlett-Packard 7DCDT-250 displacement transducer fixed into the top of the jacket tube so as to measure the difference in length of the jacket and probe-plus-specimen. The calibrated sensitivity of the transducer corresponded to an output of 7.41V per inch of deflexion at 7.0V excitation. The transducer output voltage and the thermocouple voltage (referred to that of a similar thermocouple in an ice-water bath) were recorded against one another on a Hewlett-Packard 7001A X-Y recorder. The stability of the measuring system as seen on the recorder output (at 300°K) appeared to be +8.7 x 10⁻⁶ ins in a period of 4100s. No long-term drift was apparent in this period. This corresponded to a precision of relative volume measurement of +6.9 x 10⁻⁵. The accuracy in temperature measurement is estimated to be +1°K. The recorder trace could be read to +0.05ins which corresponds to a maximum resolution of 1.33 x 10⁻⁶ ins.
The dilatometer was heated from 273°K to 387°K at an approximately constant rate of $5 \times 10^{-3}$ °K s$^{-1}$. The absolute values of the specific volume have been taken as the mean values from the measurements described in 7.12. The specific volumes of PR and MR samples determined in this way are shown as a function of temperature in fig 7.16. The volume curves show a break at about 300°K, the volume expansion coefficient below this temperature being $1.78 \times 10^{-4}$ ml.g.$^{-1}$ °K$^{-1}$ and above $2.28 \times 10^{-4}$ ml.g.$^{-1}$ °K$^{-1}$. The glass transition temperature has been set at 378°K (161) as the best value from the literature. The glass transition temperature determined (sect. 7.2b) was 380°K. A dotted line extending the expected rubbery volume/temperature slope of $4.7 \times 10^{-4}$ ml.g.$^{-1}$ °K$^{-1}$ has been drawn from the point where the extended experimental volume line (between 310°K and 350°K) passes through 378°K to the secondary transition temperature $T_2$ given by Adam and Gibbs (161) at 332°K. The rubbery volume curve found in the present work is not considered reliable. From 332°K another line of somewhat arbitrary slope ($1.20$ ml.g.$^{-1}$ °K$^{-1}$) has been drawn to lower temperatures. These two dotted lines are included after Rusch (131), taking his values for the slopes. The experimental points are not shown, as the data has been taken from single runs on the X-Y recorder and the data points would all fall on the lines given.
FIGURE 7.16
8. DISCUSSION

In this chapter the results already presented are discussed and compared with some of the results and theories of other investigators which were introduced in chapters 5 and 6.

8.1 The B-transition

The B-transition discussed in 7.6b is seen to occur for both PR and MR materials. In table 7.3 and in text figure 24 it was shown that the magnitude of the transition, $\Delta \sigma B$, was a function of strain-rate and was essentially zero when this was $10^2 \text{s}^{-1}$. The corresponding frequency (2 percent strain) is about 1.55 KHz. This compares well with the frequency ($3 \times 10^3 \text{Hz}$) at which Kopplemann (88) has shown the $\beta$-transition to merge with the glass-transition (and disappear). The estimated temperature and frequency of occurrence of the B-transition are $260^\circ K$, $1.1 \times 10^{-3} \text{Hz}$ (at strain-rate 4) to $300^\circ K$, $4.0 \times 10^2 \text{Hz}$ (at strain-rate 2). These may be compared with the values reported in table 5.1 and the relaxation map fig 5.4 for the $\beta$-relaxation. The transition frequency estimated from fig 5.4 for $260^\circ K$ is $7.8 \times 10^{-3} \text{Hz}$, and at $300^\circ K$, 2.0Hz. The certainty with which the transition temperature can be determined from fig 7.7 is less for high strain-rates than for low ones. If the activation energy of table 7.5 is used together with the estimated
occurrence at $260^\circ$K, $1.1 \times 10^{-3}$Hz then the transition frequency would be predicted to be 3.9Hz at $300^\circ$K in better accord with the relaxation map.

The activation energies obtained here (7.10) are discussed in 8.4.

The B-transition is the dominant transition observed in this work. The temperature and frequency at which it is observed and the activation energies determined leave little doubt that it should be identified with the $\beta$-relaxation described in 5.4c. The $\beta$-transition has been reported only once before for experiments of the constant-strain-rate type at small strains (Holt$^{(110)}$). The constant-strain-rate yield experiments of Roetling$^{(144)}$ and Bauwens et.al.$^{(145)}$ also reflect the $\beta$-transition.

As discussed under 8.6, the $\beta$-transition is observed in the data for both PR and MR materials with nearly equal magnitude. It is not certain whether the difference in magnitude is real or merely reflects inaccuracy in the data. The $\beta$-transition appears some $16^\circ$K higher for MR than for PR material. This is a consequence of the different material states.

8.2 The $A$-transition

In 7, various features of the stress-temperature curves were identified and associated with an 'A-transition'.

The temperature of occurrence of this transition is similar to that reported for the $\alpha'$ transition (see 5.4b).
In this work the A-transition has been observed at $330^\circ K$ (see 7.6b). The transition was evident for PR material, but not for MR material. The magnitude of the relaxation (table 7.3) and its temperature do not appear to be functions of the testing rate. The magnitude of the A-transition appears to be about 20% of that of the B-transition (as measured by the parameters $\Delta\alpha_A$ and $\Delta\epsilon_B$ of table 7.3).

The $\alpha'$ transition has been observed at $330-341^\circ K$ in dilatometry experiments (8)(7)(8)(9), at $330^\circ K$ in dielectric measurements (88)(154) at $340^\circ K$ in creep measurements (10) and at $330^\circ K$ in yield-stress experiments (145). Other values reported are $348^\circ K$ in calorimetry experiments (216) and $351^\circ K$ in creep experiments (129).

Thompson (120) has observed that the $\alpha'$ transition is only observed in experiments of long time scale. In tensile and shear creep experiments, he observed a shoulder in the retardation spectra (reference temperature $298^\circ K$) from $10^6$ to $10^{11}$ seconds which he attributes to the $\alpha'$ relaxation. He concludes from the measured shift factors that they are well described by three straight lines on an Arrhenius plot which lead to activation energies of 7.3 and 10.1 Kcal.mol.$^{-1}$ in the temperature range 123-238$^\circ K$, 17.9 and 17.7 Kcal.mol.$^{-1}$ in the temperature range 238-298$^\circ K$ and 42.6 and 41.8 Kcal.mol.$^{-1}$
in the temperature range 298-353°K (values derived from shear and tensile data respectively). The activation energy of the \( \alpha' \) relaxation would thus appear to be about 42 Kcal.mol.\(^{-1} \) on the basis of these measurements, but it is by no means certain that the \( \alpha^- \) and \( \beta^- \) relaxations have not influenced the answers obtained. Heydemann and Guicking\(^{(3)} \) found that the temperature of the \( \alpha' \) transition as observed in dilatometry experiments was not influenced by pressures up to 6 Kbar. Kopplemann\(^{(88)} \) found evidence for a transition at 330°K which he stated was a function of the thermal treatment of the material. No further details of the treatment were given. Wittman and Kovacs\(^{(6)} \) investigated polymers of varying tacticity by means of dilatometry. No \( \alpha' \) transition was found for solely isotactic polymer. The \( \alpha' \) transition was found only in polymers having syndio- and hetero-
tactic sequences. They conclude that the \( \alpha' \) relaxation must be associated with the co-existence of these sequences. A solely syndiotactic polymer was not investigated. The transition temperature did not appear to vary in an obvious or simple way with either the syndio- or hetero-
triad analysis. Although the glass transition temperature of completely isotactic polymer is about 330°K (table 5.1) it seems that the \( \alpha' \) transition cannot be due to long isotactic sequences undergoing a glass transition as the \( \alpha' \) transition does not appear for a completely isotactic
polymer and appears at a temperature greater than the
glass transition temperature for a polymer having the
triad analysis: \( i = 59, s = 11, h = 30 \). 
It is suggested here that the \( \alpha' \)-relaxation is associated
with the configuration of the ester groups described
by Havriliak\(^{(12)(116)}\). Discussion is presented in 8.8
to show how the observed variation of volume at 298°K
with temperature of quench could be explained in terms
of the theory of Havriliak. According to Havriliak,
various ester group configuration populations can be
'frozen-in' by quenching from different temperatures
above \( T_g \). Thus quenched and slowly cooled specimens
would be expected to contain different (and 'frozen')
amounts of the two configurations. Havriliak's conclusions
have been based upon the structure of a solely syndiotactic
polymer. The detailed conclusions would be different
for polymer containing hetero- and syndio-sequences.
The fact that in both the present investigation and that
of Kopplemann\(^{(88)}\) the \( \alpha' \) transition was found to depend
upon thermal treatment (cooling rate) lends strong
support to the conclusion that its occurrence depends
upon some structural feature which occurs if the cooling
is slow but not if cooling is so fast as to 'freeze-in'
a structure characteristic of a higher temperature. It
would be instructive to examine the \( \alpha' \)-transition for
samples quenched from different temperatures above \( T_g \).
It is concluded that the A-transition identified in 7.66 is identical to the \( \alpha' \) transition reported in the literature.

The \( \alpha' \) transition appears to depend upon the tacticity characteristics of the polymer. This has yet to be investigated fully and may throw light upon the exact mechanism of the \( \alpha' \)-relaxation. An attempt should be made to measure the activation energy of the \( \alpha' \)-relaxation.

8.3 Yield Stresses

The yield stresses as plotted as a function of temperature and reciprocal temperature in figs 7.8 and 7.9 show no apparent complete transitions as are evident in the curves of fig 7.7 say. At any given strain-rate the yield stress increases with decreasing temperature. The yield stresses are neither linear in temperature nor linear in reciprocal temperature. The difference in yield stress behaviour at a given strain-rate for PR and MR samples may be well described by a constant temperature difference although there is evidence that this may not hold well at high (1,2) strain-rates (see fig 7.9). This is discussed in 8.6.

The yield stress isotherms plotted for various strain-rates (fig 7.10) are well described by two lines and show a distinct 'break'. This is illustrated in text figure 25. This is in contrast to the work of Holt\(^{(110)}\) who found no break, but confirms work by Roetling\(^{(144)}\) and Homes et.al.\(^{(145)}\). If it is taken that the 'break-point' in fig 7.7 for 240\(^{\circ}\)K is in error (see text figure 25) then the 'break-point' for PR samples may be expressed as
\[ \log_{10} \text{(strain-rate of 'break')} = \frac{T - 335}{100}, \]

where \( T \) is the absolute temperature of the test. The break-points of the data of Roetling \(^{(144)}\) for poly (methyl methacrylate) show a similar linear dependence upon temperature:

\[ \log_{10} \text{(strain-rate of 'break')} = \frac{T - 388}{25}. \]

It is not believed that the 'break' is a consequence of using data obtained on two different testing machines as data is obtained either side of the 'break-point' on only one testing machine (the hydraulic machine) at each temperature.

Measurements of the yield stress of poly (methyl methacrylate) have been reported by Holt \(^{(110)}\), Roetling \(^{(144)}\), Bauwens et al. \(^{(145)}\), Beardmore \(^{(2,7)}\) and Rusch \(^{(179)}\). The measurements of Holt and Beardmore were made in uniaxial compression. Those of Bauwens et al., Roetling and Rusch were made in uniaxial tension. Rusch's definition of the yield stress means that it occurs at about 2 to 3 percent strain and thus it is not consistent with that used here and by other workers. Figure 8.1 shows the yield stress as a function of strain-rate at various temperatures. In each case the data is well fitted by one or two straight lines. It is seen that there is fair agreement with the results of Holt except at high strain-rates: the magnitude, rate- and temperature-dependence agree fairly well. The yield stresses
of Holt are somewhat higher than those reported here, this is probably a consequence of the different materials used. The data of Roetling shows much lower yield stresses near 300°K. His measurements were made in tension and there is good reason to expect that the yield phenomenon will depend upon the stress state (224). It may be seen from fig 8.1 that the 'break-point' in the data of Roetling occurs at lower strain rates and is a stronger function of temperature than in the present data. The high strain-rate rate dependence of the yield stress here is also seen to be much larger than that of the data of Roetling.

Figure 8.2 shows the temperature dependence of the yield stress at a strain-rate of 10⁻³ s⁻¹ taken from fig 7.10 and the data of Holt, Beardmore and Roetling. The temperature dependence here is seen to follow that of Holt closely although the stresses are somewhat lower. The temperature dependence of the data of Beardmore by contrast is different and agrees well with the tension test results of Roetling.

Roetling (144) and Bauwens-Crowet and Homes (145) have shown that the yield stress is expected to be a bi-linear function of log (strain-rate) if two processes of the Eyring (201) type occur. If two such processes occur, the yield stress will be given by

\[
\sigma / T = \sum_{i=1}^{\infty} \frac{1}{A_i} \sinh^{-1} \left[ \frac{C_i \dot{\varepsilon}}{T \exp(\Delta H/R T)} \right].
\]

Here \(A_i\), \(C_i\) are constants, \(\dot{\varepsilon}\) is the strain-rate, \(\Delta H\) is an activation energy, \(T\) is the temperature, \(R\) is the gas
FIGURE 8.2

- STRAIN-RATE $10^{-3}$ s$^{-1}$
- MOLT C (compression)
- RENDEMORE X (""")
- PRESENT INV. O ("")
- EDULTING A (tension)
constant and \( \sigma \) the stress at yield.

Bauwens-Crowet et al. have derived from the Eyring theory that

\[
\frac{\sigma}{T} = A \left[ \ln 2C_0 \dot{\varepsilon} + (\Delta H/RT) \right] = 4.38 \frac{k}{\gamma_0} \frac{\gamma \dot{\varepsilon}}{2 \gamma J_o} + \Delta H/RT
\]

for one process. Here \( \gamma_0 \) is the shear volume, \( \gamma \) the elementary shear and \( J_o \) is a rate constant for the jumping process when no stress acts. For the case of polystyrene Bauwens et al.\(^{(223)}\) used the formula

\[
\frac{\sigma}{T} = A_{\infty} \left[ \ln 2C_{\infty} \dot{\varepsilon} + (\Delta H/RT) \right] + A \beta \sinh^{-1} \left[ C \dot{\varepsilon} \exp(\Delta H/RT) \right]
\]

to fit the results. There was a critical value of the stress below which the data obtained did not fit the equation well.

