

RELAXATION PHENOMENA AND POLYMER STRUCTURE

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INTRODUCTION

In recent years a considerable amount of information concerning segmental motion in high polymers and the relaxation phenomena which are a consequence of the onset of such motion has been gathered and our knowledge of this behaviour has been greatly advanced. Since the extent and types of motion taking place in a solid material strongly influence all the physical properties, these investigations have practical, as well as theoretical, interest. The experimental methods used to obtain this information have included: (a) dynamic mechanical, (b) transient mechanical, such as creep or stress relaxation, (c) dynamic electrical, and (d) steady-state and transient nuclear magnetic resonance (NMR) methods. In the present paper we will be principally interested in techniques (a) and (d).

In a dynamic mechanical experiment a time varying stress is applied to a sample resulting in a strain also varying with time which can be split into two components, one in phase with the stress and one 90° out of phase with the stress; the former component is proportional to the energy stored per cycle and the latter to the energy loss per cycle. In such experiments run at near-constant frequency over a *wide* temperature range, peaks in the loss modulus and dispersions in the storage modulus result. As expected for relaxation phenomena, an increase in measuring frequency leads to a shift of these processes to higher temperatures. Attempts to ascribe these processes as due to the onset of such motions as side-chain and main-chain oscillations and/or rotations in the polymer at or near the measuring frequency have been made by comparing results obtained on a variety of different polymers and by correlating the temperature-frequency positions of these processes with those found using other methods, such as: NMR, dielectric and volume-temperature measurements¹. It also should be pointed out that the storage modulus value at any given temperature is a useful measure of the specimen rigidity or inversely the flexibility, the latter increasing with temperature due to the increasing amounts of chain motion.

Turning now to the NMR techniques, there are two quantities of interest to us, one of these is the width (or the second moment) of the steady-state NMR absorption envelope, which is a measure of the spin-spin interaction and the other is the spin-lattice relaxation time, T_1 , the time constant for the energy transfer which can occur between the nuclei in the higher energy spin states or state and the surroundings or lattice. The effect of motion on these quantities is to narrow the absorption (to decrease the second moment

of the central portion of the absorption) and to shorten the relaxation time, the latter leading to a more efficient energy transfer process. Therefore, when measurements are made over a wide temperature range, starting at low temperatures, the peak-to-peak width of the derivative NMR absorption will decrease, if motion of the magnetic nuclei at the appropriate frequency occurs, this frequency being of the order of the absorption width $\sim 10^4$ – 10^5 c/s; motion of the lattice leads to a minimum in the T_1 -temperature plot, this minimum being found at a temperature where the frequency of the motion is near the resonance frequency ($\sim 10^7$ – 10^8 c/s). Due to the higher frequency of the measurement, the T_1 minimum is expected at somewhat higher temperatures than the mid-point of the second moment decrease for any particular process.

One definite advantage of the steady state absorption method is that the second moment values can be compared with values calculated using the van Vleck equation² if the distances between the interacting nuclei are known ($\Delta H^2 \sim 1/r^6$). In the calculation a value for the rigid lattice is obtained. In addition, estimates of the reduction in this value as a consequence of simple types of motion, such as methyl rotation about the C_3 axis, can be made³. Replacement of magnetic nuclei with others whose interactions are not apparent using the particular conditions of frequency and field employed can also be helpful in determining the type of motion responsible for a given process. Since we will be concerned only with proton resonance, the best nucleus for this replacement would be deuterium since this would probably cause the least change in other physical properties of the polymer.

During the remainder of this paper, data for a number of polymers will be presented and discussed. The polymers chosen for discussion have been mainly those studied by the author and his co-workers and have been chosen to demonstrate some of the similarities and differences found in the dynamic mechanical and NMR results. In most cases the explanations given for the various relaxation processes are tentative and are by no means agreed on by all the workers in the field. It should be noted that in only a few cases have the mechanical and NMR measurements been carried out on the same batch of a given polymer from the same supplier. In general, three or four different samples have been used and therefore ambiguities in the data due to this are bound to occur.

LINEAR POLYETHYLENE

Although linear polyethylene has received considerable study to date and it is well recognized that a number of relaxation processes exist for this polymer, the exact natures of these processes are still subjects of controversy.

At the lowest temperatures for which studies have been reported⁴ to date, 4.2–6°K among sixteen polymers containing various repeat units, a melt-formed linear polyethylene specimen was found to have the lowest dynamic elastic loss modulus, E'' , (0.07 – 0.09×10^8 dynes/cm²) and the highest dynamic elastic storage modulus, E' , (1.0×10^{11} dynes/cm²). As might be expected, therefore, a linear polymer with no side chains and with a high degree of chain order shows little molecular activity at these temperatures. However, as is evident in *Figure 1*, this state of low molecular activity does not persist as the temperature is raised, since mechanical loss maxima,

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storage modulus dispersions, NMR line narrowing and T_1 minima are found with some of these occurring well below the melting point.

The mechanical data, E' and E'' , given in *Figure 1*, at temperatures from 6° to 77°K were obtained for Marlex 50 using a longitudinal vibration apparatus⁵ operating at $\sim 10^4$ c/s. The break in the loss curve at $\sim 47^\circ\text{K}$

