An NMR Study of Plasticization and Antiplasticization of a Polymeric Glass

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ABSTRACT: Films of glassy polycarbonate (BPA-PC) containing relatively low concentration of the diluent di-*n*-butyl phthalate were studied in two series of NMR experiments. In the first series proton $T_{1\rho}$ measurements were made on polycarbonate with deuterated methyl groups containing perdeuterated diluent up to a concentration of 25 wt %. Under these circumstances the proton relaxation times monitor the π flips of the phenylene groups that is related to the principle sub-glass transition mechanical loss. As the phthalate diluent is first added, the modulus increases slightly and the loss peak is suppressed. The $T_{1\rho}$ at 44 kHz data show a minimum at about −40 °C which corresponds to the mechanical loss at 1 Hz and a temperature of −100 °C. The $T_{1\rho}$ minimum is changed by the addition of diluent in a selective manner. At a diluent concentration of 5 wt % the low-temperature part of the minimum corresponding to the most mobile phenylene groups is suppressed. The remaining minimum is narrower and is shifted slightly to higher temperatures by the removal of the component of the distribution of relaxation times which leads to the low-temperature side. As the concentration of diluent is raised to 10 and 25 wt %, a second lower temperature minimum appears. This minimum is attributed to enhanced motion of repeat units in contact with microscopic clusters of diluent. A lattice model is presented which accounts for suppression of motion at low concentrations and the appearance of the second minimum at higher concentrations. Suppression is associated with improved packing caused by the presence of an isolated diluent molecule in contact with a polymeric repeat unit while enhanced mobility is caused by the presence of a microscopic diluent cluster in contact with a repeat unit. This same lattice model is used to reinterpret a carbon-13 spin diffusion study of the same diluent–polymer system where one ester group on the diluent is labeled. The lattice interpretation of the spin diffusion data reinforces the earlier interpretation in terms of a preferred spatial location of the diluent relative to the polymeric repeat unit. The new interpretation also indicates an increased rate of spin diffusion per diluent molecule at low concentrations, which indicates stronger interactions with the polymer in this regime, in agreement with the suppression of motion observed in the proton $T_{1\rho}$ data.

Introduction

The effects of low molecular weight diluents on polymeric glasses have been investigated from a number of standpoints[1-9] including NMR spectroscopy.[10-14] The motivation for considering diluents in polymeric glasses arises from the changes of bulk properties upon the addition of the diluent. Typically, the glass transition decreases with the addition of a low molecular weight compound; this is relevant to the processing of the polymer. The mechanical properties of the glass can also be altered. The modulus may either increase or decrease with the addition of diluent and indeed the modulus behavior can change depending upon the amount of diluent added. The dynamic mechanical spectrum of the polymer plus diluent can be quite different than that of the pure polymer. Either mechanical loss peaks can be introduced by the addition[11,15,16] of diluent, or peaks present in the pure polymer can be suppressed.[1-8] In general, a diluent is said to plasticize a polymeric glass if the modulus is lowered upon addition of the diluent. This would be associated with an increase in mechanical loss below the glass transition. If the diluent increases the modulus, it is characterized as an antiplasticizer; and there would be less mechanical loss.

This level of consideration does not focus on the chemical structure of the polymeric repeat unit or any associated intermolecular interactions: a fact which has encouraged NMR spectroscopists to study polymer–diluent systems. Mechanical and dielectric experiments have led to interpretations involving repeat unit level descriptions of motion or the proposal of intermolecular interactions, but these techniques do not provide direct probes of such aspects. NMR does provide direct and discriminating probes of either chain motion or diluent motion independently, and this has been used to monitor each component in a multicomponent glass.[10-14] A carbon-13 spin diffusion experiment has also provided evidence for specific interactions between the polymer chain and the diluent in antiplasticized systems.[12]

In this report, proton spin-lattice relaxation, $T_{1\rho}$, in the rotating frame will be used to monitor chain motion upon addition of diluent without any contribution of the diluent to the observed relaxation. This is achieved by complete deuteration of the diluent molecule so that the preponderant source of relaxation is among protons on the polymer and thus only motion of the polymer will contribute to relaxation. The polymer under consideration is polycarbonate, which has been well studied.[14,17-27] Here NMR has shown π flips of the phenylene groups to be the predominant repeat unit level motion, and this motion is quantitatively related to the low-temperature dynamic mechanical loss peak. In fact, proton $T_{1\rho}$ data played a key role in linking shear mechanical loss with phenylene group π flips.[19] Deuterium line-shape data show the π flips to be suppressed by the addition of diluents,[11] and the proton $T_{1\rho}$ data developed here provide a complementary view relative to the line-shape results. Proton $T_{1\rho}$ data as a function of temperature are very useful in defining the distribution of relaxation times in much the same way as dielectric or mechanical loss peaks define relaxation distributions as a function of temperature. The advantage of NMR is that only the motion of the chain will be monitored without contributions from the motion of the diluent.

The changes in the distribution of relaxation times for polymer motion determined from proton relaxation upon

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addition of diluent suggested an interpretation to the authors that is tied to the specific interactions observed in the earlier spin diffusion experiment. The spin diffusion experiment was carried out on the same system that is under consideration here, namely, polycarbonate to which di-*n*-butyl phthalate (DBP) is added as a diluent. The changes between the two experiments do involve isotopic labeling. The spin diffusion experiment employed carbon-13 labeling of the DBP while the $T_{1\rho}$ experiment requires perdeutero DBP.

To incorporate certain features of both experiments into a quantitative interpretation, a lattice model is presented. The lattice model is used to count the number of nearest-neighbor contacts between a given polymer repeat unit and diluent molecules. It is also used to calculate the fraction of diluent molecules that are in contact with other diluent molecules. Usually lattice models in polymer science are mean field models, but this model is used to correlate the specific type of local environment surrounding a repeat unit with the mobility of the repeat unit. The first contact between a diluent molecule and a repeat unit is associated with suppression of chain motion while clusters containing two or more diluent molecules around a given repeat unit are associated with increased mobility. The model provides at least a semiquantitative framework to interpret changes in the shape of the $T_{1\rho}$ minimum associated with changes in the distribution of relaxation times with concentration, changes in the specificity of carbon-13 spin diffusion with concentration, and changes in the modulus with concentration.

Experimental Section

Perdeutero DBP was prepared from perdeuteriophthalic acid and perdeuterio-1-butanol. Chemical purity was checked by high-pressure liquid chromatography and isotopic purity by high-resolution proton and deuteron spectroscopy. Carbon-13 labeled DBP enriched at one of the carboxyl sites was prepared from phthalic acid-α-^{13}C (99%) and unlabeled 1-butanol. Isotopic purity was checked by high-resolution carbon-13 spectroscopy. The polycarbonate used for the proton $T_{1\rho}$ measurements was also isotopically labeled by deuterating the methyl groups. The preparation and isotopic purity of the methyl deuterated analogue of Bisphenol A polycarbonate (BPA-PC-d_6) have been presented in another paper.[24] The structures of the various labeled species are given in Figure 1.

