Amorphous Polyolefins: A Relationship Between Molecular Structure, Submolecular Motion, and Mechanical Behavior

J. R. MARTIN* and J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*
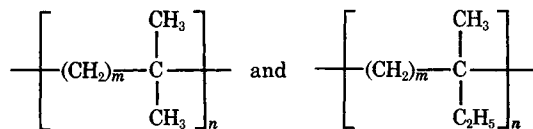
Synopsis

The thermomechanical spectra of two series of amorphous polyolefins represented by $+CH_2)_m-C(CH_3)_2+_n$ and $+(CH_2)_m-C(CH_3)(C_2H_5)+_n$, where $m = 1$, 2, and 3, are presented from $-180°C$ to above the glass transition temperatures. The polymers were obtained by cationic polymerization of α-olefins. The mechanical spectra show a maximum in glass transition temperature and secondary transition temperature for the second member of each series. This maximum is interpreted in terms of a proposed geometrical intermolecular interlocking which is considered to be at a maximum for the second member of the series and serves to restrict the submolecular motions associated with the transitions. The proposal is discussed in terms of its consequences upon free volume, density, cohesive energy density, and chain flexibility.

INTRODUCTION

In order to elucidate the molecular mechanisms of the transitions and relaxation processes in solid polymers, many investigations have been undertaken using for the most part three techniques:[1-4] mechanical spectroscopy, dielectric loss, and nuclear magnetic resonance. These studies have shown that amorphous polymers display at least two types of dispersion processes; the high temperature process, attributed to long-range segmental motions of the main chain; and the low-temperature processes, attributed to the motion of side groups and/or to local relaxation modes of the main chain. In crystalline polymers, in addition to the relaxation processes associated with the amorphous regions, additional processes occur which are associated with crystalline transitions.

This study presents an investigation of the thermomechanical spectra of two series of amorphous polyolefins represented by the formulae

$$\left[\begin{array}{c} CH_3 \\ | \\ -(CH_2)_{\overline{m}}-C- \\ | \\ CH_3 \end{array} \right]_n \quad \text{and} \quad \left[\begin{array}{c} CH_3 \\ | \\ -(CH_2)_{\overline{m}}-C- \\ | \\ C_2H_5 \end{array} \right]_n$$

* Present address: Textile Research Institute, Princeton, New Jersey.

where $m = 1, 2, 3, \ldots$ These polymers are of fundamental importance to polymer science and yet have been neglected. A reason for their importance lies in the systematic *in-chain* variation of one —CH_2— between consecutive members of each series since it is the structure and influence of the main chain per se which is central to polymeric behavior. The absence of polar forces, tacticity, and crystallinity allows the results to be interpreted solely in terms of geometric effects. One reason for the neglect of the series is that synthetic problems remain.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

The polymers were synthesized by cationic polymerization of alpha olefins.[5] The first member of each series ($m = 1$) results from 1–2 polymerization of the parent monomer. The resulting polymeric structures for the second and third members of the series do not represent simple 1–2 addition, but display structures resulting from isomerization of each terminal monomer residue unit before the propagation step. For these polymerizations, the isomerization is a hydride shift favored by the thermodynamic stability of the tertiary carbenium ion. The solution polymerizations were carried out at low temperatures ($-78°$ to $-130°C$) so that the hydride shift could occur before the propagation step and also so that other competing reactions (e.g., transfer by proton elimination which leads to low molecular weight species) were rendered less competitive. By way of illustration, the steps that determine the polymeric repeat unit which arises from the monomer 3-methyl-1-butene are summarized in Figure 1.