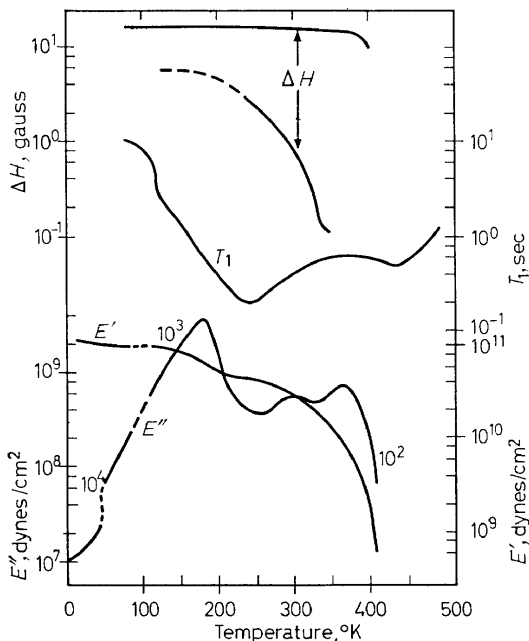


Figure 1. Dynamic elastic storage modulus, E' , dynamic elastic loss modulus, E'' , NMR line width ΔH , and spin-lattice relaxation time, T_1 , v , temperature for linear polyethylene. Data from references 4, 7, 8 and 9. (Note: the numbers 4, 7, 8 and 9. (Note: the numbers on the loss curve correspond to the approximate frequency of measurement))

corresponds to a change in method for obtaining the loss with the values at temperatures below 47°K being taken by a free decay type method and those at temperatures above 47°K by a forced vibration band-width type measurement. The data at temperatures above $\sim 110^\circ\text{K}$ were taken using a transverse vibration apparatus^{6,7}, the frequency varying from about 2×10^3 to 2×10^2 c/s as the temperature increased. In the original publication the loss data were reported in terms of Q^{-1} ; the E'' values given in *Figure 1*, and in all the following figures which contain transverse vibration data, were calculated from the appropriate expression, $E'' = Q^{-1}/E'$. The broad line NMR data in *Figure 1* were obtained⁸ for Marlex 50 at 40 Mc/s and the spin-lattice relaxation time (T_1) measurements⁹ for Rigidex 35 at 21.5 mc/s using the apparatus of Mansfield and Powles¹⁰. In the linewidth data the dashed line for the narrow component, indicates that only approximate values are available due to difficulty in resolution at low temperatures.

The γ process, found at 175°K (1.2×10^3 c/s) in the mechanical loss data, at 245°K (3.5×10^7 c/s) by T_1 measurements and probably corresponding to the appearance of the narrow component in the steady-state NMR

measurements for melt formed samples is presently believed by a number of workers in the field to be due, at least in part, to torsional oscillation of a small number (2–4) of CH_2 units in the disordered or amorphous parts. Due to the fact that a loss maximum in this frequency–temperature range is found for pressed mats of linear polyethylene crystals grown from dilute solution^{11, 12} but is absent or nearly so in unpressed crystals¹³, has led to the proposal that at least part of the γ -process may be a consequence of lattice defect motion. These defects could be of various sorts including the point dislocation proposed by Reneker¹⁴ and the single or double kinks described by Peckhold *et al*¹². Unpressed mats of polyethylene crystals exhibit a T_1 minimum at about 245°K the same as for the melt-formed sample. However, it is possible that motion of a very small portion of protons in disordered regions could lead to relaxation of the much larger number in the ordered regions.

A mechanical loss maximum in this frequency–temperature region has also been reported for various other linear polymers including polytetrafluoroethylene, some poly(alkylene oxides), a number of polyamides, a polyurethane, a polyurea and some polyesters. Such a maximum has been found for all polyamides studies to date, the material with the smallest number of consecutive CH_2 units being Nylon 4 (3CH_2 units)¹⁵. Data have been reported¹⁶ which indicate that poly(ethylene terephthalate), with two consecutive CH_2 units may exhibit such a maximum. However, due to the presence of a more pronounced peak at 210°K (1 c/s) the $\sim 130^\circ\text{K}$ peak only appears as a shoulder. Studies of other polymers containing only one or two CH_2 units between amide groups or some other relatively rigid unit should be carried out in order to determine experimentally the minimum number of CH_2 units involved.

Evidence that the processes in polytetrafluoroethylene^{17, 18} and polyoxymethylene¹⁹ are associated with motion in the disordered regions is given by the fact that samples prepared by quenching show greater modulus dispersions and somewhat higher loss modulus maxima than do annealed ones.

The γ_a mechanical loss modulus maximum at 300°K (810 c/s) has been found to decrease in size with increasing order^{20, 21} (increasing annealing) which indicates a dependence on the movement of chain segments in the disordered regions. For branched polyethylene this is generally a predominate process and therefore it has been proposed that the motion taking place can involve CH units as well as CH_2 side chain and main chain units; this means that motion of a larger number of segments than the number involved in the γ -process is taking place in the a_a process. The narrowing of the NMR sharp line at $\sim 320^\circ\text{K}$ ($\gtrsim 10^4$ c/s) (see *Figure 1*) has been associated with the a_a loss maximum. In previously unheated crystals this narrow component does not appear until heating to elevated temperatures (396°K for 12 h) has been accomplished which is evidence that defects or disordered regions are involved⁸.

The a_c loss modulus peak seen at 360°K (500 c/s) is found²¹ to increase in size upon annealing melt-formed samples, thereby indicating its dependence on the crystalline regions. Two possible mechanisms, among many, which could be responsible for this loss peak are: the onset of torsional oscillation in the crystalline regions²², and spherulite distortion and motion, known to

occur at 270°K and up²³. It is to be noted that very low frequency measurements show two separate loss maxima in the so-called a_e region^{24a}. One of these maxima (a_e') does not appear to occur at frequencies above 10² c/s prior to melting while the other (a_e) appears to be connected with the NMR broad line decrease (390°K; 10⁴ c/s) and the high temperature T_1 minimum (440°K; 3.5×10^7 c/s) leading to its assignment as due to chain torsion in the crystalline parts^{22, 24b}. It is reasonable to expect that the mechanism with the low frequency cut-off will be connected with motion of large units such as lamellae or spherulites and therefore this is assumed to account for the a_e' mechanism. It should be pointed out that the high temperature T_1 minimum is found⁹ above the melting point (410°K) for linear polyethylene when measurements are made as the specimen is heated up. When the melt is cooled from around 500°K the high temperature T_1 minimum is found at about 400°K having shifted to lower temperatures presumably due to crystallization taking place at a lower temperature than melting. This is consistent with a strong effect of crystallinity on the process leading to this minimum. Further T_1 measurements in this temperature range are necessary to specify in more detail the motional behaviour in the 10⁷–10⁸ c/s frequency region.