Films of the polymer plus diluent were prepared by dissolving DBP and BPA-PC in dichloromethane followed by evaporation and vacuum drying. Optically clear films were produced by this approach which were sealed under vacuum in 10-mm tubes for the proton relaxation experiment. The film was cut into small pieces and packed in a 7-mm rotor for the magic angle experiments.

Proton $T_{1\rho}$ data were acquired on a Bruker SXP 20-100 at a Larmor frequency of 90 MHz. A standard $\pi/2$-phase shifted locking pulse was used with a radio frequency field strength of 1.0 mT. Temperature was maintained within 2 deg with a Bruker B-ST 100/700 temperature controller that was calibrated against a thermocouple in the probe.

The carbon-13 data were acquired on a Bruker WM 250 with an IBM solids accessory for magic angle spinning. The carbon Larmor frequency was 62.9 MHz, and all experiments were performed at an ambient temperature of 21 °C. Carbon-13 T_1's were measured with the Torchia[28] pulse sequence. Spin diffusion from the enriched peak on the diluent to various sites on the polymer was observed by inverting the enriched peak using a Dante sequence after the carbon-13 $\pi/2$ pulse in the Trochia sequence. The presence of spin diffusion is determined by an increase in decay rate upon application of the Dante pulses relative to the decay rate in the Torchia sequence. Details of this spin diffusion experiment have been presented as part of a preliminary report.[12]

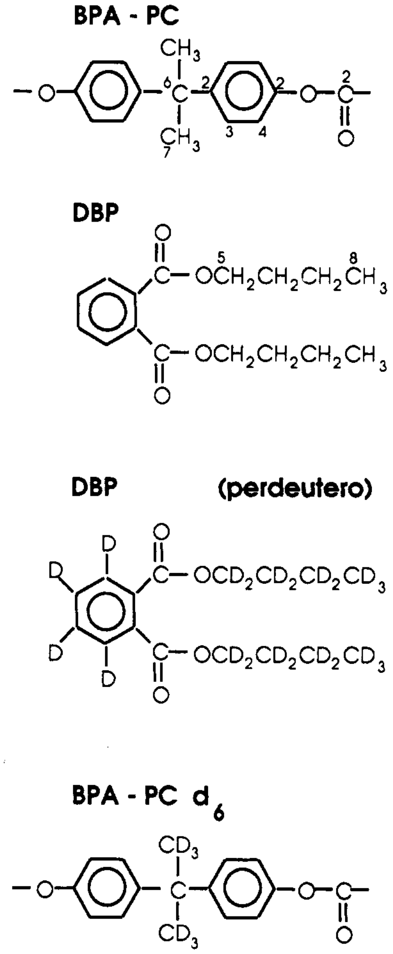

Figure 1. Chemical structures for polymer repeat units and the diluent.

Results

Proton $T_{1\rho}$'s of BPA-PC-d_6 are plotted as a function of temperature in Figure 2 for films which are 0, 5, 10, and 25 wt % perdeutero DBP. The value of each $T_{1\rho}$ is based on about eight spin lock measurements of intensity, and the plots of log intensity versus spin lock time were quite linear.[19] The high-temperature limit of the $T_{1\rho}$ reported for each concentration is near the glass transition temperature for that concentration. The individual proton $T_{1\rho}$ values have an accuracy of 15% and a precision of 5%; and care was taken so the relative values of $T_{1\rho}$ for various temperatures and concentrations can be compared on the basis of the precision.

Carbon-13 spin-lattice and spin diffusion decay curves are presented in parts a–f of Figure 3. Decay curves are given for three resolved polymer peaks following the numbering system given in Figure 1. Each part contains the decay curve for the T_1 experiment at a particular concentration of unlabeled diluent and the decay curve for the spin diffusion experiment at the same concentration but with carbon-13 labeled diluent. Any increase in decay rate observed for the latter experiment is associated with spin exchange between the labeled carbon on the diluent and the particular carbon site on the polymer.

Interpretation

The broad $T_{1\rho}$ minimum shown in Figure 2 for the pure polymer has been reported before[24] for BPA-PC-d_6. The observed relaxation was attributed to the action of π flips and libration of the phenylene group on the intermolecular dipole–dipole interaction.[24,27] A quantitative inter-

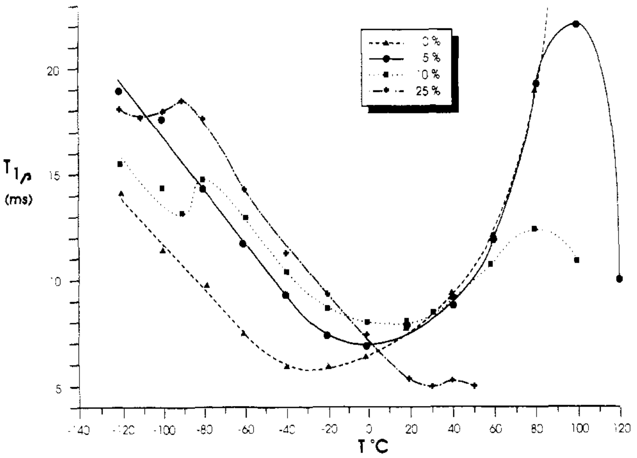

Figure 2. Proton $T_{1\rho}$ versus temperature. The triangles are for pure polymer, the circles are for the polymer plus 5% perdeutero DBP, the squares are for the polymer plus 10% perdeutero DBP, and the crosses are for pure polymer plus 25% perdeutero DBP. The lines are just smooth connections between the data points for each concentration. Note that the difference between the curve for pure polymer and the curve for 5% diluent is a loss of relaxation on the low-temperature side of the minimum: an effect associated with antiplasticization. At a concentration of 5%, the loss of relaxation ranges from 0 °C to the lowest temperatures studied. As the concentration is raised, low-temperature relaxation is lost in the region from 20 down to -80 °C. At the two highest concentrations of diluent, a second less intense minimum appears near -100 °C which is associated with molecular level clusters of diluent.

pretation was obtained on the basis of a fractional exponential correlation function for the π-flip process in combination with Gronski's model for libration. The fractional exponential correlation function arises from a heterogeneous distribution of π-flip rates associated with a distribution of local environments for the phenylene groups. To amplify this point, a heterogeneous distribution of correlation times corresponds to different correlation times for phenylene groups in different spatial locations throughout the glassy sample. A single proton $T_{1\rho}$ is observed at a given temperature because proton spin diffusion averages over all environments at a given temperature. The correlation function for π flips obtained from the proton relaxation data can be used to predict the position and breadth of the low-temperature mechanical loss peak of polycarbonate. The $T_{1\rho}$ minimum is much like an inverted mechanical or dielectric loss peak with the characteristic frequency of the minimum given by radio frequency field amplitude which is 44 kHz for the case under consideration here.