The third member of each series does not display a completely isomerized structure. Because two consecutive hydride shifts are required to form the
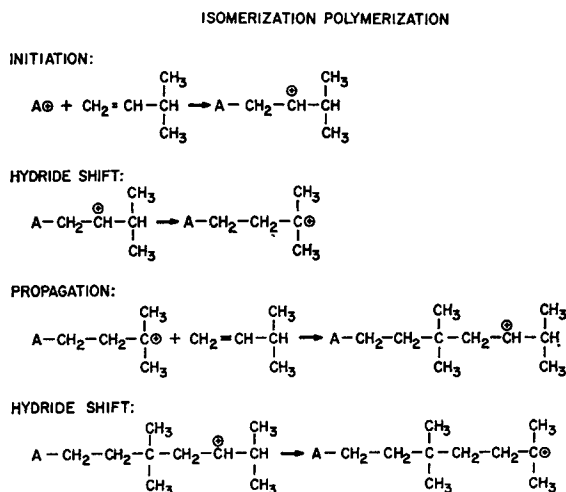

Fig. 1. Initiation, hydride shift, and propagation steps in the cationic isomerization polymerization of 3-methyl-1-butene.[5]

stable tertiary carbenium ion, some propagation occurs before complete isomerization and results in "1,2" and "1,3" repeat units being incorporated into the chain.[6]   Studies are currently being directed toward obtaining pure forms of the third member of each series by determining the effect of polymerization variables, especially temperature, counterion, and polymerization medium, upon the hydride shift reaction and ultimately upon the resulting polymer microstructure.[7]   (For sake of simplicity, the third member of each series is assumed pure in the interpretation of the mechanical re-
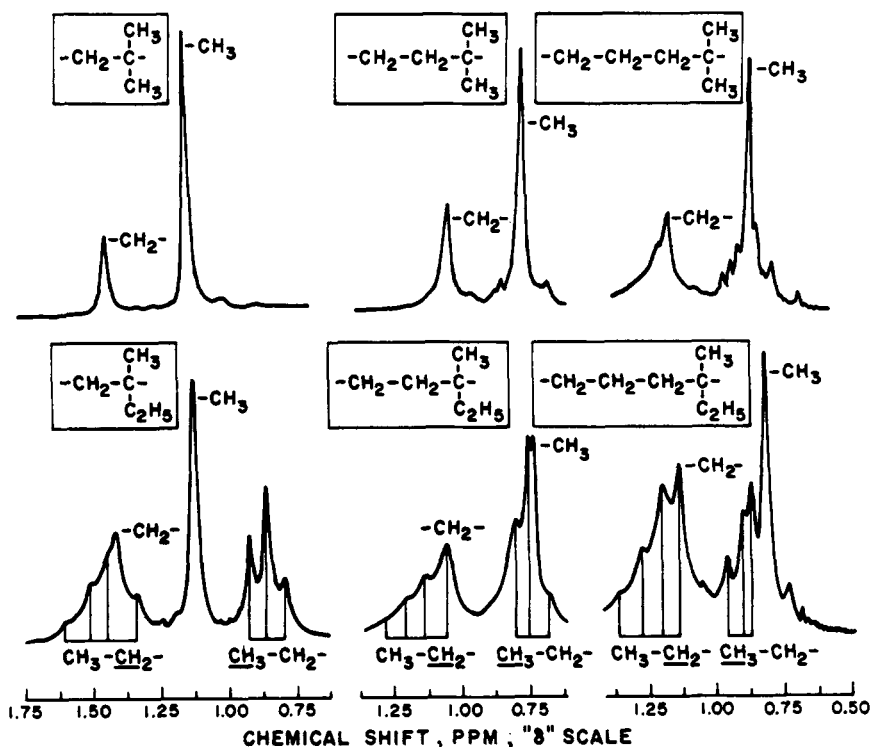

Fig. 2. High resolution 100-MHz NMR spectra obtained at 90°C, using 20% solutions of polymer in hexachloro-1,3-butadiene.[7]

sults; as discussed below, this assumption does not alter the general pattern of results.)

Molecular weights were estimated from intrinsic viscosity data using an equation for polyisobutylene.

The high-resolution solution NMR spectrum of each of the polymers is shown in Figure 2.   The spectra for the first two members of each series are consistent with the pure structures, whereas the spectra for the third members show the presence of undesired complexities.