POLY (α -OLEFINS)

A majority of the studies of the relaxation behaviour of poly(α -olefins) have been confined to polypropylene, the member with the simplest repeat unit. In *Figure 2* mechanical loss and storage modulus data from 6° to 270°K, obtained⁴ with the longitudinal vibration apparatus at $\sim 10^4$ c/s and from $\sim 120^\circ$ –440°K using the transverse beam apparatus²⁵ at frequencies of 2×10^3 to 10² c/s are shown along with measurements of the second moment of the NMR absorption (ΔH^2)²⁶ from $\sim 77^\circ$ –310°K and T_1 data²⁷ from $\sim 80^\circ$ to 470°K. A different sample of isotactic polypropylene was used in each of these investigations. It is to be noted that the E'' results obtained by the two methods gives the same values in the 235° to 270°K region. At least five separate relaxation processes are apparent in these data.

The a_a process in the loss measurements, found at 290°K (10³ c/s) is also apparent in the second moment and in the T_1 measurements ($\sim 345^\circ$ K; 3.5×10^7 c/s). A loss maximum for atactic noncrystallizable polypropylene occurs in the same temperature region and is associated with the change of the polymer from glass-like to rubber-like properties. Therefore, the a_a process in the isotactic polymer is believed to involve segmental diffusion in disordered parts due to partial rotations about C—C bonds of the main chain. The T_1 minimum at 165°K and the second moment decrease in the $\leq 77^\circ$ –130°K range have been established to be a consequence of CH₃ reorientation about the C₃ symmetry axis by measurements on poly(3,3',3"-trideuteropropylene)^{26, 27}. Although this type of motion leads to decided changes in the magnetic resonance quantities, a separate loss maximum is not found by the longitudinal vibration method at 10⁴ c/s. However, the loss does increase in the 80°–160°K region, as is shown in *Figure 3*, and this may be, at least partially, due to the onset of methyl group motion.

If the assignments for the two above mechanisms are correct, then it

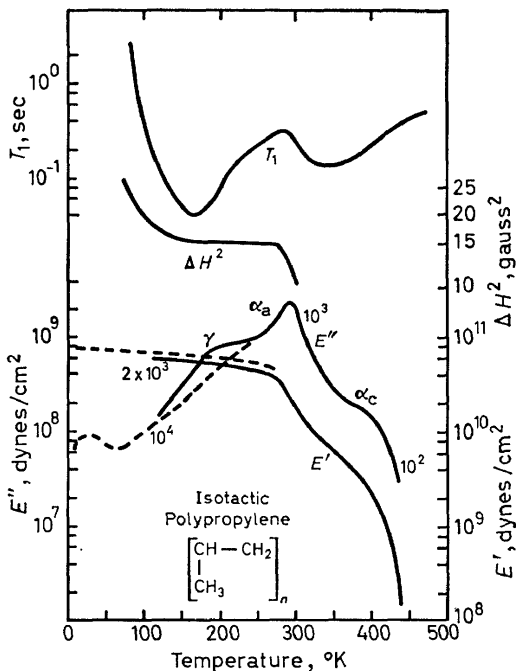


Figure 2. Dynamic elastic storage modulus, E' , dynamic elastic loss modulus, E'' , NMR second movement, ΔH^2 , and spin lattice relaxation time, T_1 , for isotactic polypropylene. Data taken from references 4, 25, 26, 27

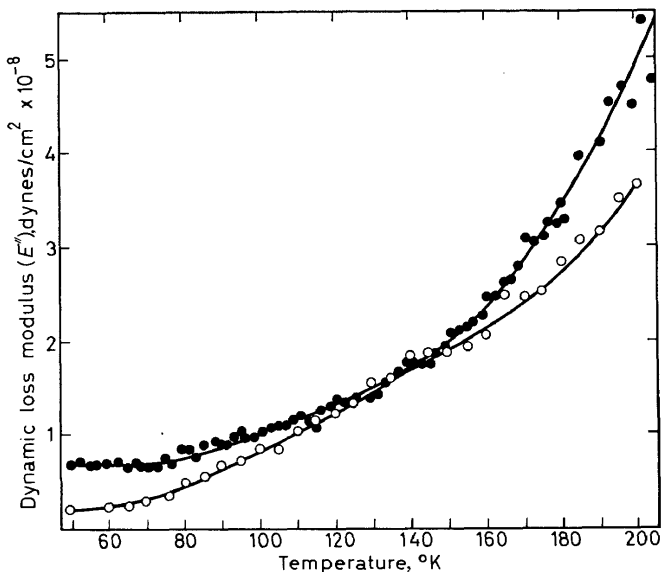


Figure 3. Dynamic loss modulus, E'' , from 50°-200°K for isotactic polypropylene (○) and non-crystallizable poly(methyl methacrylate) (●) calculated from data of Crissman^{4, 30}

appears reasonable to attribute the γ loss maximum at 245°K (2×10^3 c/s) to torsional motion of a limited number of chain units in the disordered regions, a mechanism similar to that believed responsible for the γ peak for polyethylene. The shift of this mechanism by 70° to higher temperatures in going from polyethylene to polypropylene is believed to be due to the greater mass of the repeat unit and possibly to steric reasons.

The a_c loss modulus maximum has been found to increase in size when measurements are made on solution grown crystal mats, as compared with melt-formed samples²⁸ and therefore appear to involve motion in the crystalline regions.

