by jump diffusion or Brownian diffusion and a distribution of amplitudes may be present. The ability to distinguish these subtle differences from the NMR data is uncertain.

NMR spectroscopy has clearly identified the diluent as a mobile species in the ternary system of interest. It is our proposal that the mechanical loss peak arises from the liquidlike motion of the diluent, a conclusion that reinforces the results of a survey of mechanical properties of a large number of plasticized PPE/PS blends.[2] Further quantitative work will be carried out to link the collapse of the NMR line shape to the breadth and temperature of the mechanical loss peak as has been done in an earlier study[1] of polymer motion in glasses.

With this proposal in mind, two distinct mechanisms of plasticization can be imagined. First, a diluent may expedite a local motion of the polymer and thereby lower the modulus of the glass. Second, the diluent itself may undergo local motion, changing the modulus of the glass. Of course both or neither of these mechanisms may be operative when a diluent is added to a glassy polymer. In addition we have not yet introduced modes for antiplasticization behavior. However, a focus on identifying local motions via solid-state NMR and relating these motions to bulk mechanical behavior is a powerful approach for understanding plasticization and antiplasticization.

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Registry No. PS, 9003-53-6; PPE (SRU), 24938-67-8; PPE (homopolymer), 25134-01-4; trioctyl phosphate, 78-42-2.

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Heterogeneous Microscopic Mobility near the Glass Transition from NMR Line Shapes

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ABSTRACT: At or below the glass transition, a Pake doublet is observed for polycarbonates containing only phenylene protons. The Pake doublet arises from the dipole–dipole interaction between adjacent protons on the phenylene ring, and this interaction is essentially unaveraged by sub-glass transition motions since it is parallel to the virtual bonds of the chain backbone. As the glass transition is traversed, the line shape becomes bimodal with the Pake doublet still present plus a Lorentzian line superimposed in the middle of the doublet. The Lorentzian line is approximately 10 times narrower than the Pake component just above T_g, indicative of much more mobile phenylene groups. The fraction of narrow component grows from 2% just above T_g to 17% at 50 °C above T_g. The population of the narrow component can be modeled on the basis of free volume theory or defect concentration. An alternative view is provided by considering the glass transition to be highly spatially heterogeneous with a correspondingly broad distribution of correlation times.

In amorphous polymers just above the glass transition, there is a considerable range in the amplitude of motion at the level of the repeat unit.[1–7] To a first approximation, the mobility just above the glass transition can be divided into two classes: more mobile and less mobile. This categorization has been based on observations of NMR line shapes where commonly a narrow component is seen to be superimposed on a broad component. Both the narrow and broad components arise from amorphous material, although crystalline material can contribute to the latter if the polymer is semicrystalline. The less mobile amorphous line shape is typical of that seen in a fairly rigid solid and is much like the line shape observed below the glass transition. As the temperature is raised above the

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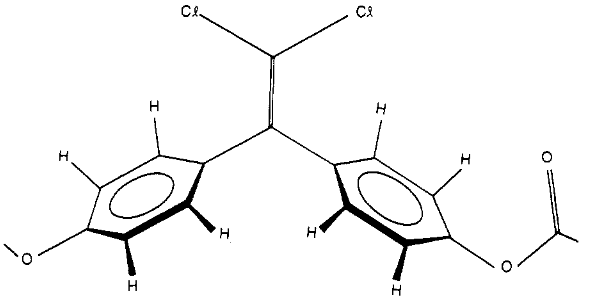

Figure 1. Structure of the repeat unit for Chloral polycarbonate (1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene).

glass transition, the portion of amorphous material which is more mobile increases at the expense of the portion which is less mobile.