EXPERIMENTAL PROCEDURE AND RESULTS

The dynamic thermomechanical spectra ($\sim$1 cps) of the polymers are shown in Figures 3 and 4; the curves are displaced vertically for purposes of clarity without altering their shapes.   The spectra were obtained from a torsional pendulum utilizing a supported sample (torsional braid analysis[8,9]). This particular technique provides a convenient method for obtaining the dynamic mechanical spectra because of the physical difficulties which would be encountered in preparing other types of specimens (e.g., films and molded bars) from linear polymeric materials that are rubbery and gummy at room temperature.   The specimens used were prepared by solvent casting onto a glass braid from a 5% to 10% solution of polymer in n-heptane (bp 98.4°C). Solvent was removed by heating to 200°C ($\Delta T/\Delta t = +2°C$/min) in a flowing nitrogen atmosphere.   Since identical spectra were obtained in both heating and cooling modes of operation, crystallinity was considered to be absent.   The essential features of the spectra, using the loss peaks for assignment of transition temperatures, are summarized in Table I.
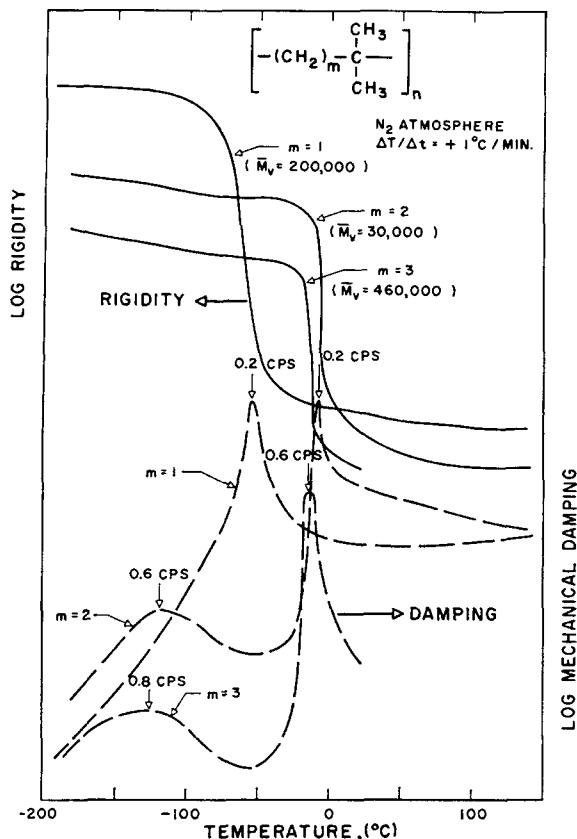

Fig. 3. Thermomechanical spectra of a series of amorphous polyolefins.

TABLE I
Summary of Formulae, Molecular Weights, Transition Temperatures and Activation Energies, and NMR Chemical Shifts

	$\overline{M}_v$	Glass Transition	Secondary Transition(s)	NMR Chemical Shifts[a] ppm "δ" Scale	
				—CH₂—	—CH₃
—CH₂—C(CH₃)(CH₃)	200,000	−65°C (0.2 cps) (22 kcal/mole)	−229°C (0.8 cps)	1.40	1.07
—CH₂—CH₂—C(CH₃)(CH₃)	30,000	−7°C (0.2 cps) (48 kcal/mole)	−115°C (0.6 cps) (12 kcal/mole); −148°C (100 Hz) (4 kcal/mole)	1.055	0.76
—CH₂—CH₂—CH₂—C(CH₃)(CH₃)	460,000	−15°C (0.4 cps) (44 kcal/mole)	−130°C (0.8 cps) (9 kcal/mole)	1.105	0.785
—CH₂—C(CH₃)(C₂H₅)	18,500	−20°C (0.4 cps) (28 kcal/mole)	−140°C (1 cps) (18 kcal/mole)	1.40	1.10
—CH₂—CH₂—C(CH₃)(C₂H₅)	25,100	+5°C (0.2 cps) (44 kcal/mole)	−100°C (0.9 cps) (9 kcal/mole); −165°C (1 cps) (6 kcal/mole)	1.075	0.75
—CH₂—CH₂—C(CH₃)(C₂H₅)	268,000	−15°C (0.2 cps)	−145°C (0.9 cps)	1.055	0.73