The lowest temperature loss maximum (22°K; 10^4 c/s) has also been reported by Sinnott (19°K; 6 c/s)²⁹ and attributed to methyl reorientations in the amorphous regions. However, the appearance of a loss maximum in the same region for poly(vinyl chloride)⁴, as seen in Figure 4, does not substantiate that assignment. As is further evident in Figures 4-6,

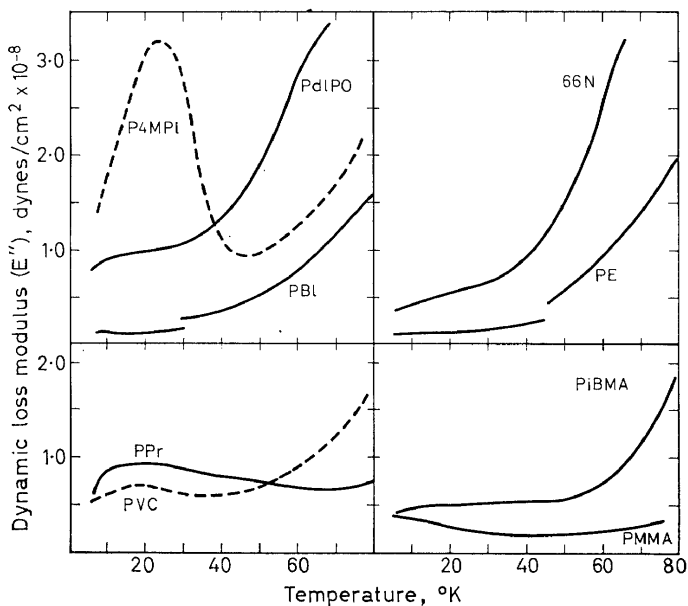


Figure 4. Dynamic loss modulus, E'' , v. temperature from 6° to 80°K for nine polymers⁴: polyethylene (PE), nylon 66 (66N), polypropylene (PPr), poly(vinyl chloride) (PVC), poly(butene-1) (PBI), poly(4 methyl pentene-1) (P4MP1), poly(*dl*-propylene oxide) (PdIPO), poly(methyl methacrylate) (PMMA) and poly(isobutyl methacrylate) (PiBMA)

a large number of polymers of varying chemical units show very low temperature loss maxima accompanied by small storage modulus decreases. The cause of these and the relationships between them are not entirely known, although in some cases they have been tentatively attributed to side chain oscillations.

Detailed studies of thermal and stress history effects, the effects of impurities, and the effect of frequency as well as further studies concerning chemical composition of the polymer should be carried out in order to elucidate the mechanisms for the very low temperature loss maxima.

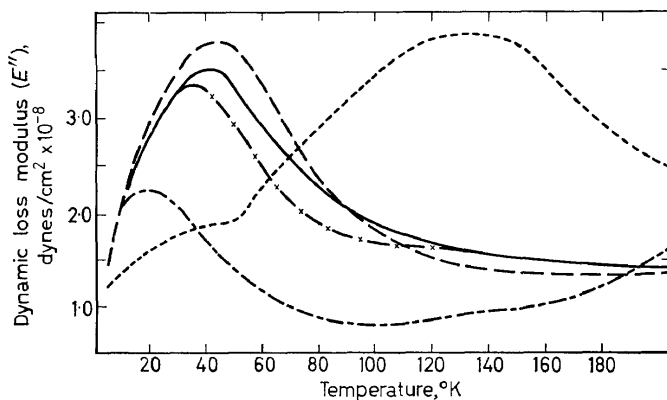


Figure 5. Dynamic loss modulus, E'' , v. temperature for polystyrene and various poly(methylstyrenes)³¹; amorphous isotactic polystyrene (—), poly(ortho methyl styrene) (—×—), poly(vinyl toluene): 70% para, 30% ortho (— · —), poly(vinyl toluene): 65% meta 35% para (· · · · ·) and poly(α -methyl styrene) (— — —)

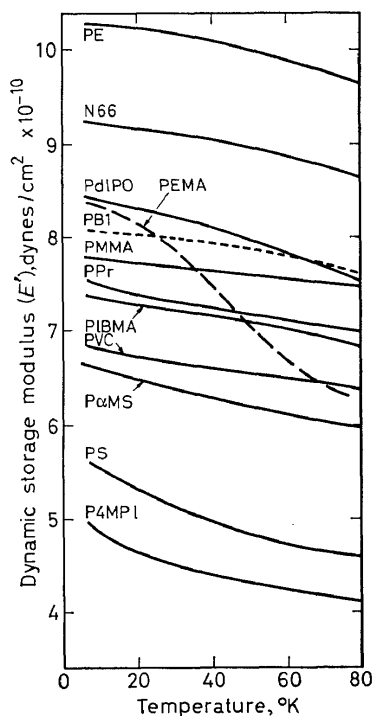
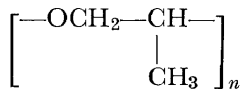


Figure 6. Dynamic storage modulus, E' , v. temperature for various polymers^{4, 31} [same legend as for Figure 4 except: poly(ethyl methacrylate)—PEMA, non-crystallizable polystyrene, PS, and poly(α -methyl styrene), P α MS]

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Some results have been obtained on poly(*dl*-propylene oxide),



a polymer with the same side group as polypropylene, but a different chain repeat unit; the data for the two polymers do bear some similarities. Dynamic loss and storage modulus results obtained in shear at 0.5 to 0.05 c/s using a torsion pendulum³² and in longitudinal vibration⁴ at $\sim 10^4$ c/s are given in *Figure 7* for samples from the same polymer batch. In addition

