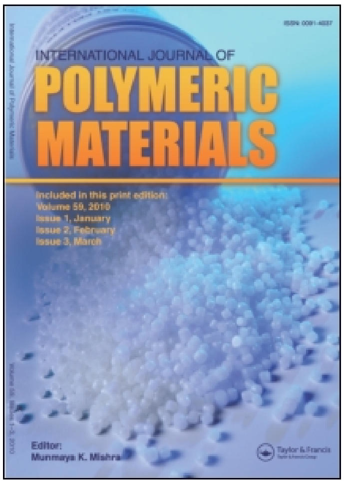


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Secondary Loss Peaks in Glassy Amorphous Polymers

J. Heijboer[a]
[a] Centraal Laboratorium TNO, Delft, The Netherlands

To cite this Article Heijboer, J.(1977) 'Secondary Loss Peaks in Glassy Amorphous Polymers', International Journal of Polymeric Materials, 6: 1, 11 — 37

To link to this Article: DOI: 10.1080/00914037708075218

URL: http://dx.doi.org/10.1080/00914037708075218

Intern. J. Polymeric Mater., 1977, Vol. 6, pp. 11–37

Printed in Reading, England

Secondary Loss Peaks in Glassy Amorphous Polymers†

J. HEIJBOER

Centraal Laboratorium TNO, Delft, The Netherlands

(*Received February 22, 1977*)

A short description is given of the determination—as a function of frequency and temperature—of secondary mechanical loss peaks in glassy amorphous polymers.

The molecular motions causing secondary loss peaks are classified. The dependence on frequency of the temperature of the maximum of the loss peak is discussed.

The effects on the secondary loss peaks of structural features such as plasticization, intermolecular steric hindrance and polarity, are illustrated by the example of the β-maximum of poly(methyl methacrylate), emphasis being laid on the difference between a glass transition and a secondary loss peak.

1 WHAT ARE SECONDARY LOSS PEAKS?

Figure 1 schematically shows the dependence of the modulus and damping of an amorphous polymer on temperature. At the *main or glass transition* T_g the modulus drops by a factor of a thousand; in the region of this transition the material changes from glassy to rubbery. This transition is accompanied by a high loss peak, the maximum of tan δ generally lying between 1 and 3. This peak is usually called the α-peak.

Apart from this main transition, which has a tremendous effect on the mechanical properties, there nearly always are minor transitions in the glassy region at which the modulus decreases by a factor of e.g. not more than two. Nevertheless these minor or *secondary transitions* may have a marked effect on the mechanical behaviour: sometimes a material is brittle below and tough above the secondary transition. In Figure 1 we see that the secondary transition stands out more clearly in the loss curve than in the

---

†Presented at the Fourth Midland Macromolecular Meeting on "Molecular Basis of Transitions and Relaxations", in honour of Dr R. F. Boyer, February 5–7, 1975.

Also presented as a symposium lecture at the IUPAC "International Symposium on Macromolecules", Madrid, September 15–20, 1974.

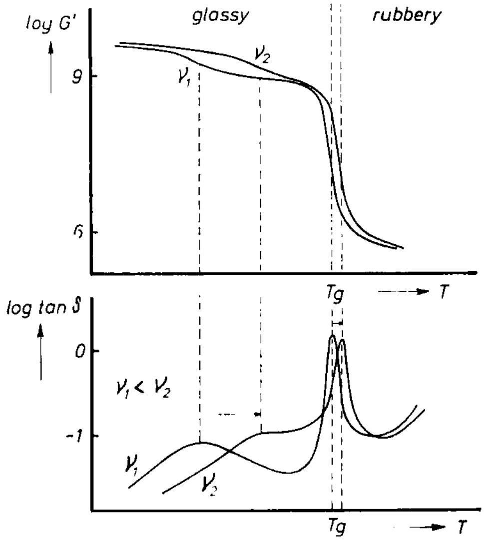


FIGURE 1 Storage modulus G' and damping tan δ as functions of temperature T at two frequencies ν_1 and ν_2 for an amorphous polymer (schematical drawing).

modulus curve: the loss curve shows a distinct maximum, whereas the modulus curve merely shows a steeper decrease.

When there are more secondary transitions, they are usually labelled from higher to lower temperatures with the successive letters of the Greek alphabet: β, γ, δ, and so on.

Tan δ is preferably plotted on a logarithmic scale, because the small loss peaks are more prominent and their slopes are more straight than they are in a linear plot. Moreover, this way of plotting is in better agreement with the relative accuracy of the damping measurement itself.

The mechanical properties of polymers are dependent on frequency; as is indicated by the two curves in the parts of Figure 1, ν_2 is a higher frequency than ν_1, the main effect of a frequency increase being a shift of the curve to the right (i.e. to a higher temperature). A secondary transition is shifted more rapidly than a glass transition, and so at higher frequencies the two may merge or coincide. When instead of tan δ one plots the loss modulus $G'' = G' \tan \delta$, the separation between the β- and α-maximum is better. This is seen on comparison of Figure 2 and Figure 1.

Figure 3 shows the relative locations of a secondary maximum and a glass transition in an Arrhenius plot. In this plot the slope of a secondary transition is steeper than that of the glass transition. This indicates that the best separation of the loss maxima is obtained at lower frequencies. Moreover, it is seen

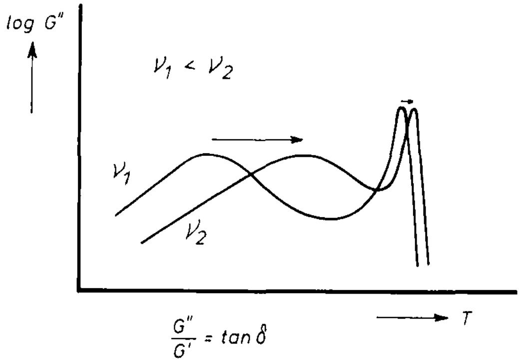


FIGURE 2 Loss modulus G'' as a function of temperature T at two frequencies ν_1 and ν_2 for an amorphous polymer. The curves pertain to the same (hypothetical) data as do those in Figure 1.

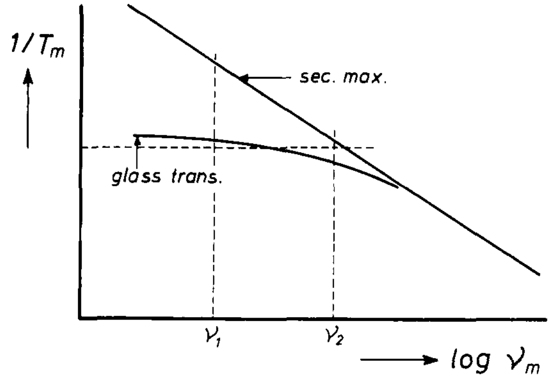


FIGURE 3 Schematic drawing of the course of a glass transition and that of a secondary maximum in a $1/T_m$ vs. log ν diagram.

that by plotting the losses as a function of frequency at a constant temperature, one might be able to separate the α- and β-maxima, even at temperatures near that at which the two maxima coincide.

2 MEASUREMENT OF SECONDARY MAXIMA

Section 1 emphasizes the importance of measurements over a broad frequency range. In dielectric measurements a single instrument, such as a Schering bridge, covers five decades. In mechanical measurements for a similar range of frequencies several instruments are required.

Figure 4 gives a survey of the equipment used at the Centraal Laboratorium TNO. On the horizontal axis is plotted the time (from left to right) or the frequency (from right to left); on the vertical axis the range of moduli covered by the various instruments.

The best known instrument is the torsional pendulum, in which a specimen carries out free vibrations. Application of different moments of inertia allows a frequency range of up to two decades to be covered. Normally, with our size of specimens, we obtain data in the region of 1 Hz.