The $T_{1\rho}$ minimum observed for the 5 wt % diluent sample shows a rather similar shape to the pure polymer result with the high-temperature side of the minimum almost exactly overlapping the pure polymer data until the glass transition is approached. The low-temperature side of the minimum is shifted significantly toward higher temperatures, and the actual minimum point is changed only slightly to higher temperature. In terms of the inhomogeneous distribution of correlation times, this corresponds to the removal of the short correlation times from the distribution of correlation times for π flips. Physically, the motion of the most mobile phenylene groups appears to be stopped by the addition of diluent to the level of 5 wt %.

In terms of classical considerations of the role of diluents in glassy polymers,[1-8] this corresponds to antiplasticization. The addition of a small amount of low molecular weight compound has produced a decrease in the local motion of the polymer chain backbone. The important feature in this experiment is the selective observation of local chain motion. Any local diluent motions that might be important to mechanical or dielectric response are completely transparent because of deuteration of the diluent. The second important point is the suppression of the motion of the most mobile phenylene groups through the addition of a diluent. This result has not been emphasized in comparable mechanical or dielectric data, and in fact these experiments on related systems (polymer–polymer blends) have indicated suppression of the high-temperature side of loss curves which corresponds to the least mobile components of a distribution of correlation times.[11,29,30] In the NMR experiment reported here it is clear that we are monitoring motion of the phenylene groups of the polymer, free from the motion of other units. Furthermore, Figure 2 clearly indicates the motion of the most mobile phenylene groups is either suppressed or shifted to higher temperatures upon addition of 5 wt % diluent.

The suppression of the most mobile components in a glass can be related to conceptual models of glasses. In particular, we will employ the picture presented by Johari[31] which is summarized by the phrase "islands of mobility". In Johari's view the glass is heterogeneous containing both high-density, low-energy regions and low-density, high-energy regions. The former have little molecular mobility, and the latter are rather mobile and are responsible for a substantial fraction of the expansivity and heat capacity of the glass. This view of the glass was used by Johari to discuss aging, but here we find it useful in considering the effects of diluent addition.

It would appear at the level of 5 wt % diluent that the low-density, high-energy, high-mobility regions of the glass are changed. These regions would be associated with the low-temperature side of a $T_{1\rho}$ minimum, and it is this portion of the minimum that is removed by a low concentration of diluent. In the formation of the glass, the high-energy regions are composed of unrelaxed, nonequilibrium chains or portions of chains. The regions are trapped in a high-energy state because of the inability of the polymer chains to rearrange at temperatures well below the glass transition except by the relatively slow aging process. However, if a small amount of low T_g diluent is present during the formation of the glass, it can relax the high-energy regions because it has greater intrinsic mobility than the polymer chain. Densification of glasses upon addition of low T_g diluents is well-known, and the $T_{1\rho}$ data presented here clearly show loss of the most mobile regions upon addition of a small amount of diluent.

The process of suppression of motion upon the addition of diluent does not continue in a simple fashion at higher concentrations. In the BPA-PC plus DBP system under study here, antiplasticization changes over to plasticization as concentration is raised as noted by a lowering of the modulus.[10] In the $T_{1\rho}$ data at 10 wt %, two competing effects are apparent. From temperatures of -80 to +20 °C, a suppression of motion is indicated in a quite analogous fashion to the 5 wt % data. This continued suppression of the most mobile phenylene groups is in line with discussion up to this point. However at a temperature of about -90 °C, a new $T_{1\rho}$ minimum has appeared. Remember that this minimum must still be associated with motion of the phenylene group since only motions of the phenylene groups are monitored by this NMR experiment.

New arguments must be presented to reconcile the appearance of this increased mobility with the interpretation just developed. To develop a more complete pic-