Holt\(^{(110)}\) has used the formula

\[
\sigma = U_0 / \nu + kT / \nu \ln \dot{\varepsilon} / \dot{\varepsilon}_0
\]

to describe his data. This also has a basis in the Eyring theory. Here \( U_0 \) is an activation energy for yielding in the absence of stress, \( \nu \) an activation volume, and \( \dot{\varepsilon}_0 \) is a function of the size and number of sites at which molecular movement occurs.

Whitney and Andrè\(^{(224)}\) and Rusch\(^{(179)}\) have discussed the influence of the volume changes during deformation upon yield. The volume change at strain \( \varepsilon \) may be written

\[
\Delta \nu = \nu (1 - 2\nu) \text{ where } \nu \text{ is Poisson's ratio. In tension, with } \nu = 0.3 \text{ and } \varepsilon = 0.1 \Delta \nu = 0.04. \text{ If } \varepsilon \text{ is negative so is } \Delta \nu. \text{ If increased volume aids the yielding then the yield stress should be greater in compression than in}
\]
tension. This is seen to be so in figs 8.1 and 8.2. An attempt has been made here to fit the expression of Roetling (144) in order to explain the observed yield data. The parameters obtained were

\[
\begin{align*}
A_\infty &= 264.2 \\
A_\beta &= 163.2 \\
\log_e C_\kappa &= -78.1 \\
\log_e C_\beta &= -38.2 \\
\Delta H_\kappa &= 50.43 \text{ Kcal.mol.} \\
\Delta H_\beta &= 38.63 \text{ Kcal.mol.}
\end{align*}
\]

these should be compared with the value obtained by Roetling

\[
\begin{align*}
A_\kappa &= 218 \\
A_\beta &= 104 \\
\log_e C_\kappa &= 90.0 \\
\log_e C_\beta &= 25.0 \\
\Delta H_\kappa &= 24.0 \text{ Kcal.mol.} \\
\Delta H_\beta &= 81.0 \text{ Kcal.mol.}
\end{align*}
\]

It has been noted already that there are differences between the present data and that of Roetling. The large differences in activation energies are attributable to the different temperature and rate dependences previously demonstrated.

Constant strain-rate testing under hydrostatic pressure
should resolve the effects of the stress state upon the yield phenomenon. It appears that the yield properties might profitably be further investigated as a function of free volume in order to see whether there is a direct dependence of one upon the other.

8.4 Stress Reduced-Strain-Rate Master Curves, Shift Factors and Activation Energies

The master curves shown in fig 7.12 are constructed from the stress-strain-rate curves shown in fig 7.2 and fig 7.3. The success of the shifting depends upon having stress-strain-rate curves over a sufficiently wide range of rates with enough data points to define the shape of the curve adequately at each temperature. Enough temperatures must be investigated so that curves at successive temperatures may be shifted onto one another confidently in order to create a master curve. (This procedure is well described by Ferry(37), for instance). If an insufficient range of strain-rates is investigated, the shape of the stress-strain-rate curve at a given temperature is not well defined, shifting of one curve onto another is made difficult and errors in the shift factors will result. These errors are cumulative. If sufficiently small temperature intervals are not taken, the exact amount of time-shift is not easy to obtain because the shifted curves will not overlap sufficiently. As the shifting procedure is
mostly subjective in any case, the final master-curve and shift-factors will suffer in accuracy. Apart from these factors, if normalized stresses (see 10.13) are being processed, errors in the normalization factors will affect the shifting procedure and thus lead to inaccurate master curves. It has not been ratified in the present work that the assumption that \( c_T = d_T \) made here (and by McCrum and Morris\(^{(109)}\), and Thompson\(^{(120)}\)) is valid. The normalization procedure and normalization factors used here are at least the same as those used by those workers.

In constant strain-rate testing only one data point (for fixed strain, rate and temperature) or time and temperature) is obtained from each test. In a relaxation or creep experiment by contrast, data is available over the whole time scale of a single test. If accurate measurements can be made at small strains in the linear viscoelastic region, then the stress-strain relation may be differentiated using the procedure described in 10.2 and data obtained over the whole time scale (for the linear region) of the experiment. It has been discussed elsewhere that small strains could not be accurately measured using the techniques available.

In this investigation, just adequate data (consistent with the capabilities of the equipment) to construct the master curves was aimed for. Even so, some 80 results from tests made on the Instron machine (total 87 tests) and 48 results from tests made on the hydraulic machine (total 68 tests) are reported here. This excludes
the initial exploratory programme and tests concerned with slenderness, end lubrication and repeatability. It is obvious from the stress-strain-rate curves and the master curves that data both more closely spaced in strain-rate and temperature would be advantageous. The master curve shifting was performed three times (each for PR and MR, 2 and 4 percent strain, normalized and un-normalized data): the error in the final curves was then estimated on the basis of the possible limits considered in each case. In the present work the construction of the master curves is made more difficult by the fact that the relaxed and unrelaxed moduli of the \( \beta \)-transition are not reached at the lowest and highest strain-rates employed. Tests at higher and lower temperatures, but the same strain-rates employed here, would begin to show the effects of other relaxations.

Figure 8.3 shows the present shift factor data (for un-normalized stresses) at 2 percent strain plotted with data from Rusch\(^{(13)(179)}\), McLoughlin and Tobolsky\(^{(22)}\), Bueche\(^{(130)}\) and Thompson\(^{(120)}\). It may be seen that the shift factors for data taken at high strains (c. 2 percent), i.e., the present data and that of Rusch\(^{(179)}\) (for 1-2 percent strain) are lower than those obtained at smaller strains. It is notable that Thompson, who obtained the highest values for the shift factors, ensured that the measurements were made in the linear viscoelastic regime. The relaxation measurements of Rusch\(^{(13)}\) were made at 0.5 percent strain in flexure. The yield measurements of Rusch\(^{(179)}\) are in fair agreement with those obtained here. It is notable that the other investigators reported here have used smaller temperature intervals than in the
The present work, as well as measuring response throughout the testing period (except Rusch (179)).

The activation energies for the β-relaxation obtained in this work and reported in 7,10 agree well with those of other workers (see table 5.1). In cases (here and in table 5.1) where values of over 20 Kcal.mol.\(^{-1}\) (usually 26-30 Kcal.mol.\(^{-1}\)) are reported, the data has not been normalized. This procedure is fully discussed in 10.13. If normalization is not carried out, the results obtained are incorrect. When normalized data are used or the activation energy derives from dynamic measurements, activation energies are of the order of 17 Kcal.mol.\(^{-1}\). The exact values of the activation energy obtained will, of course, depend upon the exact chemical and structural constitution of the polymer and also upon the shift factors obtained from the master-curve construction (and thus presumably upon the measurement strains).

### 8.5 Features of the Stress-Temperature Curves

The curves of fig 7.7 show evidence of a single large transition. That this is very probably the β-transition has been discussed in 8.1. The curves for the PR material (but not the MR material) show a smaller transition - the α' transition discussed under 8.2. Stress-temperature curves for MR material show a marked decrease at 360\(^0\)K for all strain-rates. This feature is discussed in 8.6. There remains one other notable feature: the curves for PR material at 4 percent strain (but not those for MR material) show a steady rise below 220\(^0\)K. Presumably this is characteristic of large strain behaviour and also
depends upon the material treatment. The first point in any case is well established as the corresponding 2 percent and 4 percent strain data points derive from the same test.

8.6 The Properties of Slow- and Fast-Cooled Samples

The PR and MR materials examined here show some notable differences in mechanical properties. The stress-strain-rate curves are generally similar in form for the two materials. The anomaly which is apparent in figs 7.2 and 7.3, i.e., that some stresses at 200°K are lower than those at 300°K at the same strain-rate is probably due to the fact that the normalization factors (c_T) used are too large for low temperatures. This anomaly is evident in the curves both for PR and for MR materials. Although the limiting moduli (2 percent strain) are not reached in these experiments, they have been estimated (in fig 7.6) as E_U(PR) = 705000 psi, E_U(MR) = 310000 psi, E_R(PR) = 585000 psi, E_R(MR) = 165000 psi at 300°K. The limiting moduli for MR material are thus much lower than those of the PR material. The limiting stresses for the normalized master curves at 2 percent strain of fig 7.12 differ by 2760 psi which corresponds to a secant modulus difference of 137000 psi. This modulus difference diminishes to 97500 psi in the centre of the β-transition range. This is a consequence of the fact that the MR material relaxes faster than the PR material in this region.
The MR material does not show evidence of the $\alpha'$-transition. This has been discussed under 8.2. The stress at 2 percent strain of the MR material drops away sharply at temperatures greater than $350^\circ$K. Figure 7.16 shows that in the dilatometry experiments volume contraction is also evident on heating above $350^\circ$K. The volume measurements reported in 7.12 show that MR samples heated to $366^\circ$K have retracted in volume considerably after 20 hours. The photoelastic internal stress measurements reported in 10.6 reveal (as discussed in 8.12) that the internal stress is considerably changed by heating to $366^\circ$K for 2 hours. It is believed that the reduced stresses at high temperatures are a consequence of volume retardation taking place during the test which is probably aided by the applied stress.

In fig 7.7, it is seen that the diminished stress at $360^\circ$K is maintained to the highest strain-rate investigated. It is concluded therefore that the low stresses are not a consequence merely of unaided volume contraction during the test period which is short at high strain-rates ($\sim 1$ms). If the volume had relaxed somewhat at temperature prior to the test, the stresses would be expected to be higher (closer to the stress for the PR material). It follows that the unusually low stresses are a consequence of volume relaxation aided by the stress, which occurs in such a manner that least total work is done during the test.)
The magnitude of the $\beta$-transition as measured by the parameter $\Delta\sigma$ (see 7.6) for MR material is very similar to that of the PR material. The $\beta$-transition temperature for MR material (table 7.4) is $280^\circ\text{K}$, $16^\circ\text{K}$ higher than that for the PR material ($264^\circ\text{K}$). The magnitude of the transition ($\Delta\sigma$) is shown for the MR material together with that for the PR material in text figure 26. The magnitude of the transition in the MR material is slightly less than that of the PR material, but the transition appears about $16^\circ\text{K}$ higher in temperature.

In 7.8 it was observed that the MR material had a lower initial modulus than the PR material. This was also observed by McLoughlin and Tobolsky (22) in relaxation experiments performed on poly (methyl methacrylate) treated in a similar way. It is clear from fig 7.16 that if free volume alone controls the relaxation behaviour of the polymer, then the properties of the MR material at a given temperature and strain-rate should be the same as those of the PR
material at the same strain-rate and at a higher temperature where it has the same specific volume. If the temperature of the PR material is less than 300°K then this difference will be \((0.8514-0.8476)/1.78 \times 10^{-4} = 21.4°K\) and if the temperature of the MR material is greater than 300°K the difference will be \((0.8514-0.8476)/(2.28 \times 10^{-4} = 16.7°K\) (see table 7.7 and fig 7.16). In terms of the theory of Rusch (13) this should be so whatever the form of the volume-temperature relationship of the equilibrium glass. If other dilatometric transitions than the one found here are present, then the 'temperature shift' will be different in every region of different expansivity. Whatever the volume-temperature relations for the two materials this 'temperature shift' can be found as a function of temperature.

We are neglecting here the difference in properties caused by a change in temperature alone. If this is accounted for by the expected change in the limiting moduli (i.e. by means of the normalization factor) the multiplying factor for a change of 20°K would be 1.09 at 300°K or 1.03 at 200°K. The stress difference due to this cause (say 700 psi) is small compared to the difference in stresses observed for PR and MR materials at a given temperature and strain-rate (say 3000 psi). The yield-stress-temperature curves (figs 7.8 and 7.9) of MR and PR material do seem to be related by a simple temperature difference. The value of the horizontal shift required to cause superposition of the MR and PR
yield stress curves is tabulated below:

Table 8.1

<table>
<thead>
<tr>
<th>Rate</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>220 °K</td>
<td>11</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240 °K</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>260 °K</td>
<td>14</td>
<td>19</td>
<td>14</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>280 °K</td>
<td>9</td>
<td>13</td>
<td>18</td>
<td>14</td>
<td>11</td>
<td>19</td>
</tr>
<tr>
<td>300 °K</td>
<td>9</td>
<td>16</td>
<td>18</td>
<td>16</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>320 °K</td>
<td>10</td>
<td>18</td>
<td>18</td>
<td>16</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>340 °K</td>
<td>10</td>
<td>19</td>
<td>18</td>
<td>9</td>
<td>9</td>
<td>13</td>
</tr>
</tbody>
</table>

There is seen to be fair agreement with the idea that iso-volume states result in the same yield stress (neglecting, of course, the direct temperature dependence of the yield stress).

It is immediately obvious from figures 7.5 and 7.6 that a mere horizontal shift of 21.4 or 16.7 °K will not cause a superposition of the stress-temperature curves of MR and PR materials at a given strain-rate for small strains. This may be seen to be true both in regions where the stresses approach the limiting values for the \( \beta \)-transition and also for intermediate temperatures. It follows (excepting the \( \alpha' \) transition from consideration) that no modification of the vertical shift factor \( c_T \) (which has been applied) would enable the superposition of the MR and PR stress-temperature curves (with the previously mentioned horizontal shift). This is because the factor \( c_T \) must multiply stresses for both materials. The factor
$c_T$ must be 1.00 for the reference temperature and there is no evidence in present data to suggest that $c_T$ will be of different form for PR and MR materials. It seems that the free volume must affect the limiting stresses in some way as well as affecting the relaxation times. It is also possible that the free volume may affect the magnitude of the $\beta$-transition (see previous discussion). The temperature dependence of the limiting moduli should not be confused with a possible dependence upon free volume per se.