For longer-time experiments we use the torsional creep instrument. This gives the shear compliance J as a function of time t. Creep in torsion has several advantages over creep in tension, one of which is that thermal expansion does not affect the reading, and another that in torsion the material behaves linearly up to higher stresses than it does in tension. The time range covered depends only on the experimenter's patience. The instrument is fully automated, so that measurements can be made overnight, one day being a practical limit. The shear modulus and losses can be calculated

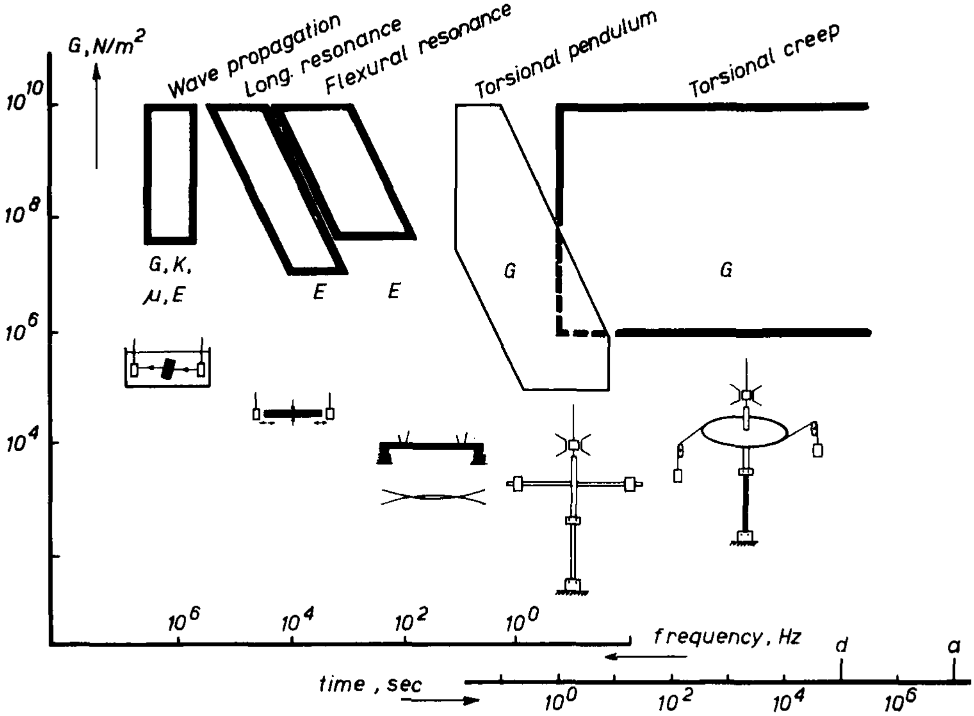


FIGURE 4 Survey of modulus and frequency ranges covered by the instruments used at the Centraal Laboratorium TNO for measurements of modulus and damping.

from the data by means of the first-order approximations[1]

$$G^*(\nu) \simeq \frac{1}{J(t)} \text{ and } \frac{d \ln J}{d \ln t} \simeq \frac{2}{\pi} \tan \delta(\nu) \text{ with } 2\pi\nu = \frac{1}{t}$$

For frequencies between 100 and 10,000 Hz, we have the method of flexural resonance vibration; here the losses are calculated from the width of the resonance peak. For these three measurements we use the same specimen.

Longitudinal resonance vibration extends the frequency range up to 100 kHz; the specimens are cylindrical bars, 10 cm long and 1 cm in diameter; or 1 cm long and 0.1 cm in diameter.

For 0.8 and 5 MHz we used propagating waves. These measurements give the shear as well as the compression modulus, from which we can also calculate Poisson's ratio μ. Waterman[2] found that Poisson's ratio behaves like a compliance; it is a complex quantity whose imaginary part shows a maximum in the temperature region of the maximum of the loss modulus.

Further details about the instruments can be found in Ref. 3, which also contains references to the original literature.

Figure 5 shows a representative example of results obtained with this series of instruments. Data are given for poly(cyclohexyl methacrylate) (PCHMA). In the glassy state this polymer has a sharp transition that must be ascribed to the flipping motion of the saturated six-membered ring.

In this figure, G' and $\tan \delta$ are plotted as functions of temperature for six frequencies. The values of G' for 200, $\simeq 10^4$ and $\simeq 10^5$ Hz have been calculated from Young's moduli, with the Poisson's ratio derived from the MHz-measurements. The figure is dominated by the γ-maximum, which shifts to higher temperatures with increasing frequency. Below $-150°$C we also see a part of the δ-maximum. Near $-60°$C the curve for 10^{-4} Hz shows a faint β-maximum. As expected, each γ-peak is accompanied by a drop in the corresponding storage modulus (G') curve. Figure 6 gives the Arrhenius plot of the γ-maximum. The points fit very well to a straight line over a temperature range of 200 K and a frequency range of 10 decades. (An idea of this time span is gained from the consideration that, if the shortest time were 1 sec, the longest would be about 300 years!) The activation energy is 11.3 kcal/mol. This value agrees very well with the value of 11.4 kcal/mol found from NMR measurements for the activation energy of the chair–chair transition of the cyclohexyl ring.[4,5]

Figure 7 shows the results of reducing to one temperature the torsional pendulum measurements of G'' for the γ-maximum of PCHMA, by shifting them along the frequency axis until they coincide. The distance over which the data have to be shifted to coincide with those at the reduction temperature is called the shift factor a_T. It is clear that for this loss peak the reduction is justified, as the direct measurements (filled circles) coincide with the

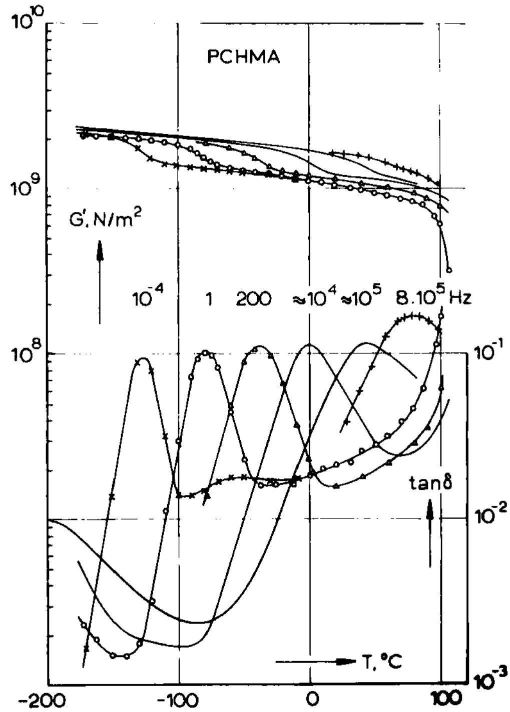


FIGURE 5 Shear modulus G' and damping tan δ as functions of temperature at six frequencies for poly(cyclohexyl methacrylate) (PCHMA).

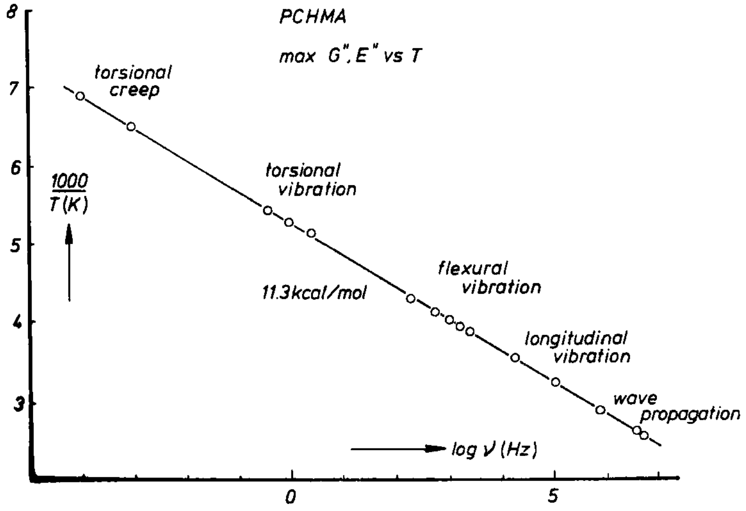


FIGURE 6 Arrhenius plot for the γ-loss maximum of poly(cyclohexyl methacrylate). The data are obtained from G'' resp. E'' vs. T-curves.

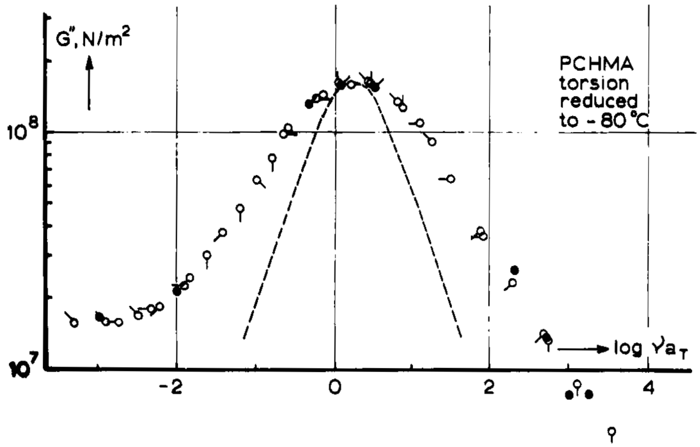


FIGURE 7 Loss modulus G'' for PCHMA at −80 C as a function of reduced frequency νa_T. Filled circles represent direct measurement at the given frequency. Dashed line: maximum for a single relaxation time.

reduced data. Although the cyclohexyl loss peak is rather sharp, its width on the logarithmic scale still is about twice that of a peak with a single relaxation time.