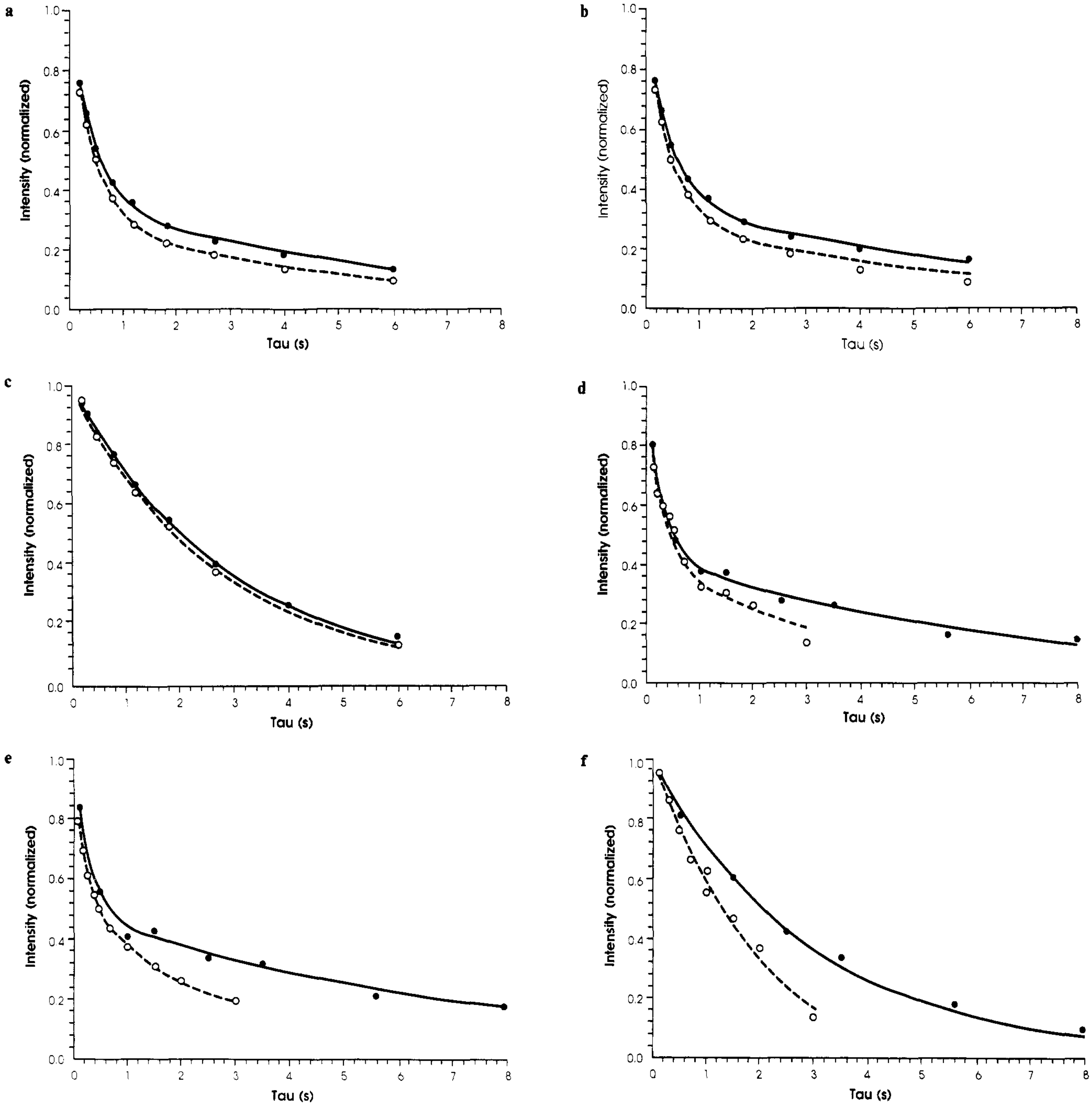

Figure 3. (a) Decay of phenylene carbon 3 Intensity versus time at a concentration of 10 wt % DBP. The solid line and solid points are for the Torchia T_1 experiment, and the dashed line and open circles are for the spin diffusion experiment. The lines are fits of the decay curves as described in the text. (b) Decay of phenylene carbon 4 intensity versus time at a concentration of 10 wt % DBP. The two curves are as in a. (c) Decay of the quaternary carbon intensity versus time at a concentration of 10 wt % DBP. (d) Decay of phenylene carbon 3 intensity versus time at a concentration of 25 wt % DBP. (e) Decay of phenylene carbon 4 intensity versus time at a concentration of 25 wt % DBP. (f) Decay of the quaternary carbon intensity versus time at a concentration of 25 wt % DBP.

ture, we wish to now introduce a simple lattice model. In this lattice model, a site will be occupied by either a BPA-PC repeat unit or a DBP molecule. Both species have comparable molecular weights. Each site has six nearest neighbors, and it is these nearest neighbors that we wish to consider. For a BPA-PC repeat unit, two of the nearest neighbors must be BPA-PC repeat units because of chain connectivity. The remaining four units may either be occupied by diluent or polymer. Using random statistics, the probability of a given polymer repeat unit having zero, one, two, three, or four nearest-neighbor diluent molecules can be calculated as a function of concentration of diluent. To do this we define occupancy probabilities, in particular: p, fraction of sites occupied by a polymer repeat unit; d, fraction of sites occupied by a diluent molecule. These occupancy probabilities can be calculated from the composition of the diluent–polymer blend. We can then calculate the fraction of polymer repeat units with zero, one, two, three and four diluent moieties as neighbors by

$$\begin{aligned} F_0 &= p^4 \\ F_1 &= 4p^3d \\ F_2 &= 6p^2d^2 \\ F_3 &= 4pd^3 \\ F_4 &= d^4 \end{aligned} \qquad (1)$$

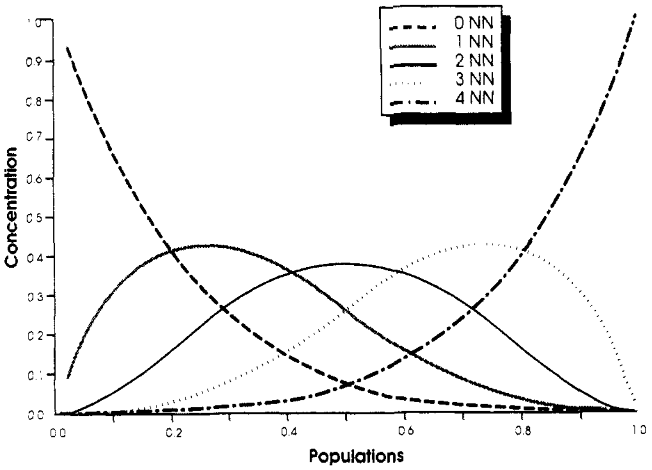

Figure 4. Populations of polymer repeat units with various types of nearest-neighbor (NN) environments versus concentration. The populations are calculated from the lattice model developed in the text. The line for the population of repeat units having zero nearest neighbors is designated 0 NN. Other populations are designated in a similar fashion.

The symbol F_i denotes the fraction of polymer repeat units with i diluents as nearest neighbors and $\sum F_i = 1$. These fractional populations are shown as a function of overall diluent–polymer composition in Figure 4.

To relate this tracking of the number of diluent molecules next to a repeat unit to the $T_{1\rho}$ data, phenylene group mobility requires a few additional associations. First for suppression of motion, the first diluent molecule to come in contact with a repeat unit will be assumed to improve local packing and to reduce the mobility of the repeat unit unless the diluent molecule is part of a cluster of diluent molecules. With regard to Figure 4, the fraction of repeat units with one nearest neighbor rises very rapidly with concentration; and in the range of concentration of 1–5% the only prevalent species are units with either zero or one diluent neighbor. This is the regime of simple antiplasticization in this model.

By the point at which the concentration of diluent reaches 10%, a significant population of polymer repeat units with two diluent molecules as nearest neighbors is present. If the diluent has a significantly lower T_g than the polymer, these polymer units are to be associated with increased mobility and account for the appearance of the second, lower temperature $T_{1\rho}$ minimum. In the lattice model clusters of diluent molecule are to be associated with regions of increased mobility given that a low T_g is a good indicator of diluent mobility. Also the diluent is assumed to be a Θ solvent for the polymer so that there is little preferential clustering of diluent with diluent or diluent with polymer and thus random statistics should be applicable. Given the structural similarity of the phthalate ester and the polycarbonate repeat unit, this may be a reasonable assumption. This particular diluent–polymer system is considered to be a single phase, and the model is only attempting to count local microscopic clusters within a single-phase system. Such microscopic clusters are well below the size needed to thermodynamically define a new phase.

The population of repeat units with more than two diluent moieties as nearest neighbors does not become significant until the concentration passes 20%. These larger clusters of diluent around a repeat unit would also be associated with increased mobility, and indeed the 25 wt % $T_{1\rho}$ also display a second lower temperature minimum. In the temperature range of −90 to +10 °C, there is continued evidence of antiplasticization that would be associated with the population of units with one nearest-neighbor diluent unit. The population of such units continues to rise until just past 25% according to Figure 4. The mobility associated with clusters larger than two diluent repeat units might well have greater mobility than those of just two units. There is a shift in the position of the second, lower temperature $T_{1\rho}$ minimum at 25% to lower temperatures, and this minimum is broader than the 10% minimum that is indicative of a greater range of mobilities. As a reference point, the T_g of pure DBP is −97 °C which is in the general vicinity of the lower temperature minimum appearing at higher diluent concentrations.[32]

The lattice model can be used to simulate the $T_{1\rho}$ data presented in Figure 2. To begin the process, the $T_{1\rho}$ minimum of the pure polymer can be fit or simulated by using a fractional exponential correlation function.

$$\phi(t) = \exp(-(t/\tau)^{\alpha}) \qquad (2)$$

This form of the correlation function has been used to fit proton $T_{1\rho}$, carbon-13 chemical shift anisotropy line shape collapse data, and carbon-13 T_1 data.[26,27] Physically, the fractional exponential form corresponds to a distribution of exponential correlation times, and this distribution is associated with the heterogeneous distribution of π flips of the phenylene group in polycarbonate. Thus, the correlation function can be written

$$\phi(t) = \sum_{k=1}^{n} P_k \exp(-t/\tau_k) \qquad (3)$$

The addition of another motion besides π flips is required to account for the relaxation data just mentioned. The second motion is libration of the phenylene group about the C_1C_4 axis. The chemical shift anisotropy data are strongly influenced by this motion at higher temperatures, and T_1 data are somewhat influenced by this motion since it is characterized by a high frequency. This motion is a minor contributor to the proton $T_{1\rho}$ data except at the lowest temperatures and will therefore be left out of the analysis of the proton $T_{1\rho}$ upon addition of the diluent DBP.

