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Relaxation Behavior of Polymers at Low Temperatures†

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SUMMARY

The relaxation behavior of polymers at low temperatures, as studied by dynamic mechanical, dielectric, and nuclear magnetic resonance methods, is reviewed. Modulus values at 4 and 77°K are tabulated for a variety of both crystalline and amorphous polymers and are compared to room temperature values as well as to theoretical values deduced from intermolecular force constants. Specific attention is given to polymers that show a δ-type relaxation. At low frequencies, this relaxation occurs in the temperature region below 100°K. The δ-processes are shown to arise from reorientational motion of side chain methyl groups, as in PMMA or PVA, side chain ethyl groups, as in PEMA or PVPr, and side chain phenyl or phenyl-substituted groups, as in PS or PmClS. Linear polymers, such as PE and PTFE, that have no side chain groups exhibit no δ-type relaxation. Consideration is also given to the effect of various internal and external variables on the low-temperature relaxation behavior. These variables include chemical structure, hydrogen atom substitution, crystallinity, impurities, drawing, and past history. An attempt is made to correlate the dielectric and nuclear magnetic resonance data with the mechanical data. Log frequency versus reciprocal temperature plots are given for several polymers of different chemical structure, and activation energies are estimated.

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INTRODUCTION

Relaxation studies on polymers at very low temperatures are few in number. Most of the reported studies, whether made by dynamic mechanical, dielectric, or nuclear magnetic resonance measurements, have been concerned primarily with temperature dependence only over the range from liquid nitrogen values to, or near, the melting point. Various reviews of much of this work are now available [1-6].

Over the temperature range from 4.2 to 77°K most of the investigations made to date have been dynamic mechanical studies. These include studies of the shear modulus and loss [7-10, 14a] by use of a torsion pendulum and studies of elastic modulus and loss [11-14] by means of a rod-like specimen driven longitudinally at its resonant frequency.

Only a few dielectric studies of polymers over the range from 4.2 to 77°K have been reported [15-17]. However, more comprehensive data are now available [18]. Over this temperature range, there do not appear to be any complete studies of the temperature dependence of nuclear magnetic resonance line widths or second moments. Some studies [19, 20] have, however, been carried down to 20°K and one study [21] reports line shapes for several polymers at 4.2°K.

One purpose of the present study is to review the available low-temperature data which have been obtained on high polymers in the range from liquid helium values to liquid nitrogen values and to present some new data on dielectric and mechanical behavior. Another purpose is to indicate the influence on low-temperature modulus and loss behavior of such variables as chemical and molecular structure, crystallinity, impurities, copolymerization, and past history, including drawing. A third purpose is to investigate the degree of correlation of the dynamic mechanical, dielectric, and nuclear magnetic resonance results and to use the information obtained from these studies to discuss possible interpretations of the observed low-temperature transitions.

Before presenting the results of low-temperature studies carried out below 100°K, it is appropriate to briefly review the general nature of the viscoelastic behavior of solid high polymers.

RELAXATION TRANSITIONS IN POLYMERS–GENERAL

It is now well recognized that all high polymers exhibit relaxation or dispersion regions. Each of these appears to be related, though not usually

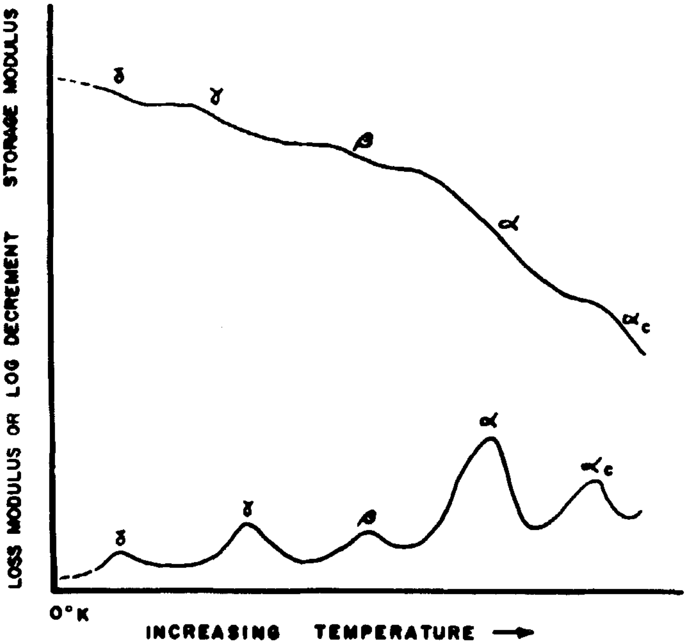

Fig. 1. Diagrammatic sketch of temperature dependence of mechanical loss and modulus of polymers.

in a simple way, with the relaxation of molecular constraints and with the onset of certain types of molecular motion. It is customary to designate these various relaxation or transition processes by the Greek letters α, β, γ, δ, . . . listed in descending order of temperature occurrence. These relaxation processes are most readily identified by peaks in the mechanical or dielectric loss vs. temperature curves and by associated changes in the modulus or dielectric constant vs. temperature relation. A diagrammatic sketch of the temperature and loss behavior of a solid high polymer is shown in Fig. 1. For purposes of clarity we have assumed that each of the relaxation processes occurs independently of the others. Actually the various processes frequently overlap. Not all polymers show all of the processes designated in Fig. 1, although most polymers, whether amorphous or crystalline, show at least two relaxation regions in this temperature range. The magnitude of each relaxation and its temperature location is a function of the composition and structure of the polymer as well as of its past history.

Although our interest in this paper is primarily with the δ-type processes that occur at low temperatures (below 100°K), it is appropriate to make a few brief comments on the general nature of the α, β, and γ-type relaxations. The α-type relaxation process may be single or multiple. As we pass through this transition region, the mechanical properties change markedly. The modulus falls from a value of the order of 10^{10} dyn/cm^2, characteristic of that of a rigid polymer, to a value of 10^7 dyn/cm^2 or less, characteristic of that of a rubber. If the polymer is completely amorphous, such as atactic polystyrene (PS), there is only a single transition and this is designated α_a to indicate that it is associated with motion in the amorphous regions. This transition involves micro-Brownian motion of the main chain, and depending upon the test frequency, it generally occurs a few degrees above the so-called glass transition, T_g, as determined from specific volume measurements. It occurs near 100°C for PS and polymethyl methacrylate (PMMA), near 15°C for polymethacrylate (PMA), and near 0°C for atactic polypropylene. In the α-transition temperature region, the NMR line width and second moment fall to very low values, indicating that translational, as well as rotational, motion is probably occurring. For most commercial polymers, the α_a-transition is located above room temperature while for rubbers it falls below room temperature.

If a polymer is partially crystalline and partially amorphous, the process occurs in two stages, which, as shown in Fig. 1, are designated by the letters α_a and α_c. The lower-temperature relaxation, α_a, is associated, as described above, with motion in the amorphous portion of the polymer. The higher-temperature process, α_c, which may itself be multiple, is associated with motion of molecular chains in the crystalline regions of the polymer. As such, it is also revealed in NMR studies by a narrowing of the broad component of the resonance line. Although this process has been thoroughly studied by various techniques in both single crystals and bulk polymer [1, 2], the exact nature of the molecular motion involved is still not resolved. In some experiments, two peaks have been observered in mechanical loss data. One is usually associated with torsional motion of chain segments in the crystalline regions and the other with interlamellar slip. In other experiments on annealed crystals, as many as four separate peaks have been observed, and some of these are considered to arise as a result of defects produced by the annealing [22]. The activation energies of α-type processes are temperature dependent and are of the order of 40-100 kcal/mole.

The β-relaxation process is usually found in the intermediate temperature region between about -50 and 50°C. It has various possible origins and, in some cases and at some test frequencies, it may be obscured by the α-process. It occurs in PMMA in both dielectric and mechanical studies and is attributed to reorientational motion of the entire side chain. It occurs near 20°C in polytetrafluoroethylene (PTFE) and is attributed to a crystal phase change. It occurs near -40°C in polyamides (PA) containing water and is attributed to motion of hydrogen-bonded water molecules or of water-amide complexes. The activation energy for the β-process varies considerably depending upon the molecular origin. Reported values vary from about 20 kcal/mole for PMMA and Nylon 6-6 to about 30-40 kcal/mole for PTFE.

The γ-relaxation process is usually centered near 150°K although it may be found, depending upon the polymer and the test frequency, at various temperatures from about 100 to 240°K. It is considered to be a local mode oscillation, or reorientation, involving only several CH_2 or equivalent groups. These groups may be in the side chain or in the main chain. γ-type transitions due to side chain motions have been observed at low frequencies near 100°K in polyethylvinylether (PEVE) and near 170°K in polyvinylstearate (PVS). γ-type transitions due to motion of short sequences of the main chain have been observed in the 150-170°K range for PE, Nylon 6-6, and polyoxetane, all of which have three or more CH_2-type groups in sequence, and in the 180-200°K range for PTFE. For glycol terephthalate polymers, this process occurs at various temperatures depending upon the number of CH_2 groups that are present. For polyethylene terephthalate (PETP) with two CH_2 groups, it is found near 240°K, but for the corresponding polymer with 10 CH_2 groups between phenylene units, it is located at about 150°K.

The γ-transition has been observed in single-crystal mats as well as in melt-crystallized polymer. Hence, it appears that this local mode oscillation or short-range segmental reorientation can occur in both crystalline and amorphous regions. In fact, recent evidence [23] indicates that the γ-peak may itself have two components—γ_a associated with motion in the amorphous or disordered phase, and γ_c associated with local twisting motions in the crystalline regions. Activation energies for the γ-process have been given by various investigators. They vary from about 10 to 18 kcal/mole.