Figure 8 shows the relation between the shift factor a_T and $1/T$ for the γ-maximum of PCHMA and for that of PCHA. The graphs are not straight, but slightly curved. This might be explained by the assumption that the apparent activation energy slightly varies, and that even within a single loss peak there is a distribution of activation energies.

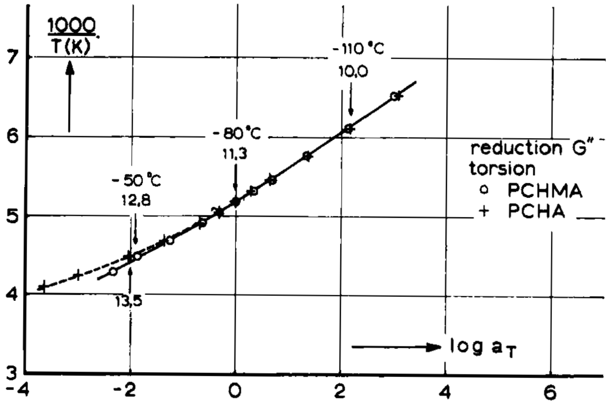


FIGURE 8 Shift factor a_T of G'' plotted vs. $1/T$ for PCHMA and poly(cyclohexyl acrylate) (PCHA). The activation energies, calculated from the local slope, are indicated in kcal/mol.

3 THE MOLECULAR ORIGIN OF SECONDARY MAXIMA

In order to deal with the molecular origin of the loss processes, we will consider what types of motion are possible in amorphous polymers below their glass transition temperature. At the glass transition motions of large parts of the main chain are frozen in. Since these motions require a considerable free volume, it is reasonable to suppose that below the glass transition the available free volume is still large enough for the motion of smaller groups.

Figure 9 gives a survey of the four main types of motion (A, B, C and D) which are possible below T_g and which give rise to secondary loss peaks.

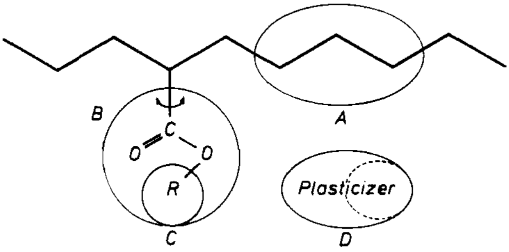


FIGURE 9 The various kinds of groups whose movements give rise to secondary mechanical loss peaks.

Type A This is a motion, still within the main polymer chain, but locally much more restricted than the motion corresponding to the glass transition. A typical example of a loss peak, connected with such a type of motion is the β-maximum of rigid PVC,[6,7] which lies near 210 K at 1 Hz (see Figure 10). It is clear that this maximum must be attributed to a main-chain motion, since there are no other possibilities: rotation about the C–Cl bond has no effect, and any motion of the chain ends would result in the height of the loss peak being dependent on the degree of polymerization, which it is not.[8] Figure 10 also shows that an increase in density of about 0.4 %, corresponding to a considerable decrease in free volume, has nevertheless practically no effect on the height of the loss peak.[9]

Another example of local main-chain motion is found in polycarbonate;[10] a comparison with dielectric loss data shows that the polar carbonate group is involved in the secondary maximum. The secondary maxima of polysulphones[11] and polyesters[12] are also caused by this type of motion.

Type A motion is an important one, since the corresponding secondary loss peak often marks the transition from brittle to tough behaviour.

Type B This type is the rotation of a side group about the bond linking it to the main chain (see Figure 9). The side group moves as one whole; its rotation need not be complete, and indeed is more likely to be a transition

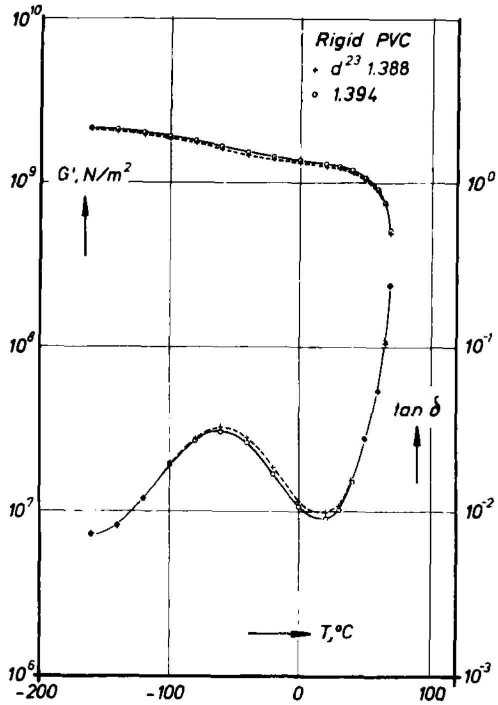


FIGURE 10 Storage modulus G' and damping tan δ at 1 Hz as functions of temperature for two samples of rigid poly(vinyl chloride); one cooled at 50 bar, the other at 1000 bar, from above T_g to room temperature. Measurements at normal pressure, starting at -160°C.

from one equilibrium position to another. The deformation of adjacent valence angles often forces the main chain to partake slightly in the side group motion. A typical example of this type of motion is found in polymethacrylates.[13] The β-maximum is caused by the motion of the entire —COOR group. Figures 11 and 12 show this β-maximum of poly(methyl methacrylate) (PMMA), together with the much smaller secondary maximum of poly(methyl acrylate) (PMA). Both the glass temperature and the secondary maximum lie at a much lower temperature for PMA than for PMMA. Comparison of Figure 12 and Figure 11 shows that secondary maxima are more pronounced in a loss modulus (G'') plot than they are in a tan δ plot; for PMMA the glass transition is even the minor peak in the G''-plot. In the next section we shall discuss the β-maximum of PMMA in more detail.

Type C This type of motion is an internal motion within the side group itself, without interaction with the main chain (See Figure 9, type C). Typical examples are the internal motions in R of the —COOR group in polymethacrylates, e.g. that of the *n*-butyl group in poly(*n*-butyl methacrylate)

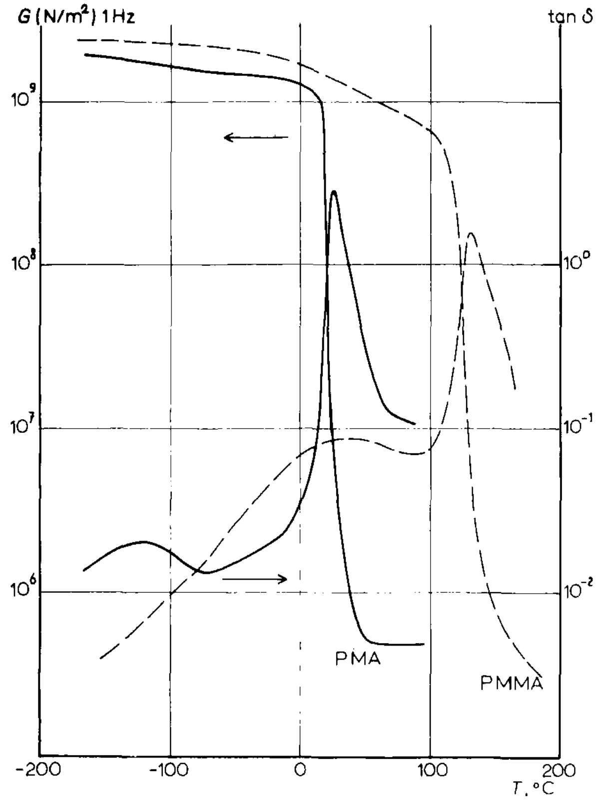


FIGURE 11 Storage modulus G' and damping tan δ at 1 Hz as functions of temperature for poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA).

and that of the cyclohexyl group in poly(cyclohexyl methacrylate).[14] In Figures 13 and 14 the loss peak of the cyclohexyl group (already shown in Figure 5) is compared with that of the *n*-butyl group. The two groups have the same length, viz. four carbon atoms, but the *n*-butyl group has a greater freedom of motion at its end. As a consequence the maximum of the *n*-butyl group lies about 100 K lower than that of the ring. The higher flexibility of the *n*-butyl group also results in the T_g of the polymer being about 80 K lower than that of PCHMA.

