weight homopolymer and expands when longer homopolymer chains are added. These effects are qualitatively explained as the result of relaxing constant density and increased volume fraction constraints by the addition of small mobile homopolymer molecules.

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Local Intermolecular Structure in an Antiplasticized Glass by Solid-State NMR

An antiplasticized glass is a combination of a polymer with a low molecular weight diluent which results in a material with a higher modulus.[1,2] The increase in modulus is associated with a suppression of local chain motion,[3] and this suppression can sometimes be directly observed as the disappearance of a low-temperature mechanical loss peak[4,5] or as the slowing of a specific local reorientation in a solid-state NMR spectrum.[5,6]

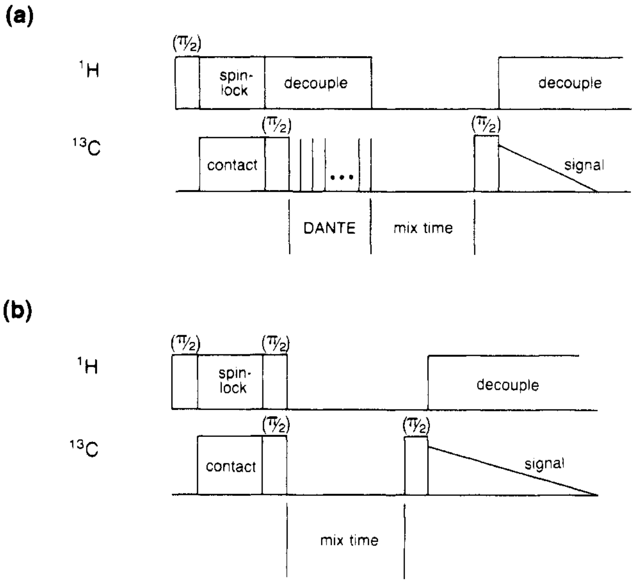

Figure 1. (a) Solid-state carbon-13 MASS pulse sequence for the measurement of spin diffusion. The pulse sequence begins with the normal cross polarization procedure. The first $\pi/2$ carbon pulse creates magnetization and the DANTE sequence selectively inverts the labeled magnetization. The mix time allows for spin diffusion between the inverted peak and the remaining resonances. The last $\pi/2$ carbon pulse just places magnetization in the xy plane for detection. (b) Solid-state carbon-13 MASS pulse sequence for the measurement of spin–lattice relaxation.[14]

Several mechanisms have been suggested for the increase in modulus and the associated suppression of sub-glass transition motion. A densification of the antiplasticized polymer is often noted[3,4] that is identified with a loss of free volume and thus a suppression of motion. At first glance, the addition of a low molecular weight diluent would be expected to increase free volume. Since just the opposite is observed for antiplasticizer, this type of diluent is supposed to go into the "holes" in the amorphous glass so as to alter the free volume distribution.[5]

To a certain extent, this explanation begs the question since it does not clearly identify the property that distinguishes a plasticizer from an antiplasticizer. Some investigators have proposed specific interactions between the polymer and the diluent as the key property of an antiplasticizer.[3,4,7] It is the purpose of this report to seek evidence for such a specific interaction by the presence of a preferred position of the antiplasticizer relative to the polymer repeat unit. The system to be examined is polycarbonate (BPA-PC) and di-*n*-butyl phthalate (DBP). The diluent, DBP, acts as an antiplasticizer at low concentrations and a plasticizer at high concentrations.[8]

The experimental approach for the determination of local structure will be carbon-13 spin diffusion between a labeled site on the DBP and various natural abundance sites in the BPA-PC repeat unit. Carbon-13 spin diffusion experiments have been developed[9,10] and have been used to demonstrate intimate mixing in blends.[11] However, no observation of spin diffusion has been made prior to this report which shows specificity at the level of chemical structure in an amorphous glass. Atomic site selectivity within a polymeric repeat unit has however been suggested as a desirable possibility in carbon-13 spin diffusion experiments.[11]

Carbon-13 labeled DBP enriched at one of the carbonyl sites was prepared from phthalic acid-α-^{13}C (99%) obtained from Merck, Inc. The phthalic acid was esterified with unlabeled 1-butanol. Diluent samples of 10 and 25 wt % were prepared by dissolving DBP and BPA-PC in

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dichloromethane followed by evaporation. Unlabeled DBP was also combined with BPA-PC in the same manner.

