0.5–0.9 and r_2 = 0.6–1.1, and those for styrene and *p*-divinylbenzene are r_1 = 0.2–0.7 and r_2 = 1.0–1.2 for incorporation of the first double bond of the divinylbenzene.[29] The divinylbenzene is consumed more rapidly than the styrene, so when polymerization is carried to complete conversion, substantial amounts of long polystyrene chains are formed during the the latter stages. These long chains can account for the near invariance of T_1 over a range of 0–6% cross-linking. The (chloromethyl)styrenes used in our syntheses do not alter the conclusions because sytrene (M_1) and (chloromethyl)styrenes form nearly ideal copolymers, r_1 = 0.72, r_2 = 1.08.[33]

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Molecular Dynamics in Solid Polycarbonate by Proton Magnetic Resonance

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ABSTRACT: The proton magnetic resonance line shape is measured for the solid polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene over a temperature range of −120 to +120 °C by pulse Fourier transform techniques. A detailed second moment analysis, including separation of the intramonomer and interchain contributions, reveals the dynamical details of the polymer behavior below the glass transition. Clear evidence is present for phenylene rotation as the only significant intramolecular motion in the bulk phase. A phenomenological treatment for motional narrowing in solid-state NMR is applied to the data and is indicative of the existence of two overall dynamical processes, one predominant at low temperatures (below −40 °C) and the other at somewhat higher temperatures. The molecular nature and cooperativity of these two thermally activated processes are discussed in relation to their contribution to NMR relaxation. These findings are in overall agreement with and yield insight into previous dynamic mechanical studies on similar systems.

Introduction

The use of proton magnetic resonance (^{1}H NMR) techniques on bulk polymers can yield insight into both structure and molecular dynamics.[1-4] This information can be used to complement direct observation of mechanical properties and in some cases provides a probe at the molecular level for the origin of specific mechanical characteristics. Molecular reorientations occurring at a rate comparable to the ^{1}H NMR line width ($\sim 10^4$ Hz) will cause line narrowing in accordance with the reorientation geometry. The ^{1}H NMR absorption line shape for a solid is dominated by the nuclear dipole–dipole interaction between neighbor and near-neighbor magnetic nuclei. Complete analysis of the absorption line shape in a complex system like a bulk polymer is not feasible, but the problem can be obviated by the measurement and analysis of the second moment of the absorption line shape.[5,6]

In this investigation the ^{1}H NMR second moment is measured for the polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (chloral) shown in Figure 1. The

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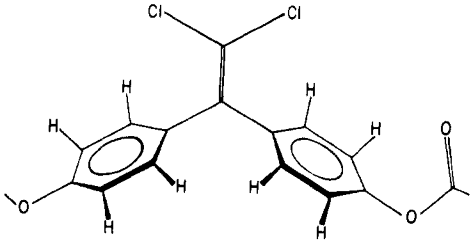

Figure 1. Structure of the repeat unit for the polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (chloral).

study was made over a wide range of temperature below the glass transition point (~164 °C) in order to fully investigate the motions occurring in the bulk phase and, if possible, to correlate this with the mechanical properties. The chloral polymer contains only equivalent phenylene protons and thus the proton NMR line shape reflects very precisely both local and long-range motion of the polymer backbone. This is true not just because of the simplicity of having only one type of proton, but also the orientation of the principal dipolar interaction parallel to the backbone direction makes this polymer an unusually informative candidate for a ^{1}H NMR study. The existence of low-temperature motions in polycarbonates has long been recognized as contributing to the impact resistance of the material,[7] though the specific molecular nature of these motions is not fully understood.