Type D This is a motion of, or taking place within, a small molecule, dissolved in the polymer. This can be a motion within a plasticizer molecule, e.g. of the *n*-butyl group in dibutyl phthalate. Figure 15 shows another example: a low temperature maximum that is caused by a motion of the oxo-substituted cyclohexyl ring of an ester, dissolved in PMMA. The maximum of the oxo-substituted cyclohexyl ring lies at a much lower tem-

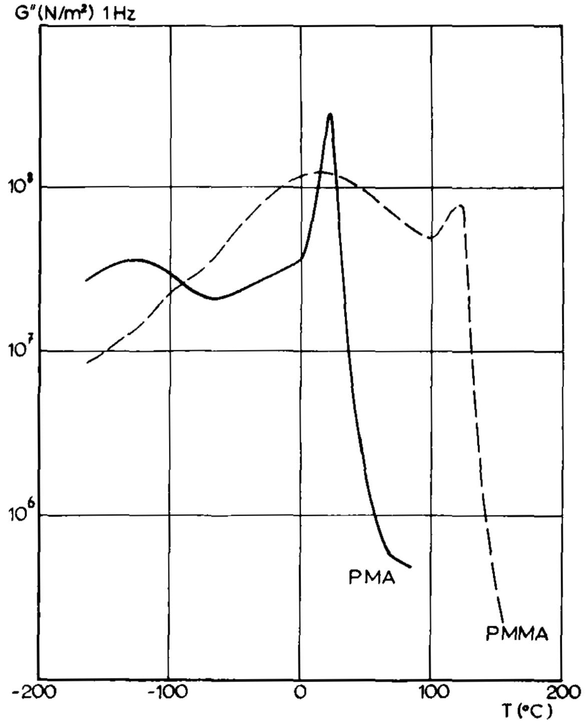


FIGURE 12 Loss modulus G'' at 1 Hz as a function of temperature for poly(methyl methacrylate) and poly(methyl acrylate).

perature than that of the unmodified cyclohexyl ring, because the barrier to the flipping motion is considerably lower.[14]

Figure 16 shows the losses, measured in creep and in free vibration, of caprolactam dissolved in PMMA. The maximum near −80°C, 1 Hz, is due to the caprolactam. The loss peak for this seven-membered ring nearly coincides with that of the six-membered ring of cyclohexyl, the reason probably being that rotation about the bond between CO and NH is blocked.[15] The cycloheptyl ring has a maximum at a much lower temperature, viz. at about −170°C, 1 Hz.[16] In Figure 16 the maximum near 0°C, 1 Hz, is the β-maximum of PMMA.

Small molecules dissolved in polymers, sometimes associate themselves with side groups, particularly if both are polar. When association takes place and there is a combined motion, we get a type C instead of a type D motion. Janáček and coworkers have thoroughly investigated the effect of the interaction of small molecules and side groups on secondary loss peaks in polymethacrylates.[17] In this paper we shall not deal further with these complexes.

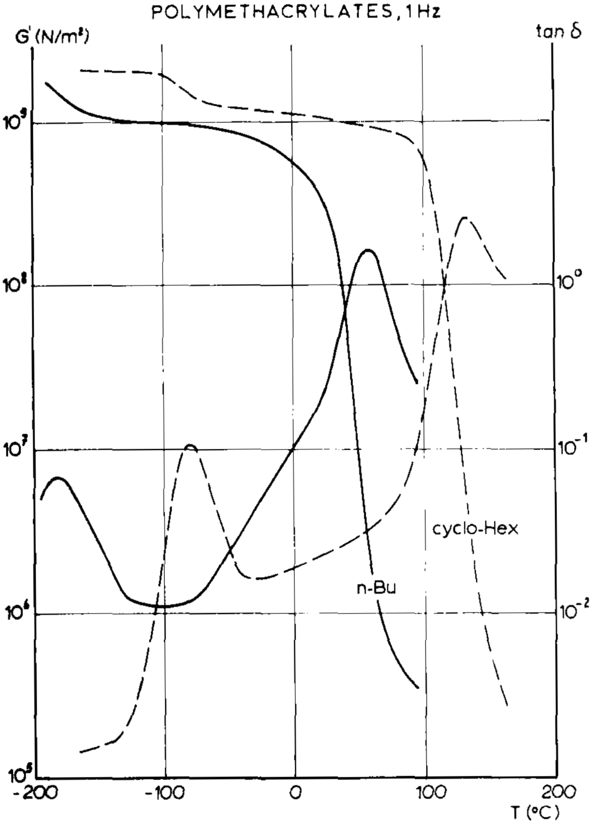


FIGURE 13 G' and tan δ at 1 Hz of poly(*n*-butyl methacrylate) and poly(cyclohexyl methacrylate).

We shall now consider the dependence on frequency of secondary loss maxima, originating from the different types of molecular motion. Loss moduli have been determined at a constant frequency as a function of temperature, and from the resulting curves the temperature T_m corresponding to the maximum loss has been read. Figure 17 gives several Arrhenius plots, in which the reciprocal of T_m (in Kelvin) is plotted as a function of the logarithm of frequency ν. The thick parts of the lines indicate the region of the measurements; the thin parts are extrapolations.

Figure 17 shows the following examples:

Type A: β-maximum of PVC
Type B: β-maximum of PMMA
Type C: γ-maximum of P*n*PrMA
γ-maximum of PCHMA

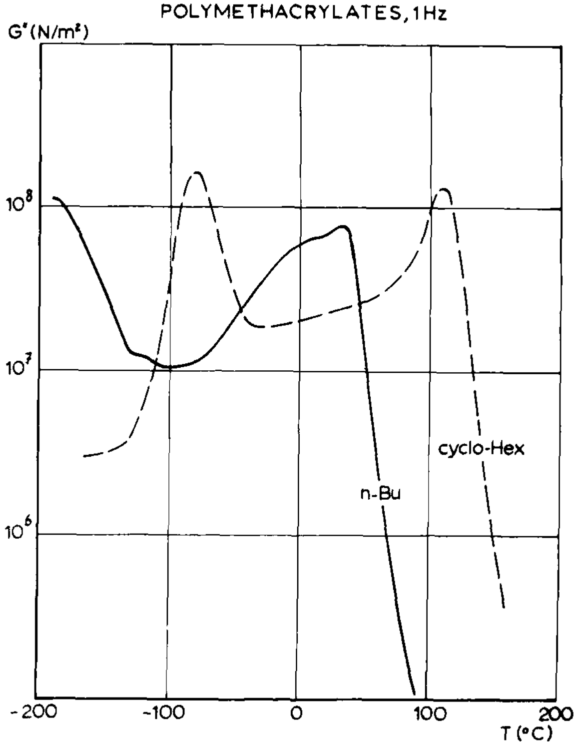


FIGURE 14 G'' at 1 Hz of the same polymers as in Figure 13.

Type D: maximum of 4-benzoyloxycyclohexanone, 25% (w/w) embedded in PMMA

The measured values fit the Arrhenius equation:

$$\ln \nu = \ln \nu_0 - E_a/RT_m \qquad (1)$$

$$(\text{or } \log \nu = \log \nu_0 - 0.4343\, E_a/RT_m)$$

where E_a is the activation energy and R the gas constant. The straight line corresponding to the loss peak of the type A motion extrapolates to $\log \nu_0 = 15$; the other lines for the types B, C and D motions all extrapolate to 13.5 ± 1.

10^{13} Hz is a reasonable frequency for a molecular vibration. The molecular picture behind an activated process described by an Arrhenius equation, is as follows: suppose the mechanism is one involving two potential wells separated by a barrier much higher than kT (Figure 18).