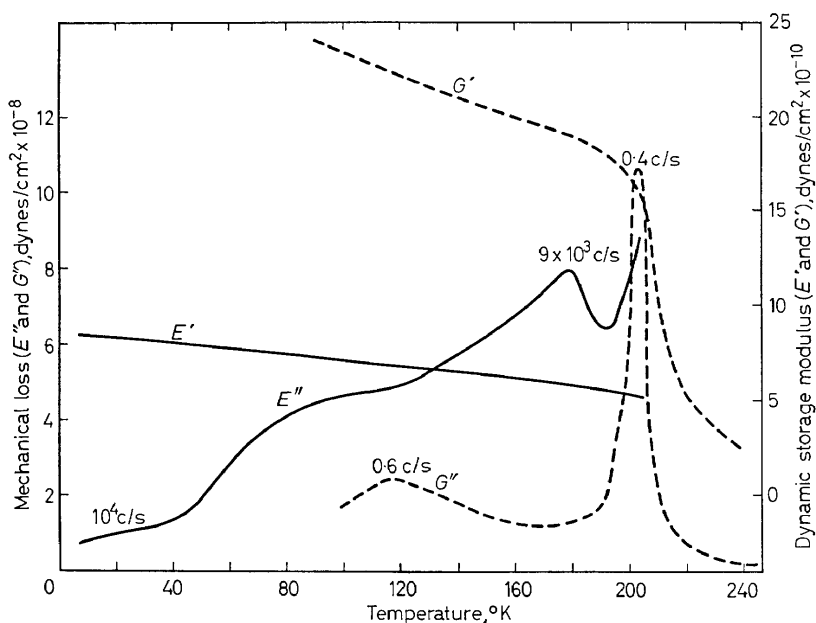


Figure 7. Dynamic elastic storage and loss modulus (E' and E'') at $\sim 10^4$ c/s and dynamic shear storage and loss modulus (G' and G'') at ~ 0.5 c/s *v.* temperature for poly(*dl*-propylene oxide). Taken from the data in references 4 and 32)

to the loss plateau at 6°–40°K, noted in *Figure 4*, the longitudinal vibration data⁴ show a loss shoulder at $\sim 100^\circ\text{K}$, a γ loss maximum at 180°K (9×10^5 c/s), and an upswing (α_a) at $\sim 200^\circ\text{K}$. The lower frequency shear measurements³², carried out over a shorter temperature range, show one loss maximum at 115°K (0.6 c/s) corresponding to the γ process and another at 205°K (0.4 c/s), the α_a process. Further measurements are given in *Figure 8* where the NMR second moment³³ and the dielectric loss tangent³⁴ at 10⁴ c/s are compared with the mechanical loss tangent⁴ at $\sim 10^4$ c/s for samples taken from the same batch but having been put through different purification procedures. It is seen that the dielectric results are in general agreement with the dynamic mechanical data, while the NMR shows two distinct processes, one attributed principally to methyl reorientation ($\leq 180^\circ\text{--}110^\circ\text{K}$) and the other to motion associated with a change from

glassy to rubber-like properties. The latter mechanism is also believed to be responsible for the highest temperature mechanical loss process shown. The mechanical and dielectric data given in *Figures 7 and 8* plus dielectric results at a number of other frequencies and at higher temperatures are represented on a log frequency ν , reciprocal temperature plot in *Figure 9*.

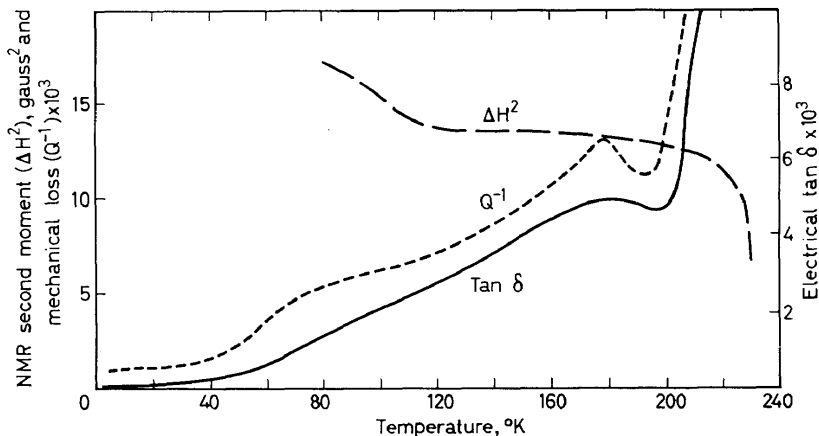


Figure 8. Mechanical loss tangent⁴ at $\sim 10^4$ c/s, dielectric loss tangent³⁴ at 10^4 c/s, and NMR second moment³³ ν . temperature for poly(*dl*-propylene oxide)

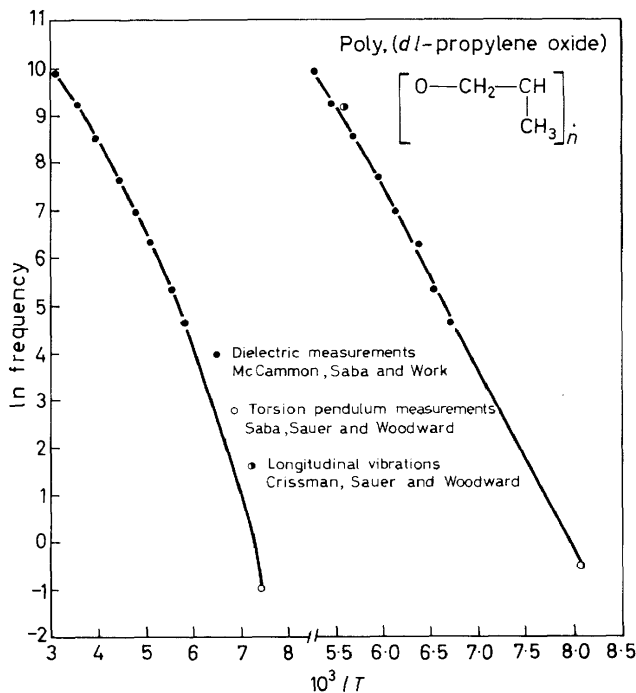


Figure 9. Log frequency ν . reciprocal temperature for poly(*dl*-propylene oxide). Taken from the data in references 4, 32, 34

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The curve on the left gives data for the a_a process while the other represents the γ process. It is noted that the plots are somewhat curved precluding the calculation of a temperature independent "apparent activation energy".