Teflon (PTFE) is an example of a specific polymer that has been investigated over the entire temperature range from 4.2 to 600°K and which exhibits three separate relaxation regions in addition to a further softening near melting temperatures. The modulus and internal friction data, taken from McCrum [8], are shown in Fig. 2 for samples of 48%

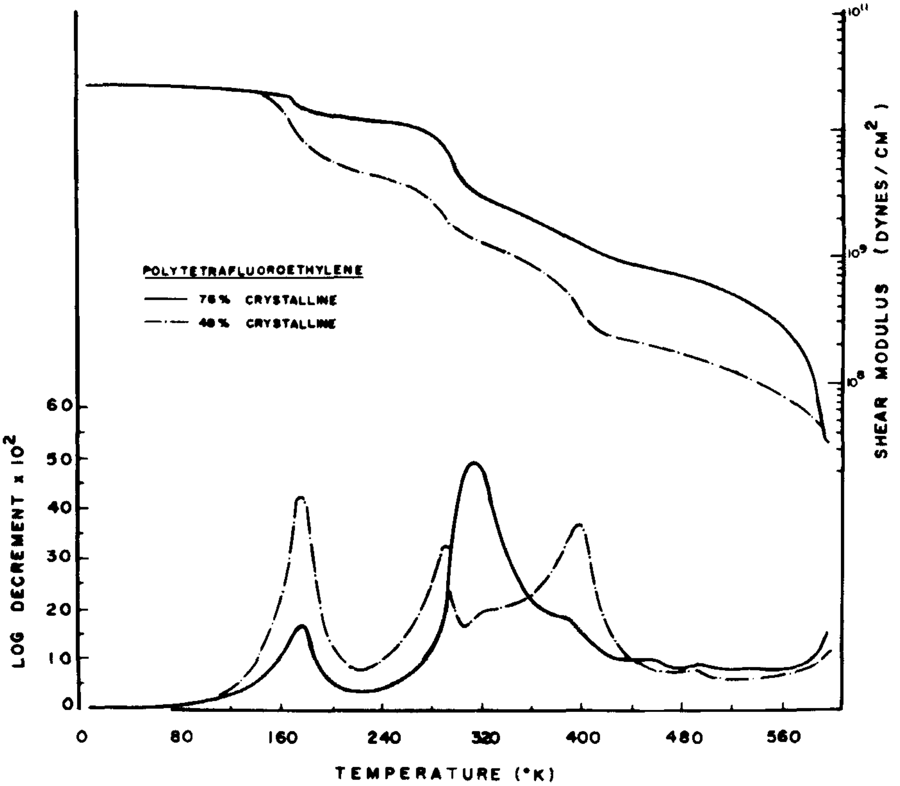

Fig. 2. Temperature dependence of shear modulus and loss of polytetrafluoroethylene. Data obtained from Ref. [8].

and 76% crystallinity. This particular polymer exhibits no δ-type process at low temperatures, but a γ-type process is evident near 180°K, a β-type process near 300°K, and an α-type process near 400°K. For this polymer, the data [8, 24] indicate that the γ-process is occurring in the amorphous or disordered regions of the polymer while the β-process is associated with a phase change of the crystalline regions. However, it has not been possible to unequivocally associate the α-process with either the crystalline or amorphous phase.

MECHANICAL BEHAVIOR AT VERY LOW TEMPERATURES

As the temperature of a polymer is lowered and molecular motions are

Table 1. Elastic Modulus of Unoriented Polymers at Low Temperatures

	Material		Elastic modulus (10^{10} dyn/cm^2)			
Type	Name	Designation	4.2°K	77°K	300°K	Ref.
Crystalline	Polyethylene (linear)	PE	10.3	9.7	2.9	[12, 25]
	Nylon 6-6	PA 6-6	9.2	8.6	4.1	[12, 26]
	Polypropylene (isotactic)	PP	7.5	7.0	2.4	[12, 27]
	Polybutene (isotactic)	PB	8.1	7.7	2.0	[12, 28]
	Polystyrene (isotactic)	PS	6.1	5.0	4.4	[13, 29]
	Poly-4-methyl-pentene-1	P4MP1	5.0	4.1	2.3	[12, 28]
	Poly-dl-propylene oxide	PPO	8.4	7.6	–	[12]
Amorphous	Polymethylmethacrylate	PMMA	7.8	7.5	–	[12]
	Polyethylmethacrylate	PEMA	8.3	6.3	–	[12]
	Polyisobutylmethacrylate	PiBMA	7.4	6.9	–	[12]
	Polyvinyl chloride	PVC	6.8	6.4	3.0	[12, 30]
	Polystyrene (isot. quenched)	PS	5.6	4.6	3.3[a]	[13, 29]
	Poly-ortho-methylstyrene	PoMS	5.8	4.8	3.9	[13]
	Poly-α-methylstyrene	PαMS	6.6	6.0	4.5	[13, 31]
	Polyimide	PI	6.2	5.9	3.4	[14b]

[a] Atactic polystyrene.

Table 2. Shear Modulus of Unoriented Polymers at Low Temperatures

Type	Material		Shear modulus (10^{10} dyn/cm^2)			Ref.
	Name	Designation	4.2°K	77°K	300°K	
Crystalline	Polyoxymethylene (68%)[a]	POM	5.2			[10]
	Polytetrafluoroethylene (55% and 64%)	PTFE	2.2	2.1	0.35	[7,8]
	Polytetrafluoroethylene (85%)	PTFE	2.7	–	–	[7]
	Poly-4-methyl-pentene-1	P4MP1	2.0	1.7	0.89	[32]
	Polypropylene (75%)	PP	2.75	2.6	–	[10]
	Polypropylene (40%)	PP	2.15	1.9	–	[10]
	Polypropylene cast film ($\rho = 0.897$)	PP	–	1.7	0.42	[33]
	Polyethylene terephthalate (56%)	PETP	2.3	2.1	1.1	[14a]

Amorphous	Polymethyl methacrylate	PMMA	3.2	3.1	–	[9]
	Polyethyl methacrylate	PEMA	2.8	1.9	–	[32]
	Polyethyl methacrylate	PEMA	2.9	2.2	–	[9]
	Polyisobutyl methacrylate	PiBMA	2.6			[10]
	Polystyrene	PS	2.3	1.8	–	[10]
	Polystyrene	PS	1.9	–	–	[32]
	Polyvinylacetate	PVA	2.0	1.8	–	[32]
	Polyvinylproprionate	PVPr	2.8	1.7	–	[32]
	Polyisobutyl vinyl ether	PiBVE	2.4	2.2	–	[32]
	Copolymer ethylene-butene-1 (4:1)		2.9	–	–	[10]
	Polyethylene terephthalate film	PETP	1.6	–	–	[32]
	PETP film (Mylar)		2.1	1.8	1.0	[14a]

[a] Value in parentheses is estimated degree of crystallinity.

frozen in, it is expected that the elastic and shear moduli will show an appreciable increase. The magnitude of the rise depends upon the particular polymer. Table 1 gives values of the elastic modulus for seven crystalline polymers and eight amorphous polymers, at 4.2°K, 77°K, and room temperature. The low-temperature values were determined on a longitudinal type of apparatus operating at a test frequency of approximately 10^4 cps; modulus values at room temperature were mostly determined in a transverse type of apparatus operating at test frequencies of the order of 10^3 cps.

The linear polymers, such as PE and Nylon 6-6, tend to have the highest values of elastic modulus at 4.2°K, viz., about 10^{11} dyn/cm^2. The increase in modulus in going from room temperature to 4.2°K is smallest ($\sim$ 70%) for PS, which has no γ- or β-relaxation. For materials that do show a γ-type relaxation near 150°K, such as PE, poly-4-methyl-pentene-1 (P4MP1), and nylon, the low-temperature value is two to three times the room-temperature value. For materials in which the α_a-transition is below room temperature, as in polybutene, the increase is greater ($\sim$ four times).

From comparison of the modulus values at 4.2 and 77°K, one can determine which polymers will show a significant δ-transition and which will not. For polymers such as PE, PP, PB, Nylon 6-6, PVC, and PI, the modulus rise from 77 to 4.2°K is small, less than 10%, and no well-defined δ-type loss peaks are present. For polymers that have a modulus increase of about 20%, such as PS, PEMA, and P4MP1, a significant δ-type process can be expected; examples of these will be shown later.

Values of the shear modulus at low temperatures of a number of unoriented polymers are given in Table 2. Slight disagreement in values at 4.2°K between results of different investigators is probably a result of different past history. All values listed in this table have been obtained with a torsion pendulum; hence the approximate frequency of the measurements is 1 cps.

The material with the highest shear modulus at 4.2°K is polyoxymethylene (POM). For all of the other polymers listed, the modulus value falls in the general range of about 1.5-3 × 10^{10} dyn/cm^2. Comparison of values for the same polymer from Tables 1 and 2 indicate that the elastic modulus is generally about 2.5-2.7 times the shear modulus. This would indicate a Poissons ratio of between 0.25 and 0.35.

It is of interest to compare these observed values of modulus at 4.2°K with predicted values based on assumed force constants. First, however, we give some modulus data on oriented polymers. Few measurements appear to have been made of the modulus of drawn polymers at very low temperatures. Table 3 lists data, taken mostly from a recent investigation

Table 3. Shear Modulus of Drawn Polymers at Low Temperatures

Material				
Name	Designation	Amount of draw	Shear modulus (10^{10} dyn/cm^2) at 4.2° K	Ref.
Polystyrene	PS	Unstretched	1.92	[32]
		Stretched 3:1	2.30	[32]
Polyvinyl acetate	PVA	Unstretched	2.04	[32]
		Stretched 4:1	2.20	[32]
Polyvinyl proprionate	PVPr	Unstretched	2.80	[32]
		Stretched 6:1	3.18	[32]
Polyisobutyl vinyl ether	PiBVE	Unstretched	2.44	[32]
		Stretched 5:1	2.76	[32]
Polyethylene terephthalate	PETP	Unstretched	1.59	[32]
		Stretched 3:1	3.63	[32]
		Biaxially stretched and heat set	3.0	
PETP (Annealed) (56% cry.)		Unstretched	2.3	[14a]
PETP (51% cry.)		Uniaxially drawn and heat set 7:1	3.8	[14a]
PETP (Mylar) (54% cry.)		Biaxially drawn and heat set	5.0	[14a]

Table 4. Comparison of Elastic Modulus of Polymers with Calculated Values

Material		Modulus of unoriented polymer at 4.2°K $(10^{10}$dyn/cm$^2)$		Modulus of oriented polymer at 300°K $(10^{10}$dyn/cm$^2)$		Calculated modulus $(10^{10}$dyn/cm$^2)$	
Name	Designation	Value	Ref.	Value	Ref.	Value	Ref.
Polyethylene	PE	10.3	[12]	235	[37]	250	[38]
Polyvinyl alcohol	PVAl	–		250	[37]	182-340	[39, 40]
Polytetrafluoro-ethylene	PTFE	6.0[a]	[7]	153	[37]	160	[40]
Cellulose		–		127	[37]	57-180	[41, 42]
Polyethylene-tetephthalate	PETP	4.2[a]	[32]	74-137	[37, 43]	122-146	[44, 45]
Polyoxymethylene	POM	13.5[a]	[10]	53	[37]	40-220	[46, 47]
Polypropylene	PP	7.5	[12]	41	[37]	10-49	[46, 47]
Polyethylene oxide	PEO	–		9.8	[37]	4.5-9.0	[37, 48]

[a] Calculated from measured shear modulus using a Poissons ratio of 0.3.

by Frosini and Woodward [32], for six different synthetic polymers. The moduli of the drawn polymers are higher than the values of the undrawn polymers but, especially for the amorphous polymers, the increase is rather small, in most cases only 10 or 15% for draws of several hundred per cent. An increase in modulus of about the same magnitude has been noted at 20°K for PS biaxially oriented [33]. For PETP, the modulus increase is considerably larger—over 100% for a 3:1 draw ratio. Kawaguchi [34] has studied the effect of drawing on the elastic modulus of this polymer at higher temperatures and he finds, at 200°K and at a draw ratio of 7:1, that the elastic modulus reaches values of about 18×10^{10} dyn/cm^2. Hall [35] has measured the modulus of polypropylene monafilament drawn about 5.5:1. His reported value at 77°K is about 14×10^{10} dyn/cm^2. A much higher modulus value has been given by Vincent [36] for a high-molecular-weight linear polyethylene drawn 16:1. He obtained a modulus value at 100°K of 62×10^{10} dyn/cm^2. This is about six times higher than the value given in Table 1 for an unoriented specimen tested at 4.2°K and is comparable to values reported for natural fibers such as ramie and hemp when tested at room temperature.