In this paper, proton line shapes are reported for the completely amorphous polycarbonate shown in Figure 1. Molecular motion below the glass transition has been well-studied by NMR and other techniques in this and related polycarbonates.[6-16] These polymers are found to be very mobile below the glass transition with strong mechanical and dielectric loss peaks.[17,18] The predominant intramolecular motion identified in polycarbonates is π flips of the phenylene groups though more complex motional descriptions incorporating this feature have also been presented.[16,20]

As a highly mobile completely amorphous polymer, this polycarbonate contrasts with the semicrystalline polymers already studied by proton NMR.[4,5] In deuterium line-shape studies, Spiess[6,7] noted that the line narrowing occurred over a smaller temperature interval in amorphous polystyrene than in semicrystalline polyethylene. This difference was attributed to the presence of crystalline regions which restricted the motion in the amorphous regions of the semicrystalline polymer. This explanation requires that the constraints imposed by the crystalline regions upon the chain segments in the amorphous regions exist over a fairly large length scale as compared to many motional models which involve only a few bonds. Furthermore, additional evidence for the large length scale ($\geq$50 Å) over which topological constraints are effective is available from studies of the effects of entanglements on the spatial anisotropy of motion in polymer melts at temperatures over 100 °C above their glass transition temperature.[21]

One other feature of this polymer makes it attractive for study. The proton line shape at the glass transition is dominated by the dipolar interaction between adjacent protons on each phenylene group.[8] This interaction is parallel to the virtual bond, the phenylene group, which composes a large part of the chain backbone. If the glass transition is associated with reorientation of the units in the chain backbone, then this dipolar interaction is an excellent probe to monitor backbone flexibility. It is also relevant to note that librational motion about the twofold axis of the phenylene group will not average the dipolar interaction. Only libration or reorientation about axes inclined to the twofold axis will produce narrowing of the Pake doublet.

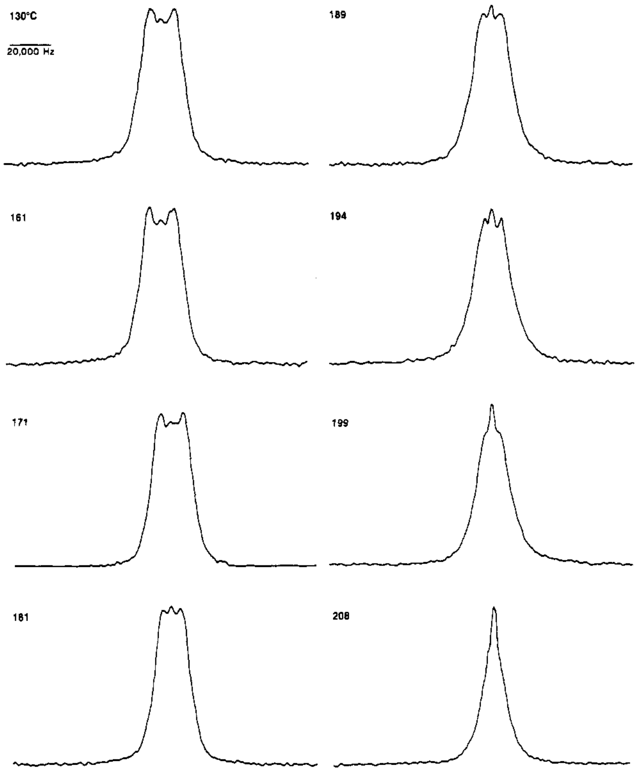

Figure 2. ^{1}H spectra for Chloral PC as a function of temperature.

The presence of a narrowed component coexisting with the broad component raises questions about polymeric glasses and the glass transition. What is the source of this superficially bimodal behavior at the molecular level? Are intermolecular constraints being released as temperature is raised but in only some regions or domains of the sample? For polymer scientists this line of thought is often couched in free volume arguments and distributions of free volume.[1-5] Another phrase that has been used to describe the phenomena leading to the presence of a narrow line is "islands of mobility".[19] Are intramolecular conformational defects[22] the source of the islands of mobility in the sample rather than a distribution of free volume or are both factors contributing? Do the more mobile and less mobile regions interchange with time at a given temperature? What are the size and lifetimes of the two regions? These questions are not answered in this report, but a quantitative determination of the less mobile and more mobile populations is presented for a completely amorphous polymer along with three expressions relating the populations to temperature. The relative breadths of the narrow and broad components imply certain motional characteristics and suggest further experiments to pursue the questions just raised.