The pure polymer $T_{1\rho}$ data can be fit with the fractional exponential form using a known value of the intermolecular second moment, $S = 1.8 \times 10^{-2}$ mT^2 and by adjusting the value of the fractional exponent, the apparent activation energy, and Arrhenius prefactor of the correlation time τ. The equation employed for $T_{1\rho}$ is

$$1/T_{1\rho} = (2/3)\gamma^2 S[1.5J_e(2\omega_e) + 2.5J_1(\omega_H) + J_2(2\omega_H)] \qquad (4)$$

where $\omega_e = \gamma H_{rf}$, γ is the gyromagnetic ratio, ω_H is the Larmor frequency, and J is the spectral density or the Fourier transform of the correlation function. The radio frequency field amplitude is H_{rf}. The fit is shown in Figure 5, and the associated parameters are listed in Table I.

The $T_{1\rho}$ data for polymer plus diluent can be simulated by using the lattice model and the fractional exponential correlation function according to the following procedure. The main $T_{1\rho}$ minimum or higher temperature minimum is associated with repeat units surrounded by other polymeric repeat units. The fraction of such repeat units is given by the quantity F_0 defined in eq 1. To accomplish the appropriate weighting, the second moment associated with the main minimum is multiplied by the fractional population F_0. Then the apparent activation energy and Arrhenius prefactor are

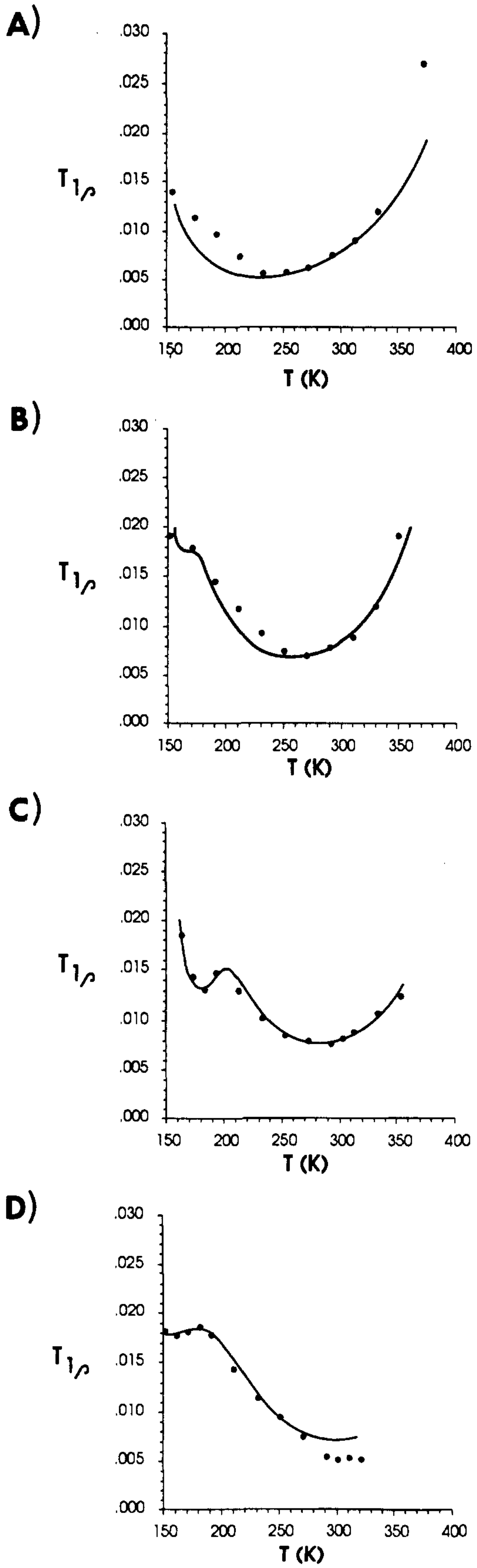

Figure 5. Proton $T_{1\rho}$ versus temperature. (A) Points are the experimental data for the pure BPA-PC, and the solid line is the fit using a fractional exponential correlation function. (B) Points are the experimental data for BPA-PC plus 5% perdeutero DBP, and the solid line is the fit using two fractional exponential correlation functions and the lattice model. (C) The same plot as B except for BPA-PC plus 10% perdeutero DBP. (D) The same plot as B except for BPA-PC plus 25% perdeutero DBP.

adjusted to simulate the main part of the $T_{1\rho}$ minimum as a function of temperature.

The fractional population associated with polymeric repeat units with one diluent moiety as a nearest neighbor is given by F_1 of eq 1. This population of repeat units is assumed not to undergo π flips below the glass transition and is simply left out of the simulation of the low-temperature $T_{1\rho}$ data. Actually a correction is made to include a portion of this population in the lower temperature minimum. Suppression of motion should only be associated with isolated diluent molecules in the lattice and enhancement of polymer motion should be associated with polymer repeat units in contact with microscopic diluent clusters. Some of the fractional population of polymer repeat units F_1 in contact with only one diluent molecule are actually in contact with a microcluster of diluent molecules through a single diluent molecule. Under these circumstances, we will associate this sub-population of the fractional population F_1 with enhanced mobility. The fractional population of diluent clusters of size i, G_i, cannot be calculated easily. Clusters of this type have been considered in percolation theory[33] and can be enumerated, but no simple formulae for clusters larger than size two exist. The lattice model can be used to calculate G_1 and G_2 assuming every moiety has six nearest neighbors. In this case the microclusters are calculated from the point of view of a diluent molecule and not a polymer repeat unit. Thus the central moiety becomes a diluent molecule.

$$G_1 = p^6$$
$$G_2 = 6p^5d \qquad (5)$$

Since microclusters of all sizes cannot be determined, we use a slightly different approach to the calculation of the number of repeat units that are in contact with a microcluster through one diluent molecule. The probability for a polymer repeat unit in contact with one diluent molecule is F_1. If the nearest-neighbor sites of the diluent are considered, one is already occupied by a reference polymer unit and is considered in the quantity F_1. There are five more nearest-neighbor units surrounding the diluent that are not included in the calculation of F_1. The probability that all of these units are occupied by polymer repeat units is p^5. The combined probability F_1p^5 gives the likelihood that a polymer repeat unit is in contact with a diluent molecule that is completely surrounded by additional polymer repeat units. This is the type of polymer unit that is to be associated with antiplasticization through improved packing and suppression of motion. The remaining polymer units in contact with one diluent molecule that is in turn in contact with other diluent molecules are given by $F_1(1 - p^5)$. Such repeat units are to be associated with increased mobility in the model along with repeat units in direct contact with multiple diluent molecules that are given by F_2, F_3, and F_4.