Although the elastic and shear moduli of polymers increase significantly, as Tables 1 and 2 show, in going from room temperature to 4.2°K, it is evident from a comparison of the experimental data with calculated values that the observed values are still far below theoretical values of modulus deduced from crystal structure and assumed inter- and intramolecular potentials. This comparison is made in Table 4 in which the third column lists experimental data taken at 4.2°K and column 7 gives the computed values for eight different crystalline polymers. These are seen to fall in the range from about 10×10^{10} dyn/cm^2 for polyethylene oxide (PEO) to about 300×10^{10} dyn/cm^2 for PE. For the linear polymers, PE, PTFE, and PETP, the calculated modulus values are seen to be about 25 times the measured modulus values at 4.2°K of the unoriented polymer. The difference is much less for the more helical polymers, such as POM and PP, but even here the observed experimental values are 5-10 times too small.

Better agreement with the theoretical values is obtained if one compares the modulus of the crystallites themselves rather than that of the whole specimen. This is possible, using X-rays, by observation of the changes in lattice spacings with applied stress. Although this procedure has not yet been done at low temperatures, measurements have been made for a number of different polymers at room temperature; the values obtained are given in column 5 of Table 4. Comparison of these values with those of column 7 shows that the agreement with theoretical values is now quite good, especially for the linear zigzag-type polymers. A more comprehensive discussion of this subject has been given in Ref. [49].

LOW-TEMPERATURE RELAXATION PROCESSES

Effect of Molecular Structure

It appears from the available low-temperature mechanical data [7-14, 32, 33, 50] that some polymers exhibit no relaxation processes below 100°K, while a number of others exhibit one or more. Examples of polymers that show no δ-type low-temperature transitions are the linear polymers with no side chains, such as PE, PTFE, POM, and Nylon 6-6. All of these exhibit large γ-type relaxation processes in the 150-200°K range due to local motion of short-chain sequences, but none of these polymers exhibits loss peaks or modulus dispersions at lower temperature (Fig. 2).

Other polymers that show no apparent modulus dispersion but which have very small, broad loss peaks ($Q^{-1} \sim 10^{-3}$) in the 10-40°K temperature range include PP, poly(dl-propylene oxide) (PdlPO), polyvinyl chloride (PVC), and poly-isobutyl methacrylate (PiBMA). The temperature dependence of the elastic and shear moduli of a polymer of this type, viz., PP, is shown in Fig. 3 taken from the data of Crissman et al. [12] and Sinnott [10]. Over the range of 4.2-77°K, the dependence is essentially a linear one and the elastic modulus is approximately 2.7 times the shear modulus.

Several polymers show a relatively large ($Q^{-1} \sim 5 \times 10^{-3}$ or larger) low-temperature relaxation process in the general neighborhood of 40-50°K. These include PS, PEMA, and polyvinylproprionate (PVPr). The temperature dependence of the elastic modulus of two of these, viz., PS and PEMA, is shown in Fig. 4. For PS, this relaxation mechanism has been observed in dielectric as well as mechanical studies and a comparison of the loss data from both methods is given in Fig. 5. Considering that these data were compiled by three different sets of investigators [10, 13, 18] using different methods and different specimens, the agreement between them is remarkably good and gives strong evidence that the dielectric and mechanical relaxations have a common cause. This is believed to be an oscillatory or wagging motion of the pendant phenyl group. For PEMA and PVPr, the δ-type relaxation is attributed to motion of the pendant ethyl group. In the data of Fig. 5 there is also a small apparent loss peak near 150°K. The origin of this peak is discussed later.

The specific influence of structure on the δ-type processes has been studied by carrying out measurements on substituted polystyrenes. Upon

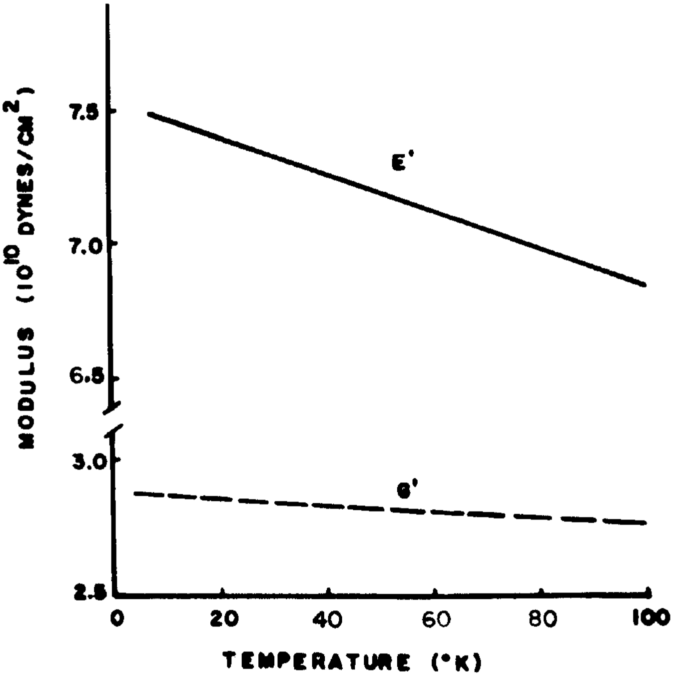

Fig. 3. Temperature dependence of shear (G′) and elastic (E′) modulus of polypropylene. Data obtained from Refs. [10, 12].

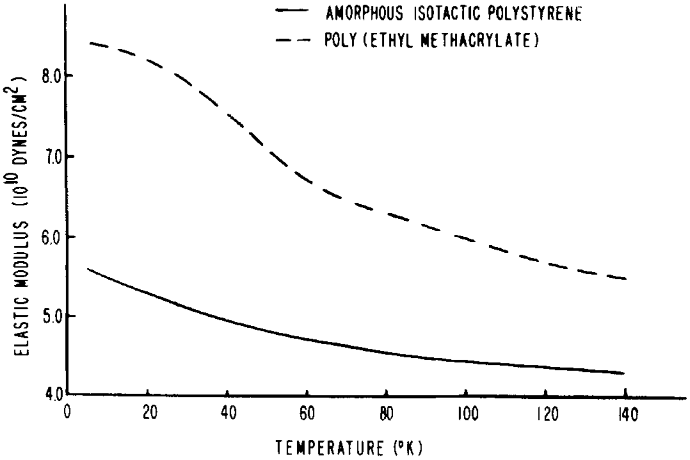

Fig. 4. Temperature dependence of elastic modulus of polystyrene and polyethyl methacrylate. Data obtained from Refs. [12, 13].

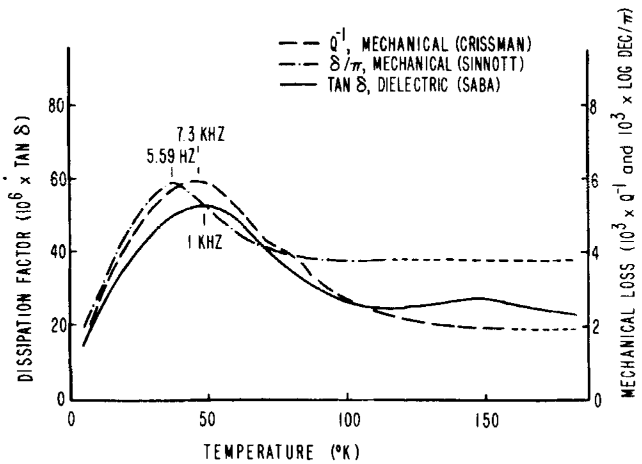

Fig. 5. Temperature dependence of mechanical and dielectric loss of polystyrene. Data obtained from Refs. [10, 13, 18].

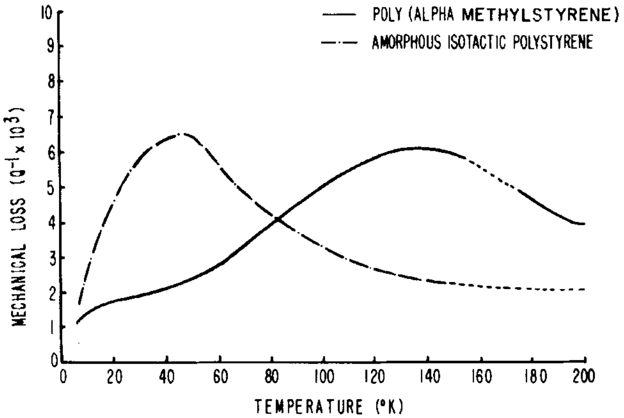

Fig. 6. Temperature dependence of mechanical loss of polystyrene and poly-α-methyl styrene. Data obtained from Ref. [13].

replacing the α-H of PS by a methyl group, the δ-peak, as shown in Fig. 6, is apparently shifted to much higher temperatures, presumably because of hindrance to phenyl motion introduced by the adjacent methyl group. From NMR data [51] it is known that the line width and second moment begin to reduce at a temperature of 140°K or so, and this reduction has

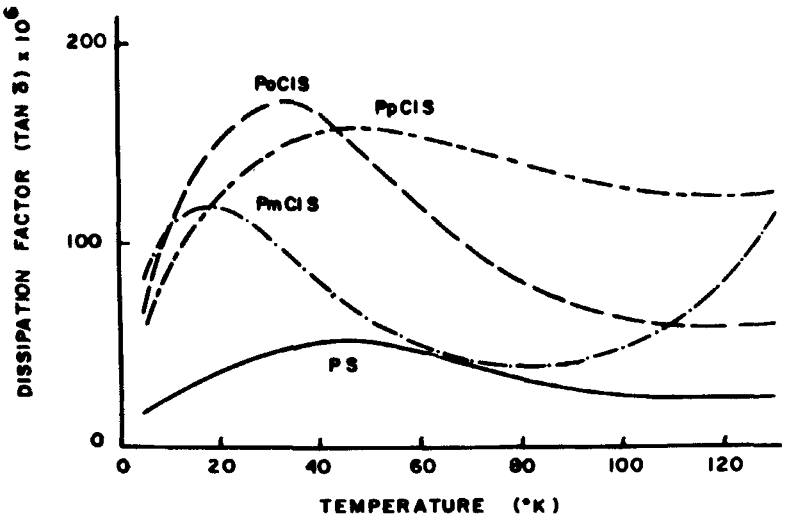

Fig. 7. Temperature dependence of dielectric loss of various polychloro styrenes. Data obtained from Ref. [18].

been attributed to hindered rotation of the α-methyl group. Hence the absorption peak centered near 150°K in Fig. 6 may reflect combined phenyl group and methyl group motion. The data also indicate that a broad low shoulder is still present in the 30-40°K region.