The mechanical and dielectric loss shoulders at $\sim 100^\circ\text{K}$ (10^4 c/s) may, in part, be associated with methyl reorientation about the C_3 axis. However, since the dipolar parts are located in the backbone chain, it is believed that some movement of atoms in the main chain also occurs. The γ loss maximum is believed to be analogous to that in polypropylene and polyethylene.

T_1 measurements have recently been reported³⁵ for the polymer with two minima at ~ 130 – 160°K and 270 – 300°K appearing for high molecular weight material. Studies of deuterated samples indicate that the lower temperature minimum is associated with methyl reorientation.

NMR and dynamic mechanical results for poly(4-methyl pentene-1), a poly(α -olefin) containing isobutyl side chains, are given in Figure 10.

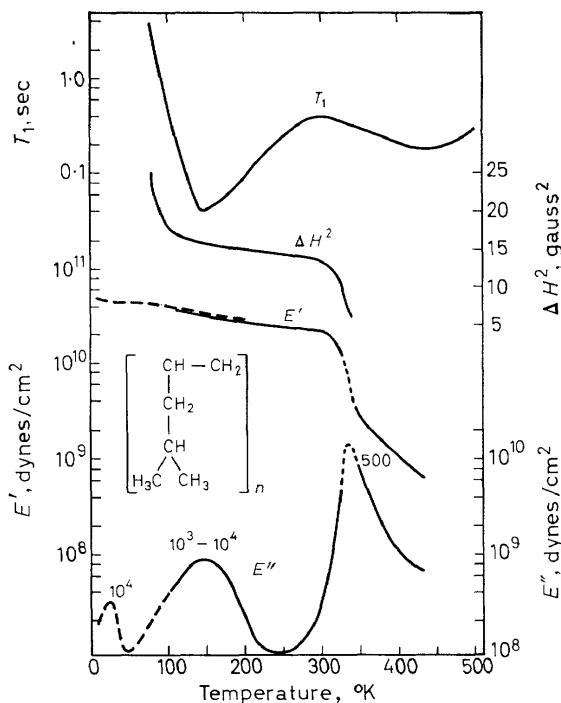


Figure 10. Dynamic elastic modulus (E''), dynamic elastic storage modulus (E'), NMR second moment, ΔH^2 , and spin-lattice relaxation time, T_1 , for isotactic poly(4-methyl pentene-1). Data taken from references 4, 9, 26, and 36

Three different P4MPI specimens were used in these studies, the broad line NMR²⁶ and the dynamic mechanical results from $\sim 100^\circ$ to 430°K using the transverse beam apparatus³⁶ being obtained on specimens from the same rod. In the 100° to 200°K region overlap of the E'' data from the two mechanical studies occurs.

At least four relaxation mechanisms are evident in the 4° to 450°K region

from the data in *Figure 10*. The dynamic mechanical results and the data using both of the NMR methods indicate a relaxation mechanism at about 330–340°K ($\sim 10^3$ – 10^4 c/s) and 430°K (3.5×10^7 c/s) believed to be associated with the onset of considerable chain motion in the disordered parts. The T_1 minimum at 145°K and the NMR line narrowing process at $\leq 80^\circ\text{K}$, in analogy with results for polypropylene, are attributed to methyl group motion, whereas the mechanical loss maximum at 150°K (10^3 – 10^4 c/s) is believed to be due to motion of other side chain segments, in addition to the methyl groups. Other poly(α -olefins), such as poly(3-methyl butene-1)³⁶, poly(butene-1)³⁷ and poly(pentene-1)³⁶ with side-chains containing two or more carbon atoms show a loss maximum in this temperature-frequency region; however, as noted above, polypropylene, the polymer with only a methyl side chain, does not. The mechanism responsible for the maximum at 24°K (10^4 c/s) has not been identified to date.

Dynamic mechanical measurements made by Dr J. A. E. Kail (Imperial Chemical Industries, Ltd., Plastics Division) on a highly crystalline specimen of poly(4-methyl pentene-1) using a vibrating reed apparatus are given in *Figure 11*. The specimen was prepared by pressing strips of a mat at

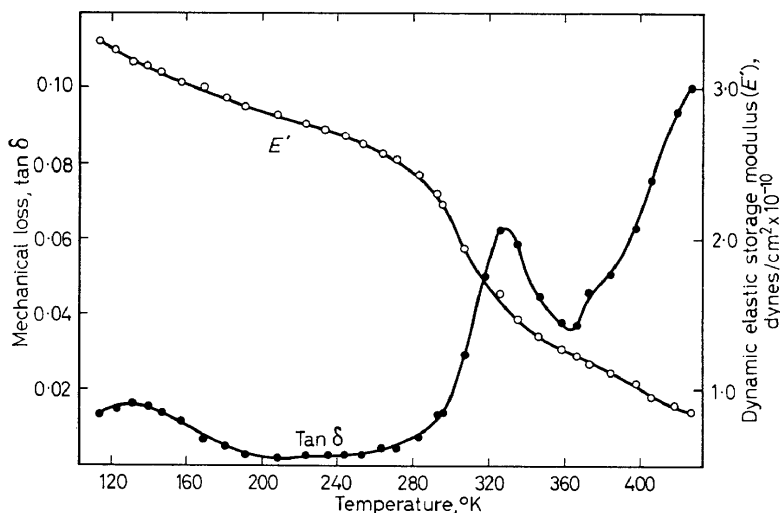


Figure 11. Mechanical loss ($\tan \delta$) and dynamic elastic storage modulus, E' , v. temperature for a poly(4-methyl pentene-1) sample prepared from dilute solution crystallized material

60°C, the mat being obtained by fast filtration of material crystallized at 64°C from a dilute solution (0.07 wt per cent in xylene). The γ and α_a loss peaks are present as in melt-formed samples, the latter being considerably reduced, presumably due to the increase in crystalline order. An additional process or processes are evident at temperatures $>370^\circ\text{K}$ which may be associated with motion in or by the crystal lamellae. Two mechanical loss peaks have previously³⁸ been reported in this temperature region (410° and 450°K; ~ 100 c/s). T_1 measurements⁹ on samples prepared from dilute solution crystallized material show two minima, as found for melt formed specimens (see *Figure 10*).