Rusch (13) has suggested that in order to cater for the dependence of the modulus upon thermal history "it is recommended that the modulus be multiplied by the ratio $T_o/T_e$. Here $T_o$ is the reference temperature for the shift-factor and $T_e$ is the effective temperature (see 6.3f). Quoting again: "Although the temperature reduction factor $T_o/T_e$ has no rigorous theoretical basis, it provides, qualitatively at least, a smooth transition between the rubbery and glassy regions and allows a correction to be made for glasses with different thermal histories". In 8.7 the values of $T_e$ have been presented. The factor $T_o/T_e$ will vary as shown in table 8.2. The factor $T_e^{MR}/T_e^{PR}$ then constitutes the relative magnification of the MR stress-temperature curve with respect to the PR curve. This small factor obviously cannot alone explain the large difference between the curves at any given temperature. It remains, therefore, to find the reason for the strong dependence of the limiting moduli upon specific volume (if indeed it is the volume alone which affects these moduli).
Table 8.2

The Factor $T_o/T_e$

<table>
<thead>
<tr>
<th>$T_o^O (K)$</th>
<th>$T_e (MR)^O (K)$</th>
<th>$T_o/T_e$</th>
<th>$T_e (PR)^O (K)$</th>
<th>$T_o/T_e$</th>
<th>$T_e (MR)/T_e (PR)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>382.5</td>
<td>0.988</td>
<td>377.0</td>
<td>1.002</td>
<td>1.014</td>
</tr>
<tr>
<td>340</td>
<td>381.1</td>
<td>0.993</td>
<td>376.0</td>
<td>1.006</td>
<td>1.013</td>
</tr>
<tr>
<td>320</td>
<td>379.5</td>
<td>0.997</td>
<td>374.5</td>
<td>1.009</td>
<td>1.012</td>
</tr>
<tr>
<td>300</td>
<td>377.2</td>
<td>1.002</td>
<td>372.7</td>
<td>1.013</td>
<td>1.011</td>
</tr>
<tr>
<td>280</td>
<td>375.0</td>
<td>1.008</td>
<td>370.5</td>
<td>1.020</td>
<td>1.011</td>
</tr>
<tr>
<td>260</td>
<td>373.2</td>
<td>1.012</td>
<td>368.5</td>
<td>1.025</td>
<td>1.011</td>
</tr>
<tr>
<td>240</td>
<td>372.0</td>
<td>1.016</td>
<td>367.2</td>
<td>1.030</td>
<td>1.011</td>
</tr>
<tr>
<td>220</td>
<td>371.0</td>
<td>1.019</td>
<td>366.5</td>
<td>1.032</td>
<td>1.011</td>
</tr>
<tr>
<td>200</td>
<td>370.5</td>
<td>1.020</td>
<td>306.0</td>
<td>1.033</td>
<td>1.011</td>
</tr>
</tbody>
</table>

8.7 The Theory of Rusch

The idea proposed by Rusch (13) that the time-temperature equivalence of the Williams-Landel-Ferry relation (which was shown in 6.2b to be equivalent to a free-volume interpretation) may be modified to describe behaviour in the glassy regime has been presented already in 6.3f. The theory has been tested here against the shift-factor and volume data available (and presented respectively in 7.9 and 7.12, 7.13). The shift-factor $\log \alpha (T)$ was used in order to determine the effective temperature $T_e$ according to Rusch,
\[ \log \alpha_T = -C_1 (T_e - T_o) / (C_2 + (T_e - T_o)), \]

which relation is assumed to hold below the glass transition temperature if the values of \( T_e(T) \) are determined by the free volume of the material alone. In the above \( C_1, C_2 \) and \( T_o \) are the normal WLF 'constants' and reference temperature. In the following, the values of 20.20, 44.6\(^\circ\)K and 378\(^\circ\)K have been assigned for poly (methyl methacrylate) these values being taken from the data of Adam and Gibbs (161). The reference temperature \( T_o \) is thus the dilatometric glass transition temperature. The values of \( \log \alpha_T \) for PR and MR samples enable the respective effective temperatures to be determined as a function of temperature. These are shown in fig 8.4. The curves of \( \log \alpha_T \) as a function of temperature for PR and MR material at 2\% strain only (reference 380\(^\circ\)K) shown in fig 7.13 were used as the source of \( \log \alpha_T \). The parameter \( w_f(T) \) (non-equilibrium free volume) (see 6.3f) may now be determined from the \( T_e(T) \) values according to Rusch's theory by using

\[ w_f(T) = (T_e - T) \Delta \alpha, \quad T \geq T_2 \]

\[ w_f(T) = (T_e - T_2) \Delta \alpha, \quad T \leq T_2. \]

Here \( T_2 \) is the second-order transition temperature of Gibbs and di Marzio (148) and has been taken here at 332\(^\circ\)K following Adam and Gibbs (loc. cit.) (Alternatively, \( T_2 \)
may be considered as the temperature at which the shift-factor $\log \alpha_T$ in the unmodified WLF formula goes to infinity; using the constants given above this would be $333.4^\circ\text{K}$. $\Delta \alpha$ is the difference between the expansivities of equilibrium liquid and equilibrium glass, i.e., $\alpha_l - \alpha_g$. It may be considered also as the 'expansivity of free volume'. This parameter is disposable and was used by Rusch to make the values of $w_f$ obtained from $\log \alpha_T$ and those obtained from volume measurements coincide. It should be pointed out here that while the equilibrium volume of the liquid is measurable (and hence so is $\alpha_l$, which is approximately constant with temperature) that of the glass ($\alpha_g$) is not measurable except within perhaps ten degrees of the glass-transition temperature. It is thus an assumption of Rusch's theory that the equilibrium glass volume is linear in temperature and consequently that $\alpha_g$ is constant. Sub-glass transitions may well interfere with this assumption (in table 5.2 dilatometric transitions in poly (methyl methacrylate) have been observed for the $\alpha'$ process at $335^\circ\text{K}$ and for the $\beta$ process at $288^\circ\text{K}$ for non-equilibrium glasses) so the theory of Rusch unmodified should be reserved for temperatures above any minor transitions. While a choice of the form of the equilibrium glassy volume-temperature curve may be made that will cause the theory to work perfectly (that is perhaps with $\alpha_g$ a function of temperature) this has not been used here, nor was it by Rusch as the equilibrium volume-temperature relationship cannot be measured directly and thus no direct verification is possible. The assumption
of a constant value for \( \alpha_g \) seems to be the simplest possible consistent with expectation.

Various arbitrary values of \( \Delta \alpha \) may thus be chosen in order to establish the form of \( w_f(T) \) as derived from the shift-factor measurements. The values of \( w_f(T) \) may now be derived directly from the volumes of the PR and MR materials (fig 7.13) by assuming values for both \( \alpha_1 \) and \( \alpha_g \) (i.e. \( \alpha_1 \) and \( \Delta \alpha \)). Text figure 23 shows how this is done. Fig 7.16 shows an equilibrium liquid line (\( \alpha_1 = 4.7 \times 10^{-4} \) K\(^{-1} \)) and equilibrium glass line (\( \alpha_g = 1.2 \times 10^{-4} \) K\(^{-1} \), \( \Delta \alpha = 3.5 \times 10^{-4} \) K\(^{-1} \)) as examples.

If the theory of Rusch is correct, there should be a realistic \( \alpha_1, \Delta \alpha \) combination consistent with other evidence for which \( w_f(T) \) determined from the shift-factor and from the volumes coincide. In fact, as \( \alpha_1 \) may be measured directly this amounts to determining \( \Delta \alpha \) (or \( \alpha_g \)) in order that there is coincidence. The value of \( 4.7 \times 10^{-4} \) K\(^{-1} \) was measured by Rusch for \( \alpha_1 \), and the value of \( \alpha_g \) determined by him to cause coincidence of \( w_f(T) \) \( 1.2 \times 10^{-4} \) K\(^{-1} \) (i.e. \( \Delta \alpha = 3.5 \times 10^{-4} \) K\(^{-1} \)) as shown in fig 7.16.

The \( w_f(T) \) values determined from the shift-factors and assumed \( \Delta \alpha \) and from the volume measurements and the (same) assumed \( \Delta \alpha \) are shown in figures 8.5, 8.6 and 8.7. It may be seen that the parameters used by Rusch (\( \alpha_1 = 4.7 \times 10^{-4} \) K\(^{-1} \), \( \Delta \alpha = 3.5 \times 10^{-4} \) K\(^{-1} \)) do not result in coincidence here. If \( \alpha_g \) is fixed at \( 4.7 \times 10^{-4} \) K\(^{-1} \), it may be seen from fig 8.6 that for PR samples the best choice for \( \Delta \alpha \) (if temperatures down to 300°K) only are considered (the
Figure 8.6

Graph showing the relationship between temperature and volume for different pressures. The graph is labeled with various data points and equations, such as

\[ V = 4.7 \times 10^4 \text{m}^3/k \]

\[ P = 2.0 \times 10^6 \text{Pa} \]

\[ \Delta V = 2.7 \]

\[ \Delta T = 2.1 \]

\[ \Delta P = 2.5 \times 10^4 \text{Pa} \]

The x-axis represents temperature in K, ranging from 0 to 600, and the y-axis represents volume in m^3, ranging from 0 to 10. The graph includes data points and linear relationships.
temperature at which a dilatometric sub-glass transition is evident in the present volume measurements) is 2.6 $\times 10^{-40} K^{-1}$. If, however, the $w_f(T)$ for MR material is also considered (fig 8.7) it is seen that $\Delta \alpha = 2.75 \times 10^{-40} K^{-1}$ is a better compromise. The agreement is seen to be fair except that there is obviously an increasing divergence at lower temperatures. This may be well due to the occurrence of a sub-glass transition, but it is difficult to see how this might be accounted for by modifying the theory as there is at present no theoretical basis in a free volume theory for such relaxations.

Even if the agreement at $\Delta \alpha = 2.75 \times 10^{-40} K^{-1}$ is considered sufficiently good, there is still a difference in the sign of the error in $w_f(T)$ for PR and MR samples. The $w_f(T)$ estimated from volumes is larger than that from $\log \alpha_T$ for MR material but less for PR material. This suggests that free volume directly or alone may not be the dominating factor in the relaxation processes.

Text figure 27 shows the effect of changing $\alpha_1$ or $\Delta \alpha$ in order to try to obtain a better agreement. At the top is shown the initial attempt which is typical of the case shown for $\alpha_1 = 4.7 \times 10^{-40} K^{-1}$, $\Delta \alpha = 3.3 \times 10^{-40} K^{-1}$ in fig 8.5. If $\alpha_1$ is raised so as to improve the fit near 320$^\circ$K, there will be serious divergence at low temperatures. If $\Delta \alpha$ and $\alpha_1$ are raised together, then the fit near 332$^\circ$K may be improved, but that below 332$^\circ$K is not. Several such attempts are shown in fig 8.5.
It may be seen that a notable improvement in the fit for PR material might be made if the case \( \alpha_1 = 4.7 \times 10^{-4} \, \text{K}^{-1} \), \( \Delta \alpha = 2.8 \times 10^{-4} \, \text{K}^{-1} \) was changed to \( \alpha_1 = 4.85 \times 10^{-4} \, \text{K}^{-1} \), \( \Delta \alpha = 2.8 \times 10^{-4} \, \text{K}^{-1} \) but fig 8.7 shows that this would make the fit for MR material worse.

Two points which are relevant to the discussion here are

1. that the relaxation data of Rusch were not normalized as discussed in 7.5 and
2. that the present data is obtained at much higher strains (2%) than that of Rusch (0.5%).

These are two reasons to expect that the \( \log \alpha_T \) values obtained here and by Rusch are different (which they are - see fig 8.3). An immediate consequence of this is that the values of \( w_f(T) \) predicted from them will not agree.

If, however, the theory of Rusch is generally applicable, neither of these facts should preclude the possibility of fitting the \( w_f(T) \) values by means of an appropriate choice of \( \Delta \alpha \). This does not seem possible here.

If temperatures above 332\(^0\)K only are considered, it is possible to determine \( w_f(T) \) from \( \log \alpha_T \) for a series of values of \( \Delta \alpha \) and \( w_f(T) \) from volume measurements as a function of \( \alpha_1 \) only. It is then possible to create a nearly exact coincidence of the \( w_f \)'s if the following values of \( \Delta \alpha \) and \( \alpha_1 \) are paired: see table 8.3., table 8.4.

It thus seems that the theory will work in the temperature range 332-378\(^0\)K for any \( \alpha_1 \) as long as \( \alpha_g = 2.1 \times 10^{-4} \, \text{K}^{-1} \) (PR) or \( 1.55 \times 10^{-4} \, \text{K}^{-1} \) (MR). This is also evident in figs 8.5-8.7. This fact still does not enable the theory to be any better satisfied by the present data below 332\(^0\)K. In any case the different values of \( \alpha_g \) required by the two different material treatments again throws suspicion on the theory.
High-Temperature Fitting of $w_f(T)$

**Table 8.3**

<table>
<thead>
<tr>
<th>$\alpha_1$</th>
<th>$\Delta \alpha$</th>
<th>$\alpha_g$</th>
<th>$(x 10^4)^{\circ} K^{-1}$</th>
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<tr>
<td>4.6</td>
<td>2.5</td>
<td>2.1</td>
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</table>
The concept of the description of the state of non-equilibrium glasses discussed in 6 lead to the conclusion that a one-parameter description of state is not likely to be adequate. Even if it were, there is the question of which parameter it would be (enthalpy, entropy, volume or other) (192)(193). The theory of Rusch is essentially a one-parameter theory where volume (more strictly free-volume in his sense) is that parameter. It seems then that on theoretical grounds that Rusch's theory is unlikely to be true generally. It seems further that it does not agree with the present measurements. It remains to be said, however,
that the theory of Rusch does provide a very valuable approach to the problem of defining time-temperature-volume relationships for non-equilibrium glasses and the answers obtained therefrom are in approximate agreement with shift-factor data.

8.8 Volume Measurements

In 7.12, the specific volume measurements reported for PR and MR samples at 300°K were respectively 0.8476 mlg⁻¹ and 0.8514 mlg⁻¹ for samples cooled from 413°K at nominal rates of 1 x 10⁻³ Ks⁻¹ and 7.4 x 10⁻¹ Ks⁻¹. The specific volume of MR samples (at 300°K) subsequently annealed for 20 hours at 366°K was 0.8483 mlg⁻¹. The specific volume of samples cooled from 413, 403 and 393°K at 7.4 x 10⁻¹ Ks⁻¹ were respectively 0.8498, 0.8520 and 0.8540 mlg⁻¹.

The value reported for PR material is in good accord with the values given in table 5.2 for material of similar tacticity: 0.8456(⁶), 0.8439(¹), 0.8148(¹¹) and 0.8369 mlg⁻¹(³). The first two of these values fall within the estimated error for the present measurements of ± 0.44%.