The one-dimensional solid-state magic-angle sample spinning NMR pulse sequence used to detect spin diffusion is shown in Figure 1. The time course of the experiment is conveniently divided into four periods, analogous to two-dimensional NMR experiments.[12] In period 1, carbon-13 magnetization is prepared by using standard cross polarization techniques. The phase-alternated 90° pulse duration was typically 5.5 μs, and the spin-lock and contact pulses were 2 ms in duration. At the end of the cross polarization, the enhanced carbon magnetization is aligned along the x axis. A 90° pulse is then applied along the y axis, rotating the magnetization parallel to the z axis. At the beginning of the evolution period, a DANTE pulse train is used to selectively invert the peak corresponding to the labeled carbon.[9] This is accomplished by centering the radio-frequency field at the selected peak and applying 18 pulses of 0.8-μs width with a pulse interval spacing of 75 μs. Hence the total time duration of the pulse train is 1.3 ms. These parameters correspond in the frequency domain to a series of pulse sidebands with a spacing of 13.3 kHz, an excitation width of approximately 670 Hz, and a resulting flip angle of 180°. Since the spectrum width is 25 kHz, only the selected peak is maximally affected by the DANTE pulse train. In addition, protons are decoupled during this period in order to prevent spin diffusion from occurring.[13] During the mixing period, the proton decoupler is turned off, broadening the carbon line widths and causing the peaks to overlap. Carbon-13 magnetization relaxes by spin diffusion and spin–lattice relaxation during this period. A 90° pulse (phase alternated in parallel with the initial 90° pulse in the preparation period) then rotates the magnetization into the xy plane for detection. Any nonlinear effects of the DANTE sequence will be constant for different mixing periods and thus decay times will be essentially unaffected.

T_1 experiments are performed on unlabeled DBP–BPA-PC blends by using the same sequence as the spin diffusion experiment but without the DANTE pulse train. The pulse sequence is essentially identical with that described by Torchia[14] for measuring T_1 and is shown in Figure 1.

A Bruker WM-250 spectrometer with an IBM solids accessory module was used to perform carbon-13 magic-angle sample spinning experiments at 62.9 MHz. The magic-angle spinning rate was 3.5 kHz, and the measurements were made at ambient temperature (21 °C). In order to perform these experiments, two modifications of the IBM solids accessory were required. The noise-blanking circuitry was modified to allow the application of multiple pulses in the carbon-13 transmitter channel. Without this modification, the length of the DANTE pulse sequence and the mixing time are severely constrained. Furthermore, a safety feature limiting the total time span of any single experiment to approximately 1 s was altered to permit single experiments requiring up to 10 s. This is necessary to obtain data with mixing times greater than 1 s.

A spectrum for the antiplasticized polycarbonate is shown in Figure 2 along with peak assignments. The spectra generated by a typical one-dimensional spin diffusion experiment are shown in Figure 3 where the labeled peak is inverted and the intensities of the BPA-PC resonances are monitored as a function of mix time. Figure 4 displays several decay curves of signal amplitude vs. mix time for some of the resonances corresponding to single BPA-PC atomic sites. These data are compared with the decay of signal amplitude observed in the T_1 experiment on the same sites in the comparable unlabeled sample.