To summarize, the fractional population of polymer repeat units in contact with more than one diluent molecule will be considered to have enhanced mobility to simulate the lower temperature minimum that appears at higher concentrations. This includes the fractional populations F_2, F_3, and F_4 plus $F_1(1 - p^5)$. The latter population is associated with polymer repeat units in contact with one diluent molecule but that diluent molecule is in contact with other diluent molecules. The sum of these four fractional populations will be used as the weighting fractor for the second minimum relative to the main minimum. The lower temperature minimum is simu-

Table I
Parameters for $T_{1\rho}$ Fit

	high-temp minimum				low-temp minimum			
concn of DBP, wt %	pop.	τ_∞, s	E^*, J	α	pop.	τ_∞, s	E^*, J	α
0	1	1.0×10^{17}	49 000	0.13	0			
5	0.8145	5.5×10^{21}	71 000	0.12	0.0359	2.7×10^{15}	26 300	0.58
10	0.6561	2.4×10^{20}	74 000	0.14	0.1275	4.6×10^{28}	41 200	0.31
25	0.3164	3.5×10^{13}	37 700	0.35	0.3586	3.0×10^{20}	41 800	0.11

lated with this weighting times the second moment, plus the variation of the apparent activation energy, fractional exponent, and Arrhenius prefactor.

The amount of second moment associated with the relaxation of polymer repeat units with enhanced mobility must be reduced according to the number of nearest neighbors that are deuterated diluent molecules. Deuteration reduces intermolecular relaxation by the square of the gyromagnetic ratio of deuterium divided by that of hydrogen. This factor is sufficiently small so that the presence of the deuterated diluents will simply be neglected in the estimation of the second moment. The second moment of the polymer repeat units with diluent neighbors will be scaled according to the fraction of the four units that remain protonated.

All the aspects of the simulation of the $T_{1\rho}$ data via the lattice model have now been presented. The resulting simulations are shown in Figure 5, and the relative qualitative trends are reproduced. Since the simulation involves the presence of two fractional exponential correlation functions, each of which has three associated parameters, the simulation is not necessarily unique nor could it necessarily be achieved by a nonlinear least-squares procedure without expansion of the data base.

This lattice model is only being presented for lower ranges of concentration, 0–25%, and is not expected by the authors to have utility at higher concentrations. It does however provide a useful framework for discussion of the $T_{1\rho}$ data. It can also be used to refine the analysis of the carbon-13 spin diffusion data presented in an earlier report for this same polymer diluent system.

To accomplish this, the formalism presented by Linder et al.[33] will be used to describe the change in carbon-13 magnetizations with time. For an N carbon system, each carbon magnetization is labeled S_N and the return of the magnetization to equilibrium can be written in matrix form as

$$\dot{\mathbf{S}}(t) = -\mathbf{R}\cdot\mathbf{S}(t) \tag{6}$$

where $\mathbf{R}$ is the rate matrix and $\mathbf{S}$ is a column vector. Diagonal elements of the rate matrix are of the general form $(R_i + \sum R_{ij})$ and off-diagonal elements, of the general form $-R_{ij}$. The spin–lattice relaxation rate is R_i, and the cross relaxation rate is R_{ij} which is the spin slip interchange rate or spin diffusion rate ($i \neq j$).

If all carbons in the system are included in eq 6, the formulation is too complex to apply to the data. Following Linder et al.,[34] the treatment will be reduced to consideration of 2 × 2 matrices by focusing on the interaction of the labeled carbon and a given unlabeled carbon in a series of pairwise solutions. Since spin diffusion from the labeled carbon on the diluent to resolved carbons on the polymer chain is of interest, the time evolution of three polymer carbons corresponding to the data of Figure 3 at two concentrations will be analyzed. The resolved polymer carbons of interest are the protonated phenylene carbons (3 and 4) and the quaternary aliphatic carbon (see Figure 1). The methyl carbon of the BPA-PC is also resolved, but the spin–lattice relaxation rate is so large that no spin diffusion to it could be observed.

Considering the labeled carbon to be 1, the rate equation (eq 6) reduces to

$$\begin{aligned} \dot{S}_1(t) &= -(R_1 + R_{1j})S_1(t) + R_{1j}S_j(t) \\ \dot{S}_j(t) &= -(R_j + R_{1j})S_j(t) + R_{1j}S_1(t) \end{aligned} \tag{7}$$

where j represents a natural abundance carbon on the polymer. For a particular natural abundance carbon 2, solutions for these equations[34] were presented in terms of the three rates and the initial conditions.

$$\begin{gathered} S_1(t) = A\exp(-\lambda_1 t) + B\exp(-\lambda_2 t) \\ S_2(t) = C\exp(-\lambda_1 t) + D\exp(-\lambda_2 t) \\ \lambda_{1,2} = \{(R_1 + R_2 + R_{12}) \pm [[R_1 - R_2]^2 + 4R_{12}{}^2]^{1/2}\}/2 \\ A = [(R_1 + R_{12} - \lambda_2)S_1(0) - R_{12}S_2(0)]/(\lambda_1 - \lambda_2) \\ \lambda_1 \geq \lambda_2 \\ B = S_1(0) - A \\ C = [(R_2 + R_{12} - \lambda_2)S_2(0) - R_{12}S_1(0)]/(\lambda_1 - \lambda_2) \\ D = S_2(0) - C \end{gathered} \tag{8}$$

Similar equations were developed by Linder et al.[34] for the case where two labeled carbons are present that have strong coupling between them plus weaker coupling to a third natural abundance carbon. This system leads to a description much like the simple two-site equation.

$$\begin{gathered} \lambda_{1,2} = (1/2)(R_1 + R_2 + 3R_{12} \pm \{[R_1 - R_2 - R_{12}]^2 + 8R_{12}\}^{1/2}) \\ A = \{[R_1 + R_{12} - \lambda_2]S(0) - 2R_{12}S_2(0)\}/(\lambda_1 - \lambda_2) \\ B = S_1(0) - A \\ C = [(R_2 + 2R_{12} - \lambda_2)S_1(0) - R_{12}S_1(0)]/(\lambda_1 - \lambda_2) \\ D = S_2(0) - C \end{gathered} \tag{9}$$

Note that S_1 is the sum of both labeled carbon magnetizations and both are assumed to have the same cross relaxation rate to the unlabeled carbon magnetization S_2.