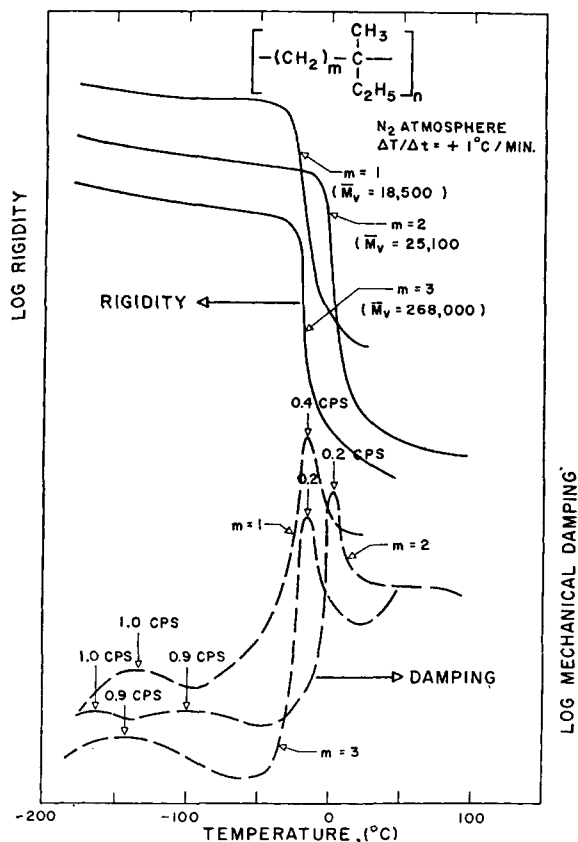a 20% Solution in hexachloro-1,3-butadiene; 100 MHz; 90°C.

Fig. 4. Thermomechanical spectra of a series of amorphous polyolefins.

The dielectrically obtained frequency dependence of the transitions of polyolefins in the first series is presented in Figure 5 as Arrhenius plots. These dielectric measurements[10] confirm (by extrapolation) the assignments of the mechanically determined transitions and, in addition, reveal in the second member an additional secondary transition which was not observed mechanically at 1 cps. The apparent activation energies for the loss processes which are included in Table I were determined from these dielectric data (within the frequency range investigated). Table I also includes a value for a secondary transition ($-229°C$; 0.8 cps) for polyisobutylene. This was obtained with a torsional braid specimen with measurements made above $+4°K$ in a suitable apparatus.[11]

DISCUSSION

The glass transition is identifiable by a sharp damping peak with a concomitant abrupt drop in storage modulus as the material passes from the glassy to the rubbery state. From a molecular viewpoint, the glass transition represents the onset of large-scale rotations and oscillations of
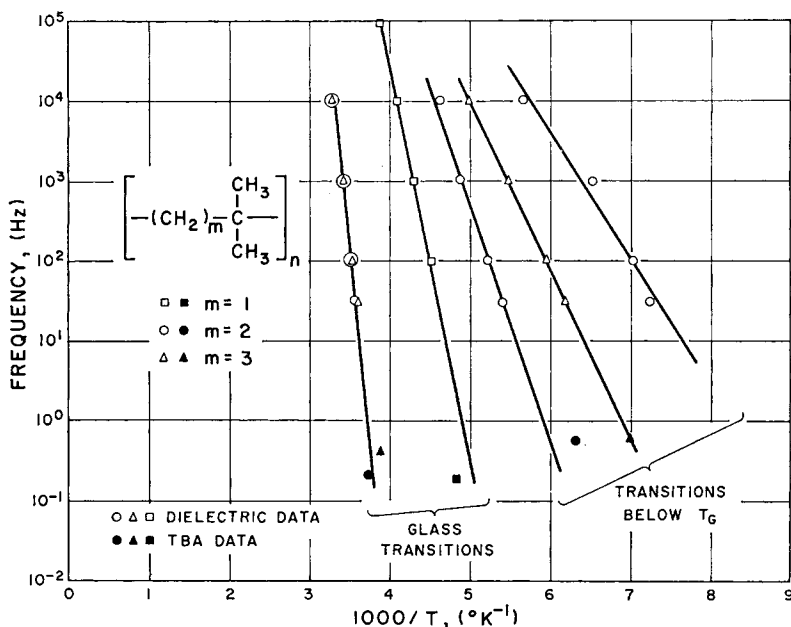
Fig. 5. Frequency dependence of transitions in a series of amorphous polyolefins.[10]