The effect of both Cl and CH_3 substitution on the phenyl ring has also been investigated [13, 16, 18]. Fig. 7 gives the temperature dependence of the dielectric loss of unsubstituted PS and of the same polymer with substitution of Cl for H in the ortho position (PoClS), the meta position (PmClS), and the para position (PpClS). Substitution in the para position apparently has no effect on the temperature location of the δ-peak, but the presence of this peak in both PS and P_pCls is itself evidence that the molecular motion involved cannot be pure rotation but must involve wagging. Upon substitution in either the ortho or meta position, the transition shifts to lower temperature. Since a partial or hindered rotation of the side group would be dielectrically active in PoCls and PmClS, the motion responsible for the δ-process is believed to be a coupled motion involving both partial rotation and wagging [16, 18].

The effect of methyl substitution on the phenyl ring has been studied by mechanical methods for three different samples [13, 52]. The results are presented in Fig. 8 for polyorthomethylstyrene (PoMS) and two

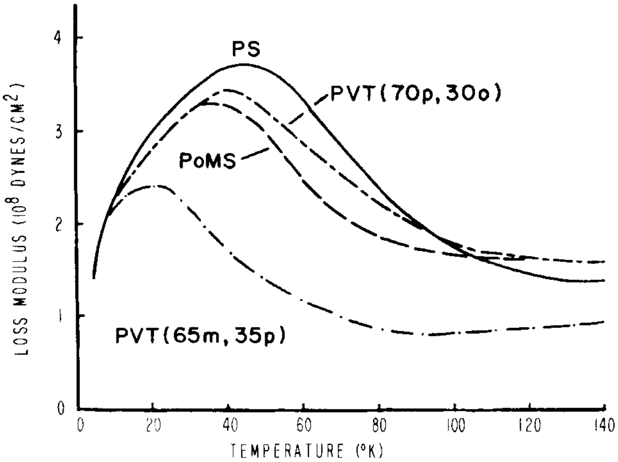

Fig. 8. Temperature dependence of mechanical loss modulus of various polymethyl styrenes. Data obtained from Ref. [2]. Code: ——— PS; — — — PoMS; — – — Polyvinyl toluene 70% para, 30% ortho; — - —polyvinyl toluene 65% meta, 35% para.

polyvinyltoluene (PVT) copolymers, one a 70% para, 30% ortho copolymer and the other a 35% para, 65% meta copolymer. The results of the CH_3 substitution on mechanical loss behavior is analogous to the results of Cl substitution on the dielectric behavior. The PoMS sample has a loss peak similar to that of PS but its maximum is centered somewhat below that of unsubstituted PS. The largely meta copolymer has its loss peak at about 20°K (~1 kc/sec).

Although the dynamic mechanical tests were not run, except for PoMS, on pure methyl styrenes, the high degree of correlation that exists between Figs. 7 and 8 strongly indicates that comparable motions are involved in the two cases. The mechanical relaxation may involve methyl rotation as well as phenyl group oscillation and wagging but, if so, the methyl rotation probably occurs well below 20°K and contributes little to the measured loss values.

Other effects of molecular structure are discussed in the next section.

Effect of Crystallinity

Not many experiments have been made at low temperatures on samples of different degrees of crystallinity. However, available data appear to be consistent [7, 12-14a]. Table 2 shows that a higher degree of crystallinity

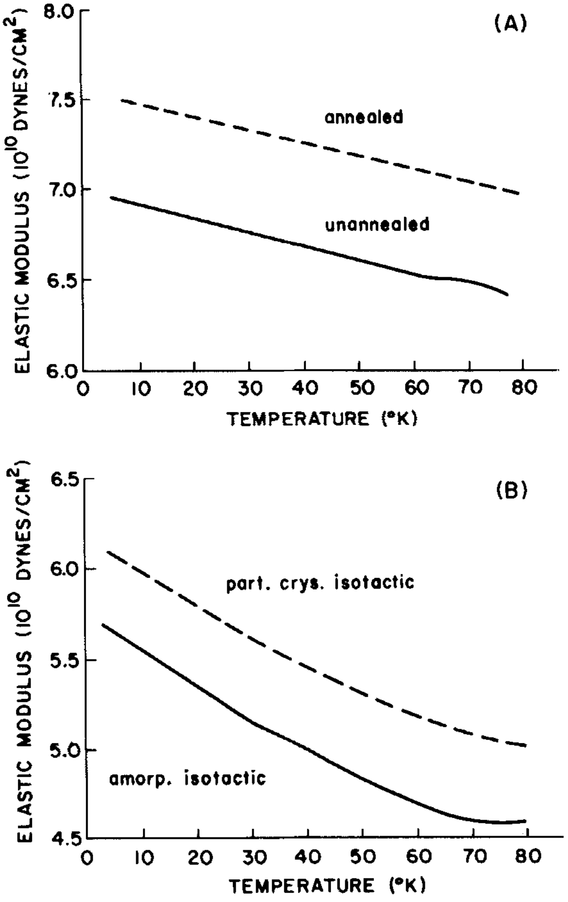

Fig. 9. (A) Temperature dependence of elastic modulus of polypropylene. Data obtained from Ref. [12]. (B) Temperature dependence of elastic modulus of polystyrene. Data obtained from Ref. [13].

for PTFE (85% vs. 55%) leads to higher modulus value at 4.2°K (2.7×10^{10} vs. 2.2×10^{10} dyn/cm^2). The data also show a significant increase in modulus at both 4.2 and 77°K for PETP film in going from the amorphous to the partially crystalline state. Figure 9A shows that the effect of increasing the crystallinity of PP, by annealing at 160°C, from 61 to 74% is to raise the modulus over the entire temperature range. A similar effect of crystallinity is shown in Fig. 9B, where the modulus and loss are plotted for a

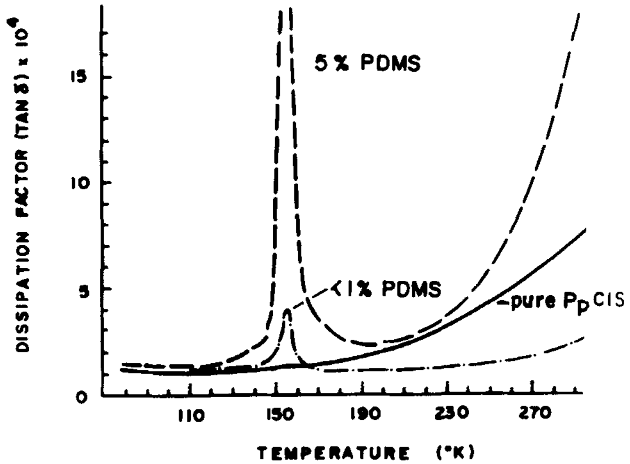

Fig. 10. Temperature dependence of dielectric loss of polypara-chloro styrene of various degrees of purity. Data obtained from Ref. [53]. Code: — — — 5% poly(dimethyl siloxane) (PDMS) (Dow Corning silicone lubricant); — · — < 1% PDMS (calculated); ——— purified sample.

noncrystalline isotactic sample of PS and for a sample that has been annealed at 175°C. Again the modulus is higher, and the internal friction is lower, for the more crystalline sample.

Effect of Impurities

The low-temperature relaxation behavior of polymers can be markedly affected by impurities. Several examples of this effect are now presented. It was mentioned earlier that in the low-temperature dielectric measurements on PS (Fig. 5) a small loss peak was noted near 150°K. Although the origin of this peak was not known at the time, it was later thought to arise from the presence in the polymer of a Dow Corning lubricant, poly(dimethyl siloxane). Data obtained by Schetzina [53] (see Fig. 10) on PpClS show that addition of 5% of this vacuum grease to the polymer causes a large increase in the dissipation near 150°K. The initial sample is estimated to have contained 1% or less of this impurity. A third sample, carefully prepared to avoid the presence of this impurity, was also studied. It can be seen from Fig. 10 that for the purified sample the 150° maximum has essentially disappeared.

Impurity effects in PS have also been observed by Frosini and Woodward [32]. Using a torsion pendulum apparatus, they found two peaks at

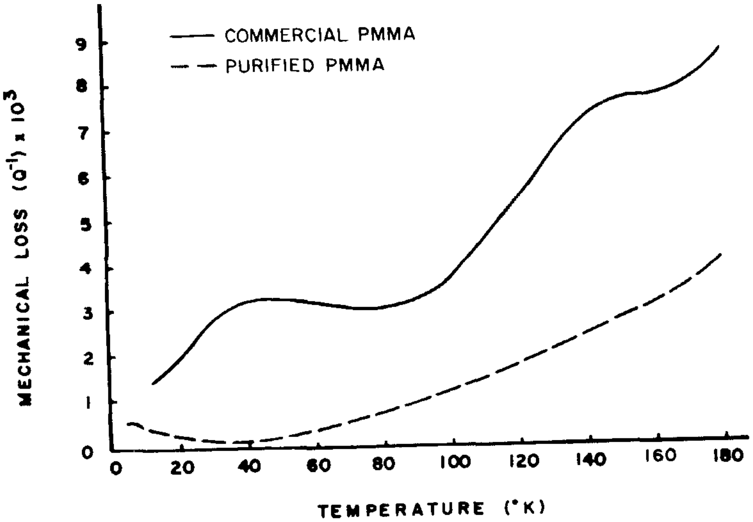

Fig. 11. Temperature dependence of mechanical loss of polymethyl methacrylate. Data obtained from Refs. [12, 52].

about 23 and 99°K in a commercial PS sample but only a single peak at 36°K, in agreement with the data of Sinnott [10], who used a carefully prepared sample. In view of these results, it appears quite likely that the additional dielectric peaks reported to occur in the low-temperature region by several investigators [17, 54] are not a result of polymer chain motion but are due to the effect of impurities. Some differences in mechanical relaxation behavior between PETP films [32] and Mylar films [14a] may arise from the same cause.

Impurities have, in fact, been observed to greatly affect the mechanical relaxation behavior of PMMA at low temperatures. This is shown by the data in Fig. 11, which gives values of internal friction, Q^{-1}, as a function of temperature for a commercial sample of PMMA and for a purified sample. The commercial sample shows two extra loss peaks not present in the pure polymer, and the presence of these extra peaks obscures the real relaxation process that is present in the pure polymer at very low temperatures. This latter process has been observed by both Sinnott [9] and Crissman et al. [12], and it is considered to be a result of motion of the ester methyl group. It is known from NMR results [51] taken at temperatures from 77°K that the ester methyl is rotating below this temperature, and more recent data [21] indicate that it is still undergoing hindered rotation even at liquid helium temperatures.