POLYSTYRENE AND POLY(α -METHYL STYRENE)

T_1 ⁹, NMR line width⁴⁰, and dynamic mechanical data, obtained for polystyrene using both longitudinal vibrations³¹(--) and transverse vibrations³⁹(—), are plotted in *Figure 12*; four separate free radical polymerized (non-crystallizable) polystyrene samples were used. In the ~ 90 – 260°K region overlap in E' values occurs although the E'' values differ. At

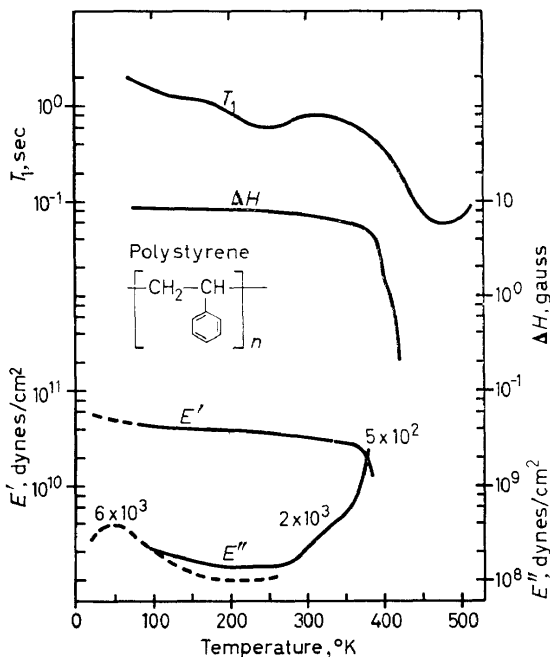


Figure 12. Dynamic elastic modulus (E'), dynamic elastic storage modulus (E''), NMR line-width, ΔH , and spin-lattice relaxation time, T_1 , for free-radical polymerized polystyrene. Data taken from references 5, 9, 39 and 40

least two and possibly three relaxation processes are apparent in these data. The process found at the highest temperatures used in the three investigations is attributed to segmental diffusion arising as a consequence of the glass to rubber transition reported at about 100°C . Whether the mechanical loss maximum at 45°K is related to either the T_1 minimum at 265°K on the plateau at $\sim 130^\circ\text{K}$ is not known. Higher frequency mechanical measurements would help to clarify this point. A partially isotactic polystyrene sample in both the quenched and annealed conditions showed³¹ the 45°K loss modulus peak, although the size of the peak is decreased to some extent. This does not appear to be in agreement with recent studies of Baccaredda, Butta and Frosini⁴¹ who found that the low temperature loss maximum occurs at temperatures of $\geq 110^\circ\text{K}$ higher for isotactic than for non-crystallizable polystyrene. It has been suggested²⁹ that this loss peak is due to phenyl group oscillation or wagging. This is consistent with broad-line NMR results⁴⁰ which indicate little motion at 77°K and below. As is seen in *Figure 5*, the polymers of various methyl substituted styrenes show a

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loss maximum in the low temperature region ranging from values of 20°–45°K. It is not presently known if all of these maxima can be attributed to the same mechanism.

NMR second moment and line width results⁴², T_1 data⁹ and mechanical loss and storage modulus data obtained with a transverse beam apparatus from 200°K⁴³ in addition to the mechanical results obtained with the longitudinal bar apparatus³¹ (Figures 5 and 6) are shown in Figure 13 for poly(α -methyl styrene). Two and possibly three relaxation processes are evident

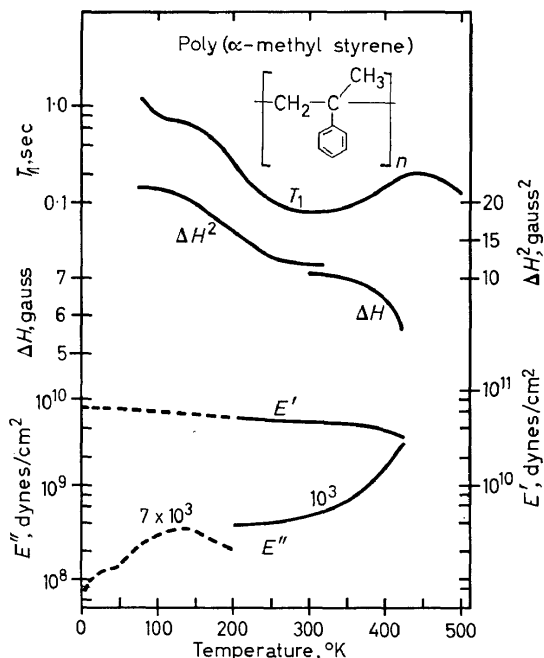


Figure 13. Dynamic elastic loss modulus (E''), dynamic elastic storage modulus (E'), NMR second moment, ΔH^2 , and spin-lattice relaxation time, T_1 , for poly(α -methyl styrene). Data taken from references 9, 31, 42, 43

from these data. The downswings in T_1 , line width and E' and the upswing in E'' at the highest temperatures employed are believed to be manifestations of the glass to rubber transition. The T_1 minimum at about 305°K and the drop in second moment centred at about 200°K have been attributed to methyl group motion based on second moment calculations⁴². The loss maximum at 135°K (7×10^3 c/s) has been tentatively attributed³¹ to phenyl group oscillations possibly coupled with methyl reorientations. The occurring of the phenyl motion in poly(α -methyl styrene) at temperatures 80–90 degrees higher than for the same motion in polystyrene could be a consequence of steric hindrance caused by the methyl group. The origins of the plateau in T_1 at 130°K are not presently known.