Various possibilities for the nature of these motions have been proposed. Isolated motion of the carbonate group and motion of the phenylene and carbonate units together have been postulated in some systems.[8] Motion of the two phenyl rings with the ethylene linkage as a unit is conceivable,[9,10] as is overall torsional motion of the entire monomer unit. Isolated or concerted phenylene rotation or rotational oscillation represents one of the least restricted motions, and essentially free independent rotation of the phenylene rings about the 1,4 axis has been suggested by Tonelli.[11]

For the first motion mentioned above, it has been noted that the size of the carbonate group is unlikely to account for the mechanical properties. Backbone motions involving part or all of the monomer unit moving in a cooperative manner encompass the familiar "crankshaft" motions proposed by many investigators[12-14] and their effect on the NMR second moment of the rigid solid, concomitant with their onset, can be predicted in many cases. Predictions of the effect of phenylene rotational motions on the NMR second moment are also possible.

In this investigation we attempt to explicitly determine which processes are consistent with the ^{1}H NMR second moment in the bulk polycarbonate chloral below the glass transition and at which temperatures these processes dominate the dynamics.

Experimental Section

The polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene was obtained as an 8-mm-diameter cylindrical plug from Dr. John T. Bendler of the Research and Development Center, General Electric, Schenectady, N.Y. The isotropic samples were prepared by compression molding and dried under vacuum at 90 °C prior to sealing in 10-mm NMR tubes; both annealed and nonannealed samples were prepared. Dilute solutions of 7 and 15 wt % in perdeuteriotetrachloroethane were prepared and subjected to five freeze–pump–thaw cycles before sealing in 10-mm NMR tubes.

The proton absorption line shapes are measured at 90 MHz by using Fourier transform techniques on a Bruker SXP 20-100 NMR spectrometer. The instrument is used under external deuterium lock conditions with quadrature detection and a sweep width of 50 kHz. A $\pi/2$ pulse of 1–2 μs was typical. Such a pulse is more than sufficient to cover a 50-kHz region but the digitization rate associated with a 50-kHz sweep was just sufficient for the broadest lines encountered at low temperatures. The temperature is controlled to ±1 °C with a Bruker B-ST 100/100 thermoregulator calibrated with the usual chemical standards and a thermocouple. Boiling liquid nitrogen is used as the coolant gas and approximately 30 min is allowed for temperature equilibration. Measurements made at a separate frequency (30 MHz) show similar trends with little absolute difference in second moment. Second moments derived from the spectra reflect an average of up to five separate determinations and are determined by numerical integration (using the Simpson rule) of the absorption line shape. The accuracy of the second moments is limited by the digitizing rate and, as pointed out above, for the broadest lines at low temperatures (<200 K) the uncertainty in the second moment could be greater than the precision estimate of ±0.1 G^2. This, however, would have little effect on the basic conclusions presented below.

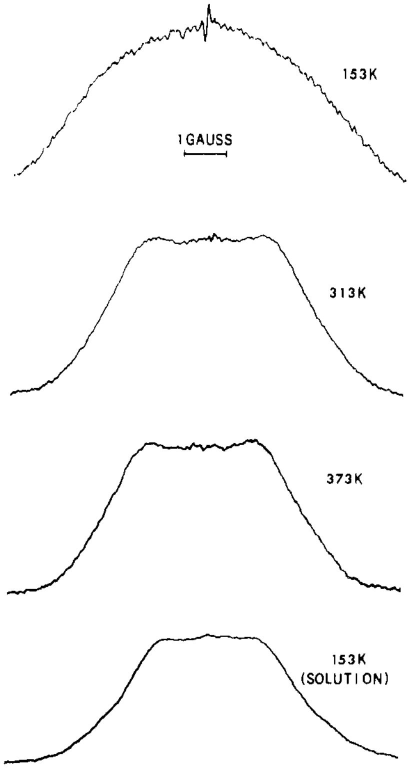

Figure 2. Proton resonance absorption spectra for the polycarbonate chloral at 90 MHz as a function of temperature for the bulk polymer and the frozen solution in $C_2D_2Cl_4$.