Effect of Copolymerization

Sinnott [7] has studied the effect of copolymerization on a polymer (PTFE) that shows no low-temperature δ-process. It was found that a copolymer of 5 mole % hexafluoropropylene and of comparable crystallinity had no transitions but had a slightly higher shear modulus value at 4.2°K (2.43×10^{10} vs. 2.25×10^{10} dyn/cm^2). The effects of copolymerization on a polymer that has a δ-relaxation have also been reported [52]. This polymer is a styrene-acrylonitrile copolymer (76% styrene, 24% acrylonitrile); its elastic modulus and loss over the low-temperature region are shown in Fig. 12. From comparison of the data with those on the homopolymer, it is clear that the δ-transition has been shifted to lower temperatures by addition of the acrylonitrile. This behavior may be a consequence of reduced interaction between phenyl groups.

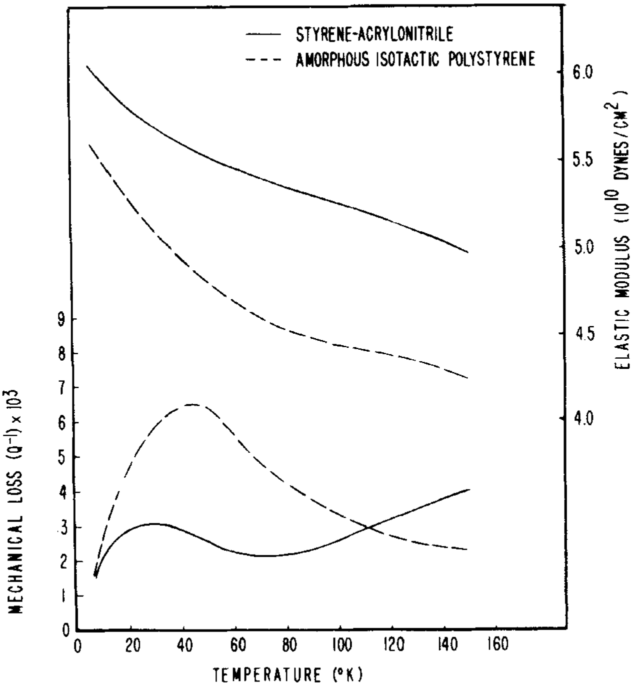

Fig. 12. Temperature dependence of elastic modulus and loss for styrene-acrylonitrile copolymer (76% styrene, 24% acrylonitrile). Data obtained from Refs. [13, 52].

Effects of Drawing

The effects of orientation on the mechanical relaxation spectrum of polymers have been studied by various investigators at temperatures above 77°K, but little information is available below 77°K. Armeniades et al. [14a] studied undrawn and drawn Mylar and found an appreciable modulus increase as well as some changes in the γ loss peak near 200°K and in the loss temperature behavior below 80°K. Frosini and Woodward [32] have obtained data on drawn samples of various polymers. Their data for PS at a draw of 3:1 are shown in Fig. 13. For this polymer the δ-peak has been decreased by orientation. Data have also been obtained on stretched and unstretched samples of PVA, PiBVE, and PVPr. All three of these materials, whether undrawn or drawn, were found to have two low-temperature loss peaks, a δ-type process at low temperatures and a γ-type process above 100°K. The low-temperature loss peaks were found near 10, 10, and 49°K while the γ-type loss peaks occurred at about 150, 116, and 149°K. Although the loss peaks were not appreciably moved in temperature location for the drawn samples, the magnitudes of the loss peaks were altered. For all three polymers the γ-peak consistently decreased upon drawing (at rates of 3-5 to 1) but the δ-peak was reduced (PS), remained the same (PVA), or increased (PiBMA and PVPr).

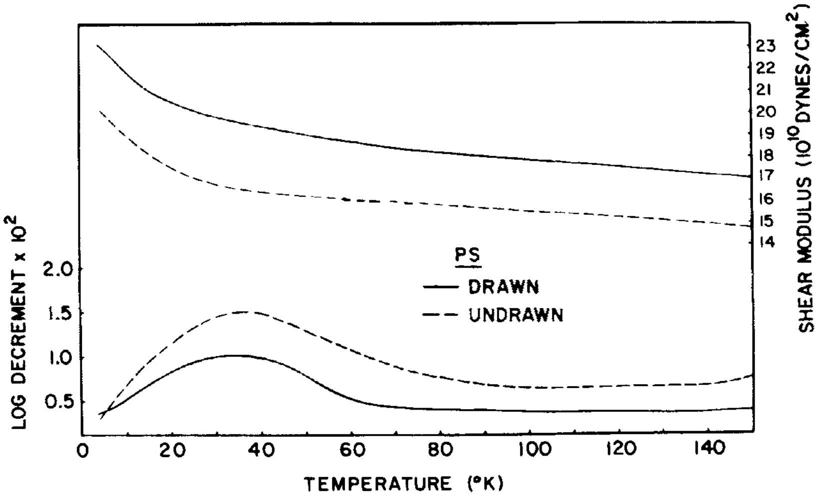

Fig. 13. Temperature dependence of shear modulus and loss of polystyrene. Data obtained from Ref. [32].

CORRELATION OF MECHANICAL, DIELECTRIC, AND NMR LOW-TEMPERATURE DATA

Some examples have already been given of the extent to which the data of different methods of measurement can be correlated. First of all, with respect only to the dynamic mechanical measurements, comparable information is obtained concerning the low-temperature behavior whether the measurements are of Young's modulus or of shear modulus. This is evident from the data for PP shown in Fig. 3 and from comparison for various polymers of the data of Tables 1 and 2. Except for the overall reduction in modulus value, the only other difference is to shift the δ-transition, if present, to somewhat lower temperatures. This is expected in view of the fact that the shear measurements are made at a frequency of approximately 1 cps while the elastic modulus measurements are obtained at a test frequency of about 10^4 cps.

Also, as shown in Fig. 5 for PS, dielectric measurements, which are sensitive to dipolar motions, and mechanical measurements, which are sensitive to most all types of molecular motion, agree very closely with one another if tests are run at comparable frequencies. One advantage of the dielectric measurements is that they can be carried out relatively easily over a wide range of frequencies and activation energies thus can be estimated from a plot of ln frequency at the loss peak vs. reciprocal temperature.

NMR data are also now available for many polymers. Although these studies have been made for the most part as a function of temperature only above 80°K, they still provide useful information concerning the presence and possible cause of low-temperature δ-relaxations. First of all, from comparison of the observed NMR second moment, ΔH^2, at 77°K with the calculated rigid lattice value, one can say whether certain molecular groups, such as methyl or ethyl side chains, are rotating at this temperature. Secondly, from observation of the temperature dependence of the spin-lattice relaxation time, T_1, one obtains information concerning molecular motions occurring at megacycle frequencies. When a given polymer group, or segment, attains the resonance frequency, interaction of the spin system with the lattice becomes more effective and a minimum occurs in the T_1 vs. temperature relation.

The extent of the correlation between the different methods of observation is now presented for several different polymers.

Figure 14 shows a dispersion map of ln frequency vs. reciprocal temperature for PS. Included on the graph is dielectric data of Saba [18] at various frequencies, mechanical data of Crissman et al. [13] at 10^4cps,

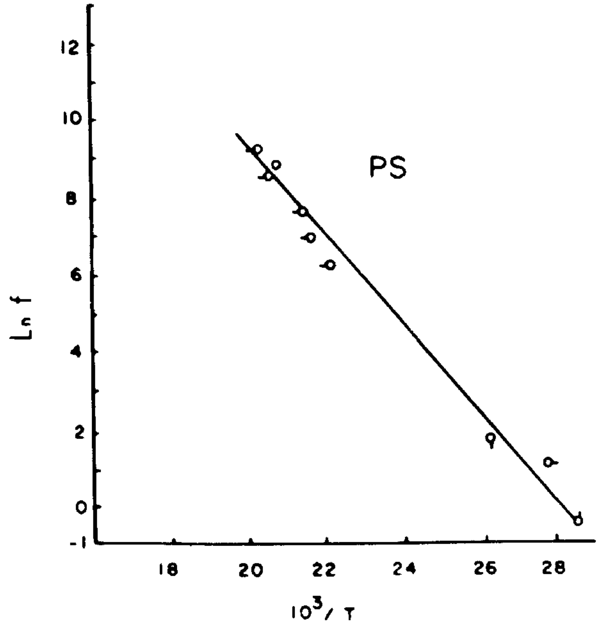

Fig. 14. Ln frequency vs. reciprocal temperature for polystyrene. Data obtained from Refs. [10, 32, 33, 13, 18]. Code: Mechanical ϙ, o-, ό, o dielectric -O.

and mechanical data at low frequencies of Sinnott [10], Frosini, and Woodward [32], and Chung [33]. Good agreement of the data is obtained over the entire frequency range, and the apparent activation energy for the δ-process in polystyrene is 2. 3 kcal/mole. NMR data of Hunt et al. [55] show two T_1 minima, or shoulders, one at 135°K and the other at about 260°K. Neither of these values fall on extension of the straight line drawn through the low-frequency data.

Figure 15 shows the temperature dependence of dielectric measurements [15], mechanical measurements [12, 56], and NMR measurements [52] for poly(dl-propylene oxide) over the temperature range from 4.2°K to about 200°K. This polymer shows an α_a-type transition above 200°K, a γ-type transition centered at 180°K at 10^4 cps and at 120°K at ~1 cps, and at least one, and perhaps two, low-temperature transitions. Both mechanical and dielectric data show a relaxation near 80°K and there is also a broad hump of low intensity in the mechanical data in the 10-40°K range.

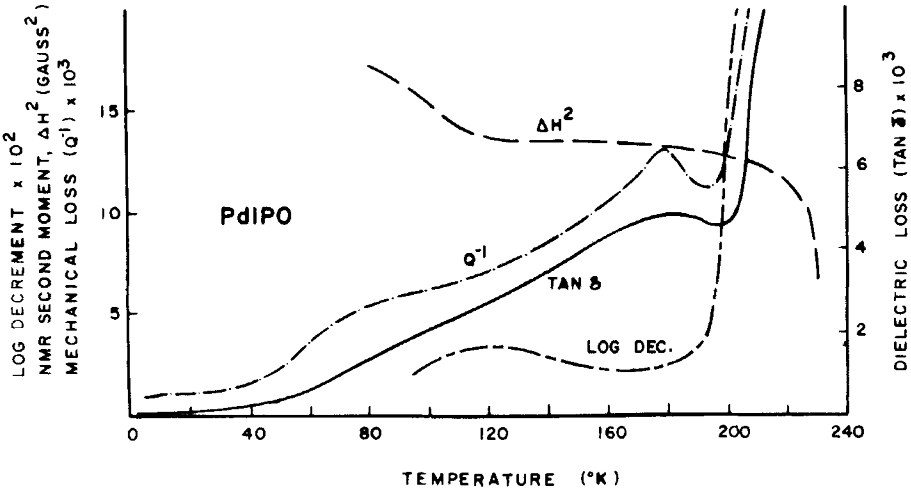

Fig. 15. Temperature dependence of mechanical and dielectric loss and NMR second moment of poly(dl-propylene oxide). Data obtained from Refs. [56, 12, 15, 52]. Code: Mechanical —— – —— ~ 0.5 Hz, —— • —— ~10^4 Hz; Dielectric ———— ~10^3 Hz; NMR, ΔH^2 —— —— —— .