SOME POLY(ACRYLATES) AND RELATED POLYMERS

NMR second moment results⁴⁴ for free radical polymerized noncrystallizable samples of poly(ethyl acrylate), poly(butyl acrylate), poly(vinyl

propionate) and poly(ethyl vinyl ether) are given in *Figure 14*. The three polymers, for which the hydrocarbon portion of the side chain is an ethyl group, show similar behaviour and it is concluded that the motions contributing to the various line narrowing effects for each polymer are similar.

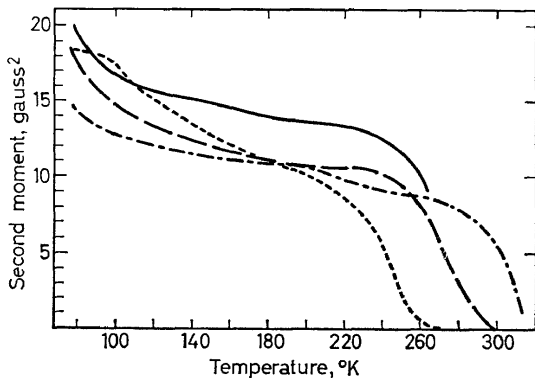


Figure 14. NMR second moment *v.* temperature for poly(ethyl acrylate) (— · —), poly(butyl acrylate) (---), poly(vinyl propionate) (— — —), and poly(ethyl vinyl ether) (—)⁴⁴

The greater number of protons per repeat unit is believed to be responsible for the higher second moment values for poly(ethyl vinyl ether) as compared to those for poly(ethyl acrylate) and poly(vinyl propionate). The narrowing process in the $\leq 77^{\circ}\text{--}120^{\circ}\text{K}$ region is believed to be brought about by either methyl or ethyl reorientations since the experimental values in this temperature region fall approximately between the estimated rigid lattice and ethyl rotation values of $\sim 22\text{--}23$ gauss² and ~ 12 gauss², respectively.

The relatively gradual decrease in second moment from $\sim 120^{\circ}\text{K}$ to temperatures just below the final precipitous drop is either due to further side chain re-orientations, possibly involving all the protons of the ethyl group, or to small amounts of chain torsion. The final process for all three polymers occurs at temperatures above the glass transition and indicates the large amount of chain motion which becomes possible in the liquid or rubbery state.

The greater slope of the second moment—temperature plot in the $100\text{--}220^{\circ}\text{K}$ region for poly(butyl acrylate) as compared to that for the others polymers is attributed to the occurrence of propyl and butyl motions in addition to those possible for the ethyl unit. Poly(vinyl stearate) a highly crystalline polymer with a C₁₇ hydrocarbon side-chain, shows a similar second moment decrease to that for poly(butyl acrylate) as well as a mechanical loss peak, attributed to side chain reorientations⁴⁴.

A torsion pendulum investigation³² of poly(ethyl vinyl ether), using a sample from the same preparation as that used for the NMR study, has shown that a mechanical loss peak exists at 100°K (0.9 c/s); this has been attributed to motions involving the side branch and including the cooperative action of 3–4 consecutive segments. Because of the higher correlation frequency, the associated change in the NMR plots would be expected in the region above 100°K and it is in this region where gradual decreases are found in the experimental line width and second moment.

POLY(METHACRYLATE ESTERS)

From the dynamic loss modulus data given in *Figure 4* it is seen that poly(methyl methacrylate) shows a small loss maximum at $\sim 4^\circ\text{K}$ (10^4 c/s) attributed to ester methyl group motion. There is also a plateau in the loss for poly(isobutyl methacrylate) in the $6^\circ\text{--}50^\circ\text{K}$ range, the cause of which is not known⁴. Poly(ethyl methacrylate) on the other hand has a much larger E'' peak at $\sim 50^\circ\text{K}$, as is seen in *Figure 15*, presumably due to ester ethyl

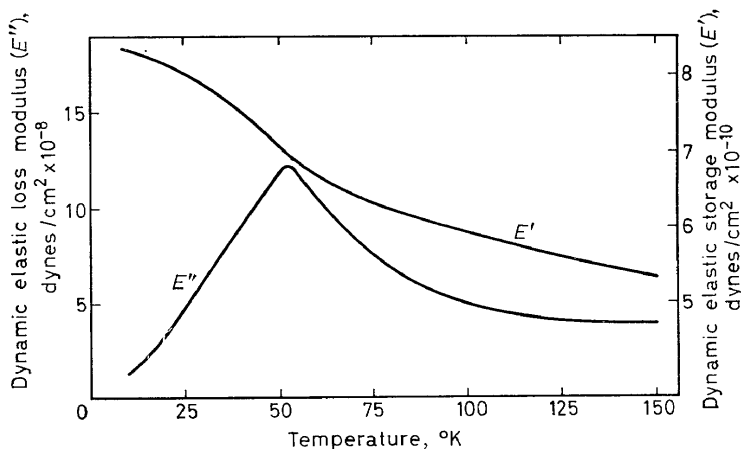


Figure 15. Dynamic elastic storage (E') and loss modulus (E'') v. temperature for poly(ethyl methacrylate). Data taken from reference 4

movements. T_1 minima have been reported at $\sim 80^\circ\text{K}$ for poly(methyl methacrylate)⁴⁵ and 145°K for poly(ethyl methacrylate)⁴⁶ and have been attributed to motions similar to those suggested from the dynamic mechanical results.

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