submolecular segments which, through thermal expansion, have acquired the necessary free volume for the process to occur.

In both series studied, the glass transition temperature rises in going from the first to the second member of the series and then decreases in going from the second to the third member of the series. The effect is less pronounced in the second series, $+(CH_2)_m—C(CH_3)(C_2H_5)+_n$ (Fig. 4), than in the first $+(CH_2)_m—C(CH_3)_2+_n$ (Fig. 3). Although the molecular weights within a series are not strictly comparable, a higher molecular weight for the second member of the first series would, if anything, raise the glass transition temperature and not affect the general pattern of results. Similarly, a lower molecular weight for the third member of the second series would, if anything, lower the glass transition temperature, with the maximum in the second member of the series still being retained. Mechanically obtained glass transition temperatures ($\sim$1 cps) have been reported for members of the first series[12] and for the first member of the second series.[13] Within the limits of experimental error, these results are in agreement with the results presented here.

The molecular structure of the first member of each series exhibits a high degree of intramolecular steric hindrance which could be expected to decrease along each series with increasing number of in-chain contiguous methylene groups. Other things being equal, the effect of this intramolecular steric hindrance should be to raise the glass transition temperature so that the glass transition temperature would decrease along each series. Such an effect is observed in the glass transition temperatures of a series of

poly(methylene terephthalates)[14] and poly(methylene oxides)[15] where the dominance of intramolecular effects causes the glass transition temperature to decrease with increasing number of in-chain contiguous methylene groups. Since, in the polymer series investigated here, this regular decrease in glass transition temperature along each series is not observed (i.e., the glass transition temperature is at a maximum for the second member of each series), it would seem that in these polymers the dominant factors determining the glass transition temperature are intermolecular rather than intramolecular. Since the polymers are nonpolar, the observed intermolecular effects must arise from geometric rather than polar effects.

This conclusion, which attributes the observed behavior to intermolecular effects, rests upon the supposition of increased intramolecular flexibility with increasing number of in-chain contiguous methylene groups. In invoking the concept of molecular flexibility, the meaning of the term "flexibility" must be considered. Considering this flexibility as a *kinetic* phenomenon, as in the case of dynamic mechanical spectra, the decrease in glass transition temperature with increasing number of in-chain contiguous methylene groups for the poly(methylene terephthalate) and poly(methylene oxide) series provides evidence for the assumption of increased intramolecular flexibility along such a polymer series. The behavior of the high-resolution NMR spectra of the polymers studied here provides evidence for the high intramolecular steric hindrance in the first member of the series.[7] As illustrated in Figure 2 and tabulated in Table I, both the methyl and methylene peaks are shifted significantly downfield for the first member of each series. This behavior has previously been reported[16] for members of the first series. Similar behavior is also displayed by the NMR spectra of a series of low molecular weight paraffins with structure analogous to the polymer series.[17] The downfield shift results from intramolecular interference of the neighboring pairs of geminal methyl groups which appears as a maximum when these groups are separated by a single methylene linkage.