Results

Typical spectra from solid chloral and the frozen solution in $C_2D_2Cl_4$ are shown in Figure 2 and the values of the second moment of the line shape as a function of temperature in the range 150–400 K are presented in Figure 3. The spectra of the bulk polymer show a broad, almost Gaussian, line shape at low temperatures, corresponding to the rigid polymer. Line narrowing due to the onset of the motion occurs initially at 200 K followed by the gradual appearance of the classic Pake doublet[15] at 260 K. The doublet persists independent of motional narrowing and is also evident in the frozen-solution spectra at 153 K. The data show approximately a 35% decrease in second moment from the rigid solid value of 4.6 G^2 over the temperature range of 250 K due to motional narrowing. The decrease consists of an initial rapid decrease in the range 200–230 K followed by a more gradual decrease up to 400 K. This two-stage behavior has been observed by

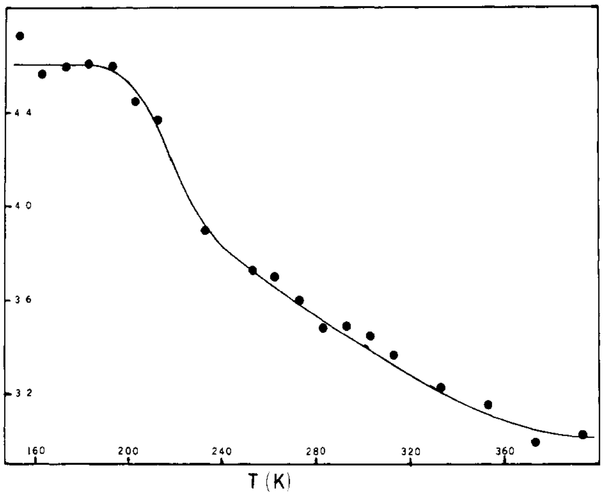

Figure 3. NMR second moment (S) vs. temperature. Moments are determined for the bulk polymer chloral from the proton absorption line shape at 90 MHz.

other investigators[2,4] and has been interpreted as indicative of the onset of two motional processes in the solid. Measurements on three different preparations of the solid, both annealed and nonannealed, show only small differences in overall line shape behavior.

The doublet splitting of 2.5 ± 0.2 G measured in the region above 300 K is constant and reflects the interaction between two adjacent protons separated by 2.6 ± 0.1 Å.[15] The assignment of this interaction to the 2,3-phenylene protons is unequivocal. Conventional bond distances assign a separation of 2.5 Å to these protons. No other proton–proton separation of this order is present in the monomer and interchain interactions are ruled out by the appearance of the doublet in the frozen solutions, where intermolecular interactions are reduced considerably. The doublet splitting in the frozen solution may be slightly narrower than in the glass though the two values are within experimental error. The frozen-solution signal is weaker and of somewhat different shape, which also complicates comparisons. The persistence of the 2.5-G splitting independent of motional narrowing implies that the dynamical processes occurring must be such that they do not significantly affect dipole–dipole interactions parallel to the 1,4-phenylene axis (the 2,3-phenylene proton vector) in the polymer backbone. Further consideration will show that this places severe restrictions on the type of motions we may consider to be present in the bulk polycarbonate chloral. In order to interpret the effect of motional narrowing further we must now theoretically consider the second moment of chloral and the effect of molecular motion upon the second moment.

Interpretation

The Van Vleck theoretical second moment of the NMR absorption corresponding to a rigid lattice (i.e., in the absence of any NMR-active molecular motion) can be written[5]

$$S = \frac{3}{2}I(I+1)g_n^2\beta_n^2\frac{1}{n}\sum_{j>k}[(3\cos^2\theta_{jk}-1)r_{jk}^{-3}]^2 \qquad (1)$$

where I is the nuclear spin quantum number, g_n the nuclear g factor, β_n the nuclear magneton, n the total number of interacting nuclei, r_{jk} the length of the vector joining nuclei j and k, and θ_{jk} the angle between the vector r_{jk} and the external magnetic field. If nonresonant magnetic nuclei are present in the sample a term

$$S = \frac{1}{3}g'^2_n\beta_n^2I'(I'+1)\frac{1}{n}\sum_{j>k'}[(3\cos^2\theta_{jk'}-1)r_{jk'}^{-3}]^2 \qquad (2)$$

can be added to eq 1 to take these interactions into account. For an isotropic sample, expression 1 must be spherically averaged for all θ_{jk} and leads to the expression

$$S = \frac{6}{5}I(I+1)g_n^2\beta_n^2\frac{1}{n}\sum_{j>k}r_{jk}^{-6} \qquad (3)$$