The tendency for the specific volume in quenched specimens to depend upon the quench temperature was shown in 7.12 to be statistically significant. A tentative explanation of this is offered here. Havriliak(¹²) and Havriliak and Roman(¹¹⁶) have reported work on the dielectric and
infra-red properties of poly (methyl methacrylate) (see 5.4c). They conclude that the two configurations of the ester groups are occupied above the glass-transition temperature in a way which depends upon temperature: the ratio of the infra-red absorption peaks corresponding to the two states varies linearly with temperature. Configurations corresponding to such temperatures may be 'frozen-in' by rapidly cooling the samples. If it is conjectured that the volume is a function of the ester group internal configuration then the observed density variations in samples rapidly cooled from various temperatures may be attributed to the various configurations 'frozen-in'. This seems a reasonable assumption as Havriliak and Roman regard the effect as due to inter-molecular rather than intra-molecular forces and it would thus be expected to affect the specific volume. The dilatometry experiments reported here revealed only one transition in the volume-temperature relationship - at about 300°K. An extended investigation at higher instrument sensitivity did not reveal any discontinuity between 320 and 350°K. The thermal coefficients of expansion observed: 2.28 x 10^{-4}°K^{-1} from 310 to 360°K and 1.78 x 10^{-4}°K^{-1} from 250 to 290°K are in good accord with the values observed (3)(6) and recorded in table 5.2: for the temperature ranges 340 to 360°K (2.25 x 10^{-4}°K^{-1}, 2.02 x 10^{-4}°K^{-1}, 2.36 x 10^{-4}°K^{-1}, 2.78 x 10^{-4}°K^{-1}) and from 280 to 320°K (1.65 x 10^{-4}°K^{-1}, 1.60 x 10^{-4}°K^{-1}, 1.84 x 10^{-4}°K^{-1}, 2.05 x 10^{-4}°K^{-1}).
Dilatometric transitions near 300°K have been reported by Martin et al. (212) at 293°K, Sherby and Dorn (213) at 303°K, Holt and Edwards (214) at 296°K and Atkinson and Grant (215) at 303°K.

If all of the free volume at the quench temperature was retained on quenching, the maximum difference in volume to be expected of fast and slow cooled samples would be (413-378)Δα for samples cooled from 413°K. Here Tg = 378°K and Δα is the 'coefficient of expansion of free volume'. If Δα is taken as 2.0 x 10^-40°K^-1 (a minimum value) the volume difference would be 0.0070 ml/°K, that observed is 0.0038 ml/°K. Thus the fast cooling (MR) process here is not fast enough to prevent an approach towards equilibrium during the cooling. The values of f(Tg) (the fractional free volume at the commencement of the glass transition) have been given as a function of cooling rate (σ) by Saito et al. (14), according to their theory as 0.0289 (σ = 10^-2), 0.0272 (σ = 10^-3), 0.0256 (σ = 10^-4) and 0.0243 ml/°K (σ = 10^-50°Ks^-1). (they assigned Δα = 4.8 x 10^-4o°K^-1). The expected difference in volumes of samples cooled at 10^-2 and 10^-4o°Ks^-1 is thus 0.0033 ml/°K, and of samples cooled at 10^-2 and 10^-50°Ks^-1 0.0047 ml/°K. If the f(Tg) values of Saito et.al. are extrapolated to $σ = 7.4 \times 10^{-10}$°Ks^-1 f (Tg) is found to be 0.0303 ml/°K. The difference in volume of samples cooled at $7.4 \times 10^{-1}$°K and $1.0 \times 10^{-30}$°Ks^-1 (the programmes used here) is then expected to be 0.0031 ml/°K.
(The value observed is 0.0038 mlg⁻¹). The observed volume difference is thus close to that predicted by Saito et al.

As shown in fig 7.16, at temperatures above 350⁰K the MR material is sufficiently close to the glass transition temperature to enable volume relaxation to occur and the volume approaches that of the PR material. This is supported by the observations concerning measured mechanical properties discussed in 8.6 and the observations on the release of internal stress discussed in 8.12.

An improvement in the experiments presented here would be to cool the specimens in a chamber controlled so as to give a constant rate of cooling. Lower rates of cooling could thus be achieved. There would be some point in investigating the final variation of specific volume throughout the specimen for fast cooling rates in order that some of the outside of the specimen could be machined away. This would leave a core of more homogeneous properties for testing. Specimens heated above the glass transition temperature, pressurized and then cooled below the transition temperature would be expected to show lower specific volumes than samples cooled under atmospheric pressure. This would enable lower specific volumes to be achieved than could otherwise be conveniently obtained. The density measurement techniques used here could undoubtedly be improved on by overcoming some of the difficulties presently found with
other techniques. The interesting variation of density with quenching temperature should be investigated more fully. The results should be correlated with infra-red measurements made at the quench temperature and after quenching. Evidence from these experiments should lead to useful information concerning the $\alpha'$ relaxation.

8.9 Thermodynamic Description of State

In chapter 6 this problem has been discussed at length. There is sufficient information about glassy polymers to expect that the relaxation properties in the glassy state will not be adequately described by one parameter (186)(187)(209). There is some evidence which leads to the conclusion that the entropy or enthalpy of the non-equilibrium states of glassy materials would be a more suitable parameter to investigate than the (free) volume (192)(193).

It has been shown in 8.7 that the proposition of Rusch (13) that free volume and temperature may be used to adequately describe the material state is true in approximation since it enables a crude prediction of shift-factors from measured volumes. Evidence is given there to show that this theory does not provide a dependence of the parameter $w_f$ upon the temperature which is consistent with the experimental shift factor dependence. In 8.6 it has been
shown that there is a gross error in the limiting moduli for materials in different states which cannot be adequately accounted for by Rusch's theory. It has also been shown in 8.6 that an iso-volume description of state cannot adequately describe the mechanical properties for small strains.

It seems that better information about a possible specification of material state may be found by measuring the enthalpy of the polymer cooled at various rates or otherwise manipulated into different states. This could be done by measuring the heat required to raise the sample from some temperature below to some temperature above the glass transition temperature. The measurement of this property would be in better sympathy with the theories of Gibbs-di Marzio and Goldstein than the measurement of volume. It may be that some other property such as refractive index would be more easily measured accurately than the volume in order to investigate the material state. Some form of correlation between this property and some fundamental property such as volume or enthalpy would have to be established.

8.10 The Constant Strain-Rate Technique

The mechanical viscoelastic properties of a solid may be investigated by many different techniques. A stress history or a strain history may be prescribed and the strain or stress response observed. The prescribed history may be a
step-function, a periodic function or a ramp function. As long as the material is linear in the Boltzmann sense (37) all such measured properties are related. There is thus ab initio no reason to prefer any special technique over any other. Practically, however, one testing technique may be greatly preferred over another because of convenience or availability of equipment. Here the constant rate of increase of strain with time is the test method used. In 10.2 it is shown how the secant modulus for a constant strain-rate test may be approximately equal to the stress relaxation modulus. The stress-strain-rate and stress-temperature curves presented here may thus be compared directly with storage modulus and stress relaxation modulus curves in the literature.

Although the experiments are relatively easy to perform over a range of strain-rates and temperatures, they are subject to several errors which do not occur in other experiments. One of these is the variation in strain-rate during the test. This has been discussed in 7A and also at length in 10.3. The variation in strain-rate is solely a deficiency in the performance of the two testing machines employed. In the case of the Instron machine, the error in strain-rate may be up to 40% under unfavourable conditions. In the case of either machine the error in the determination of stress at a given strain may be large because of the relatively large error in determining the strain when the conventional techniques of machine operation are used. Careful attention to technique can minimize these errors considerably, but the
use of an accurate extensometer directly fixed to the specimen is the only satisfactory solution.

The restriction on the relations between secant moduli from constant strain-rate tests and relaxation moduli and the variations in strain-rate in the (nominally) constant strain-rate tests as conducted here thus mean that caution should be used in relating the present results to literature data obtained by other techniques. Relaxation or creep experiments are better methods than constant strain-rate experiments for gathering data concerning relaxation mechanisms in polymers if time-temperature superposition must be attempted. This is because they provide data over the whole time-scale of the experiment and better define the curve at a given temperature. They have a disadvantage when compared with constant strain-rate tests in providing data over smaller time scales. Measurements could probably be made over six decades of time (up to say $4 \times 10^4$ s).

Constant strain-rate experiments can be made over about 8 decades in time, say to $10^3$ s$^{-1}$, at least three different testing machines would be needed however and many experiments. The relaxation method would make data available over the whole time scale by using only one testing machine and one experiment at each temperature.
8.11 Stress-Strain Curves

Figure 7.11 shows some typical stress-strain curves. The stress at a given strain and strain-rate is seen to increase as the temperature is decreased. The stress at a given strain and temperature increases as the strain-rate is increased. Thus the mechanical properties of poly (methyl methacrylate) are sensitive to both temperature and strain-rate, as is to be expected if a time-temperature equivalence is to be sought. The difference in the secant moduli of PR and MR material appears to be maintained to small strains.

The stress-strain curve near yield is seen to be defined by larger second derivatives at low temperatures or high strain-rates than at high temperatures or low strain-rates. Figure 7.11 shows that as the temperature is decreased to 300°K the yield strain increases and then decreases at lower temperatures for PR material. This was also observed by Beardmore (217) who found that the temperature of greatest yield strain for compression tests was 270°K and the greatest yield strain 4.4 percent. The temperature of maximum yield strain corresponds to the temperature of the β-transition. No accurate assessment of this temperature can be made here as measurements of the yield strain were not made.

At low temperatures the stress-strain curves have a greater
gradient between 2 and 4 percent strain than at high temperatures. This gradient is also a function of strain-rate at high temperatures. This is shown in text figure 28 where the ratio of stresses at 4 and 2 percent strain for PR material is plotted for 200, 300 and 360 °K against log strain-rate.

These temperatures avoid the $\beta$-transition region as far as possible. At 200 °K the ratio is close to 2.0 and falls somewhat as the strain-rate increases. At 300 °K the ratio is somewhat lower and increases slightly with strain-rate. At 360 °K the ratio is 1.05 at the lowest rate and increases steeply with rate. The result of this is that at high strain rates the stress-strain curves at different strain-rates are of similar form while at
low strain-rates the form is similar at low temperatures but at 360°K the gradient decreases to nearly zero at strains of the order of 4 percent. This may also be seen in fig 7.11. This is presumably due to the proximity of the glass transition at this temperature and time. The rate of stress relaxation under these conditions must then approximate the rate of stress application. The mean values of \( \sigma_4/\sigma_2 \) for the PR material (in strain-rate) for the temperatures 200, 300 and 360°K are 1.96, 1.84 and (1.54). The corresponding values for MR material are 2.31, 2.09 and (1.76). The ratio \( \sigma_4/\sigma_2 \) for MR material shows a similar behaviour to that of the PR material at each temperature.

The rate of decrease of gradient with strain is less for MR material than for PR material as shown by the values of \( \sigma_4/\sigma_2 \). This is largely a consequence of the lower initial modulus of the MR material. This is reflected in the ratio of the PR stress to MR stress at given strain and temperature - \( \sigma_p/\sigma_M \). The mean values (in rate) are

| Table 8.5 |
| Stress Ratio \( \sigma_p/\sigma_M \) |
| 2% Strain       | 4% Strain |
| 200°K           | 1.319     | 1.133     |
| 300°K           | 1.311     | 1.170     |
| 360°K           | 1.679     | 1.617     |
The value of the ratio is less at 4 percent strain than at 2 percent strain. There is a notable difference in the behaviour of the materials at 360°K which is not present at lower temperatures. The ratio $\sigma_p/\sigma_M$ rises from 1.315 to 1.68 (2 percent) or 1.15 to 1.62 (4 percent). This is because the MR stresses are unusually low at 360°K. This is believed to be due to the onset of the volume contraction of the MR specimens under the influence of stress at a temperature close to the glass transition temperature. This is borne out by the dilatometry, ageing-out of volume and ageing-out of internal stress experiments described elsewhere.

8.12 Temperature Gradients and Internal Stresses

The cooling programmes used in this investigation have been described in 7.1 and 10.4 and the expected time variation in surface temperature of hot or cold specimens exposed to the atmosphere is also discussed in 10.4. It is expected that the (PR) specimens cooled at the (nominal) rate of $1.0 \times 10^{-3}$°K s$^{-1}$ will contain insignificant temperature gradients during cooling. The cooling curve in fig 10.4 will thus be representative for all parts of the specimen. Because the polymer has a finite thermal conductivity there will be thermal gradients present during the fast cooling (MR) programme which are of greater magnitude. The cooling curve presented in fig 10.4
will be representative of the history of the specimen centre. If the specimen is treated as a long cylinder, the formulae presented in 10.4 may be used to estimate the surface temperature history. This has been done here for two cases: air cooling at the outer surface with \( h = 1.275 \text{ cal s}^{-1} \text{ cm}^{-2} \text{ o}^{-1} \text{ K}^{-1} \), and water cooling at the outer surface \( h = 100 \text{ cal s}^{-1} \text{ cm}^{-2} \text{ o}^{-1} \text{ K}^{-1} \). These cooling curves are presented in text figure 29. The surface rates of cooling at the glass transition temperature are \( 1.56 \times 10^{-2} \text{ o}^{-1} \text{ K}s^{-1} \) and \( 2.75 \text{ o}^{-1} \text{ K}s^{-1} \) respectively. The cooling rate at \( T_g \) for the water-quenched (MR) material is thus \( 156/0.74 = 210 \) times as fast as the surface as at the centre. The estimated difference in free volume of the outside and inside (using an extrapolation of the data of Saito et al. (14) and presented in 6.2b) is then \( 0.0064 \text{ mlg}^{-1} \). If the specimen is air-cooled, then the ratio of cooling rates at outside and centre is only \( 2.75/0.25 = 11 \) and the expected difference in free volume only \( 0.0024 \text{ mlg}^{-1} \). The total free volume is of the order of \( 0.0272 \text{ mlg}^{-1} \) (at \( T_g^+ \)) at a cooling rate of \( 10^{-3} \text{ o}^{-1} \text{ K}s^{-1} \) (14). As the temperature gradient in the radial direction will be very steep, only near the surface will the cooling programme be very different from that measured at the centre. The calculated (outside) and measured (inside) temperature and cooling-rate-time relations are given schematically in text figure 30 for a water-quenched sample. It is, of course, impossible to achieve nearly homogeneous cooling conditions for cooling-rates of this
order with a material of such low thermal conductivity (c. $4 \times 10^{-4}$ cal K$^{-1}$ cm$^{-1}$ s$^{-1}$). The MR material as tested is thus not homogeneous, but the volume of material deviating in free volume from the mean free volume by greater than 5 percent say is small compared to the total volume.