The terminology "molecular flexibility" is also used in connection with equilibrium phenomena, and, for example, the dimensions of the time-averaged overall configuration of polymer molecules are used as a measure of it. Dimensions of isolated molecules can be obtained experimentally from polymer solutions using light-scattering and intrinsic viscosity measurements[18] and from lightly crosslinked elastomers using force-temperature measurements (made above the glass transition temperature) by application of the equation of state for rubber networks.[19] Theoretical calculations also quantitatively describe the overall dimensions of isolated polymer molecules,[20] and, although the application of these calculations to sterically hindered molecules such as polyisobutylene is quite complex, it is currently an active area of investigation.[21] The equilibrium dimensions cannot be used as a measure of flexibility between different species of molecules since the overall dimensions are a measure of the relative levels of the intramolecular conformational energy minima. On the other hand, kinetic flexibil-
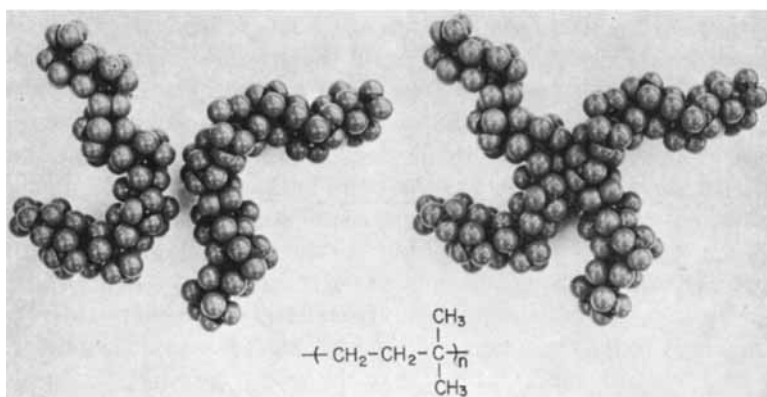
Fig. 6. Fisher-Taylor-Hirchfelder molecular models showing segments of separated and interlocked molecules.

ity of isolated molecules is determined by the conformational energy barriers to bond rotation. In this connection it is noteworthy that the normalized molecular dimensions of polyethylene and polyisobutylene are approximately equal[22,23] in spite of the obvious difference in dynamic flexibility.

The intermolecular geometric factors, which result in a maximum in glass transition temperature with the second member of each series, are interpreted in terms of intermolecular interlocking which, through molecular models, can be shown to result in maximum restriction to segmental motion in the second member of each series and thus raise the glass transition temperature. This segmental interlocking is illustrated in Figure 6, which shows molecular models for two molecules, both separated and interlocked, for the second member of the first series. The interlocking occurs by a snug fitting of the pendent methyl groups into the spaces between the pendent methyl groups on the adjacent molecule. The interlocking at the point of juncture, which may be considered as being a form of molecular entanglement, is such that motion of one interlocked molecular segment with respect to the other is restricted. The interlocking in the third member of the series (not shown) is not as restrictive and allows slight relative motion at the point of juncture.

The internally hindered polyisobutylene molecule can be conceived of as a backbone chain sheathed by methyl groups with no available sites between pendent methyl groups to allow interlocking with neighboring molecules. Because of the steric hindrance and bond-angle strain involved in the molecules of the first member of each series, standard molecular models of these molecules cannot be constructed.[18] However, it is precisely this heavy substitution which appears to prevent intermolecular interlocking and leads to a glass transition temperature lower than the other members of the series.

Based on these considerations, one can predict that if the series were extended, the glass transition temperature would continue to decrease with increasing number of in-chain contiguous methylene groups. As a limiting

case, the glass transition would approach the low amorphous glass transition temperature of polyethylene[24] which, in the absence of crystallinity, could be expected to exhibit minimal inter- and intramolecular effects. (The inclusion of polyethylene into the series, at $m = \infty$, makes the structural impurities in the third member of each series unimportant since the glass transition temperature must at some point in the series pass through a maximum whether it be at $m = 2$ or with some later member of the series.)

Similar arguments would contribute to the explanation of the high glass transition temperature of amorphous polypropylene ($-10°C$) relative to the values for amorphous polyisobutylene and amorphous polyethylene, and similarly to the explanation of the high glass transition temperature of poly(vinyl chloride) ($87°C$) relative to the values for poly(vinylidene chloride) ($-17°C$) and polyethylene.