Additional data for PPO are shown in Fig. 16. The apparatus designed by McCammon and Work [15] enables one to make simultaneous measurements of both dielectric constant (K) and loss as well as thermal expansion; values of K, at two different frequencies, and thermal expansion are shown from 4.2°K to above 250°K. Both sets of data show the α_a-transition above 200°K, and a δ-transition, between 60 and 80°K. The γ-transition near the 160-180°K range is evident in the K-data but is more striking in the tan δ-plot shown in Fig. 15.

NMR studies [57] made on a PPO sample of $M_W = 10^4$ give a spin-lattice relaxation time minimum near 140°K, as well as a second minimum near 270°K. Assuming the first of these is related to the δ-process and the second to the γ-process enables one to construct the dispersion map shown in Fig. 17. All the data for both transitions fall approximately on a straight line. Estimated activation energies are 3.5 kcal/mole for the δ-process and 7.9 kcal/mole for the γ-process. It should be noted, however, that the high-temperature T_1 minimum is considered [57] to reflect the primary transition, α_a, and, in fact, it falls also in the extension of the dispersion plot for this transition given by Woodward [2]. Evidently,

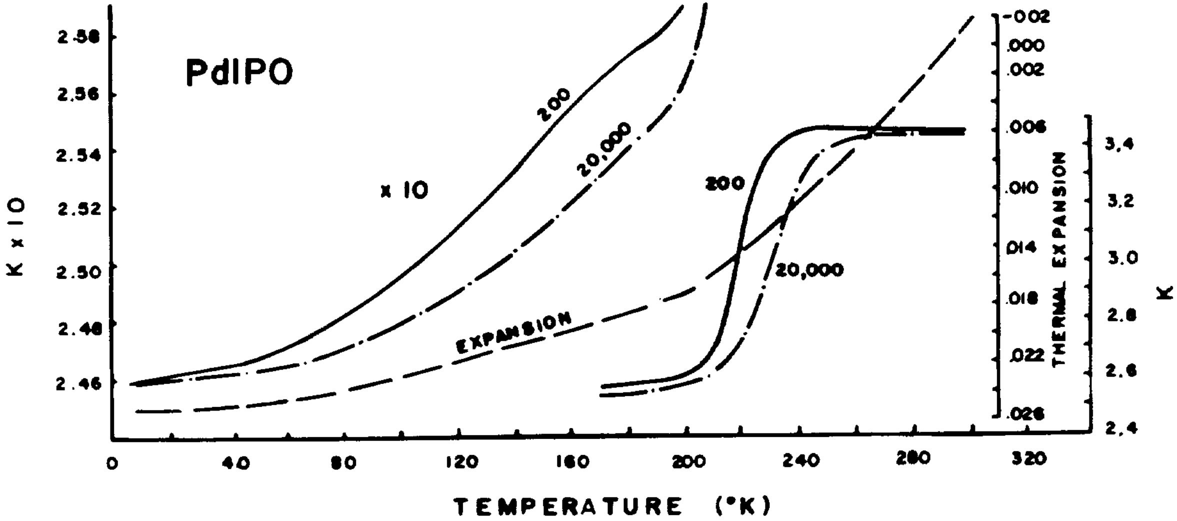

Fig. 16. Temperature dependence of dielectric constant and thermal expansion of poly-dl-propylene oxide. Data obtained from Ref. [15]. Code: ———— 200 Hz; —— • —— 20,000 Hz; —— —— —— thermal expansion.

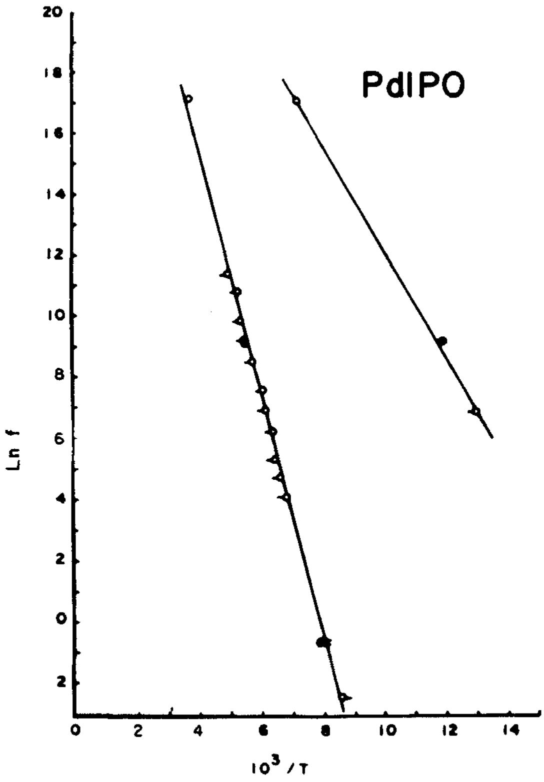

Fig. 17. Ln frequency vs. reciprocal temperature of poly-dl-propylene oxide. Data obtained from Refs. [12, 56, 15, 57]. Code: mechancial ●, O-; dielectric -O; NMR O.

at the NMR frequency, the γ- and α_a-motions coincide. It should also be noted that in the plot of Fig. 17 we have arbitrarily used the 80°K shoulder in the mechanical data as indicative of the δ-process rather than the lower-temperature hump. However, if the lower process is an indication of CH_3 motion, it would be more appropriate to plot it.

Mechanical data [12] and NMR data [2, 55] on another polymer (P4MPl) that shows a δ-transition are shown in Fig. 18. Since the T_1 minimum at 150°K and the ΔH^2 drop in the 80-100°K range of Fig. 18 have been attributed to methyl group rotation, it is appropriate to associate the modulus drop and the low-temperature loss peak near 25°K to the same process. If one does this, and in addition includes the loss peak obtained at

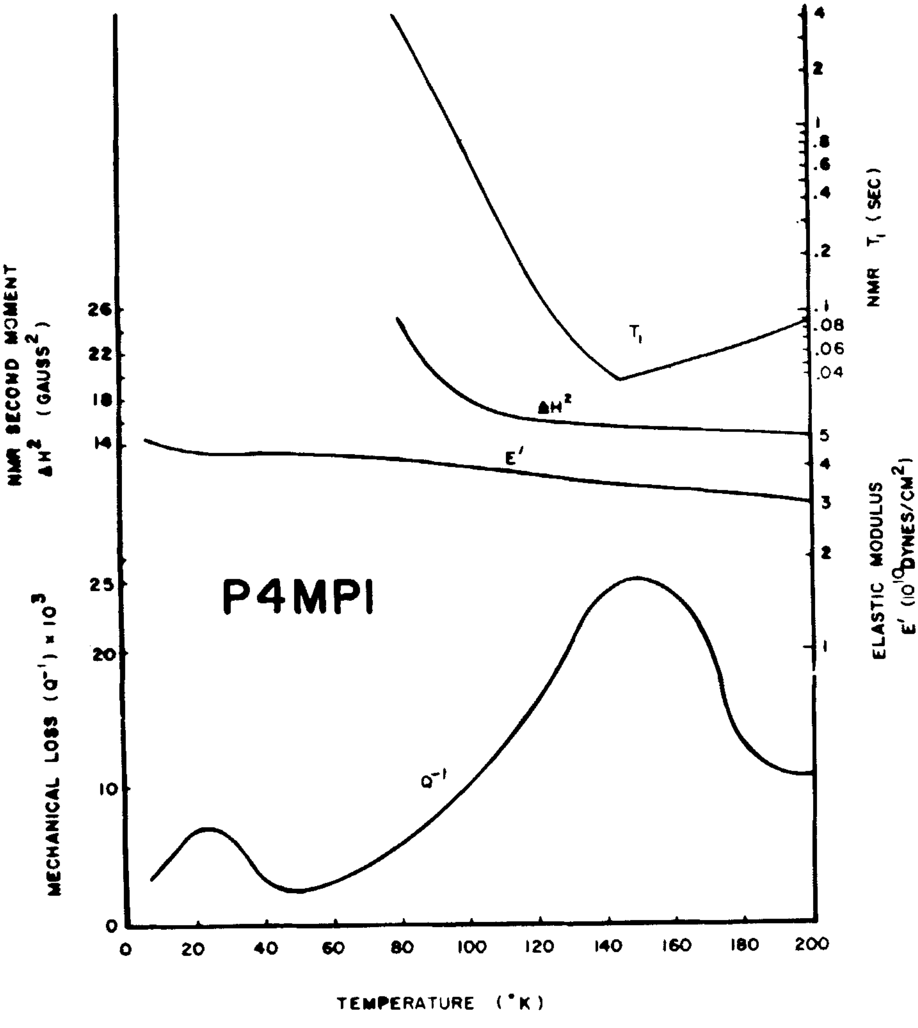

Fig. 18. Temperature dependence of NMR spin-lattice relaxation time and second moment and elastic modulus and loss of poly-4-methyl-pentene-1. Data obtained from Refs. [2, 12].

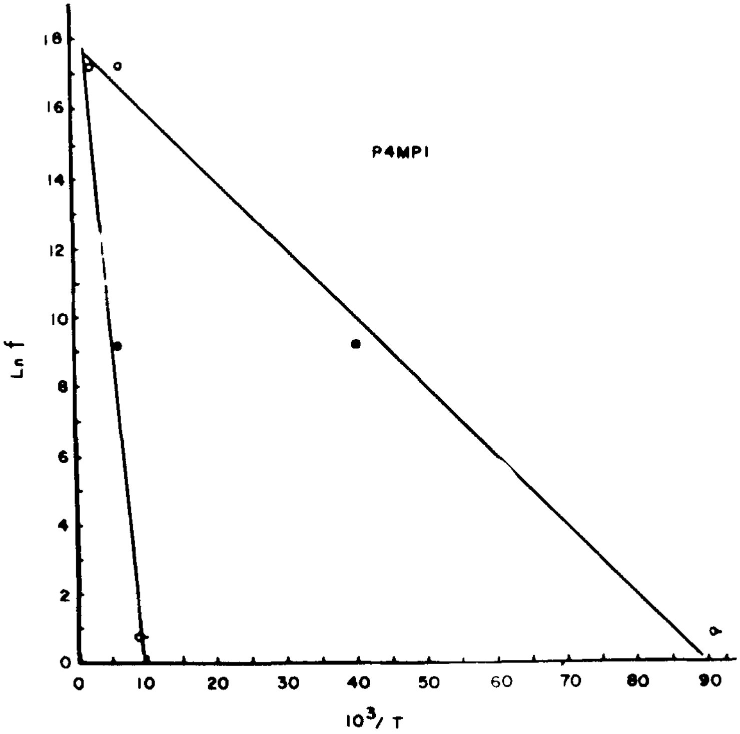

Fig. 19. Ln frequency vs. reciprocal temperature for poly-4-methyl-pentene-1. Data obtained from Refs. [32, 12, 55]. Code: Mechanical O-, ● ; NMR O.