The inhomogeneous cooling of a material undergoing the glass transition (such as the MR material here) inevitably leads to a residual stress state. Evidence for this is presented in 10.6. A question which is pertinent here is whether or not this internal stress will affect the measured stresses, i.e., whether the measured stresses reflect not only the material state, but also the internal stress.
A completely linear elastic medium may be loaded with or without internal stresses being present and the measured stress-strain relation will be the same. By means of Alfrey's elastic-viscoelastic analogy, it may be argued that as long as the material remains linear in behaviour (that is in the Boltzmann sense, see Ferry) internal residual stress will not affect the measured properties. That the material is nearly linear may be seen from the data presented in 8.11, where it is shown that in the temperature range from 200-300°K over the whole range of strain-rates investigated the ratio of stresses at 4 and 2 percent strain is close to 2.0, the greatest deviation being at 300°K and a strain-rate where the factor is 1.75. Had reliable data for 1 percent strain been available (in order to test this ratio for 2 percent strain), the ratio would undoubtedly be closer to 2.0. The degree of non-linearity is thus small at 2 percent strain and the assumption that the internal stress will not affect the stresses measured at that strain is at least true to a large degree. The differences in the measured stresses for MR and for PR materials are then largely a consequence of the difference in material state only.

In section 10.6, it is shown that the internal stress is almost removed if the temperature is raised to 366°K for two hours. This is confirmed by the relaxation of volume discussed under 8.8. The retraction of oriented poly (methyl methacrylate) has been studied by Cleeram, Karam and Williams. Their results are reproduced
in text figure 31 here. The results agree well with present observations.

8.13 The Dynamic Modulus and $c_T$

In 7.11, the results of the dynamic modulus experiments were presented. The measurement frequency varied from 871 Hz at 375°K to 1172 Hz at 260°K. Kopplemann (88) has shown that the maximum in tan$\delta$ for the mechanical measurement of the $\beta$-relaxation is at 293°K (1 Hz) and 373°K (1 KHz). The $\beta$-relaxation should thus be indistinguishable from the $\alpha$-relaxation at this frequency. The $\alpha'$ transition is not noticeably evident in the dynamic modulus data but there is evidence in the data of fig 7.15 near 330°K which could be
interpreted as being due to the $\alpha'$ transition. The onset of the glass transition is quite evident at 375°K. The present technique and specimen size is not, however, suited to measurements when the modulus is very low, that is, at higher temperatures.

The dynamic modulus from fig. 7.15 is plotted together with the secant modulus derived from the constant strain-rate results for rates of $\bar{4}$, $\bar{1}$ and 2 (presented in fig. 7.7) in fig. 8.8. It may be seen that there is a resemblance between the dynamic modulus curve and the others. The dynamic moduli are everywhere lower than the secant moduli. This is not expected from data taken at a smaller strain (than 2%) for the secant moduli and at higher effective frequency. This implies in terms of the equations presented in 10.2 that the parameter $b$ is not small compared with the parameter $a$ in this case and that the secant and relaxation (or dynamic) moduli are not simply related.

The values of $c_T$ derived from the dynamic moduli (assuming that the dynamic modulus is a good approximation to the unrelaxed modulus) have been plotted as points together with the data of Wada et al. (9) in fig. 10.7. It may be seen that there is good agreement below 300°K, but considerable divergence above 320°K. This is probably because the measurement frequency here is not so high that the moduli approach the unrelaxed moduli. The
monotonic increase of $c_T$ as given by Wada et al. seems a more probable variation with temperature. This is supported by the observation that at 1 KHz the evidence of the $\beta$-relaxation has only just disappeared. A higher frequency of measurement (say 10 KHz) would thus ensure that only the unrelaxed moduli were being measured.
9. CONCLUSIONS

The $\beta$-relaxation in poly (methyl methacrylate) is of the simple thermally-activated Arrhenius type (p.125). The activation energy of the $\beta$-relaxation is $15.0\pm 0.75$ Kcal/mol. in the material investigated (p.125). The relaxation may not be distinguished in constant strain-rate tests when the effective frequency exceeds 1500 Hz (p.111). The limiting moduli of the $\beta$-transition are functions of the specific volume of the material (p.102), (p.154). There is also a dependence of relaxation times upon specific volume. This dependence may not be adequately described by a simple free volume theory nor by the modified WLF expression of Rusch (p.157f.f.), (p.160f.f.).

An adequate single parameter (volume) description of the state of non-equilibrium polymer glasses is most unlikely to exist (p.172).

There exists in slowly cooled poly (methyl methacrylate), a relaxation ($\alpha'$) which is not present in fast-cooled material (p.138). This relaxation is found only in experiments of relatively long time scale (p.139). The transition temperature of the $\alpha'$-transition does not appear to be a function of the testing rate (p.139). There is an unidentified transition which occurs at high strains below 240°K in slowly-cooled poly (methyl methacrylate), but not in fast-cooled material (p.153).

The specific volume of fast-cooled poly (methyl methacrylate) is a function of the temperature from which the sample is
quenched (p.132).
This is probably related to the configurations taken up at various temperatures by the oxygen-ester bonds in the side chains of the polymer (p.173).
Volume relaxation of fast-cooled samples of poly (methyl methacrylate) commences at temperatures as low as 360°K under the influence of stress and 366°K when no stress is applied (p.155).
The yield-stress strain-rate relation for poly (methyl methacrylate) is bi-linear (p.142). The yield process is controlled by two different thermally activated processes of the Eyring high-stress type (p.145). Yield is also related directly to the specific volume of the material in a simple way (p.156).
10. APPENDICES

10.1 Estimation of Accuracy

10.1a Calibration of testing machines

The semiconductor strain-gauged load transducer described by Dao\(^{(160)}\) was used in the hydraulic testing machine. The transducer was calibrated directly against a DSIR-certified proof ring of 10000lb capacity. The shunt resistances equivalent to various loads are given below in table 10.1. The transducer impedance was 360\(\Omega\).

Table 10.1

<table>
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<th>Load 1lbf</th>
<th>Shunt Resistance K(\Omega)</th>
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<tr>
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</table>

The linearity of the voltage-load response measured on the d.c. bridge described in 7.3b was 0.75% to 5000lb
and 1.1% to 100001b. Loads used in practice did not exceed 3000lb. The hysteresis on unloading from 10001b was 0.5%, from 5000lb 0.3%. Creep of the transducer was less than 1% in 300s at 5000lb load. The estimated accuracy of loads read from the oscilloscope traces enlarged from Polaroid film is ±1.5%.

The Hewlett-Packard 6LVI velocity transducer was calibrated in the Instron testing machine four times at each of 0.2, 2.0 and 10.0 in min⁻¹. The mean sensitivity found was 579.2 mV in⁻¹ sec⁻¹. The makers given calibration was 596 mV in⁻¹ sec⁻¹. The estimated accuracy of velocities from negative enlargements is ±2%.

The displacement transducer described in 5.3b was constructed from an aluminium alloy of measured 0.2% offset strength 45000 psi. The dimensions were - length 2ins, width 0.375ins, thickness 0.124ins. One Budd wire-resistance strain gauge of 350Ω resistance and gauge factor 3.2 was used as the sensing element. The designed safe working range was 0.075ins for a load of 16.8 lbf. The calculated period of natural resonance (first mode) was 228μs. The voltage response using the d.c. bridge was found linear to within 2.3% at 0.075ins displacement. The calibration resistances are given below in table 10.2.
Table 10.2

<table>
<thead>
<tr>
<th>Displacement (ins)</th>
<th>Shunt Resistance (KA)</th>
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<tr>
<td>0.050</td>
<td>85.6</td>
</tr>
<tr>
<td>0.060</td>
<td>71.5</td>
</tr>
<tr>
<td>0.075</td>
<td>58.3</td>
</tr>
<tr>
<td>0.085</td>
<td>51.1</td>
</tr>
</tbody>
</table>

The estimated accuracy of strains read from the enlarged traces is ±3.5%.

The Instron testing machine was used in the conventional manner. The estimated accuracy of loads measured from the recorder trace is ±2% or better as load cell capacity is approached. The question of strain measurement which was determined from the machine stiffness characteristic and the chart record (chart driven synchronously with cross-head) is discussed under 10.5.

10.1b Stress-strain determinations

The specimen dimensions were measured by means of a bench micrometer at room temperature and the dimensions corrected to test temperature by assuming a linear expansion coefficient of $9 \times 10^{-5} \text{K}^{-1}$. Six measurements of diameter were made and these usually fell within ±0.0005ins. The error in area is thus ±0.6%. The major error in determining the stresses presented in this investigation arose from the estimation of the strain. The strain is estimated to be in error by up to ±5% if the displacement
transducer is used on the hydraulic testing machine (partly because the instant of commencement of the test is hard to determine). If the integrating method is used with a velocity trace, the error is expected to be $\pm 4.5\%$. The error in determination of the stress from Instron chart records is discussed in 10.5 and may be $\pm 7\%$ for small strains (2%). If strains are large, the error in stress is usually only due to the errors in load and area - together at best about $\pm 2\%$. Under the worst conditions (for 2% strain), the error may rise to a total of about $\pm 12\%$. It seems that a method which uses an extensometer fixed to the specimen is preferable to any other method by a considerable margin. The errors in determining specimen temperature are usually only $\pm 1^oK$ except for tests in the hydraulic testing machine at temperatures farthest from ambient when the error may rise to about $\pm 3^oK$.

**10.1c Volumetric measurements**

As discussed above, the error in measuring area for 0.25ins diameter specimens is about $\pm 0.6\%$, the error in volume measurement for double-size specimens will thus be about $\pm 0.4\%$. This constitutes the major error in the measurements of absolute specific volume. The error arising from a $\pm 1^oK$ deviation in temperature is only $\pm 0.04\%$. The accuracy of relative volume measurement is very small as indicated in 7.13.
10.1d Master curves

The master curves are obtained by an entirely subjective shifting of the stress strain-rate curves at different temperatures onto one another. As the superposition is not perfect, this will lead to error. This is especially so of two nearly horizontal curves. Further, the error is additive as successive curves are shifted. The error expected is shown on the master curves by error bars (fig 7.12). The error bars have been obtained from consideration of the three attempts made to construct each master curve.

10.1e Activation Energies

The errors in the shift factors first discussed in 10.1d may be quite large (up to one time decade, or one unit on a log_{10} scale). These errors will lead to an error in the activation energies determined therefrom and have been estimated at ±7% for non-normalized data and ±5% for normalized data (see 7.10).

10.2 Relation of Constant Strain-Rate Tests and Secant Moduli to Stress-Relaxation Moduli

Ferry (37) has shown that if a specimen of a linear viscoelastic material is deformed at constant strain-rate to strain $\varepsilon$ in time $t$ then the stress will be

$$\sigma_A = (\varepsilon/t) \int_0^t E(z)dz = \dot{\varepsilon} \int_0^t E(z)dz$$
where \( E(z) \) is the stress relaxation modulus. If strained instantaneously to strain \( \varepsilon \) and allowed to relax for time \( t \) the stress would be, by definition,

\[
\sigma_B = \varepsilon E(t)
\]

thus

\[
\frac{d\sigma_B}{dt} = \varepsilon E(t),
\]

then the secant modulus

\[
\frac{\sigma_A}{\varepsilon} = \frac{1}{t} \int_0^t E(z) dz.
\]

Further, if (as is approximately true for poly (methyl methacrylate) in the glassy range) the relaxation modulus may be represented as

\[
E = a - b \ln(z),
\]

where \( a, b \) are constants, then

\[
\sigma_A = (a + b)\varepsilon - b\varepsilon \ln(t)
\]

and

\[
\sigma_B = a\varepsilon - b\varepsilon \ln(t)
\]

and if, as is true over small time ranges in the glassy state \( a \gg b \), then the stresses \( \sigma_A \) and \( \sigma_B \) are nearly equal as are the secant and stress-relaxation moduli.

#### 10.3 Variation of Strain-Rate During Tests

Although the compression tests have previously been referred to as constant strain-rate tests, this is only approximately true. In all tests there is a variation in strain-rate from the nominal value.
In the Instron tester the strain-rate is only equal to the nominal value while the specimen deformation-rate equals the head-rate, that is while the rate of deformation of the machine and load-cell are zero. This can only be so when the specimen is deforming at constant load. The deviation from the nominal strain-rate will otherwise be greatest for the cases where the load supported is greatest (i.e. at low temperatures and high head speeds) and greatest at small specimen strains. Figure 10.1 shows stress, strain and strain-rate as a fraction of the nominal strain-rate as functions of time for three tests. In the worst case, the deviation of strain-rate from nominal is 37%. The deviation in strain-rate in this machine is always negative and greatest for small strains.

In the hydraulic testing machine, the potential drive force is always much greater than the force used to deform the specimen. This machine is also very stiff and thus overall much less sensitive to specimen behaviour as shown by strain-rate changes.

Figure 10.2 shows typical stress, strain and strain-rate records as functions of time. At lower strain-rates the head velocity is decreased at first by the increasing specimen load and later increases somewhat. At higher rates the piston rod is still accelerating as the test commences (approximately \( \frac{1}{8} \)ins run-in is given at high rates) and continues to do so throughout the test. If the load is high enough (as at low temperatures), the
FIGURE 10.2
head speed may even decrease somewhat throughout the test. The maximum deviation from nominal strain rate ever observed in this machine was 43%. It may be seen that for a great part of the testing time that the strain-rate is within ±10% or less of the nominal rate. The strain-rates obtained during tests in the hydraulic machine are thus seen generally to be more constant than those obtained during tests in the Instron tester. Although the rate variations (maximum c. 40%) may seem large it must be observed here that the steps in strain-rate in the testing sequence are usually of order 10 and at the least 6.6 and in comparison, the rate variations reported are negligible. Figure 10.3 shows Polaroid-Land film records taken from hydraulic machine tests to show various experimental arrangements as they affect the oscilloscope traces obtained. Upper left is shown a test at low speed in which the velocity transducer has been used to record the strain-rate. Appropriate parameters are shown. Upper right is shown a trace in which the lower beam records the output from the cantilever displacement transducer. Timing marks are used to modulate the oscilloscope beam. Lower left shows a case where only a single oscilloscope beam has been used, but the oscilloscope used in the X-Y mode. The displacement transducer in this case drives the beam in the horizontal direction. Lower right shows a typical trace obtained at high head speed using the velocity transducer. The initial downward dip in
strain-rate followed by a general upwards trend may be seen.