Contributions from interacting nuclei more than 5 Å apart are normally neglected in any calculation using these equations. If motion takes place, a reduction in the second moment is observed when the frequency associated with the motion exceeds the width of the resonance measured in frequency units. To take this into account we must first average eq 1, i.e., ($3\cos^2\theta_{jk} - 1$), over the motion to obtain the second moment for a given crystal orientation. Then we must spherically average to obtain S for the isotropic sample. For rotational motions about a fixed axis the net result for the isotropic second moment is[6]

$$S = S^{\mathrm{RL}}\left(\frac{3\cos^2\gamma_{jk}-1}{2}\right)^2 \qquad (4)$$

where S^{RL} is the rigid lattice second moment and γ_{jk} is the angle between the internuclear vector r_{jk} and the axis about which rotation takes place. Equation 4 is valid for an n-fold rotation as well as the classic free rotation. The effect of an incomplete rotation or rotational oscillation can also be predicted[16] and shows a partial reduction in S compared to that corresponding to the full rotation. Calculations of the influence of more complex types of motion on the second moment have also been attempted.[1,3,16]

The equations presented in the preceding section allow us to estimate the value of the second moment in chloral. Using conventional bond lengths we first estimate contribution from the monomer. For an isotropic sample the phenylene group rigid second moment is 1.65 G^2 from eq 3, dominated by the 2,3 interaction with the cross ring contribution being approximately 10%. The interphenyl contribution within a repeat unit, assuming a symmetric disposition of the phenylene rings with their planes perpendicular to the carbonate group and the Cl–C–Cl plane,[17] is estimated at 0.49 G^2, corresponding to an interproton distance of 3.0 Å. This yields a second moment for the monomer consisting of eight protons of $^1/_8[8 \times 1.65 + 4 \times 0.49] = 1.9$ G^2. The only other intramonomer contribution feasible is from the chlorines interacting with the neighboring ring protons. Even with the assumption of a minimum separation consistent with the van der Waals radii of 3 Å, eq 2 predicts a negligible contribution, less than 1%, to the second moment. The use of eq 2 does assume a quadrupolar coupling smaller than the Zeeman interaction and for a simple C–Cl bond this is expected. Also, a full analysis performed previously on this type of effect indicates that the error in using the Van Vleck formulation is normally at most a factor of 2.[22]

The difference between the monomer value of 1.9 G^2 and the experimental rigid solid value of 4.6 G^2 is due to interchain contributions to S. It is not possible in the absence of a crystal structure or a detailed knowledge of the stacking configuration in the bulk polymer to separately predict from theory the interchain contribution. However, the value of 2.7 G^2 assigned here compares favorably with that estimated by Davenport and Manuel[4] (2.8 G^2) in a similar polycarbonate where some crystal structure information did exist.

The decrease in the second moment with temperature due to the effect of motional averaging will now be considered. As mentioned previously, the persistence of a doublet of separation 2.5 G due to the 2,3-phenylene proton interaction implies that interactions along this vector are not significantly motionally averaged. For rotational motion, either full or oscillatory, this means that in eq 4, $S = S^{\mathrm{RL}}$, i.e., $\gamma_{jk} = 0$, and all rotatory motions must take place along the 1,4 axis of the phenylene ring. This limits such motions to solely phenylene rotations either concerted or isolated. The effect of phenylene rotation on the intramonomer second moment will be to average only the cross ring interactions (which are only 10% of the intramonomer second moment) and the interphenylene interaction (which will be reduced by a factor of 0.39, corresponding to $\gamma_{jk} = 30°$), leaving the main contribution of the 2,3 protons unaltered and a resulting intramonomer second moment of 1.7 G^2. The effect of phenylene rotation on the interchain contribution will be large. Interchain interactions are expected to have a proton dipole–dipole interaction vector inclined at approximately 90° to the 1,4-phenylene axis, leading to reduction in the second moment by 0.25 of the rigid lattice value. This would decrease the value of 2.7 G^2 assigned to the interchain contribution to 0.8 G^2. This value is an estimate since the exact inclination of the interchain proton–proton vector is not known; but even if an assignment of 90° relative to the 1,4 axis is within 30%, the value will not be appreciably affected. The phenyl reorientation also modulates the interchain proton–proton separation, reducing the second moment still further. Since the interchain distance is unknown, however, this cannot easily be estimated and thus the narrowed value of 0.8 G^2 should be considered as an upper estimate. These conditions lead to a motionally narrowed value of 2.5 G^2 for the second moment under the influence of phenylene rotation. In view of the uncertainties in estimating the interchain contribution this is in reasonable agreement with the experimental data in Figure 3.