11°K in low-frequency mechancal measurements [32], the dispersion map of Fig. 19 is obtained. If one represents these data by the straight line shown, then the apparent activation energy for the δ-process in this polymer is 0.4 kcal/mole. Also shown in the same plot are points representing the loss peaks of the γ-process from mechanical measurements. If we associate the upper T_1 minimum, as for PPO, to combined γ- and α_a-processes, then we get an activation energy for the γ-process of 5.2 kcal/mole.

Dynamic mechanical data at both low (~1 cps) and high frequencies (~10^4) and NMR T_1 data at still higher frequencies (~10^7) are available for both PMMA and PEMA. Some of the data for PMMA are plotted in Fig. 20. The mechanical modulus and loss data are from Crissman et al. [12], the NMR T_1 data from Slichter [58], and second moment data from

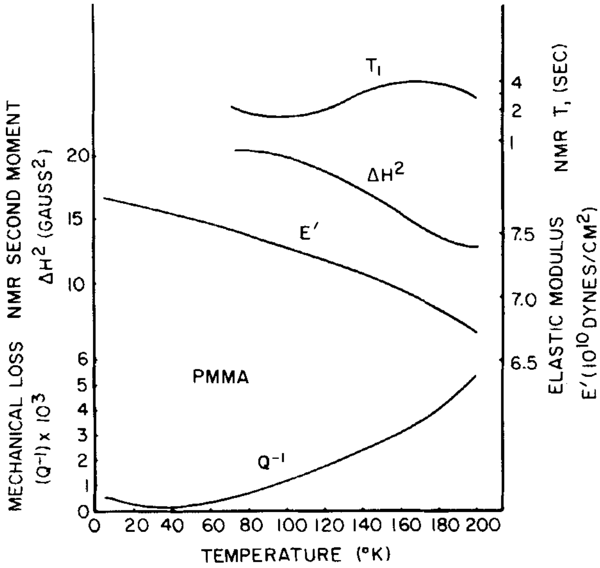

Fig. 20. Temperature dependence of NMR spin-lattice relaxation time and second moment and elastic modulus and loss of polymethyl methacrylate. Data obtained from Refs. [58, 51, 12].

Odajima et al. [51]. From comparison of observed second moment values at 77°K with values computed for the rigid lattice, it is known that the methyl group rotates at lower temperatures. We thus associate the very-low-temperature mechanical rise, which is also evident in the data of Sinnott [9], to methyl group motion and also the T_1 minimum shown in Fig. 20 at 100°K. No dispersion map has been drawn and no activation energy is here given for methyl rotation in PMMA, for two reasons. First, there is some disagreement about the location of the T_1 minima [58-61], with some investigators placing it between 70 and 80°K rather than 100°K; and secondly, the low-temperature peak at 5°K or below is not fully resolved in the mechanical data.

There appear to be sufficient data available for PEMA, however, to construct a dispersion map for the δ-process in this material. This is done in Fig. 21, which gives mechanical data from three sources [9, 12, 32] and NMR T_1 data from two sources [59, 60]. The estimated activation energy for this process, which is attributed to ethyl group motion, is 1.5 kcal/mole.

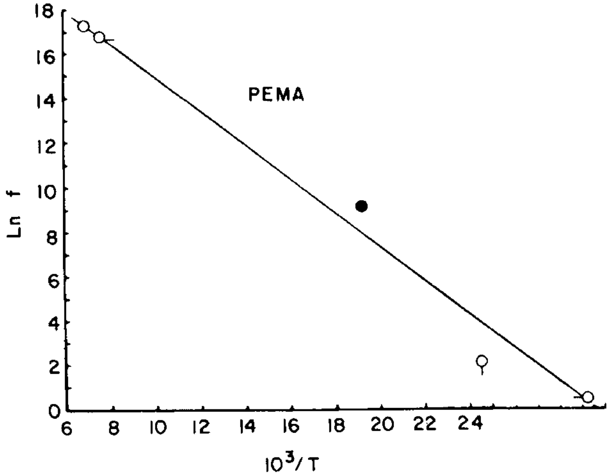

Fig. 21. Ln frequency vs. reciprocal temperature for poly-ethyl methacrylate. Data obtained from Refs. [32, 9, 12, 59, 60]. Code: Mechanical -O, O, ●; NMR O, O-.

DISCUSSION AND CONCLUSIONS

From a study of all of the test results that have been acquired at low temperatures, some of which have been presented in the previous sections, it appears possible to draw some tentative conclusions concerning the nature and the underlying molecular mechanisms of δ-type relaxation processes. This is done below along with an indication of some of the areas in which additional evidence is needed in order to improve our understanding and to clarify apparent conflicts.

Our conclusions are:

1. A relaxation mechanism at very low temperatures will arise from reorientational motion of pendant methyl groups. This has sometimes been referred to as an ϵ-relaxation. The specific temperature location of this relaxation will depend not only on the measuring frequency but on the location of the methyl group on the polymer chain. At low frequencies, this motion will occur and will give rise to a small mechanical loss peak, in the 0-30°K range. For PMMA, where the methyl is attached to the side chain ester group, it apparently occurs below 4.2°K. For PVA, it occurs at about 10°K. It is probably also the cause of the 10°K peak in

PiBVE. It doesn't appear to occur in polybutene, PB, but there is a definite minimum in the damping near 12°K and a gradual rise as the temperature goes down to 4.2°K. Hence, methyl group reorientation may occur below this temperature. Methyl rotation may also be the cause of the low, broad peak that is found in PP in the range 20-30°K. Its occurrence at a higher temperature for this material is to be expected because of additional restraints produced by its proximity to the main chain. Methyl rotation is probably also the cause of the prominent low-temperature peak in P4MP1 and the broad hump in PiBMA in the 20°K region. Here, too, the barrier to rotation should be higher than for the ester methyl in PMMA because of the presence of two methyl groups on the same carbon atom. Methyl reorientation appears also to have been detected by dielectric measurements in PMMA where an upswing in tan δ was observed in the low-temperature region [62].

2. Methyl rotation is more easily detectable in NMR data than in mechanical or dielectric data. It should give rise in many polymers to a line narrowing in the 4-80°K range, but this has not been directly observed probably because of the scarcity of NMR data below 80°K. For PMMA, in view of the mechanical data of Sinnott [9] and Crissman et al. [12] and the NMR data of Filipovich et al. [21], it may occur at temperatures below 4.2°K. Methyl rotation should also give rise to a T_1 minimum, but because of the high resonance frequency used in NMR, this minimum will occur at higher temperatures. It has been reported as occurring at 100°K in one study [58], and as falling below 80°K in two other investigations [59, 60]. A recent study [61] made at temperatures down to 4.2°K shows it to occur in the 70-75°K temperature range depending upon the amount of paramagnetic oxygen that is present in the sample. T_1 minima, presumable due to methyl rotation, have also been reported in the 80-200°K range for a number of other polymers with CH_3 groups on the side chain, such as PP [19], PPO [57], PMA [60], and P4MP1 [55]. In addition, mechanical loss maxima at 10^7 cps have been found in PP at 160°K and have been attributed to the same cause [63].

In di-substituted polymers with α-methyl groups, such as PMMA, the α-methyl appears to be much more hindered than the ester methyl, and line width data show it to rotate at line width frequencies in the 150°K region and to give a T_1 minimum at about 260°K. This minimum is also present in PEMA and polybutylmethacrylate (PnBMA) but is absent in PMA and polyethacrylate (PEA) [60]. Mechanical loss maxima, attributed to α-methyl motion, have also been found near 220°K at 10^7 cps in PMMA and PEMA [63]. In PαMS, the upper temperature minimum is thought to arise from the α-methyl while the lower temperature minimum may come from phenyl oscillation.

3. Activation energies for the methyl rotation process, based on frequency shift methods, give values in the range of 0.4-3.5 kcal/mole. These values are somewhat higher than values estimated directly from NMR data, but this is to be expected. The difference is due to the presence of a distribution of relaxation times [64] rather than to a single time.

4. Low-temperature δ-type processes can also arise from reorientational motions of the ethyl C_2H_5 group. Since the barrier to rotation of this group is expected to be higher than for CH_3 rotation, the relaxation is also observed at higher temperatures, in the neighborhood of 50°K. This process is much more pronounced in mechanical measurements than is CH_3 rotation, presumably because the latter only can occur without significant distortion of the surrounding lattice. Relaxation peaks due to side chain ethyl motion have been found in PEMA and in PVPr, which has a similar pendant group on the side chain. An ethyl group is also present in PB, and no low-temperature relaxation is noted near 50°K. However, here the ethyl group is directly attached to the main chain and hence the barrier to its rotation is expected to be considerably higher. Motion of the side group will still occur but at a higher temperature. The γ-peak in this material in the 130-150°K range is attributed to this cause.

5. Ethyl rotation also gives rise to an NMR T_1 minimum. For PEMA this occurs at about 135°K. The estimated activation energy from frequency shift methods using low-frequency mechanical data, as well as NMR data, gives a value of 1.5 kcal/mole. For an α-ethyl group rather than an ester ethyl group, the T_1 minimum is much higher. Also, the increased barrier to α-ethyl rotation relative to α-methyl rotation is evident in the disappearance of the 260°K T_1 minimum in going from PMMA to polymethylethacrylate (PMEA) [60].

6. Low-temperature relaxations in the temperature range 20-50°K may arise from motion of a side chain phenyl group, as in PS, or in the methyl or chloro-substituted polystyrenes. Activation energies based on mechanical and dielectric data are about 2.3 kcal/mole. It appears that the motion involved in this case is not phenyl rotation but phenyl-group oscillation and wagging. The loss modulus of PS does not appear to be significantly affected by crystallinity or by uniaxial stretching. However, the storage modulus is appreciably increased by both factors.

7. Low-temperature relaxations may arise from impurities in the polymer and these may give rise to one or more loss peaks in the 4.2-150°K range. In view of this, greater care is needed in characterization of the starting material of many investigations. Otherwise, erroneous conclusions may be drawn relative to the relation of polymer structure and relaxation behavior.

8. No low-temperature relaxations occur in linear polymers such as PE, PTFE, and nylon which have no easily rotatable side groups and no oxygen atoms in the main chain. For PE, dielectric studies carried down to 5°K on oxidized samples also show no loss peaks, in agreement with the mechanical data [63].

9. For linear polymers with oxygen atoms in the main chain, such as PPO or PETP, low-temperature transitions do appear to be present. In fact, in both materials there seem to be two separate low-temperature relaxation processes occurring in the temperature range 0-100°K [12, 14a].