Each of the groups is vibrating at its molecular frequency in a well, and sometimes it jumps across the barrier to the other position. If entropy

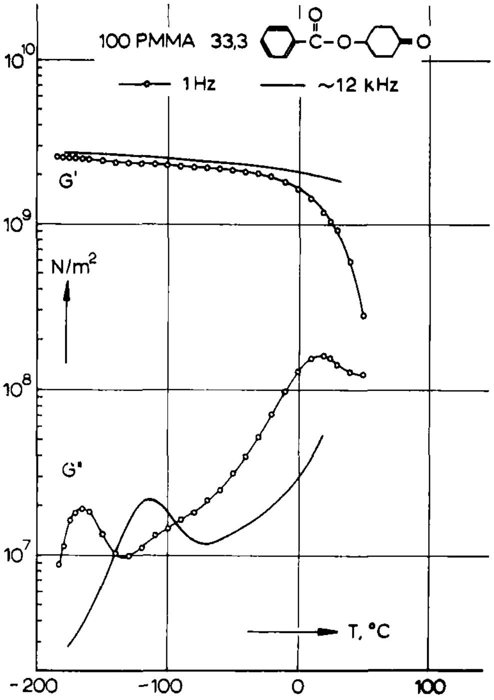


FIGURE 15 G' and G'' at 1 Hz and at about 12 kHz for PMMA containing 25% of 4-benzoyloxycyclohexanone.

differences between the two positions are neglected, the relative numbers of the groups in each of the two positions in the state of equilibrium are determined by Boltzmann's equation. Application of a stress causes the differences in depth of the two wells to change; the equilibrium is disturbed and a redistribution of the groups over the two positions starts. The rate of redistribution is determined by the temperature and by the height of the barrier, which is therefore the activation energy E_a. When during the time of redistribution the stress field changes its direction, energy is dissipated. This molecular picture implies that the location of *the secondary loss peak is determined by the local barrier within the molecule.*

Figure 17 also shows a glass transition, viz. that of the rubbery part of acrylonitrile-butadiene-styrene (ABS). Clearly, the behaviour of this maximum is quite different from that of the secondary maxima: the slope of the curve is much less steep, indicating a much higher activation energy. We conclude that *secondary maxima behave quite differently from glass transitions.*

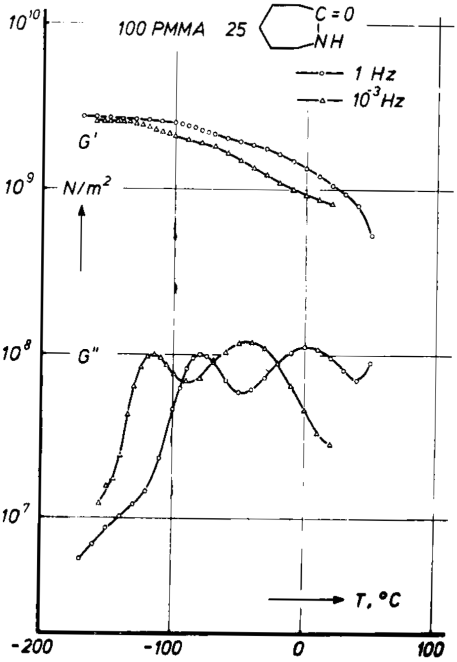


FIGURE 16 G' and G'' at 1 Hz and 10^{-3} Hz of PMMA containing 20% of caprolactam.

If we assume that in Eq. (1) $\log \nu_o = 13$ we can estimate the activation energy E_a (in kcal/mol) from $T_m(K)$ at a frequency of 1 Hz by the simple equation:

$$E_a = 0.060\, T_m \text{ (1 Hz)} \tag{2}$$

For other frequencies we have:

$$E_a = (0.060 - 0.0046 \log \nu)\, T_m(\nu) \tag{3}$$

Figure 19 gives an impression of the validity of Eq. (2). In the figure E_a values for secondary maxima of different molecular origin are plotted against their T_m at 1 Hz. The plotted values are rather accurate, because E_a is measured over at least 3 decades. Most of the data are derived from our own measurements, mainly on poly(meth)acrylates; only the numbered ones have been taken from the literature. We see that for type B, C, and D motions the relationship is obeyed to within 10%. Only for type A motions are the activation energies higher; the $1/T_m$ vs. $\log \nu_m$ extrapolates to $\log \nu_o$ values significantly higher than 13, e.g. to 15. This is probably due to a considerable entropy contribution to the transition state, which is not surprising for

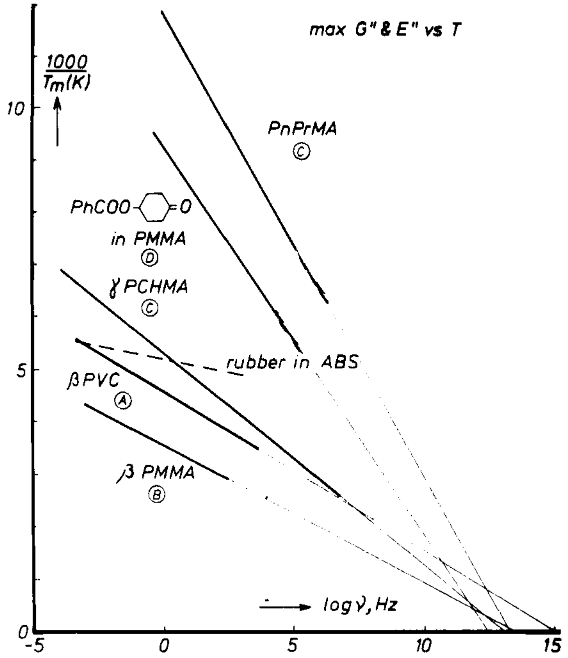


FIGURE 17 Arrhenius plots of secondary maxima. The type of motion is indicated. For purposes of comparison a glass transition (rubber in ABS) is included.

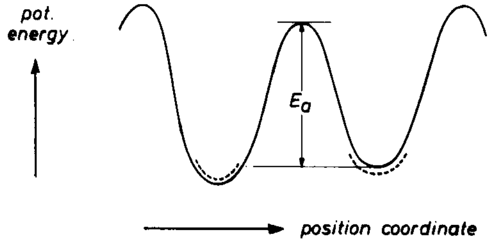


FIGURE 18 Two-well potential model.

main-chain motions. Nevertheless, even the data for type A motions obey Eq. (2) to within 20%. Equation (2) probably gives a more accurate value for E_a than does the usual determination from measurements over a narrow frequency range (say, 1 decade).

E_a-values for glass transitions are much higher than predicted by Eq. (3), e.g. 200%. The points for the γ-transition in PE and in POM also lie very far from the line in Figure 19 for secondary maxima in glassy amorphous polymers.

From this section it is clear that my viewpoint strongly differs from that

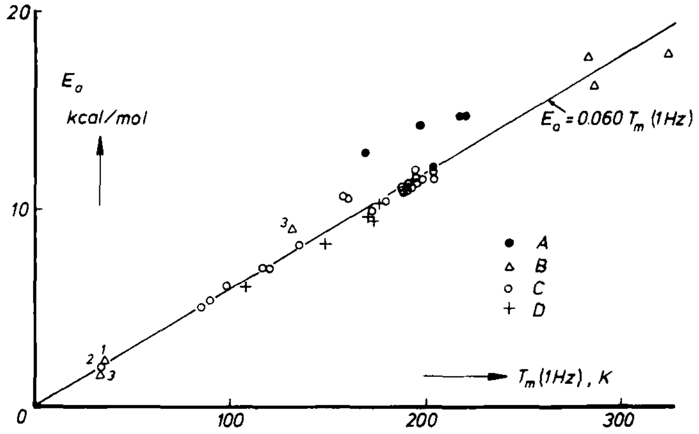
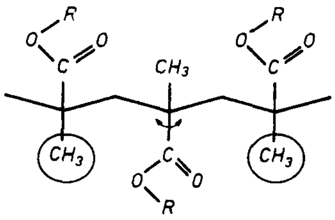


FIGURE 19 Activation energy E_a as a function of the temperature of the secondary loss maximum at 1 Hz for different types of molecular motion. The numbered points are literature data. 1: Ref. 18; 2: Ref. 19; 3: Ref. 20.

of Yohari and Goldstein,[21] who advocate *inter*molecular interactions as providing the potential barriers for secondary loss peaks.

4 DEPENDENCE ON STRUCTURE OF SECONDARY MAXIMA

We will now examine in more detail the effect of molecular structure on a secondary maximum, taking as an example a type B maximum, viz. the β-maximum of poly(methyl methacrylate) (PMMA).[13] The molecular mechanism of this maximum is usually considered to be the (partial) rotation of the oxycarbonyl group (COO) about the C–C bond linking the group to the main chain. The potential barrier is provided by the adjacent methyl groups in the neighbouring mers attached to the main chain; see the structural formula:



Molecular models (Stewart) clearly reveal the proximity of these methyl groups to the —COO group. It is not yet clear to what extent the main chain takes part in the side group motion.[22] Havriliak[23] even supposes that the

β-maximum of PMMA is due to a main-chain motion and the α-maximum to side-chain motions, but for several reasons this idea is rather unlikely.