Experimental Section and Results

A sample of the polycarbonate shown in Figure 1 was supplied by General Electric Research and Development. The sample was dried at 120 °C for 2 days in a vacuum oven and then sealed under vacuum in a 10-mm NMR tube. Proton spectra were taken at a frequency of 90 MHz on a Bruker SXP 20/100. The $\pi/2$ pulse was between 2 and 3 μs, and a dwell time of 7 μs was employed. Relative intensities of the two components comprising the observed line shape have been corrected both for finite pulse widths and receiver blanking (14.0 μs). The correlation was effected by taking theoretical line shapes based on the broad and narrow component and their populations and carrying out a numerical, discrete inverse Fourier transform to generate the time domain spectrum. The appropriate amount of early time response in accordance with the blanking was deleted and the resultant time domain signal Fourier transformed to yield a frequency spectrum which was then compared with the experimental line shapes for fitting. All operations were done corresponding to quadrature detection. Temperature control was maintained to within 2 deg with a Bruker BST 100/700 temperature controller which was calibrated against a thermocouple.

Figure 2 shows the proton spectra for this polycarbonate from the glass transition temperature (DSC) of 157 °C up to about 210 °C.

Table I

temp (°C)	fractn of broad component	Pake splitting (G)	Gaussian broadening for broad component (Hz)	Lorentzian broadening for narrow component part (Hz)
161	0.981	2.684	6300	3200
166	0.970	2.600	6200	3200
171	0.966	2.515	5900	3200
177	0.955	2.410	5800	3200
181	0.945	2.240	5500	3100
186	0.927	1.902	4800	2800
194	0.892	1.395	4400	2300
199	0.874	0.930	4300	1900
204	0.850	0.634	4100	1400
208	0.834	0.423	3400	1000

Interpretation

From 160 to over 200 °C the polycarbonate spectra are obviously bimodal with both narrow and broad components. Above 200 °C, the narrow component becomes so dominant that it is difficult to see the broader components though careful inspection still indicates its presence. Just above T_g, the width of the broad component is about 20 kHz while the narrow component is almost 10 times narrower. This aspect leads to the strongly bimodal appearance of the lines, and the very narrow component must represent repeat units that are undergoing nearly isotropic motion. On the other hand, the broad component just above T_g is essentially the same width as just below the glass transition which indicates very little reorientation save π flips of the phenylene groups of the chain backbone.

To quantitatively characterize the spectra, the line shapes will be represented as the sum of two components: a broadened Pake doublet and a narrow Lorentzian both centered at the same position. The broadened Pake doublet is much like the line shape observed below the glass transition and is thought to arise from the dipolar interaction of adjacent pairs of phenylene protons plus a general broadening from interchain proton–proton interactions.[8] The interchain interactions are quite well-averaged by the π-flip process which occurs rapidly with respect to the frequency of dipolar interactions at these temperatures. The narrow Lorentzian component is much like the line shape for a polymer melt well above the glass transition where motion is nearly isotropic but slower than in a small molecule liquid. Simulating the observed line shapes with only these two components is a first approximation, but the line shapes can be rather well reproduced by the recipe just discussed as can be noted from Figure 3.

Four parameters go into the line-shape simulations. The first is the Pake doublet splitting which equals $3\gamma h/2r^3$ where r is the proton–proton internuclear distance corresponding to the separation of adjacent protons in the phenylene group. The second parameter is the Gaussian broadening of the Pake doublet arising from interchain proton–proton interactions, and this is reported as full width at half-height. The third parameter is the Lorentzian width of the narrow component, and the last parameter is the fractional population corresponding to the broad component. Values of these parameters are listed in Table I as a function of temperature.