10. Additional dielectric data on various polymers in the 0-100°K range are most desirable. Only for PS and PPO are data available on purified samples, and for these materials the agreement between the dielectric and mechanical methods of measurement is excellent. It would be particularly helpful to have dielectric measurements on the polymethacrylates and on other materials, such as PVPr, PVA, and PiBVE, which have both polar and nonpolar groups in the same side chain. PVPr, for example, shows both a δ- and γ-process, and hence, if we attribute the δ-process to ethyl group motion, it would appear that the γ-process might involve motion of the polar carbonyl group. However, in PMMA, there is no γ-process and motion of the entire side chain gives rise to the higher-temperature β-process. It would also be helpful to have NMR studies carried down to liquid helium temperatures, as in many cases T_1 minima are indicated but not located at data taken only to 77°K.

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REFERENCES

[1] A. E. Woodward and J. A. Sauer, in *Physics and Chemistry of the Organic Solid State* (D. Fox, M. M. Labes, and A. Weissberger, eds.), Part II, Chap. 7, Wiley-Interscience, New York, 1965, pp. 637-723, 925-947.

[2] A. E. Woodward, *Pure and Appl. Chem.,* 12, 341 (1966); *Advan. Chem. Ser.,* No. 63, 298 (1967).

[3] G. M. Bartenev and Y. V. Zelenev, *Mater. Sci. Eng.,* 2, 136 (1967).

[4] M. C. Shen and A. Eisenberg, *Progress in Solid State Chemistry,* Part 3, Pergamon, New York, 1966, p. 407.

[5] N. Saito, K. Okana, S. Iwayanagi, and T. Hideshima, in *Solid State Physics* (F. Seitz and D. Turnbull, Eds.), Vol 14, Academic, New York, 1963.

[6] A. J. Curtis, *Progress in Dielectrics,* Vol. 2, Wiley, New York, 1960, p. 29.

[7] K. M. Sinnott, *J. Appl. Phys.,* **29**, 1433 (1958).

[8] N. G. McCrum, *J. Polymer Sci.,* **36**, 355 (1959).

[9] K. M. Sinnott, *J. Polymer Sci.,* **35**, 273 (1959).

[10] K. M. Sinnott, *SPE Trans.,* **2**, 65 (1962); also unpublished results.

[11] R. D. McCammon and J. M. Crissman, *J. Acoust. Soc. Am.,* **34**, 1703 (1962).

[12] J. M. Crissman, J. A. Sauer, and A. E. Woodward, *J. Polymer Sci.,* **A2**, 5075 (1964).

[13] J. M. Crissman, A. E. Woodward, and J. A. Sauer, *J. Polymer Sci.,* **A3**, 2693 (1965).

[14a] C. D. Armeniades, I. Kuriyama, J. M. Roe, and E. Baer, *J. Macromol. Sci.,* **B1**, 777 (1967).

[14b] G. A. Bernier and D. E. Kline, *J. Appl. Polymer Sci.,* **12**, 593 (1968).

[15] R. D. McCammon and R. N. Work, *Rev. Sci. Instr.,* **36**, 1169 (1965).

[16] R. N. Work, R. D. McCammon, and R. G. Saba, papers presented at ACS 1st Middle Atlantic Regional Meeting, Philadelphia, 1966, and at Conf. on Electrical Insulation, Natl. Acad. Sci., NRC Publ. 1356 (1965).

[17] M. J. Chant, *Cryogenics,* **7**, 351 (December, 1967).

[18] R. G. Saba, Ph.D. Dissertation, Pennsylvania State Univ., 1967; R. D. McCammon, R. G. Saba, and R. N. Work (submitted for publication).

[19] M. P. McDonald and I. M. Ward, *Proc. Phys. Soc.,* **80**, 1249 (1962).

[20] D. W. Jones, *Polymer,* **2**, 203 (1961).

[21] G. Filipovich, C. D. Knutson, and D. M. Spitzer, Jr., *Polymer Letters,* **3**, 1065 (1965).

[22] M. Takayanagi and T. Matsuo, *J. Macromol. Sci.,* **B1**, 407 (1967).

[23] K. M. Sinnott, *J. Appl. Phys.,* **37**, 3385 (1966).

[24] G. A. Bernier, D. E. Kline, and J. A. Sauer, *J. Macromol. Sci.,* **B1**, 335 (1967).

[25] C. W. Deeley, J. A. Sauer, and A. E. Woodward, *J. Appl. Phys.,* **29**, 1415 (1958).

[26] A. E. Woodward, J. M. Crissman, and J. A. Sauer, *J. Polymer Sci.,* **44**, 23 (1960).

[27] J. A. Sauer, L. J. Merrill, and A. E. Woodward, *J. Polymer Sci.,* **58,** 19 (1962).

[28] A. E. Woodward, J. A. Sauer, and R. A. Wall, *J. Chem. Phys.,* **30,** 854 (1959); *J. Polymer Sci.,* **50,** 117 (1961).

[29] R. A. Wall, J. A. Sauer, and A. E. Woodward, *J. Polymer Sci.,* **35,** 281 (1959).

[30] R. P. Kreahling and D. E. Kline, *Kolloid Z. Z. Poly.,* **206,** 1 (1965).

[31] J. A. Sauer and D. E. Kline, *Proc. IX Intern. Congr. Appl. Mech., Brussels,* 5, 368 (1967).

[32] V. Frosini and A. E. Woodward, *J. Polymer Sci.,* A-2(7), 525 (1969); *J. Macromol. Sci.-Phys.,* **B3,** 91 (1969).

[33] C. Chung, Ph.D. Dissertation, Rutgers Univ., 1969.

[34] T. Kawaguchi, *J. Polymer Sci.,* **32,** 417 (1958).

[35] I. H. Hall, *J. Polymer Sci.,* **54,** 505 (1961).

[36] P. I. Vincent, *Proc. Roy. Soc.* **A282,** 113 (1964).

[37] I. Sakurada, T. Ho, and K. Nakamae, *J. Polymer Sci.,* **C15,** 75 (1966).

[38] A. Odajima and T. Maeda, *Rept. Polymer Phys. Japan,* **8,** 33 (1965); **9,** 169 (1966).

[39] L. R. G. Treloar, *Polymer,* **1,** 95 (1960).

[40] T. Shimanouchi, M. Asahina, and S. Enomoto, *J. Polymer Sci.,* **59,** 93 (1962).

[41] L. R. G. Treloar, *Polymer,* **1,** 290 (1960).

[42] W. J. Lyons, *J. Appl. Phys.,* **30,** 796 (1959).

[43] W. J. Dalmage and L. E. Contois, *J. Polymer Sci.,* **28,** 275 (1958).

[44] L. R. G. Treloar, *Polymer,* **1,** 279 (1960).

[45] W. J. Lyons, *J. Appl. Phys.,* **29,** 1429 (1958).

[46] T. Miyazawa, 13th Symp. High Polymer Chem., Tokyo, November, 1964.

[47] M. Asahino and S. Enomoto, *J. Polymer Sci.,* **59,** 101 (1962).

[48] S. Enomoto and M. Asahino, *J. Polymer Sci.,* **59,** 113 (1962).

[49] J. A. Sauer and A. E. Woodward, in *Polymer Thermal Analysis,* Part II, Chap. 8, Marcel Dekker, New York, to be published.

[50] M. Baccaredda, E. Butta, and V. Frosini, *J. Polymer Sci.,* **A2(4),** 789 (1966).

[51] A. Odajima, A. E. Woodward, and J. A. Sauer, *J. Polymer Sci.,* **55,** 181 (1961).

[52] A. E. Woodward, *J. Polymer Sci.,* **C(14),** 89 (1966).

[53] J. F. Schetzina, M.S. Thesis, Pennsylvania State Univ., 1965.

[54] T. Hara, M. Nozaki, and S. Okamoto, *Japan J. Appl. Phys.,* **6,** 1138 (1967).

[55] B. I. Hunt, J. G. Powles, and A. E. Woodward, *Polymer,* **5**, 323 (1964).
[56] R. G. Saba, J. A. Sauer, and A. E. Woodward, *J. Polymer Sci.,* **A1**, 1483 (1963).
[57] T. M. Connor, D. J. Blears, and G. Allen, *Trans. Faraday Soc.,* **61**, 1097 (1965).
[58] W. P. Slichter, *J. Polymer Sci.,* **C(14)**, 33 (1966).
[59] T. Kawai, *J. Phys. Soc. Japan,* **16**, 1220 (1961).
[60] J. G. Powles, B. I. Hunt, and D. J. H. Sandiford, *Polymer,* **5**, 505 (1964).
[61] J. G. Powles and B. I. Hunt, *Phys. Letters,* **14**, 202 (1965).
[62] T. Hara, *Japan. J. Appl. Phys.,* **6**, 147 (1967).
[63] J. Hirose and Y. Wada, *Rept. Progr. Polymer Phys. Japan,* **IX**, 287 (1966).
[64] J. G. Powles and P. Mansfield, *Polymer,* **3**, 337 (1962).

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Discussion of Paper by J. A. Sauer and R. G. Saba

Relaxation Behavior of Polymers at Low Temperatures

W. J. Schell: Is the transition in PMMA below 4.2°K by mechanical loss measurements due to the side chain methyl group or the main chain methyl group? Because PMMA and PEMA both have main chain methyls is there a similar transition in both at approximately the same temperature?

J. A. Sauer: The transition at or below 4.2°K is due to motion of the ester methyl group. This can be seen, for example, by comparison of the NMR T_1 data for PMMA and for PMA [55], where only a side chain methyl is present. The NMR data for these two materials are similar and the T_1 minimum is reported as occuring below 80°K.

Motion of the α-methyl group also gives rise to a T_1 minimum, but this occurs at a much higher temperature, around 260°K in both PMMA and PEMA. Also, if one replaces the α-methyl by an α-ethyl group as for PMEA, then the 260°K minimum is shifted to a much higher temperature, indicating that the barrier to rotation of the α-ethyl group is much higher than for the α-methyl group.

M. Shen: The low-temperature transition in polymethyl methacrylate has been attributed to the rotation of the methyl group on the ester side group. Why is it observable in dielectric data, since the methyl group is nonpolar?

J. A. Sauer: Good dielectric data appear to be available at low temperatures only for PS and PdlPO, and not yet for PMMA. However, dielectric measurements have been made on polypropylene[*] which also has a side chain methyl group and is generally considered nonpolar. Actually, as Curtis[†] pointed out several years ago, there is a small dipole moment associated with the methyl group. With good instrumentation, many so-called nonpolar materials can now be studied. It is possible, therefore, that the ester methyl group motion in PMMA may also show up in dielectric data if measurements are taken down to very low temperatures.

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[*] R. N. Work, R. D. McCammon, and R. G. Saba, *J. Chem. Phys.*, **41**, 2950 (1964).

[†] A. J. Curtis, *J. Chem. Phys.*, **36**, 3500 (1962).