Any other rotatory type of motion, such as crankshaft motions or motion of the phenylene–ethylenic unit as a group, would involve a γ_{jk} relative to the 2,3-proton vector of approximately 60 or 120° and would reduce the second moment by a factor of the order of $^1/_{64}$, leading to an extremely narrow line and a large decrease in the doublet separation. The absence of any such observation eliminates the possibility of large or even moderate amplitude motions of this type occurring in the solid polymer.

To investigate the possibility of any other type of motion, presumably nonoscillatory in character but still limited by the restriction concerning little reorientation of the 1,4 axis, we have used a phenomenological equation for motional narrowing in solids (recently developed by Hendrickson and Bray).[18] The motional narrowing is given by

$$\ln\left(\frac{1}{W} - \frac{1}{A}\right) = -\frac{E_a}{kT} + \ln\left(\frac{1}{B} - \frac{1}{A}\right) \qquad (5)$$

where W is the line width at temperature T, A is the line width at low temperatures corresponding to the rigid lattice, and B is the high-temperature line width corresponding to the thermally activated state. A plot of eq 5 normally reveals the existence of different relaxation mechanisms corresponding to distinct dynamical processes. Our data are shown, plotted according to eq 5, in Figure 4 except that we are using the square roots of the second moment instead of line widths in the interest of precision. The data show the existence of two distinct linear regions above and below 233 K. The activation energies corresponding to these regions are 5 and 1 kcal/mol for the low- and high-temperature region, respectively. Similar observations have been made by Manuel and Davenport,[4] though their observations on bisphenol-A are dominated by methyl group rotation and hence not as reflective of backbone motion. The numerical values must be treated with caution in view of the assumptions of the theory. However, these low values compare favorably with predictions by Tonelli[11] for phenylene rotation. The plot suggests the existence of two dynamical processes occurring in the bulk polymer, one of which is activated at low temperature (190 K) and the other at a somewhat higher temperature (above 233 K). Our previous considerations suggest that the low-temperature process is phenylene rotation as it is responsible for the majority of the motional narrowing. The high-temperature process has a much smaller effect on line narrowing and is presumably intermolecular in nature. Since it cannot affect the 2,3-proton interaction, some form of chain-sliding[3] or volume-fluctuation process is a possible candidate. This process may be cooperative with the establishment of phenylene rotation but its exact nature cannot be ascertained from our data. However, the dominant intramolecular dynamical process occurring in the bulk polymer is phenylene rotation. It is also evident that the process of annealing has little effect on the dynamical properties observed here for the solid polymer below the glass transition.

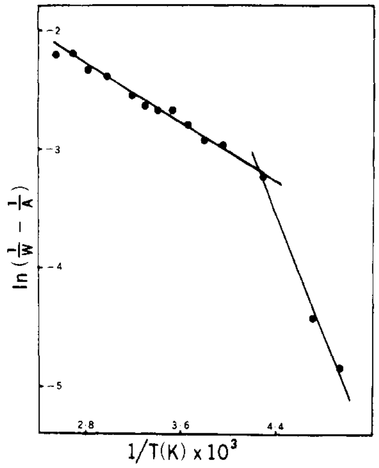

Figure 4. Semilogarithmic plot of $(1/W - 1/A)$ against $1/T$ (K). $W = (S)^{1/2}$ at temperature T, $A = (S^{\mathrm{RL}})^{1/2}$ at low temperature, and S is the second moment in G^2.