To actually interpret a spin diffusion decay curve, these rate equations must be combined with the lattice model populations and spin–lattice relaxation times determined from the Torchia sequence on unlabeled samples. At a given concentration, the proportion of the decay rate that follows simple spin–lattice relaxation with no influence from spin exchange between the diluent and the polymer site is set equal to the fraction of polymer repeat units that have no diluent molecules as nearest neighbors. The proportion of the decay rate that follows eq 8 will be the fraction of polymer repeat units that have one labeled diluent molecule as a nearest neighbor. The proportion of the decay rate that follows eq 9 will be the fraction of polymer repeat units that have two labeled diluent molecules as nearest neighbors. The values of the magnetizations at time zero can be taken from the short time relaxation data, or this can be floated as a parameter as long as good fits at short times are obtained. To summarize, the R_j's are determined from a Torchia

Table II
Relaxation Rates of BPA-PC Carbon Resonances[a]

site	concn, wt % DBP	spin–lattice relax rate, s^{-1}	spin diff rate, s^{-1}
quat.	25	0.34	0.074
Ph 3	25	4.00 and 0.15 $\phi = 0.55$	0.032
Ph 4	25	3.70 and 0.14 $\phi = 0.50$	0.040
quat.	10	0.33	0.030
Ph 3	10	2.26 and 0.17 $\phi = 0.62$	0.411
Ph 4	10	2.22 and 0.15 $\phi = 0.62$	0.446

[a] ϕ = population of fast component of double exponential fit.

T_1 experiment, the magnetizations at time zero are determined by short delay time data, and the spin exchange rate is determined by fitting the decay curves observed when the Dante inversion is applied to the labeled peak. The form of the spin exchange equations is given by the 2 × 2 matrix solutions just given, and the fraction of the decay assigned to a particular form of these equations is determined by the lattice model. The key adjustable parameter in the fits are the R_{ij}'s. Each fit involves the change of the labeled peak intensity with time and one of the resolve unlabeled polymer peaks as a function of time. The fraction of repeat units with three or more diluent neighbors is sufficiently small at all concentrations that it can be neglected over the concentration range of this investigation.

One additional complication arises in the determination of the T_1 data from the Torchia sequence. In pure polycarbonate[27] and in the polycarbonate plus diluent cases,[10] the relaxation of the phenylene carbons is heterogeneous and cannot be described as exponential decay. Over the range of delay times used here, the spin–lattice decay can be adequately described in terms of two decay rates or two time constants. The two values determined have no real physical significance but can be used to characterize spin–lattice relaxation. For our purposes, the spin–lattice relaxation is the base line; and it is additional relaxation from spin exchange that is to be determined. Thus any numerical description of spin–lattice relaxation that is reasonably accurate allows for a determination of the spin exchange rate. Spin–lattice relaxation rates and spin diffusion or exchange rates resulting from this procedure are given in Table II.

Discussion

A semiquantitative interpretation of the proton $T_{1\rho}$ data for BPA-PC upon the addition of diluent was interpreted in terms of competitive contributions from antiplasticization and plasticization with the relative weighting of the contributions determined from a lattice model. The lattice model simulates the data quite well as shown in Figure 5 though the simulation is not as good as a line drawn through the data points as was done in Figure 2. It should be remembered that we have not included the librational motion of the phenylene group in the correlation function, and the inclusion of this motion would improve the fit of at least the pure polymer data. The general trends in the data that were qualitatively interpreted in the preceding section are reproduced by the simulation. Notably, the lattice model appears to predict the correct amount of suppression based on the assumption that the first diluent molecule adjacent to a repeat unit improves packing and suppresses motion as long as it is an isolated diluent molecule. The depth of the lower temperature minimum at higher concentrations associated with increased mobility induced by very localized diluent clusters is also at least approximately predicted by the lattice model.

The actual parameters of the lattice model are listed in Table I. The Arrhenius prefactor associated with the fractional exponential correlation function has a complex meaning[19] and is not simply related to the attempt time scale as it might be in simpler systems. The trends in the apparent activation energy and prefactor should be considered qualitative. The increase in activation energy of the higher temperature minimum at diluent concentration of 5 and 10% produces the narrowing of the minimum required to simulate the data and reflects the increased restriction of polymer motion in this concentration regime. At these low concentrations, the higher activation energy for sub-glass transition motions seems physically sensible relative to the concepts of antiplasticization. The drop in the apparent activation energy at a diluent concentration of 25% may be associated with the nearness of the glass transition that commences before the temperature sweep of the sub-glass transition processes is complete. With the resulting overlap of the higher temperature sub-glass transition minimum and the glass transition minimum, the simulation parameters are particularly difficult to establish with confidence. The values for α demonstrate once more the broad distribution of mobilities existing in both the pure polymer and its diluent blends.

The correlation function parameters associated with the lower temperature minimum attributed to molecular level diluent clusters are also interesting to consider but probably of limited significance. At a diluent concentration of 5%, no lower temperature minimum is present because the population of clusters is so low that it is not much of a factor. Also at the low concentration of diluent, most diluent clusters consist of only two diluent molecules. At the higher concentrations the lower minimum is apparent in the data and can be matched by the model. The apparent activation energy for this minimum is lower than the pure polymer sub-glass transition motions which is reasonable given the greater intrinsic mobility of the diluent relative to the polymer. The fractional exponent decreases as concentration is raised. In the context of the model, this is plausible since diluent clusters of all sizes are lumped together in one lower temperature minimum. At concentrations of 10 and 25%, significant populations of clusters of several sizes are present according to the lattice model. They might well have different mobilities, but in the data all we see is a single minimum that does appear to be broader at the highest concentration. The simulation of the data reflects the same broadening of the lower temperature minimum in the decreasing value of the fractional exponent.

The proton $T_{1\rho}$ data indicate antiplasticization by suppression of the most mobile fraction of the phenylene groups at low concentrations of diluent. In this concentration regime, polymer repeat units either have zero or one diluent molecule as a nearest neighbor if a random dispersion of diluent in the glass is assumed. At low concentrations both an earlier crude analysis of carbon-13 spin exchange between labeled diluent and a more complex though comparably parameterized analysis developed here show a preferential location of the diluent molecule relative to the polymer repeat unit. This is seen in Table II in terms of a high rate for spin diffusion between the diluent and the protonated aromatic carbon nearest the carbonate group, a slightly lower rate to the neighboring protonated carbon, and the lowest rate to the quaternary aliphatic carbon. This is taken as evidence for a specific interaction between the carbonate of the polymer repeat unit and the carbonyl of the diluent. In the lattice model, the first diluent molecule next to a given polymer repeat unit is assumed to allow for improved packing resulting in densification[1-8] and a reduction in repeat unit level motions. Certainly a specific interaction between the diluent and a polymer chain resulting in local order is consistent with improved packing and subsequently a reduction in chain mobility. The order of magnitude higher spin diffusion rate at lower concentration is additional striking evidence for closer molecular contact which is again consistent with densification, improved packing, and suppression of motion. An order of magnitude change in spin diffusion corresponds to a 47% change in intermolecular separation if one ascribes the change to the inverse sixth dependence on distance. Increases in molecular motion at the higher concentrations would also reduce spin diffusion by reducing the overlap of resonance lines.