Discussion

The simulations of the observed line shapes shown in Figure 2 closely approximate the observed line shapes although the arbitrary division into a broad and a narrow line is a fairly drastic assumption. Also it is a fairly severe assumption to describe the broad component as a Pake doublet. At or below the glass transition, this component is truly a Pake doublet since the phenylene groups are not reorientating except for π flips about the twofold axis which does not average the predominant dipolar interaction leading to the Pake doublet. Above the glass transition the apparent Pake splitting diminishes as temperature is raised. An unspecified motion is now averaging the dipolar interaction, and as this averaging becomes significant, the line shape is unlikely to be a Pake doublet. A variety of line shapes can evolve from motional averaging of the dipolar interaction depending on the geometry, rate, and amplitude of the motion and the potential existence of a distribution of immobile regimes having slightly differing geometry, rates, and amplitudes. Modeling the broad component of the line shape as a Pake doublet is not completely accurate but is a sufficiently good approximation to allow an estimation of the fractional populations of the two components. However, one must not take the values of the Pake splitting above the glass transition literally although they do serve as a relative measure of the breadth of the broad component. The value of the Pake splitting at the glass transition corresponds to a distance of 2.5 Å which is comparable to other determinations of the phenylene proton separation.[23-25]

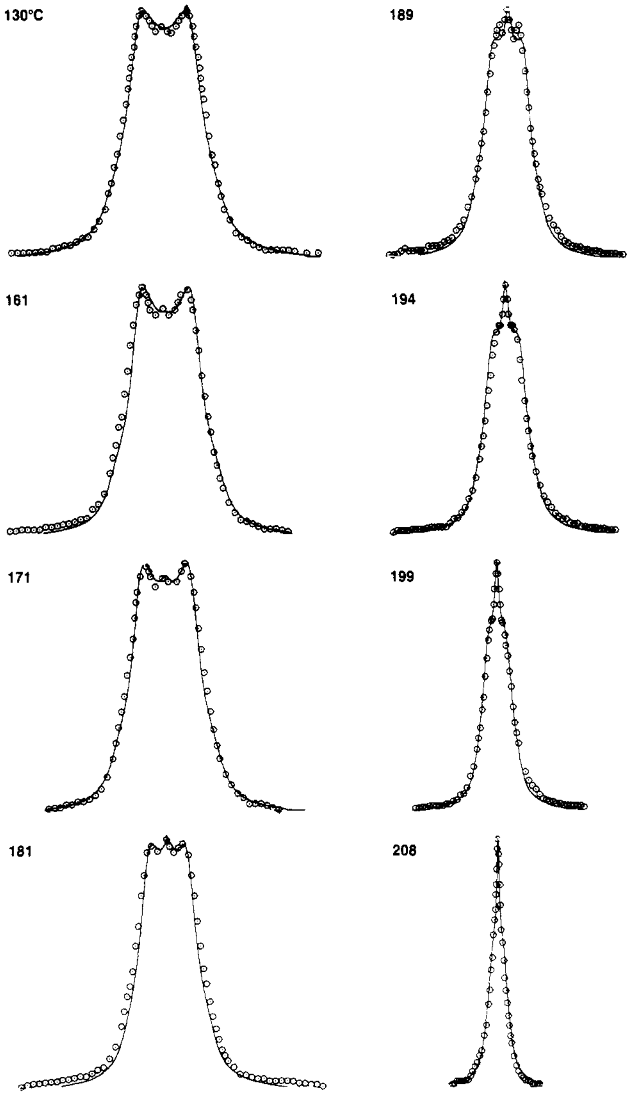

Figure 3. ^1H spectra for Chloral PC with theoretical fits (○) corresponding to the bimodal treatment in text.

Since the Pake line shape is not to be taken literally above the glass transition, the broadening of the Pake form should also not be taken as anything but a relative measure. On the other hand, the Lorentzian line representing the narrow component is a plausible form for a line shape of a mobile component above the glass transition and may therefore yield a more meaningful number. The fractional population of broad and narrow component are reliable numbers since the line shapes are well-simulated and this conclusion does not rest upon the Pake form being a meaningful representation of the broad component. The narrow component appears to be present at the glass transition, and the associated population grows with temperature. It may also be present below the glass transition, but it is at a level of 1% or less and is so close to experimental error that it cannot be definitively identified. Also a very low intensity mobile peak could arise from water, residual monomer, or chain ends and not be a mobile fraction of repeat units. The rapid increase in the mobile component just above the glass transition from 1% to 20% indicates the presence of mobile material in excess of sorbed water, residual monomer, and chain ends.