Strong arguments against it follow from a comparison of the relative sizes of the mechanical and dielectric damping maxima of PMMA and poly(methyl α-chloroacrylate) (PMeClA).[24] (In the latter, the main chain carries Cl atoms instead of CH_3 groups.)

Relative size of tan δ maxima of poly(methyl methacrylate) and poly(methyl α-chloroacrylate)

		α-maximum	β-maximum
PMMA	mechanical	large	small
	dielectric	small	large
PMeClA	mechanical	large	small
	dielectric	large	large

First, it is not to be expected that mechanically the motion of a relatively small side group would have a more marked effect than an extended main-chain motion; it seems therefore likely that the α-maximum is related to a main-chain motion. Secondly, the relative sizes of the dielectric loss maxima of PMMA suggest that the β-maximum must be ascribed to the loosening of the polar part (the side groups) and the α-maximum to the motion of the relatively non-polar main chain. This is confirmed by the relative importance of the dielectric loss maxima of PMeClA: in this polymer not only the side group but also the main chain is polar, and its dielectric α-maximum therefore also is large.

Havriliak's arguments for the molecular mechanism he proposes are based on a careful study of the infrared spectrum in the range of 1,050 to 1,030 cm^{-1}. He observed that the intensities of two absorption peaks associated with the ester group are independent of temperature below T_g and vary with temperature above T_g, whereas the sum of the intensities remains constant over the entire experimental range. From this observation Havriliak concludes that only above T_g can the ester group rotate. However, an alternative explanation is possible. With respect to rotation there are two favourable positions of the ester group in PMMA, each giving a different infrared spectrum. The spectrum only gives information about the relative populations of the two positions, the jumping from one position to another not being observed. The potential wells of the two positions are determined by the configuration of the main chain in the immediate vicinity of the side group. Above T_g these potential wells will depend rather strongly on temperature, becoming more and more equivalent with increasing temperature, due to the motion of the main chain. Below T_g the motion of the main chain is strongly suppressed and on further cooling the immediate environment of the ester group does not change very much; consequently the relative depths of the wells become nearly independent of temperature. When the difference in depths of the potential wells is not large, this means that the distribution of the ester groups over the two positions is nearly constant below T_g, regardless of the possibility of jumping from one position to the other. By contrast, above T_g the distribution over the two positions changes, becoming more and more equal with increasing temperature. The observed dependence of the infrared spectra on temperature can thus be satisfactorily explained, without it being necessary to assume that the rotation of the ester group is blocked below T_g.[25]

Nevertheless, this discussion illustrates the paucity of our knowledge about the detailed molecular mechanisms of secondary loss peaks: most of the evidence is indirect. Schaeffer's lecture[26] shows that direct observation of mobility by sophisticated NMR techniques can give important contributions to the unambiguous elucidation of the molecular mechanisms responsible for secondary loss peaks.

Returning to the effect of structure on the β-maximum of polymethacrylates, we note (Figure 20) that in the series of tan δ curves of poly(n-alkyl methacrylates) the β-maximum merges with the α-maximum as soon as the side chain reaches a length of three C-atoms. A better separation is obtained in the plot of G'' (Figure 21), which shows that the β-maximum remains near $+10$°C at 1 Hz. Both figures show that the glass transition shifts to lower temperatures with increasing length of the n-alkyl group. It is clear that these polymers, with their long flexible side chains, do not obey the rule $T_\beta/T_g \simeq 0.75$.[27]

A still better separation of the glass transition from the β-maximum is shown in Figure 22, which gives the loss modulus obtained from creep measurements, whose equivalent frequency is 10^{-3} Hz; at this low frequency, even the β-maximum of the n-butyl ester stands clearly separate from the glass transition. Once more we see that the temperature of the β-maximum is not changed by elongation of the side chain. The shift to lower temperatures of the glass transition by the lengthening of side chains is sometimes called internal plasticization. It is seen that in this respect the β-maximum behaves in a completely different way from the glass transition: internal plasticization does not shift the β-maximum to lower temperatures.

From Figure 3 in Section 1 it was concluded that in a plot of damping as a function of frequency at constant temperature, maxima can be separated at temperatures near those at which they merge. Figure 23 illustrates how powerful this method is: even at 40°C a separate β-maximum is obtained for poly(ethyl methacrylate). When we compare Figure 20, and consider the higher frequency of the maximum (about 100 Hz), this separation is quite remarkable.

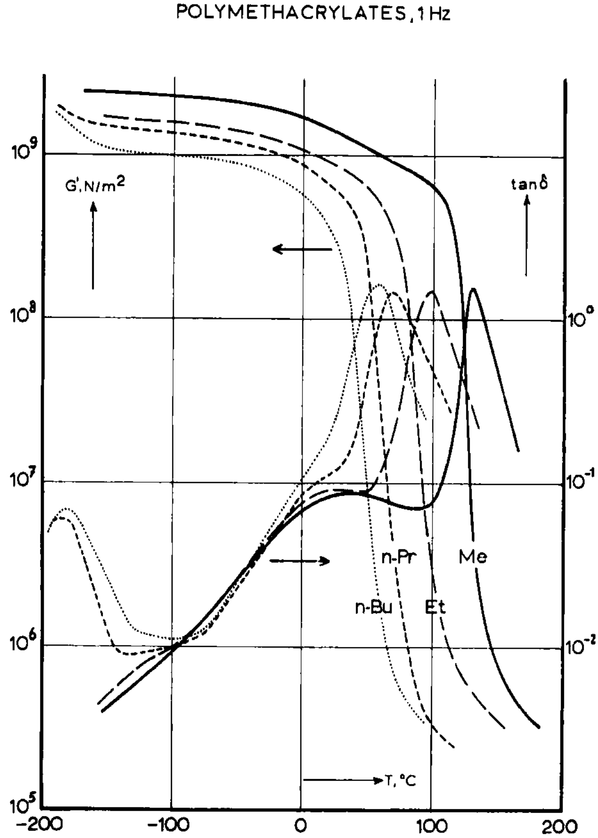


FIGURE 20 Shear modulus G' and losses tan δ at 1 Hz for poly(*n*-alkyl methacrylates). Me = methyl, Et = ethyl, n-Pr = *n*-propyl, n-Bu = *n*-butyl.

Figures 22 and 23 show the effect of a bulky *tert*-butyl group on the β-maximum: it is depressed, but remains at the same temperature and frequency. The still bulkier cyclohexyl group suppresses the β-maximum nearly completely. It is often argued that steric hindrance ought to shift maxima to a higher temperature. This is true for the glass transition, but not for this β-maximum. *Intermolecular* interactions do no more than depress the maximum, without shifting it to higher temperatures or to lower frequencies.

External plasticization, which decreases intermolecular interaction, does not affect the location of the β-maximum either. This is illustrated by Figure 24, which is derived from creep data: when PMMA is plasticized by dibutyl phthalate the G''-maximum remains near —40°C, 10^{-3} Hz. The location of the β-maximum is determined by the local *intra*molecular barrier, the *inter*molecular interaction has no effect.

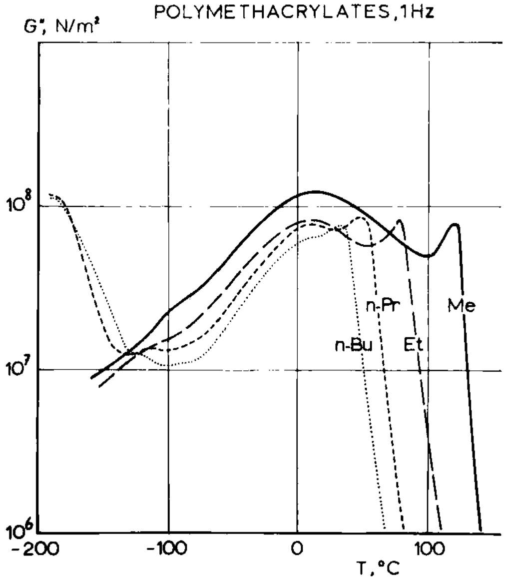


FIGURE 21 Loss modulus G'' at 1 Hz for the same polymers as in Figure 20.