Since the diluent and the polymer repeat unit are similar structurally, repeat units should also interact with other repeat units. It is the higher mobility of the diluent that allows for improved packing in the formation of the glass with a favorable interaction being a necessary but not sufficient condition.

As concentration of the diluent is increased from 10 to 25 wt %, the aromatic carbon spin diffusion rate on a per diluent molecule basis decreases markedly showing weaker association and/or an increase in molecular motion. The order of magnitude change in the spin diffusion rate of the aromatic carbon with concentration is particularly striking relative to the spin diffusion rate of the aliphatic carbon which changes by about a factor of 2 in the other direction. At higher concentrations there must be more labeled diluent closer to the aliphatic carbon than at lower concentrations where the diluent is specifically located nearer the aromatic carbons. The loss of specific spatial location at higher concentrations could either be the result of motion of the diluent or be the result of random relative placement because of weaker intermolecular interaction. In fact these two factors could go together, and ceratainly an increase in molecular motion at higher concentration is also consistent with the appearance of the second minimum in the proton $T_{1\rho}$ data and the increase in the fraction of repeat units with two or more diluent neighbors in the lattice model.

Other experimental results and associated models on polymer–diluent systems are related to the views developed here. The dual model model[35-37] for gases in glassy polymers invokes the present of two types of gases: a strongly bound Langmuir type and a more weakly associated dissolved type. At low concentrations, the majority of the sorbed gas is the Langmuir type; and, as concentration is raised, the relative proportion of the dissolved type increases. This type of relative population shift is contained in the lattice model though the lattice model seems more relevant to a case where the diluent and the polymer repeat unit are of the same size and therefore would occupy equivalent sites. Also, the difference between the glass transition temperature of the pure gas and the pure polymer is much greater than the corresponding difference between DBP and BPA-PC. Furthermore, gases would generally have less polarizability and therefore less ability to interact with the polymer. These factors tend to reduce the antiplasticization effect likely when a gas is added to the polymer relative to a higher molecular weight diluent. However in a general sense, it may be useful to regard gases as only very low molecular weight diluents.

Recent NMR line shape results on diluents in glasses also indicate mobility ranges that could be viewed from the lattice model.[13] If a local or microcluster of two or more diluent molecules allows for greater mobility of the polymer chain repeat units, the local cluster of diluent molecules also ought to allow for greater rotational mobility of the diluent molecules as well relative to diluent molecules completely surrounded by polymer repeat units. ^{31}P chemical shift anisotropy line shapes of phosphate ester diluents in polymeric glasses show a wide range of mobility leading to at least superficially bimodal line shape. At a concentration of 20 wt % diluent, the bimodal line shape consists of a broad line showing very little collapse plus a superimposed narrow line showing near total collapse. This indicates at least two very different phosphate ester mobilities though it is difficult to distinguish between a broad distribution of mobilities and a bimodal distribution by line-shape data alone. Concentration and spin–lattice relaxation measurements on the phosphate ester systems will enable an evaluation of the applicability of the lattice model to diluent mobility.

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Registry No. (BPA)(PC) (copolymer), 25037-45-0; (BPA)(PC) (SRU), 24936-68-3; DBP, 84-74-2.

^{13}C NMR Study of Radiation-Induced Cross-Linking of Linear Polyethylene

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ABSTRACT: Structural changes of linear polyethylene induced by ^{60}Co γ-ray irradiation have been studied by solution-state ^{13}C NMR spectroscopy. Relatively low molecular weight fractions were irradiated in the molten state in vacuo to different doses below the gel dose. As a result, sharp resonance lines assignable to the CH, α-CH_2, and β-CH_2 carbons associated with H-type cross-links have been evidently observed for each irradiated sample, in contrast to the previous reports. Concomitantly, Y-type long branches are also found to be significantly formed during the irradiation. The *G*-values of the H-links and Y-branches are estimated to be 0.74 and 0.27, respectively, indicating that H-links are more effectively produced in the molten state than Y-branches. Spin–lattice relaxation times, T_1, and nuclear Overhauser enhancement (NOE) have been also measured for the respective carbons of the H-links and Y-branches. These values suggest the less mobility of these carbons compared to the main-chain carbons and chain ends, but it does not significantly reduce the signal intensity of the H-links and Y-branches. Radiation effects of other structural units are also discussed.

Introduction

Although the effect of high-energy irradiation on polyethylene has been extensively studied, many fundamental problems still remain unsolved.[1] One of these is the chemical structure of cross-linking points of irradiated polyethylene samples. Bennett et al.[2] determined ^{13}C chemical shifts of the CH carbon and the neighboring CH_2 carbons for the H-type cross-link, which is connected by a C–C single bond, using a model compound in solution. According to this assignment, many H-links were found to be produced for *n*-alkanes by the irradiation in the crystalline or molten state.[3-7] Nevertheless, almost no line associated with the H-links could be observed for irradiated polyethylenes with considerably high molecular weights.[5-7] In contrast, the resonance lines assignable to long branches significantly increase in intensity with increasing irradiation dose, although such long branches, which are referred to as Y-branches, are not distinguished from the long branches usually involved in unirradiated polyethylene samples by ^{13}C NMR spectroscopy. Therefore, Randall et al. proposed that the production of the Y-branches would be a main cause of the gelation of polyethylene.[6]

The irradiation dose used in their work was suppressed to a level (10–40 kGy) less than the gel dose to obtain a soluble sample for solution-state ^{13}C NMR measurements. Therefore, the concentration of the H-links seems to be very close to the sensitivity limit of ^{13}C NMR. In this paper we report that the H-links are also produced in linear polyethylene samples by the irradiation in the molten state. In our experiments relatively lower molecular weight fractions, which were obtained by liquid–liquid fractionation, were used to increase the irradiation dose up to 100–500 kGy. The *G*-values of H-links and Y-branches are also estimated for these samples.

Experimental Section

Samples. A high-density linear polyethylene, Showadenko AZ3442, was fractionated into 10 fractions in a *p*-xylene–poly(ethylene glycol 400) system. The molecular weights and the molecular weight distributions of the fractions, which were determined by GPC using the calibration curve modified for polyethylene, are shown in Table I. For comparison, a low molecular weight polyethylene, Mitsui Hi-wax 200p (HW) ($\bar{M}_v = 5440$), and *n*-hexatriacontane (n-$C_{36}H_{74}$) purchased from Nakarai

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