10.4 Cooling Rates and Temperature Gradients

The four cooling programmes described in 7.1, viz. 1) quenching from 413°K into ice-water, 2) air-cooling, 3) free-air cooling in glycerol in a 500ml beaker, 4) cooling in a quart-size thermos flask in glycerol to 313°K were those used. Of these PR samples resulted from treatment 4), and MR samples from treatment 1).

The actual cooling rates were measured by drilling a 1/16ins diameter hole axially through the centre of a specimen (1/4ins diameter and 3/8ins long) and cementing a 36swg. copper-constantan thermocouple within the hole using Perspex in chloroform as cement. The thermocouple junction was thus at the geometric centre of the specimen. The cooling rates given (fig 10.4) are thus minimum values for the sample cooling programmes. The thermocouple voltage was measured against that of a similar thermocouple in ice-water using either a Philips PR 3500 chart recorder or a Hewlett-Packard 7001 A X-Y recorder. The cooling rates at various temperatures including the glass transition temperature are shown on the temperature-time plot of fig 10.4.

The surface temperature $T$ of a solid cylinder having volume $V$, surface area $A$ initially at temperature $T_b$ when suddenly
FIGURE 10.4
placed in an atmosphere of temperature $T_f$ may be given as

$$-\ln\left(\frac{T_f - T}{T_f - T_b}\right) = \frac{(Aht)}{(V\rho c_p)}$$

if $h$ is the heat transfer coefficient, $c_p$ is the specific heat of the material and $t$ is the time (164). The heat transfer coefficient may be calculated for loss in free air from the formula of Mayhew and Rogers (165) as

$$h = 0.27\left(\frac{T_f - T_b}{d}\right)^{0.25}.$$

If the values $T_f = 300^\circ K$, $T_b = 200^\circ K$, $\rho = 1.12$ g.ml$^{-1}$, $V = 0.032$ ml, $A = 2.54$ cm$^2$ and $c_p = 0.35$ cal$^\circ$K ml$^{-1}$ are used then $h = 2.24$ BTU cm$^{-1}$ ft$^{-2}$c$^{-1}$. If the same parameters are used in the first equation with $t = 6s$ and $t = 15s$ the value of $T - T_b$ is found to be 3.4 and 8.4$^\circ$K respectively. These are the greatest expected variations in temperature at the surface of the specimen at the conclusion of fast and slow hydraulic machine tests respectively.

10.5 Slenderness Ratio, Lubrication and Strain Measurement

An initial test series using ½in diameter specimens was conducted to examine the influence of specimen slenderness ratio and end lubrication upon the shape of the stress-strain curves. This test series was conducted at $293^\circ K$ and a nominal strain-rate of $5.55 \times 10^{-4} s^{-1}$. The specimen length was varied with the head speed in order that the strain-rate remained constant while the
slenderness ratio (4 x length/diameter) was varied from 2.33 to 12.0 (2.33, 2.88, 4.76, 8.00, 12.00). Each test was performed four times, twice with only kerosene lubricating the ends and twice with a 2.0 mil teflon tape covering the ends. The results (mean of two values) are given below in Table 10.3.

Table 10.3
Slenderness Ratio Test Results

<table>
<thead>
<tr>
<th>Slenderness Ratio</th>
<th>Stress (psi) at strains of</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Slenderness Ratio</th>
<th>Stress (psi) at strains of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2%</td>
<td>4%</td>
<td>6%</td>
<td>8%</td>
<td>Yield</td>
<td>2%</td>
<td>4%</td>
<td>6%</td>
<td>8%</td>
</tr>
<tr>
<td>2.33</td>
<td>10600</td>
<td>15300</td>
<td>17820</td>
<td>19250</td>
<td>20300</td>
<td>5100</td>
<td>10000</td>
<td>13880</td>
<td>16100</td>
</tr>
<tr>
<td>2.88</td>
<td>10100</td>
<td>15100</td>
<td>17710</td>
<td>19100</td>
<td>19940</td>
<td>6600</td>
<td>11500</td>
<td>15010</td>
<td>16790</td>
</tr>
<tr>
<td>4.76</td>
<td>8070</td>
<td>13950</td>
<td>16755</td>
<td>17940</td>
<td>18100</td>
<td>6565</td>
<td>12420</td>
<td>15720</td>
<td>17180</td>
</tr>
<tr>
<td>8.00</td>
<td>8500</td>
<td>14850</td>
<td>16560</td>
<td>17650</td>
<td>17970</td>
<td>6800</td>
<td>12000</td>
<td>14960</td>
<td>16470</td>
</tr>
<tr>
<td>12.00</td>
<td>8400</td>
<td>14620</td>
<td>16340</td>
<td>17460</td>
<td>17720</td>
<td>8400</td>
<td>14370</td>
<td>17370</td>
<td>18020</td>
</tr>
<tr>
<td></td>
<td>Kerosene Lubricated</td>
<td>Teflon Lubricated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It may be seen that the stress at a given strain and slenderness ratio is always larger for kerosene lubrication than for teflon lubrication. The stresses at given strain for kerosene lubrication decrease as slenderness ratio increases. A limit of about 5 must, however, be placed upon the slenderness ratio because buckling is evident on some of the curve obtained at slenderness ratio 8 (teflon lubrication). At lower slenderness ratios than 4.76 the stresses (kerosene
lubrication) increase indicating that radial end constraint interferes with the test noticeably. The slenderness ratio finally selected was 6 (3/8ins length, ¼ins diameter). Although the end lubrication is noticeably better for the teflon-ended specimens (lower stresses) there is a strong tendency for the stresses at given strain to decrease as the specimen slenderness ratio decreases. This is unexpected. It is believed due to the fact that the teflon ends then become of relatively larger thickness with respect to the specimen length and the measured properties reflect more and more the properties of the teflon. The stresses obtained are not otherwise easily explained. For this reason teflon lubrication was not used in the major test series. Rather, molybdenum disulphide lubricant was sprayed onto the ends in order to provide a minimum of lubricating material with a maximum of lubrication. The shape of sample/³ deformed to relatively large strains (c. 20%) looked much more like that of specimens deformed a similar amount using teflon-lubricated ends than like those which were lubricated only with kerosene. It was concluded that the lubrication by means of molybdenum disulphide was of similar efficiency to that of teflon tape.

Some 14 tests were conducted under the normal conditions at a rate of 3 at 293°K to see what repeatability was obtained. The standard deviations, together with the mean stresses, are listed below in table 10.4.
It may be seen from this that the standard deviations for 1% strain are very large. The decreased magnitude of the standard deviation at larger strains has partly to do with the change in gradients of the stress-strain curve and partly with the increased accuracy of strain determination. A large part of the error in determination of the stress arises from the estimation of the machine deflexion. This has been performed by running a pseudo-test under identical conditions to the actual compression test (either before or after it) in order to measure the machine loading characteristic. The stress at a given strain (say 2% strain on 0.375 ins gauge length = 0.0075 ins, at 0.2 in-min⁻¹ head speed and 50 in-min⁻¹ chart speed represents 1.87 chart inches) is then found by determining the ordinate at which the two curves differ by 1.87 ins when their starting points are matched as closely as possible.

Let us now assume that the machine loading characteristic is linear and the load-time curve drawn during the test is a sinusoid. Then, if the two curves are matched perfectly, the situation may be represented as follows (test figure 32)

<table>
<thead>
<tr>
<th>Strain</th>
<th>PR Series</th>
<th>MR Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>(3673 ± 19.0%)</td>
<td>(3059 ± 18.2%) psi</td>
</tr>
<tr>
<td>2%</td>
<td>(9418 ± 11.6%)</td>
<td>(7700 ± 9.76%)</td>
</tr>
<tr>
<td>4%</td>
<td>(17138 ± 5.6%)</td>
<td>(14475 ± 4.84%)</td>
</tr>
<tr>
<td>6%</td>
<td>(19640 ± 1.1%)</td>
<td>(17214 ± 3.43%)</td>
</tr>
<tr>
<td>8%</td>
<td>(21316 ± 1.1%)</td>
<td>(18044 ± 2.92%)</td>
</tr>
</tbody>
</table>
Here $y_o$ is the load determined for strain $s$ (without error due to misalignment of the curves) and $y_o = \sigma_Y \sin(r + s)$ ($\sigma_Y$ is a yield stress). If, however, the curves are misplaced by $\Delta x$ : (text figure 33)
The stress now determined

\[ y = \sigma_y \sin (r + s - x) \]

is in error. The error may be represented as \( (y - y_0)/y \)

\[ E = \frac{\sin (r + s - \Delta x)}{\sin (r + s)} - 1 \]

or if \( t = r + s \)

\[ E = \frac{\sin (t - \Delta x)}{\sin t} - 1. \]

A typical case would be that shown below, the load-time curve for the test being shown as a line for small values of load \( y \) (text figure 34)
This represents the situation when the load \( y \) is at 20% of recorder span and the error (\( \Delta x \)) is 0.2 ins. The test load-time line slope is 1.0 and the machine load-time curve slope 2.0. The value of \( \Delta x/t \) will be lower the greater the value of \( y \). These parameters are reasonable estimates of the worst expected conditions for estimating stress at, say, 2% strain. The error \( E \) may now be worked out for values of \( \Delta x/t \) in the order of 0.1. If the yield load is reached at recorder full-scale, \( y = 10 \text{ins} \) then \( t \) must be taken as 1.5 radians at 10 ins. Typical values of \( \Delta x \) are 0.1 ins or 0.015 rad. By taking \( t \) at 6 degree intervals (approximately 0.1 rad.) and \( \Delta x \) values of 0.6, 1.2 and 1.8 degrees (approximately 0.01, 0.02, 0.03 rad.) we may determine the following table: 10.5.

**Table 10.5**

Error \( E \% \) in Stress

<table>
<thead>
<tr>
<th>( t^\circ )</th>
<th>( x^\circ )</th>
<th>+0.6</th>
<th>+1.2</th>
<th>+1.8</th>
<th>-0.6</th>
<th>-1.2</th>
<th>-1.8</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>-10.0</td>
<td>-18.0</td>
<td>-29.8</td>
<td>+10.0</td>
<td>+20.0</td>
<td>+30.0</td>
<td></td>
<td>0.105</td>
</tr>
<tr>
<td>12</td>
<td>-5.0</td>
<td>-9.7</td>
<td>-15.0</td>
<td>+5.0</td>
<td>+10.0</td>
<td>+14.0</td>
<td></td>
<td>0.208</td>
</tr>
<tr>
<td>18</td>
<td>-3.2</td>
<td>-6.4</td>
<td>-9.7</td>
<td>+3.2</td>
<td>+6.4</td>
<td>+9.5</td>
<td></td>
<td>0.309</td>
</tr>
<tr>
<td>24</td>
<td>-2.4</td>
<td>-4.7</td>
<td>-7.0</td>
<td>+2.8</td>
<td>+4.7</td>
<td>+7.0</td>
<td></td>
<td>0.407</td>
</tr>
<tr>
<td>30</td>
<td>-1.7</td>
<td>-3.6</td>
<td>-5.4</td>
<td>+2.2</td>
<td>+3.8</td>
<td>+5.6</td>
<td></td>
<td>0.500</td>
</tr>
<tr>
<td>36</td>
<td>-1.2</td>
<td>-2.8</td>
<td>-4.3</td>
<td>+1.8</td>
<td>+3.0</td>
<td>+3.3</td>
<td></td>
<td>0.589</td>
</tr>
</tbody>
</table>
The error for \( \Delta x/t = \pm 0.1 \) is seen to be about \( \pm 10\% \), for \( \Delta x/t = \pm 0.05 \) about \( \pm 6\% \). As both curves start almost tangent to the axis, the starting-point of each cannot be located to better than \( \pm 0.1 \) in. The maximum error expected according to the analysis is then \( \pm 10\% \). The most probable error from this source should then give rise to a standard deviation in the measured 2\% strain stress of about \( \pm 7\% \). Those in fact observed in total were \( \pm 11.6\% \) and \( \pm 9.76\% \).

10.6 Internal Stress in Quenched Specimens

Both quenched and slow-cooled specimens were examined between crossed polaroids in order to see what difference in internal stress resulted from the different cooling programmes. A slow-cooled specimen showing no initial fringes was stressed to 7800 psi and examined between crossed polaroids. This crude calibration of the stress-optical coefficient gave a sensitivity of 3100 psi fringe\(^{-1} \). Or 775 psi fringe\(^{-1} \) in \(^{-1} \). The value given by Holister\(^{(166)} \) for Perspex is 815 psi fringe\(^{-1} \) in \(^{-1} \). An as-quenched specimen showed one fringe approximately and the maximum magnitude of the principal stress difference is thus about 3200 psi. A specimen that had been quenched and had stood for three months showed considerably reduced stress. All specimens subjected to mechanical tests were freshly quenched. As the specimen must remain in equilibrium, the outside will be expected to be largely in compression while the inside will be in tension as in quenched glass\(^{(167)} \). This is borne out when a freshly quenched specimen is rapidly heated to above
the glass transition temperature by dropping it into hot glycerol. Fracture then often takes place in the very centre of the specimen in the form of a 'penny-shaped' planar crack of circular shape (radius about half the specimen radius) which is situated in the specimen with the crack plane perpendicular to the specimen axis. The problem of the internal stress induced in the rapid cooling of a viscoelastic material having temperature dependent mechanical properties has been investigated by Lee and Rogers (168). The problem is further complicated here because the glass-transition is encountered during the cooling programme. The thermal properties are thus strong functions of temperature and also the viscoelastic properties will depend upon the cooling rate. If the sample was approximated as an infinite sheet and the internal stress distribution of reference 167 is taken, it may be seen that the integrated product of stress times volume is nearly zero. If the question of yield was then investigated and a Rankine-type yield theory was used, the conclusion would be that the macroscopic yield stress of the whole thickness would be unaltered relative to a stress-free specimen. The question of whether such a yield criterion is suitable, and if not what the full stress distribution would be and the conclusion then is outside the scope of the present work. The plate shows specimens photographed between crossed polaroids. The specimen at the top is slowly cooled. The next has been quenched according to the MR programme. The third from top has been quenched and aged at room temperature for three months. The bottom specimen has been quenched and aged in glycerol at 366°K for 2 hours.
10.7 X-Ray Diffraction Experiments

The experiments described in 7.2d were performed on a Philips PW1050 diffractometer. A Philips PW1010 generator supplied Ni-filtered CuK radiation (wavelength $1.54 \times 10^{-10}$ m) at tube voltage of 36KV, tube current 12mA. The diffractometer settings were - collimating slit 1°, receiving slits 0.2min and 1°. The scanning speed was $2° \text{min}^{-1}$. The counter tube was of the proportional type operating at 1650V. The pulse height analyzer settings were: attenuation $2^3$, window 300-350 units. The rate-meter scale was 400Hz and the time constant 1 sec.