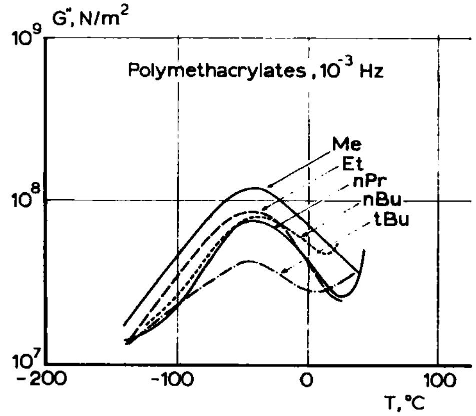


FIGURE 22 Shear modulus G'' at 10^{-3} Hz from creep data for the same polymers as in Figure 20. The curve for poly(*tert*-butyl methacrylate) (tBu) is also given.

Figure 25 shows that this statement also holds for the cyclohexyl maximum (γ-maximum) of a copolymer of CHMA and MMA. This figure brings out the different effects of a plasticizer on the glass and on the secondary transitions: the two secondary peaks are barely moved by the addition of DBP, whereas the α-peak is clearly shifted to a lower temperature. Moreover, there appears a maximum due to the motion of the *n*-butyl group of the plasticizer.

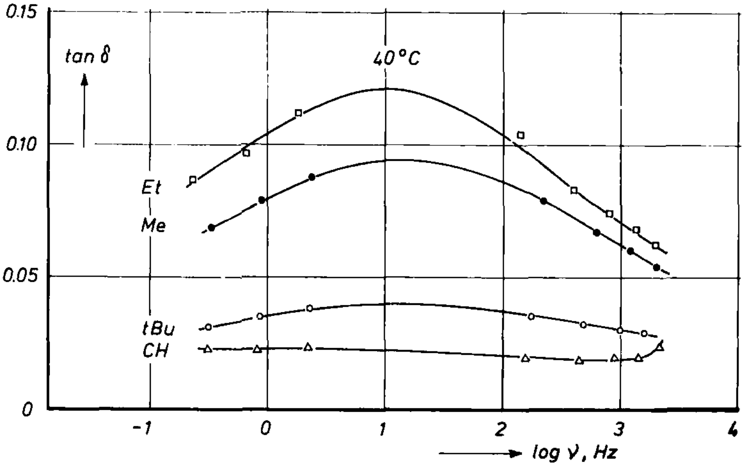


FIGURE 23 Mechanical loss tan δ as a function of frequency at 40°C for four poly(methacrylic esters). Et: ethyl ester; Me: methylester; tBu: *tert*-butyl ester; CH: cyclohexyl ester.

For the cyclohexyl as well as the oxycarbonyl motion it is the local *intra*-molecular barrier, not the intermolecular interaction, which determines the location of the loss peak.

It has been shown before[28] that a decrease of the intramolecular barrier by substituting hydrogen for methyl on the main chain shifts the β-transition of PMMA to a lower temperature, e.g., by copolymerization with styrene, whereas copolymerization with α-Me styrene, in which the methyl is still on the main chain, leaves the maximum at the same temperature.

We can also change the local barrier by attaching Cl instead of methyl to the main chain; this causes the barrier to increase and indeed, Figure 26 shows that the maximum shifts to a higher temperature.

There is one structural feature which affects the location of the β loss peak of PMMA without it being clear that the local barrier is changed, namely the polarity of the ester group. Each part of Figure 27 shows the loss moduli of a series of polymethacrylates containing polar and nonpolar groups of about the same length: the chloromethyl and cyanomethyl ester are compared with the ethyl ester, and the 2-chloroethyl, 2-bromoethyl, 2-cyanoethyl and 2-hydroxyethyl ester with the *n*-propyl ester. Although at this low frequency the effect of polarity is only slight, there nevertheless is a shift to higher temperatures and a considerable broadening of the β-maximum. These effects are probably caused by *inter*molecular interactions; so with distant polar ester groups the secondary maximum is not determined exclusively by the local *intra*molecular potential barrier.

Of course, the effect of polarity on the γ-maximum, which is due to a

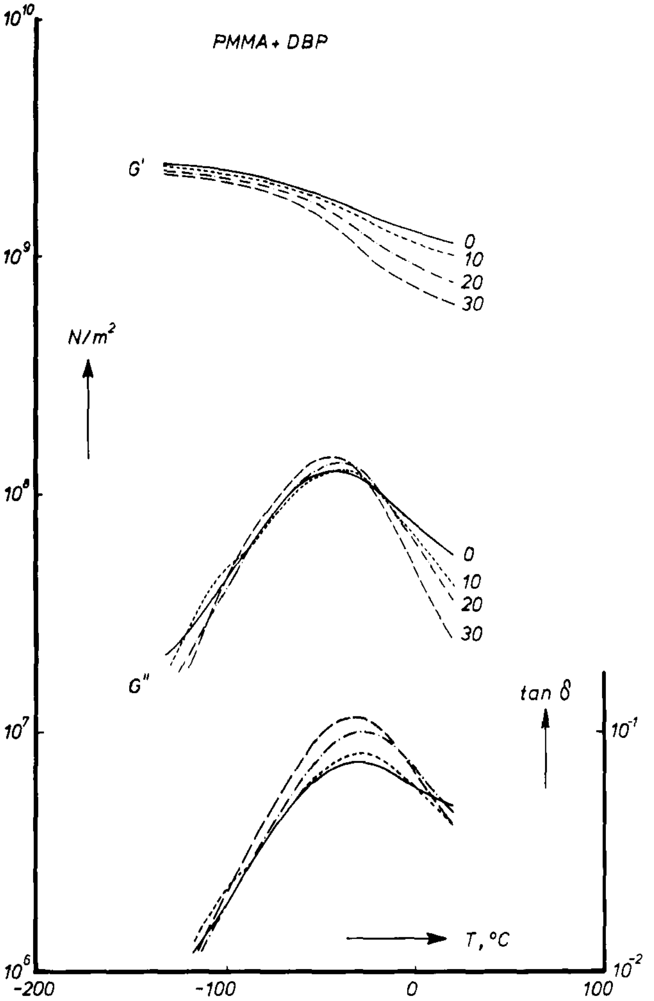


FIGURE 24 Storage modulus G', loss modulus G'' and losses tan δ at 10^{-3} Hz as functions of temperature for PMMA plasticized with dibutyl phthalate (DBP). Parts DBP (w/w) per 100 PMMA are indicated.

motion within the alkyl group itself, is essentially different; for this motion the polarity contributes directly to the local barrier, and there is a very pronounced shift to higher temperatures with increasing polarity.[29]

Some amorphous polymers show other secondary maxima whose location depends not only on intramolecular interaction but also on intermolecular interactions. A well-defined example is the γ-maximum of 2-methyl-6-alkyl

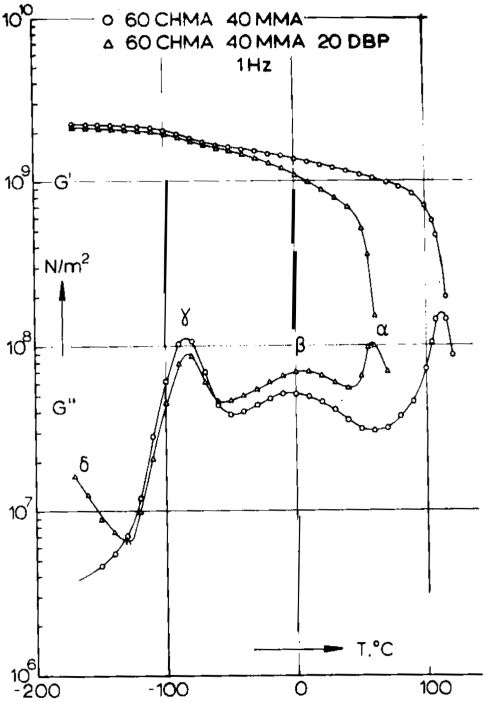


FIGURE 25 Storage modulus G' and loss modulus G'' at 1 Hz as a function of temperature for a copolymer of CHMA and MMA and for the same copolymer plasticized by 20 parts of DBP to 100 parts of copolymer.

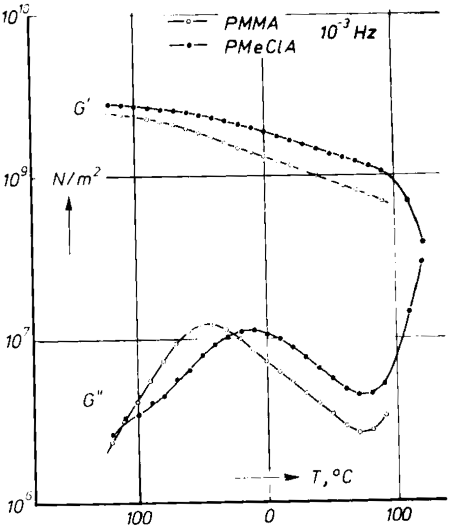


FIGURE 26 Storage modulus G' and loss modulus G'' at 10^{-3} Hz for PMMA and for poly(methyl α-chloroacrylate) (PMeClA). Data from creep measurements.