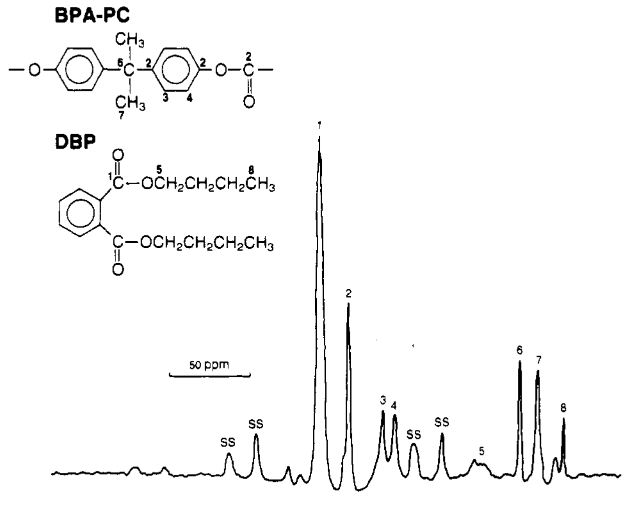

Figure 2. MASS spectrum of polycarbonate antiplasticized with di-n-butyl phthalate. Various resonances are identified with the molecular structure. (Chemical shifts: C_1, 167; C_2, 149; C_3, 127; C_4, 120; C_5, 62; C_6, 42; C_7, 31; C_8, 13 ppm). Note that peak 2 is a composite of three chemically distinct carbons that can be resolved in solution.

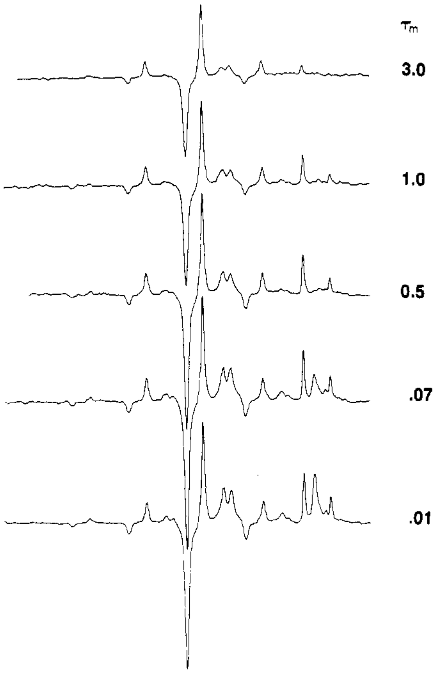

Figure 3. Typical spectra obtained during the spin diffusion experiment with inversion of the labeled carbon site.

The presence of spin diffusion is indicated by an accelerated decay rate of the magnetizations of BPA-PC sites in the DANTE experiment relative to the decay rate observed in the simple T_1 experiment. This is clearly seen in Figure 4a where the quaternary aliphatic carbon in the 25 wt % sample decays more rapidly in the experiment with the inverted DBP carbonyl magnetization than in the simple T_1 experiment. The change in decay rate can be roughly quantified by fitting both types of decay curves to a single-exponential time constant over equivalent time regimes with the typical linear least-squares procedure. Since some of the decay curves are nonexponential, this procedure is only suitable for qualitative comparisons, and the resulting time constants are listed in Table I.

A perusal of the decay curves in Figure 4 and the decay rates in Table I shows a clear difference between the 10