10.8 Nuclear Magnetic Resonance Measurements

The procedure was described in 7.2c. Text figure 35 shows a tracing of the part of the spectrum appropriate to the determination of the triad analysis with the three component curves fitted. The areas of the peaks were isotactic (i) (at 8.86°) 67, heterotactic (h) (at 8.95°) 196.4, syndiotactic (s) (at 9.09°) 264.4. The analysis was thus i 12.7%, h 37.2%, s 50.1%. The settings of the Varian A60 spectrometer for this determination were: filter bandwidth 2Hz, R.F. field 0.075 mG., sweep time 250s, sweep width 500Hz, spectrum amplification 16.0.
10.9 Molecular Weight Determination

The molecular weights were determined by the viscosity method. The resulting molecular weight falls between the true number-average and weight-average molecular weights (139). The initial solution concentration (chloroform Analar grade solutions) was 2.87 g/100ml. The viscosity was measured in a B.S. Otswald viscometer contained in a water bath controlled at 298°K. The viscosities of the successively diluted solutions $\eta$, may be determined by the method of BSS 188:1962 in which
\[ \eta = A t - B/t \] where \( t \) is the run time in seconds and \( A \) and \( B \) are viscometer constants determined for two liquids of known viscosity or by using \( \eta/\eta_o = (t - t_o)/t_o \) where \( t_o \) and \( \eta_o \) are the run times and viscosity of the solvent alone (155). The relative viscosity \( \eta_{rel} \) is defined as \( \eta_{rel} = \eta/\eta_o \) and the specific viscosity as \( \eta_{sp} = \eta_{rel} - 1 \), here \( \eta_o \) is the viscosity of the solvent alone. The intrinsic viscosity \( [\eta] = \lim_{c \to 0} (\eta_{sp}/c) \) where \( c \) is the solute concentration. The Huggins relationship

\[ \eta_{sp}/c = [\eta] + K' [\eta]^2 c \]

predicts that \( \eta_{sp}/c \) should be a linear function of \( c \), \( K' \) is the Huggins constant. This plot then intercepts the axis at \( [\eta] \), thus \( [\eta] \) is determined from several data points by drawing the best straight line through them to find the intercept. The viscosity-average molecular weight is then found from the Mark-Houwink relation (139)

\[ [\eta] = K M^\kappa \eta \]

here \( K \) and \( \kappa \) are experimentally determined constants. Figure 10.5 shows the plot of \( \eta_{sp}/c \) as a function of \( c \) for both the full BS188 method and the approximate method. The data points are well fitted by straight lines. The viscometer available was not suitable for the determination of viscosities less than 0.55cp.
FIGURE 10.5
10.10 Monomer Content

The experimentally determined glass transition temperature was 380±0 K (7.2b). The expected glass transition temperature from the tacticity (see 10.8) would be 376-378 K (see 5.4a). Dudek and Lohr (124) noted that 0.5% unpolymerized monomer lowered $T_g$ from 381°C to 378 K, and 1.1% monomer from 381°C to 366 K. It thus seems that the monomer content is less than 0.5%. The conventional commercial polymerization technique which involves some time at temperatures above the glass transition temperature (5.5b) should completely polymerize the material as polymerization proceeds very rapidly near the glass transition temperature (124).

10.11 Hydraulic Test Machine Head Velocities

During preliminary work for planning the constant strain-rate compression test series described in section 7, the velocities of the piston rod of the hydraulic test-machine were investigated as a function of drive pressure and exit orifice area. It was found that the nominal strain-rate achieved (8/3 of the head velocity in inches per second) could well be represented if log (strain rate) was plotted against log (exit area). This is shown in fig 10.6.
FIGURE 10.6
10.12 The Normalization Factor $c_T$

As discussed under 10.13, it is necessary to normalize the stresses obtained before the shifting procedure attempted. The factor $c(T)$ here is the ratio of the unrelaxed modulus at temperature $T$ to that at the reference temperature (here $300^\circ$K). Figure 10.7 shows $c(T)$ as a function of temperature, the data having been taken from the work of Wada et.al. (9). The crosses represent the values of $c(T)$ determined from the dynamic modulus experiments described in 7.11 in which the measuring frequency was $c$ 1kHz.

10.13 Normalization and Shifting of Stress-Strain-Rate Curves

It is necessary in order to obtain the apparent activation energy of relaxations controlling the mechanical behaviour to determine the way in which the mechanical response changes with time and with temperature. It is then possible to derive the apparent activation energy from mechanical test data taken over a limited range of time at several temperatures. The Williams-Landel-Ferry (WLF) empirical relation connects the multiplying factor on the response time $\alpha_T$ with the temperature and some reference temperature $T_0$ (at which $\alpha_T = 1$). The mechanical time response of the material $R_T(t)$ at temperature $T$ is related to that at the reference temperature $R_{T_0}(t)$ by
FIGURE 10.7
\[ R_T(t) = R_{T_o}(\alpha_T t), \]

the WLF relationship then gives \( \alpha_T \) by

\[
\log_{10} (\alpha_T) = -(C_1(T - T_o))/(C_2 + T - T_o)
\]

where \( C_1 \) and \( C_2 \) are 'universal constants', namely 16.7 and 55 K if \( T_o \) is taken as the dilatometric glass transition temperature. In fact Adam and Gibbs\(^{161}\) give the values of \( C_1, C_2 \) and \( T_g \) for poly (methyl methacrylate) as 20.20, 44.6 K and 378 K.

The WLF relation takes no account of the fact that the limiting values of response of a given relaxation may be functions of temperature. This, in the rubbery regime where the WLF relation is normally applied is of little consequence because the limiting values of the response vary little with temperature. If, however, the limiting values are strong functions of temperature then the empirical shifting of response curves at different temperatures onto one another in order to obtain the shift factor and hence the apparent activation energy becomes invalid unless the temperature dependence of the limiting values is accounted for.

Gross\(^{162}\) has generalized the argument. He relates the response function \( R_T(t) \) at temperature \( T \) to a standard response \( \Psi(t) \)

\[ R(T,t) = c(T)\Psi(t \times \alpha(T)) \]

or for a given temperature \( T \)
\[ R_T(t) = C_T \Psi(\alpha_T t) \]

where \( C \) and \( \alpha \) are functions of temperature. Thus if \( C \) and \( \alpha \) are known over a range of temperature then \( R \) may be specified over that range. \( C(T) \) here represents the temperature dependence of the limiting values of the response (assumed the same) and \( \alpha_T \) is the time-temperature shift factor. The linear response function can be represented in an integral form

\[ R_T(t) = \int_0^\infty F(T,\tau) c^{-t/\tau} \, d\tau/\tau, \]

here \( F \) is a distribution of response times. \( F \) can be expected to be a function of temperature, \( \tau \) is assumed to be a function of temperature and of a time and temperature independent distribution parameter \( \sigma \). If the two equations above are to hold simultaneously, then both \( F \) and \( \tau \) must separate into product functions of \( T \) and \( \sigma \):

\[ F(T,\tau) = c(T)f(\sigma) \]

\[ = g(\sigma)/\alpha(T) \]

thus

\[ R_T(t) = c_T \int_0^\infty f(\sigma) \exp \left(-t\sigma/g(\sigma)\right) \left(\frac{dg(\sigma)}{g(\sigma)}\right) \]

McCrum, Read and Williams\(^{(11)}\) have shown the need for two extra functions of temperature when the limiting responses vary each in a different way. They suppose
the response at a temperature $T$ to arise from a
distribution of response times (say a distribution
of retardation times for a creep response) $\Phi^T_J (\ln \tau)$. Then the time-temperature relationship may be written

$$\Phi^T_J (\ln \tau) = \Phi^0_J (\ln \tau / \alpha^T_I),$$

and then $\ln \alpha^T_I$ is usually given by the Arrhenius equation

$$\ln \alpha^T_I = (H/R)(1/T - 1/T_o),$$

where $H$ is the energy of activation and $R$ the gas constant or the WLF equation given previously.
The three parameters of McCrum and Morris$^{(90)}$ take account
of the temperature variation of the relaxed and unrelaxed
creep compliance (say) in the following way

$$J^T_R - J^T_U = b_T (J^T_o - J^T_U),$$

$$J^T_U = c_T J^T_o,$$

$$J^T_R = d_T J^T_o,$$

only two of the three parameters being independent. Then

$$J^T_o(t/\alpha^T_T) = J^T(t)((J^T_o - J^T_U)/(d_T J^T_o - c_T J^T_U)) + J^T_o J^T_U$$

$$((d_T - c_T)/(d_T J^T_o - c_T J^T_U))$$

if it is further assumed that $c_T = d_T$, which amounts to
saying that the fraction of the unrelaxed response released
by the relaxation under question is not a function of
temperature then

\[ J^T_0(t/\alpha_T) = (1/c_T)J^T(t). \]

This assumption was made by McCrum and Morris (loc.cit.) when they created a master curve for the creep of poly (methyl methacrylate) in the \( \beta \)-relaxation time range. The procedure is illustrated in fig 10.8.
In fig 10.8 the temperature dependence of the limiting compliances is shown on the left and the observed parts of the response (from say log \( t = 0 \) to log \( t = 5 \)) at reference temperature \( T_o \) by CD and at temperature \( T \) by AB. The normalized compliance at temperature \( T, J_p^T(t) \) is shown as a dotted line. A simple shift of time, \( (\alpha_T) \), now causes partial superposition with AB. A repetition of this limited-time data reduction for other temperatures \( T \) then enables construction of the complete compliance curve at any temperature in the range investigated from the unrelaxed to relaxed states.

This process of correcting for the temperature dependence of limiting response has been used in this work to reduce the data for the constant-strain-rate stresses (at given strain) as a function of strain-rate to create a master stress-strain-rate curve. The process of correcting for the temperature dependence of limiting stresses has been referred to as normalizing, the data before this operation have been referred to as 'raw' data and those after, as 'normalized' data. The shift factors and master curve have then been obtained as outlined in fig 7.1. The assumption that \( c_T = d_T \) has been made and \( c_T \) obtained from the data of Wada et al. [9]. The valuation of \( c_T \) with temperature is represented in fig 10.7.
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Text figures 1-8 are taken from Heijboer (86), text figures 9-16, from Kopplemann (88).
Moreover if there be not a least thing, all the tiniest bodies will be composed of infinite parts, since indeed the half of a half will always have a half, nor will anything set a limit. What difference then will there be between the sum of things and the least of things? There will be no difference; for however completely the whole sum be infinite, yet things that are tiniest will be composed of infinite parts just the same. And since true reasoning cries out against this, and denies that the mind can believe it, you must ... confess that there are those things that consist of no parts at all and are of the least nature.

Lucretius Carus Titus
De Rerum Natura
Book 1, line 615

... of pure science I am tempted to say "If a thing is not worth doing, it is only worth doing well"

J. M. Ziman
the Rutherford Memorial Lecture
13. APPENDAGE

During the course of preliminary investigations into the use of the split Hopkinson-bar technique\(^{(226)}\) for compressive testing of polymers at strain-rates above those otherwise reported here three computer programmes were developed. The programmes were written for the IBM 1130 computer with magnetic-disc storage and 8192 location core in sub-set FORTRAN IV for the 1130, version 1. The first of these programmes, HOTAN, processed the graphic and other data from a Hopkinson-bar experiment and determined the stress, strain and strain-rate in the specimen as functions of time. The calculation technique followed was similar to that of Maiden and Green\(^{(226)}\). The programme could make correction for radial inertia of the specimen as outlined by Davies and Hunter\(^{(227)}\). Data listing and also a line-printer graphic output was provided. The programme listing, description and sample outputs are held in the Engineering Library, University of Auckland.

The second computer programme, SWERD, is a finite element scheme for computing the stress and velocity in two adjoining one-dimensional elastic rods during the impression of an impulse at the end of one rod. The programme follows the stress-wave ensuing and caters for all reflections resulting. The programme is derived from one by Davids and Mehta\(^{(228)}\). The rods may be of different areas, densities and moduli and the programme
may be easily modified for more than two adjacent rods, rods of non-constant cross-section and for fixed- or free-end conditions. The present configuration allows for up to 100 space elements each of length equal to the wave-speed time-increment product and for up to 250 time increments. The programme output is in the form of a time-series print-out of the stress and velocity in every cell in the form of two space-time maps. The maps are automatically partitioned for print-out to suit the printer line width. A full programme listing, description and sample output are filed in the Engineering Library, University of Auckland.

The third computer programme, SWERV, is a finite element scheme for computing stress and velocity in a single linear viscoelastic rod. The computation scheme is similar to one described by Wenner (229). The relaxation modulus-time relation for the viscoelastic material is specified as input data. The programme output is similar to that described for the programme SWERD. At present 14 spatial elements and 90 time-elements only can be handled by the 8192 word core 1130 machine as the whole problem history must be carried in the core. The rod is loaded by an input pulse of specified magnitude and time-duration. The opposite rod-end may be either fixed or free. Modification for more complicated pulse conditions or geometries would be simple.

The original intention in the development of the finite-
element programmes was to integrate SWERD and SWERV in order to be able to simulate the compressive testing of a linear viscoelastic material in the split Hopkinson-bar. The computer configuration available was not of sufficient size that the integration could effectively be performed. Direct comparison of actual test results from a Hopkinson-bar experiment with those predicted be a simulation using the integrated finite-element scheme and a proposed material constitutive relationship could then have been made.

Another preliminary investigation concerned creep testing, that is at lower strain-rates than those otherwise reported. A six-station machine was constructed which enabled compressive creep tests to be conducted at controlled temperatures in the range 260 - 380°K and automatically recorded. Each specimen was supported by between a fixed and a moving anvil each made from hard-chromium plated type 303 stainless steel. The moving anvil was accurately guided either by a lapped plain bush or by an R&M A162536 axial re-circulating ball type bushing. The fixed anvil was adjustable in height. The platens were maintained accurately parallel. Loading was by means of a 12:1 class 1 lever system constructed of HE 30 WP aluminium alloy. Loads of up to 480lbwt could thus be applied to the specimen.