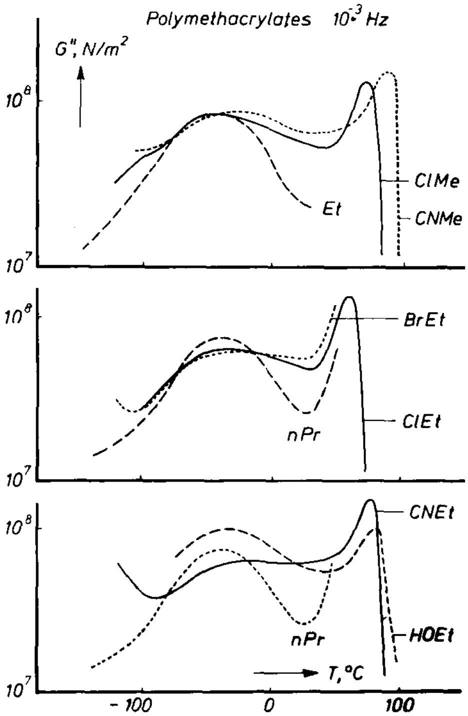


FIGURE 27 Loss modulus G'' of polymethacrylic esters with polar side chains as a function of temperature at 10^{-3} Hz. Ester groups—Et: ethyl; ClMe: chloromethyl; CNMe: cyanomethyl; nPr: *n*-propyl; ClEt: 2-chloroethyl; BrEt: 2-bromoethyl; CNEt: 2-cyanoethyl; HOEt: 2-hydroxyethyl.

substituted poly(phenylene ethers), studied by Eisenberg *et al.*[30] This maximum, which is supposed to be due to oscillations of the alkyl chain in its planar zig-zag form, shifts from 171 K to 224 K (1 Hz) on elongation of the alkyl group from 4 to 9 carbon atoms, whereas the activation energy increases considerably. It is very likely that intermolecular interactions of the alkyl group contribute to an important extent to the potential barrier for this motion.

Kolařík[31] found that the γ-maximum due to the hydroxyethyl group in copolymers of 2-hydroxyethyl methacrylate and MMA, shifts to a lower temperature with increasing MMA content. This can only be understood if, in addition to the intramolecular barrier, there is an interaction with the environment. Boyer[32,33] states that in the secondary maxima of polystyrene a combination of intra- and intermolecular hindrances is involved.

Although it is clear therefore that several secondary loss peaks must in part be ascribed to *inter*molecular interactions, the insensitivity of many of them to annealing leads one to the conclusion that very often it is the *intra*-molecular interactions which predominate. This holds especially for the cyclohexyl-maximum[14] and for the β-maximum of PMMA. The minor effect of a strong densification of PVC on the A-type motion (Figure 10) also points in this direction. When considering these effects one should bear in mind that the low-temperature tail of the glass transition is very sensitive to annealing.

CONCLUSIONS

The behaviour of secondary maxima in glassy amorphous polymers is different from that of glass transitions:

a) They obey an Arrhenius relationship over a broad frequency range.

b) For other than local main-chain motions the activation energy E_a of the molecular process underlying the loss maximum, can be calculated from $E_a = 0.060\ T_m$ with an accuracy of 10%. For local main-chain motions E_a usually is slightly higher, say 20%.

c) For many secondary maxima the origin of E_a is mainly *intra*molecular.

d) Plasticization mostly does not affect the temperature location of a secondary maximum.

e) Sufficiently strong *inter*molecular hindrance mostly decreases the height of the loss maximum, but does not shift it to higher temperatures.

Acknowledgement

My thanks are due to Mr L. C. E. Struik for illuminating discussions.

References

1. A. J. Staverman and F. Schwarzl, Linear deformation behaviour of high polymers, in H. A. Stuart, Ed., *Die Physik der Hochpolymeren*, Springer Verlag, Berlin (1956), Bd IV.
2. H. A. Waterman, *Kolloid-Z.* **192,** 1 and 9 (1963).
3. J. Heijboer, Mechanical properties of glassy polymers containing saturated rings, Doctoral Thesis, Leiden, 1972, Centraal Laboratorium TNO Communication 435, Chapter 3.
4. F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.* **89,** 760 (1967).
5. G. Binsch, *Topics in stereochemistry*, Interscience Publ., New York, **3,** 97 (1968).
6. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and dielectric effects in polymeric solids*, John Wiley, London (1967), p. 434.
7. a. G. Pezzin, G. Ajroldi, and C. Garbuglio, *J. Appl. Polym. Sci.* **11,** 2553 (1967).
   b. J. A. Mason, S. A. Iobst, and R. Acosta, *J. Macromol. Sci.-Phys.* **B9,** 301 (1974).
8. a. Y. Ishida, *Kolloid-Z.* **171,** 71 (1960).
   b. J. Beautemps, *Rev. Gen. Caout. Plast.* **47** (1), 95 (1970).
9. H. W. Bree, J. Heijboer, L. C. E. Struik, and A. G. M. Tak, *J. Polym. Sci.-Phys.* **12,** 1857 (1974).

10. Ref. 6, p. 532.
11. M. Baccaredda, E. Butta, V. Frosini, and S. de Petris, *J. Polym. Sci.* **A-2, 5,** 1296 (1967).
12. Ref. 6, p. 517.
13. Ref. 6, p. 242.
14. See J. Heijboer, Fourth Midland Macromolecular Meeting, 1975.
15. S. I. Mizushima *et al., J. Amer. Chem. Soc.* **72,** 3490 (1950).
16. J. Heijboer, *J. Polym. Sci.* **C16,** 3413 (1968).
17. See among others: J. Janáček and J. Kolařík, *J. Polym. Sci.* **C16,** 279 (1967); J. Janáček, *J. Polym. Sci.* **C23,** 373 (1968); J. Kolařík and J. Janáček, *J. Polym. Sci.* **A-2, 10,** 11 (1972); F. Lednický and J. Janáček, *J. Macromol. Sci.-Phys.* **B6,** 335 (1971); J. Janáček, *J. Macromol. Sci.-Revs.* **C9,** 1 (1973).
18. J. A. Sauer and R. G. Saba, *J. Macromol. Sci.-Chem.* **A3,** 1217 (1969).
19. K. Shimizu, O. Yano, Y. Wada, and Y. Kawamura, *J. Polym. Sci.-Phys.* **11,** 1641 (1973).
20. O. Yano and Y. Wada, *J. Polym. Sci.* **A-2, 9,** 669 (1971).
21. G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53,** 2372 (1970) and **55,** 4245 (1971).
22. See J.-F. Jansson, *J. Appl. Polym. Sci.* **17,** 2997 (1973).
23. S. Havriliak and N. Roman, *Polymer* **7,** 387 (1966).
24. K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polym. Sci.* **13,** 565 (1954).
25. H. Looijenga, Personal communication.
26. J. F. Schaeffer, Fourth Midland Macromolecular Meeting, 1975.
27. R. F. Boyer, *J. Polym. Sci.—Polym. Symp.* **50,** 189 (1975).
28. J. Heijboer, *Proc. Int. Conf. Physics non-crystalline solids,* N. Holland Publ. Co., Amsterdam (1965), p. 231.
29. H. A. Waterman, L. C. E. Struik, J. Heijboer, and M. P. van Duijkeren, in R. W. Douglas and B. Ellis, Ed., *Amorphous Materials, 3rd Int. Conf. Phys. non-crystalline solids, Sheffield,* 1970, Wiley (1972), p. 29.
30. B. Cayrol, A. Eisenberg, J. F. Harrod, and P. Rocaniere, *Macromolecules* **5,** 676 (1972).
31. J. Kolařík, *J. Macromol. Sci.-Phys.* **B5,** 355 (1971).
32. R. F. Boyer in N. Bikales, Ed., *Encyc. Polym. Sci. Techn.* **13,** Wiley-Interscience, New York (1970), p. 277.
33. R. F. Boyer, *J. Macromol. Sci.-Phys.* **B9,** 187 (1974).