The parameter of principal interest in this report is the relative population of the more mobile component and changes in this population with temperature. Simple free volume theory leads to the Vogel–Tamman–Fulcher (VTF) form which has had some success in describing the population of the more mobile component above the glass transition in semicrystalline polymers. If the fraction of more mobile material is δ, then the temperature dependence may be written as

$$\delta = \delta_0 \exp\{-[\gamma V_{\mathrm{fkr}}/(\alpha V_{\mathrm{m}}(T - T_0))]\} \qquad (1)$$

if a polymer is completely amorphous, δ_0 equals 1 which is appropriate for the case at hand. The critical value for the free volume above which the polymer would be so mobile as to appear in the mobile component is V_{fkr}. The compressibility is α as usual, the volume per segment is V_{m}, the temperature at which the mobile component is first present is T_0, and γ is an adjustable parameter. Since most of these quantities are not known, the equation can be simplified to a two parameter fit

$$\delta = \exp(-B'/(T - T_0')) \qquad (2)$$

where B' and T_0' are the adjustable parameters. This approach yields a good description of the temperature dependence of the populations with the values $B' = 152.6$ and $T_0' = 125$ °C.

A slightly modified form of the VTF function has been derived by Bendler and Shlesinger[22] from a consideration of the free energy barriers impeding defect motion. In this context, δ is now the concentration of defects and the functional dependence on temperature is

$$\delta = \exp(-B/(T - T_0)^{3/2}) \qquad (3)$$

and fitting to this form yields $B = 2.13 \times 10^3$ and $T_0 = 97$ °C. The quality of these two fits is comparable and acceptable.

An alternative formulation to the simple VTF form has been found to be superior in determining the fraction of crystalline material in partially crystalline polymers.[4,5] A formalism for extracting the pressure and temperature dependence of the "excess" free volume has been presented by Simha and Somcynsky[26,27] using an equation of state analysis of pressure, volume, and temperature data. Such an analysis of the thermophysical data obtained for the polycarbonate of Figure 1 yields the reducing parameters of $P^* = 1266.2$ MPa, $T^* = 10830$ K, and $V^* = 0.6806$ cm^3/g. These parameters can then be used to calculate the excess free volume $\Psi = (1 - y)$.[26,27] Following the approach of English and Zoller,[4,5] we assume that there exists some value of Ψ below which δ is zero and above which δ will increase to a plateau value of δ_0 which would likely be one in this amorphous system. The mathematical form that has been[4,5] most useful is

$$\delta(T) = \delta_0(1 - \exp\{-[(\Psi(T) - \Psi(T_0))/\Psi(T_0)]\}) \qquad (4)$$

In this formulation, the parameters δ_0 and T_0 are determined by fitting the experimentally determined values of δ and the calculated values of Ψ according to eq 4. The fitting yields a value near 1 for δ_0 (0.93) as would be expected and a value of $T_0 = 165$ °C ($\Psi(T_0) = 0.126$). This value of T_0 may be compared to $T_{\mathrm{g}} = 158$ °C as determined by DSC or the value of 157 °C as determined from dynamical mechanical data.

For the semicrystalline polymers studied, T_0 is 40–80 deg above the glass transition.[4,5] This completely amorphous polymer is therefore quite different from the partially crystalline systems. The estimates of T_0 from the VTF form and the Bendler–Shlesinger form are even lower. This seems to imply the presence of mobile material near the glass transition or even below the glass transition. Polycarbonate does have a high degree of mobility as a glassy polymer, but the main motions are quite restricted geometrically and fall well short of the nearly isotropic motion associated with the narrow component of the line shape above the glass transition. The VTF form and Bendler–Shlesinger form suggest the presence of small amounts of more mobile material below the glass transition, which would be associated with nearly isotropic motional freedom. Are these chain ends, small molecule impurities or more interestingly are they free volume or conformational defects? The examination of more amorphous systems would seem worth while in this regard. In deuterium line-shape studies, Spiess[6,7] noted that mobility grew in much more rapidly in amorphous polystyrene than in partially crystalline polyethylene. This was ascribed to the restrictions on motion of chain segments in the amorphous regions introduced by parts of the chain molecules being locked into crystallites. However, the motions discussed in this report and many others focus on rearrangements involving only a few bonds (3–7 bond units),[6,7] and it is hard to see how the crystallites could influence such rearrangements in portions of the amorphous chain removed from the crystallites by several bonds. Comparisons between forms of a polymer which can be prepared both as a semicrystalline and completely amorphous material would help address this question. In Spiess' study of amorphous atactic polystyrene, the line narrowing appeared not to involve a shift in population between a narrow line and a broad line but rather appeared to involve narrowing by a single process.[6,7] This distinction between polycarbonate and polystyrene is worth noting with a view to further consideration.