The specimen deformation was in each case recorded by means of a beryllium–copper alloy cantilever beam transducer fitted with two Philips type PR9813 120 ohm foil strain-
gauges. The transducers could be located so as to have a full scale deflection of 0.050, 0.200, or 0.500 in. The strain gauges formed part of a full Wheatstone bridge excited at 4.8V and the bridge outputs were recorded sequentially on a 12 channel Honeywell–Brown type 153 Electronik recorder having 10mV range and a special slow chart drive speed. Specimen deformation could also be recorded by means of dial indicator gauges or by means of a Sanborn 7DCDT-250 displacement transducer and recorded on a Hewlett-Packard 7001A X–Y recorder. The precision of measurement using the strain-gauge displacement transducers was approximately $5 \times 10^{-4}$ in. The dial indicators could be read to $5 \times 10^{-5}$ in. The Sanborn displacement transducer output could be read to $5 \times 10^{-6}$ in. The Sanborn transducer and X-Y recorder was the only measurement system capable of giving readings within one second of specimen loading.

The temperature of the specimens was controlled by immersing them in a re-circulating flow of kerosene maintained from an insulated reservoir tank. A centrifugal washing machine pump driven at 300rpm maintained a constant flow to the bottom of the six specimen container tanks, the overflow returning to the reservoir. The kerosene temperature was measured by means of a 100 ohm copper resistance-thermometer element located at the centrifugal pump outlet. The reservoir temperature is maintained to ±0.05°C between 280 and 340°C and otherwise to ±0.1°C by injecting small quantities of hot (or cold) (temperature = control temperature ± ~15°C) kerosene from a hot reservoir tank into the centrifugal pump inlet.
The hot reservoir tank is heated by a 600W element and a small reciprocating pump (driven at 50rpm) maintains circulation. On demand from the temperature controller part of the flow pump is by-passed to the injection port. Overflow from the specimen chamber system returns to the hot reservoir.

The resistance thermometer element forms part of a Wheatstone bridge. The temperature set-point is achieved by means of a Bournes type A 100 ohm Helipot in the opposite arm of the bridge. The bridge output is amplified by a d.c. transistor amplifier having a gain of 2000 times. The amplifier and bridge are independently temperature controlled for stability. The total instrument warm-up time is about 30 mins. The amplifier output feeds a d.c. power amplifier which controls a differential d.c. moving coil relay which in turn supplies 230V power to a solenoid. The solenoid lifts a valve in order to divert flow from the reciprocating pump to the injection port. A further manual control valve varies the delivery rate to the injection port.

Temperature deviation and absolute temperature may be read out from the Brown recorder. Hunting of the control system is minimized by adjusting the injected delivery rate until injection occurs for about half the total time. For temperatures below ambient the hot well tank is cooled by means of solid carbon dioxide.

Full working drawings of the creep tester and ancillary equipment are held in the Strength of Materials Laboratory, School of Engineering, University of Auckland.
References to Appendage

226) C.J. Maiden, S.J. Green
General Motors Defence Research Laboratories Report TR65-26
May 1965

227) E.H.D. Davies, S.C. Hunter

228) N. Davids, P. Mehta
Eng. Research Bulletin B92
The Pennsylvania State Univ., (1965)

229) N. Davids
private communication
Temperature Controlled Creep Machine Layout

a) Six channel strain-gauge bridge
b) Twelve channel Honeywell recorder, showing typical records
c) Hot-well pumping unit
d) Filler cap to hot-well
e) Reciprocating injection pump
f) Drive motor for pumps
g) Delivery-rate control valve
h) Injection solenoid
i) Pulley of centrifugal circulating pump
j) Insulated box containing centrifugal pump and injection manifold
k) Hoses connecting to inlet and exhaust manifolds on creep machine
l) Resistance thermometer element in delivery line
m) Overflow line
n) Drain line
o) Cover to retain fibre-glass insulation
p) Resistance thermometer bridge
q) Temperature controller
View of Six Station Creep Machine with Temperature Controlling Jackets Removed

a) 12:1 class 1 lever system
b) Hanger and (one) weight
c) Plain bushing
d) Strain-gauge cantilever transducer
e) Lower specimen anvil
f) Specimen
g) Upper specimen anvil
h) Adjustment for lower anvils
Close-up View of One Station on Creep Machine

a) Tubular nylon creep specimen
b) Plain bushing
c) Upper anvil
d) Specimen under load at station 1
e) Lower anvil
f) Transducer drive pin
g) Transducer beam
h) Transducer beam clamp
i) Transducer mounting pillar
INTRODUCTION TO "THE MECHANICAL PROPERTIES OF GLASSY
POLY(METHYL METHACRYLATE)"

This thesis concerns the mechanical properties of a
polymeric solid and explores certain of the relation-
ships between observable mechanical behaviour and
molecular motions within the material.
A polymer is a material consisting of very large
molecules (macromolecules). Each macromolecule consists
of hundreds to thousands ofmer or atomic groups
(repeat units) usually linked together to form a
long chain. In the material described here the mer
is the ester methyl methacrylate. The material reveals
no crystalline structure in diffraction experiments -
it is amorphous. The backbone of the long-chain molecule
is formed by carbon-carbon atomic bonds alone, the
ester (-COOCH₃) groups taking pendant positions:

The macromolecules themselves are not linked together
in an amorphous polymer but are intercoiled in a
complicated manner. The configuration of any one chain
may be described as being comprised of 'kinks' occurring

*The material used in the experiments was commercial "Persper"
on a local scale rearrangements of these occurring very rapidly, 'curls' occurring on a larger scale and changing more slowly, and 'convolutions' occurring very slowly and being very large in scale compared with atomic dimensions.

Under stress, a new assortment of configurations is obtained; the response to the local aspects of the new distribution is rapid, the response to the long-range aspects is slow, and all told there is a very wide and continuous range of time-scale covering the response of the system to external stress. The motions of adjacent chains are co-operative.

Every polymeric system has a glass transition temperature below which the writhing thermal motions essentially cease. Here long-range convolutional re-adjustments are severely restricted; there is still a wide range of response rates to external stress, but different in nature.

All of these configurational features are in fact possible because there is more than one steric carbon-carbon atomic bond arrangement possible in the back-bone. From measurements of the mechanical properties of polymers information can be obtained about the nature and rates of the configurational re-arrangements and the disposition and interaction of the macromolecules both in their short-range and their long-range inter-relations. The small-strain mechanical properties of polymers are typically comprised of elastic, viscous and visco-elastic responses. If a relaxation experiment is conducted
- that is at time zero the specimen is subjected to a small uniaxial strain $\varepsilon$ which is subsequently maintained constant - the stress $\sigma(t)$ will rise instantaneously and subsequently decay (or relax). The relaxation modulus $E(t) = \sigma(t)/\varepsilon$ is thus a function of time. There is an instantaneous response and a delayed response:

The essential components of the response may be seen to be described qualitatively by a three element model consisting of a Maxwell element in parallel with a spring:
pot viscosity $\eta_2$, the parallel spring has stiffness $E_1$. The relaxation modulus is

$$E(t) = E_1 + E_2 e^{-\left(\frac{E_1}{\eta_2}\right)t}$$

Here the single relaxation time $\tau = \frac{\eta_2}{E_2}$. If there are a whole series of Maxwell elements (i):

then

$$E(t) = E_1 + \sum_{i=2}^{\infty} E_i e^{-\frac{t}{\tau_i}}$$

If there is taken to be a spectrum of relaxation times having strength $\eta_i$ between times $\ln\tau$ and $\ln(\tau+\Delta\tau)$ (using now a natural logarithmic scale for time) then

$$E(t) = E_1 + \int_{\ln\tau}^{\ln(\tau+\Delta\tau)} \eta e^{-\frac{t}{\tau}} d\ln\tau$$

It is usually found that real viscoelastic materials behave as though a spectrum of relaxation times existed. The continuous distribution required implies only that the reaction of the macromolecules to an impressed strain is reflected by rearrangements which take place over a wide time-scale in such a manner as to reduce the stress. The stress acts in such a way as to favour configurations leading to smallest total energy (i.e. a decrease in the stress) and this process then takes place by thermal activation of the macromolecular segments to their new configuration.
The molecular rearrangement itself is most commonly referred to as a relaxation. The change in mechanical properties observed as the relaxation proceeds (here in relaxation modulus) is known as a transition. In this case the strain is applied (in theory) in an infinitesimal time and the first observable change in relaxation modulus from an initial value $E_u$ (the unrelaxed modulus) occurs at some later time. As the relaxation proceeds at increasing times the modulus falls, finally reaching a value $E_R$ (the relaxed modulus) all molecular relaxation than having ceased. The $E_u$ and $E_R$ correspond to $E_1 + E_2$ and $E_1$ of the simple three-element model.

Molecular relaxations are thus evident as transitions in the mechanical properties (say the relaxation modulus) as time functions. Each relaxation normally results in a transition which spreads over several decades of time. If there is more than one relaxation taking place in the time scale investigated more than one transition will be evident.

It is possible to investigate mechanical properties by applying to the sample an oscillatory strain (or stress) and observing the oscillatory stress (or strain) resulting. Such an experiment is normally known as a dynamic experiment. If a dynamic sinusoidal strain

$$\varepsilon = \varepsilon_0 \sin \omega t$$

is applied a sinusoidal stress $\sigma = \sigma_0 \sin(\omega t - \delta)$ may result. The dynamic modulus $E(\omega)$ is then complex and may be expressed in terms of real and imaginary parts:

$$E^*(\omega) = E'(\omega) + iE''(\omega)$$

the ratio of maximum stress to maximum strain is

$$|E^*(\omega)| = \sqrt{E'(\omega)^2 + E''(\omega)^2}.$$
and

\[ E' = |E| \cos \delta \]
\[ E'' = |E| \sin \delta \]
\[ E''/E' = \tan \delta \]

Here \( \omega \) is the investigating frequency and \( E' \) and \( E'' \) are known as the storage and loss moduli respectively. \( \delta \) is known as the loss angle. In this case frequency rather than time is the experimental variable. If one relaxation takes place over the range of periodic times investigated then \( E' \), \( E'' \) and \( \tan \delta \) normally behave as shown below for a given temperature.

![Graph showing \( \log E', \log E'', \log \tan \delta \) vs \( \log \omega \)]

At limiting frequencies \( E' \) approaches \( E^* \) which approaches \( E_R \) or \( E_U \). \( E'' \) is small at limiting frequencies and peaks at some characteristic frequency (depending upon the relaxation and the temperature). \( \tan \delta \) peaks at a somewhat lower frequency than this for an experiment where strain is prescribed.

At frequencies in the centre of the transition where \( \tan \delta \) is large the material will dissipate the energy supplied as heat. At frequencies removed from this
the energy required to sustain an oscillation of the same amplitude is much reduced.

If the experiment is repeated at higher temperature the transition in $E'$ and the peaks in $E''$ and tan$\delta$ will move together towards a higher frequency. At a lower temperature they appear at a lower frequency. This is because the temperature has a direct effect upon the rate of molecular relaxation. The rate at which segments of the macromolecule attempt to attain new configurations is directly related to the thermal energy supplied to activate them and thus to the temperature.

If the transition centre frequency shifts smoothly with temperature there is said to be a time-temperature equivalence. A change in temperature is entirely equivalent to a change in time scale of the experiment. If in addition $E_u$ and $E_R$ are not themselves functions of temperature the material is said to be "thermorheologically simple".

The transitions in mechanical properties which result from molecular relaxations, the manner in which the relaxation rates depend upon temperature, and the magnitude and temperature dependence of the relaxed and unrelaxed moduli are each of fundamental importance to the study of mechanical properties and of molecular relaxations in polymers. This investigation has been focussed upon these matters for a specific polymer (poly(methyl methacrylate)) and for a specific relaxation (the $\beta$ relaxation).
The Characteristic Transitions of PMMA

The material poly(methyl methacrylate) or PMMA, of which Perspex is one commercial form shows a large reduction in modulus (about five thousand times) as the temperature is raised from 270 to 400°K. At temperatures below this transition range the material is referred to as "glassy," above it is usually called "rubbery." This, the most obvious transition of PMMA is known as the primary, glass-rubber or \( \alpha \) transition. Section 5.4(a), pages 11-12, summarize what is already known of it.

In the rubbery state, that is above the \( \alpha \) transition range, mechanical properties change smoothly with temperature and no specific transitions are apparent.

Below the \( \alpha \) transition range, there are less obvious transitions in the glassy condition. The " \( \alpha' \) transition" observed only in PMMA slowly cooled from the rubbery state and only for low rates of strain has been reported at temperatures near 330 to 340°K. The literature on this is summarized in section 5.4(b), pages 13-14. Another transition, the " \( \beta \) transition" may be observed over a wide frequency range at temperatures from 280 to 350°K, depending upon the frequency. The information available on this transition is summarized in 5.4(c), pages 15-40. The molecular relaxations which result in the \( \alpha, \alpha' \), and \( \beta \) transitions (\( \alpha, \alpha' \), and \( \beta \) relaxations) are presumably of different natures, the theories that have been advanced in explanation are outlined in section 5, pages 3-51. The character of the \( \alpha \) transition is further explored in section 6, pages 52-90.
Experimental Work

The measurements made on Perspex are described in section 7, pages 91-136. In order to investigate the manner in which the properties depend upon thermal history the material was either cooled slowly from the rubbery to glassy condition ("PR") or cooled quickly ("MR"). Measurements of stress and strain were made for uniaxial compression tests conducted over a range of straining-rates (9x10^{-5} per second to 33 per second) and over a range of temperatures (200 to 360°C). These were supplemented by measurements of the density and of the thermal coefficient of expansion. The molecular weight was measured by means of the viscosity of dilute solutions in chloroform and the "tacticity" (or characterisation of the symmetry of adjacent mers in the polymer) by means of a nuclear magnetic resonance method. X-ray diffraction methods were used to check whether there was any macroscopic anisotropy.

Discussion

Chapter 8, pages 137-192, is principally concerned with examining the influence of temperature upon the β transition revealed in the modulus as a function of straining-rate. In the temperature range above the α transition there is a simple and unique relation between the temperature and the strain-rate marking the centre of the transition. In the temperature range below the α transition the relation depends upon the rate of cooling of the sample. The formula of Rusch which attempts to explain this is examined in terms
of the experimental data. The inference is that a theory such as that of Rusch which uses a single extra parameter (volume) in order to describe the effect of different cooling rates is not adequate to explain the results near the $\beta$ transition.

The Appendage to the thesis describes an apparatus which was constructed in order to test PMMA at very slow rates of strain. Lack of time limited severely the number of tests which could be conducted in this apparatus and these are not reported here.