Conclusion

In this favorable case, a ^{1}H NMR line shape study was able to clarify the nature of motions in a polymeric glass. Though there is considerable change in the line width and shape as temperature changes from −120 to +120 °C, the undiminished persistence of the Pake doublet at high temperatures provides definitive evidence for the geometry of reorientation. Specifically, this has led to the elimination of any motion which has a significant component perpendicular to the 1,4-phenylene axis, leaving simple phenylene group rotation or oscillation as the only obvious candidate. However, since a more detailed analysis of the line shape indicates the presence of two motions, a second, less obvious candidate must be contrived. An intermolecular motion of unspecified character is a possibility which is at least consistent with the data. The presence of two or more overlapping relaxations in the low-temperature region has been raised before since the relaxation peak often appears broad and asymmetric;[8,19,20] the main contribution of this study is to confirm the presence of two motions while limiting the type of reorientations which may be proposed.

In attempting to understand a property like impact resistance, the prospect of two overlapping low-temperature motions is important. It might be difficult to account for impact resistance solely on the basis of local, isolated phenylene group rotation over a relatively low intramolecular barrier,[21] but an associated intermolecular process with a potentially longer range character provides a more plausible ingredient. The second, long-range motion may depend on the presence of rapid phenylene group rotation or oscillation, thus linking impact resistance to phenylene group motion as has been proposed.

Questions as yet unanswered are the precise extent of phenylene group rotation or oscillation and the exact nature of the second process. The amount of narrowing of the ^{1}H NMR line tends to indicate fairly large amplitude oscillation if not rotation but another approach will be required to quantify this statement. This is because the dominant dipolar interaction in the present case is not affected by the principal motion, and so a precise probe of the extent of motion is lacking. The development of a detailed model of the intermolecular process seems difficult. The best approach including ^{1}H NMR line shape analysis would be to characterize the intramolecular motional contributions to narrowing as precisely as possible to separate out the effects of the intermolecular process for analysis.

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Rates of Conformational Transitions in Branched Chain Molecules

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ABSTRACT: A recently developed theory of the kinetics of conformational transitions based on a multidimensional extension of Kramers' rate theory is applied to branched polyethylene-like molecules. In particular, the influence of branching on the mechanism and rates of the trans → gauche transition is investigated. As in linear molecules, the reaction coordinate is a localized mode. Thus, the presence of an attached side chain introduces conformational rigidity into one of the tails connected to the transforming rotational angle, and the localized mode behaves akin to related linear molecules. In general, it is found that branches somewhat reduce the transition rate relative to the linear molecule; nevertheless the effect is fairly minor. Therefore, it is concluded that the time scale of conformational transitions in branched and linear chains is the same.

I. Introduction

The nature of local motions in polymers has been the object of considerable recent attention. Experiments have been designed to probe such molecular weight independent processes,[1–5] and computer simulations have given insight into kinetic properties of small-scale rearrangements in polymers.[6–10] These simulations provide a proving ground for various theoretical models of polymer dynamics, such as those of Fixman,[9] Fixman and Evans,[11] and Adler and Freed.[12] The mechanism of small-scale motions in linear chain molecules has been recently addressed.[13] We focus here on properties of a specific class of local motions (conformational transitions from one rotational isomeric state to another) in simple chains containing branches.

The approach used has its origin in a recent study[13] in which a multidimensional version of Kramers' reaction rate theory was formulated and applied to conformational transitions in linear molecules. Based on evidence extracted from experiment and computer simulations, the theory adopted the viewpoint that conformational changes occur via single, independent transition events. The method provided the capability of predicting the dependence of the transition rate, k, on chain geometry, size, solvent viscosity, and activation energy. The reaction coordinate in the vicinity of the barrier to conformational transitions (a saddle point in the multidimensional position phase

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