Additional evidence for this proposed intermolecular interlocking lies in consideration of the structure of the third member of the first series as an alternating copolymer of ethylene and isobutylene. The relationship between glass transition temperature and copolymer composition is, in most cases, closely approximated by a linear relationship. However, a plot of copolymer composition versus glass transition temperature for this hypothetical copolymer of ethylene and isobutylene, in which the minor component is evenly distributed along the chain, would clearly pass through a maximum near the point of equimolar composition as represented by the structure of the third member of the first series. Such a maximum is indicative of some sort of intermolecular interaction. A similar maximum is also observed in the transition–composition plots of acrylonitrile–styrene[25] and vinylidene chloride–methyl acrylate[26] copolymers near the point of equimolar composition of the two comonomers. Although these copolymers contain polar groups which can be expected to contribute to intermolecular interactions, the interlocking phenomenon can still be considered contributory particularly in the case of the copolymer involving vinylidene chloride units which, like isobutylene units, are by themselves sterically hindered and heavily substituted enough to render interlocking prohibitive. It is interesting (see below) to note that for the vinylidene chloride–methyl acrylate system, the free volume at the glass transition temperature, calculated from expansion coefficients presented with the glass transition temperatures,[26] is lower than the generally accepted iso-free volume values[27] on either side of the maximum, but approaches the generally accepted "average" value at the maximum in glass transition temperature.

Molecular interlocking bears significantly upon the free-volume theory which sets for a particular polymer a specific free volume as the criterion determining the glass transition temperature.[27] Although the free-volume theory as a corresponding-states approach to the glass transition is a generally accepted theory, the premise of an iso-free volume applicable to all polymers at the glass transition is not so widely accepted.[27] There are notable exceptions to the iso-free volume theory where the free volume at the glass transition temperature is both larger, e.g., poly(ethylene terephthalate)

and poly(bisphenol A carbonate), and smaller, e.g., polyisobutylene, hevea, and poly(methyl acrylate), than the generally accepted average value. In considering the importance of geometric intermolecular effects, it seems apparent that the *shape of the free volume* must be taken into account when relating free volume to the glass transition temperature. These geometric considerations seem particularly important in light of the fact that many of the polymers deviating from the iso-free volume state are those which are highly substituted enough to prevent intermolecular interlocking, e.g., polyisobutylene and vinylidene chloride–methacrylate copolymers rich in vinylidene chloride, or those systems containing bulky groups within the main chain, e.g., poly(ethylene terephthalate) and poly(bisphenol A carbonate). On this basis, it would appear that interlocking may be a requisite for polymers exhibiting iso-free volume behavior.

It follows from the above discussion that geometric interlocking can increase the free volume and decrease the density by constraining interlocked segments to fixed conformations. Such reasoning[29] could contribute to an explanation of the observation that amorphous syndiotactic poly(methyl methacrylate) has a higher glass transition temperature ($+127°C$; 0.25 cps) than amorphous isotactic poly(methyl methacrylate) ($+55°C$; 0.31 cps), and yet the former has the lower density at $30°C$.[30-32] This does not contradict the iso-free volume theory as defined by $T_g(\alpha_R - \alpha_G) = $ constant, where α_R and α_G are the thermal expansion coefficients for the rubbery and glassy states, respectively, since the absolute values of glassy-state densities may differ.

Intermolecular interactions between polymer molecules have usually been attributed to polar groups within the molecule. These polar groups serve to form intermolecular bonds which inhibit segmental motion and at the same time decrease the free volume. Both of these effects result in an increase in the glass transition temperature. These intermolecular effects are quantitatively dealt with through use of the cohesive energy density related, for simple liquids, to the energy of vaporization and, for polymers, to the solubility parameter.[28] Although correlations between kinetic and equilibrium phenomena must be treated with caution, generalized correlations for many polymers[27] show two linear relationships between glass transition temperature and the square root of cohesive energy density; one for symmetrically substituted molecules, e.g., poly(vinylidene chloride), polyisobutylene, poly(tetrafluoroethylene), poly(dimethylsiloxane), and another for unsymmetrically substituted molecules, e.g., polystyrene, poly(methyl methacrylate), poly(vinyl chloride). The existence of these two correlations may well be attributed in part to bulk-phase intermolecular interlocking occurring in the unsymmetrically substituted molecules which would not be observed in the equilibrium polymer–solvent studies generally used to determine the cohesive energy density. (Intramolecular effects undoubtedly do play an important role in symmetrically substituted molecules for which the intramolecular barrier to rotation is less than that for unsymmetrically substituted molecules.)