The T_0 determined from the temperature dependence of the mobile fraction using the English and Zoller formulation is 9 deg above the T_{g} determined by DSC or dynamic mechanical response[19] at 1 Hz. If this T_0 is viewed as a measure of T_{g}, the temperature difference is reasonably associated with the frequency difference of the experiments. The proton line-shape experiment is associated with frequencies near 10 kHz since the line width is about 20 kHz. No single frequency is associated with the process of line-shape collapse so an exact consideration of the shift of the glass transition cannot be made. Matsuoka[28] has measured the apparent shift of the glass transition of the polycarbonate of bisphenol-A at various frequencies in a dielectric experiment and his results are consistent with the temperature shift observed here. It is relevant to comment here that in terms of the treatment of the data using the three formulations (eq 2–4), all three treatments can fit the data well and with similar quality. It is therefore not possible to assess the relative validity of the three treatments with respect to the present work. The meaning of T_0 is different for the different treatments. In the VTF and Bendler/Shlesinger treatments T_0 can be viewed as the point at which microscopic motion is first initiated in the glass whereas in the English/Zoller approach it refers to the temperature at which the excess free volume has decreased to a point such that the mobile fraction is no longer experimentally measurable.

A summary of the results at this stage indicate other future experiments. In the completely amorphous polycarbonate considered here, more mobile and less mobile fractions coexist over a significant range of temperatures above the glass transition. The more mobile component appears to be undergoing almost isotropic motion while the less mobile component hardly differs from the restricted motion present below the glass transition. The more mobile component grows in rapidly especially in comparison to semicrystalline polymer since it begins to appear at temperatures just above the glass transition. The growth of the more mobile component with temperature can be numerically described by two functions based on free volume considerations and one other closely related form based on barrier heights for defect motion. The bimodal character of the mobility and the line shape is a distinctive feature of this polycarbonate and differs from the character of line-shape collapse at the glass transition observed in amorphous polystyrene.[6,7] The observed bimodality of the NMR line shapes is indicative of the *heterogeneity of environments which exist above the glass transition temperature* in this completely amorphous polymer. This bimodal character is clearly evident at temperatures above 200 °C (Figure 2) which is well above the glass transition region even allowing for apparent shifts due to an increase in the effective frequency of measurement.[28] This observation is not inconsistent with continuous distributions of the rates and/or amplitudes of motion. The continuous distributions would appear as bimodal if some portion of the distribution were either in the slow exchange and/or restricted amplitude regime, another portion was in fast exchange with large amplitude, and a negligible portion was at an intermediate exchange rate with a significant amplitude of motion.

The size of the more mobile and less mobile regions could be probed by proton spin diffusion experiments following the pioneering report of Assink on polyurethane microphases.[29] The rate of transfer of spin energy between two populations, the more mobile and the less mobile, can be measured in a Goldman–Shen experiment.[30] This information can be used to determine a diffusion path length which can be identified with an interdomain spacing. In an amorphous sample above the glass transition, diffraction or scattering experiments are not readily applicable and spin diffusion experiments may be the best method for studying the spacing between the two populations.

Differences in the rate and amplitude of the motions present in the two populations can be better assessed from additional line shape and relaxation studies involving either carbon-13 or deuterium. Spin diffusion is less prevalent with these nuclei, and specific geometric information is readily available from the pattern of line shape collapse.[6,7,9–12]

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Registry No. (Carbonic acid)(4,4′-dichloroethenylidenebisphenol) (copolymer), 29057-43-0; (carbonic acid)(4,4′-dichloroethenylidenebisphenol) (SRU), 31546-39-1.

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