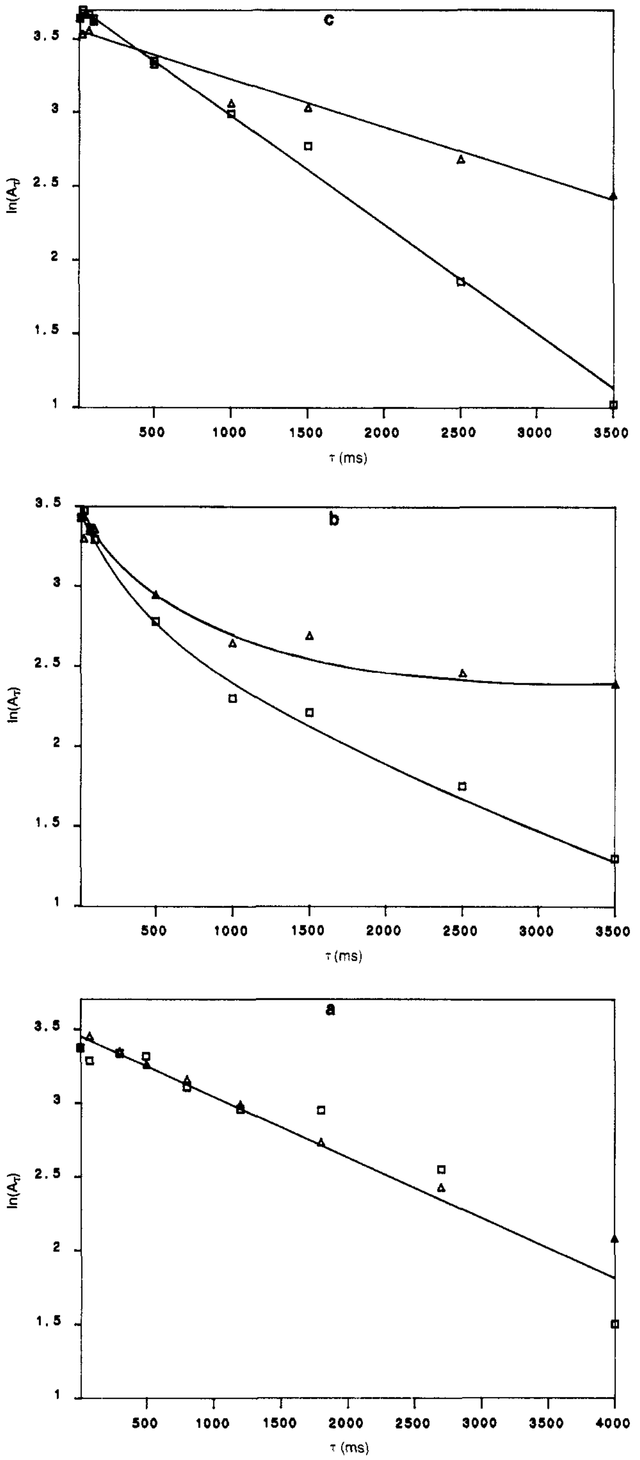

Figure 4. Decay curves observed in the spin diffusion experiment (□) with the labeled DBP and the spin-lattice relaxation experiment (△) with unlabeled DBP: (a) amplitude of the BPA-PC quaternary aliphatic carbon resonance at 25 wt % DBP; (b) amplitude of the BPA-PC protonated aromatic carbon (4) resonance at 25 wt % DBP; (c) amplitude of the BPA-PC quaternary aliphatic resonance at 10 wt % DBP.

wt % sample and 25 wt % sample. In the plasticized sample at 25 wt %, resolved lines corresponding to the two protonated aromatic peaks and the quaternary aliphatic peak all show significant spin diffusion in the form of an increased decay rate in the DANTE experiment on the labeled system relative to the T_1 experiment on the unlabeled system. This indicates molecular level mixing with spatial proximity on a distance scale of angstroms.[11] At the lower concentration of 10 wt %, corresponding to antiplasticization, the relative rate situation to the several BPA-PC sites is distinctly different. Significant spin diffusion is still seen for the two protonated aromatic sites, but little spin diffusion is noted at the quaternary aliphatic site. This distinction between the aromatic and the aliphatic sites is evident in Table I or the decay curves.

Table I
Decay Times (in s)

	25 wt % DBP		10 wt % DBP	
BPA-PC site	DANTE	T_1	DANTE	T_1
methyl	0.08	0.11	0.08	0.09
quaternary aliphatic	1.59	3.37	3.23	3.13
phenyl 3	1.77	4.99	1.83	5.05
phenyl 4	1.90	4.89	1.95	4.70

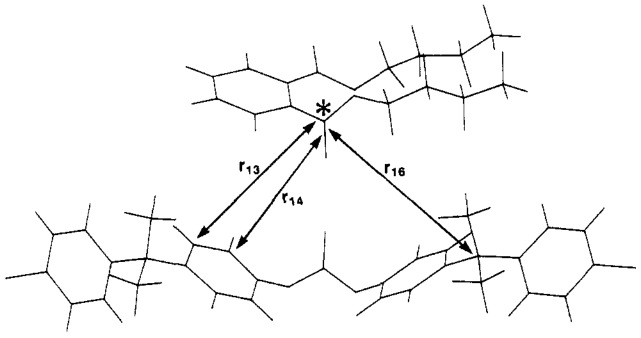

Figure 5. Pictorial representation of the relative location of DBP to the repeat unit of BPA-PC. The heavy lines indicate intermolecular distance from the labeled carbonyl: r_{13} is to the protonated aromatic carbon nearest the quaternary aliphatic carbon, r_{14} is to the protonated aromatic carbon nearest the carbonate group, and r_{16} is to the quaternary aliphatic carbon. The location of DBP is such that $r_{16} > r_{13} > r_{14}$, in agreement with the observed spin diffusion rates. The asterisk indicates the labeled carbonyl.