The secondary transitions observed in these polymer studies display similar behavior to that of the glass transition temperatures. Based on the similarity of temperature location and activation energies, these secondary transitions appear to arise from the same source as the main secondary transition observed in polyethylene and other polyolefins.[4,33] The molecular basis of this glassy state amorphous transition is generally considered to involve a small number of monomer residue units within the main chain. The presence of three to five contiguous in-chain methylene groups has been suggested to be a necessary criterion for this transition to occur.[33,34] The precise molecular motion related to these secondary transitions is uncertain although several discrete mechanisms have been proposed. Among these mechanisms are the "crankshaft mechanism" involving crankshaft motion[34] of four to eight consecutive methylene units (or lightly substituted methylene units) about two colinear carbon atoms; localized vibrational modes[35] involving the vibration of a small number of consecutive monomer residue units; and loosening of some sort of intermolecular packing or seating.[36]

The temperatures of these secondary transitions follow a pattern similar to that of the glass transition temperature in that, in going from the first to the second member of the series, the transition temperature increases and then decreases in going to the third member of the series. Assuming that all these secondary transitions arise from the same localized molecular mechanism, the occurrence of this effect in the secondary transition indicates that the interlocking is rather extensive in the glassy state. The results presented here seem to provide additional evidence for the concept of dissociation of molecular packing and, from the heavy substitution in these polymers displaying the secondary transition, provide evidence that the crankshaft mechanism is invalid.

One of the polymers shown above, poly(isomer of 3-methyl-1-pentene), displays two secondary transition peaks below the glass transition observed both mechanically and dielectrically. The corresponding member of the first series, poly(isomer of 3-methyl-1-butene), displays two dielectrically observed relaxations below the glass transition temperature.[10] The lower transition in this polymer is not mechanically active. The location of the lower secondary peak correlates with studies of α-methyl group rotation in α-alkyl ester polymers.[37] Based on the latter results, the lower transition could be assigned to motion of the pendent groups on the main chain. It might be presumed that the other polymers investigated also display such an additional secondary transition below the temperature limits of the experimental technique.

CONCLUSIONS

The proposed theory of intermolecular interlocking is based on the premise that molecular flexibility increases along each series. The relationship of transitions to flexibility depends on the fundamental definition of chain

flexibility. The actual submolecular motions responsible for transitions are speculative, and it may well be that different submolecular motions may be responsible for the "same" transition in different polymers. For example, in polyisobutylene, complete rotation of the carbon–carbon bond in the main chain is energetically difficult, and cooperative rotation of separated groups of carbon–carbon bonds in the main chain is even more difficult; therefore, the glass transition in polyisobutylene is likely to arise from motions more restrictive than complete rotation. Similarly, the glass transition phenomena in semiladder polymers which are used at high temperatures must involve torsional oscillations rather than complete segmental rotation.

Different mechanisms for processes would be expected to result in different activation energies. The activation energy reported in Table I for the glass transition of polyisobutylene (22 kcal/mole) is different from those of the next members of the series (48 and 44 kcal/mole, respectively). Similarly the activation energy of poly(2-methyl 1-butene) is lower than that of the second member of the second series.

These results and the discussion point to different molecular mechanisms for the glass transitions of the first members of each series with respect to the other members. Not until the nature of the dispersion phenomena in these most basic series of polymers is understood can we expect to have confidence in explanations of relaxation behavior in the wider field of polymers.

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