We believe the change in spin diffusion between the 10 wt % case and the 25 wt % case reflects a change in the level of structurally specific relative positions between an antiplasticized system and a plasticized system. Spin diffusion is determined by several factors including spatial proximity, relative orientation, and overlap of line shapes.[11] Since an amorphous glass is under study, a sum over all orientations is observed, removing this as a possible source of the difference. Changes in the overlap of line shapes are an unlikely source of the difference since the quaternary aliphatic line shape would be the same at 10 and 25 wt %, both of which are glasses at room temperature. If anything, the line width at 25 wt % should be reduced, assuming enhanced mobility in the plasticized regime, but this is where more spin diffusion is observed. This leaves spatial proximity as the remaining factor, and indeed spin diffusion depends on distance to the minus sixth power, which could certainly lead to pronounced effects.

If spatial proximity is the controlling factor, then the labeled carbonyl of DBP must be closer to the quaternary aliphatic carbon on the average in the 25 wt % case than in the 10 wt % case. Spin diffusion to the protonated aromatic carbons is still seen at 10 wt % just as it is at 25 wt %, so the spatial proximity to the phenylene groups must persist at 10 wt %. Thus the carbonyl ester of DBP must be near the phenylene groups but removed from the quaternary aliphatic site at 10 wt %. At 25 wt % this intermolecular structural specificity is lost and the labeled carbonyl is near both the phenylene and quaternary aliphatic sites.

Figure 5 depicts the position of the labeled DBP carbonyl at 10 wt % relative to the BPA-PC repeat units so that spatial proximity to the phenylene groups is maximized while spatial proximity to the quaternary aliphatic group is minimized. This picture is a greatly simplified representation and the proposed order is also localized. However, the spatial criteria for the placement of the DBP carbonyl derived from spin diffusion lead to a location of this functional group near the carbonate of BPA-PC. This is consistent with the presence of a specific interaction between the antiplasticizer and the polymer as postulated in some of the classic models of antiplasticization.[3,4,7]

At higher concentrations of DBP structurally selective spin diffusion is not observed and plasticization behavior commences. This indicates a loss of specific relative spatial positioning, and, in our view, this corresponds to the presence of DBP molecules near BPA-PC units that are not at a specific relative position and are not interacting with a particular functional group of the BPA-PC unit in question. The presence of nonspecifically interacting diluent is the cause of the onset of plasticization behavior, again in agreement with the premise of certain of the antiplasticizer–plasticizer models.[3,4,7]

In this report we have qualitatively connected structurally selective spin diffusion with preferential disposition of diluent molecules relative to the polymer chain in an antiplasticized glass. Currently a more quantitative approach involving numerical analysis of the decay curves based on coupled differential equations describing the concurrent contributions of spin–lattice relaxation and spin diffusion[11] in conjunction with a lattice model to count diluent–polymer contacts is under development. At this stage, carbon-13 spin diffusion appears to be at least capable of identifying local structure in multicomponent amorphous glasses. The method holds promise for the determination of intermolecular structure in other amorphous systems such as polymer blends where local interactions are presumed[15] but only identified in special cases such as hydrogen bonding.[16] More detailed models of intermolecular structure could result from a quantitative analysis of spin diffusion and from studies involving labeling several chemical positions of a given component.

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

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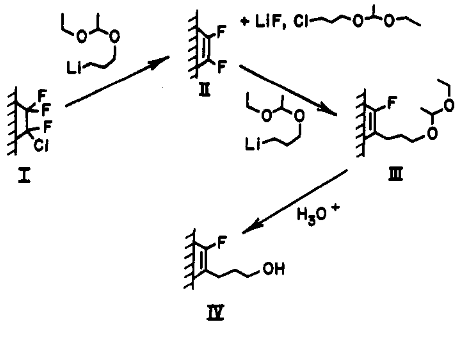
Poly(chlorotrifluoroethylene)-Containing Surface-Confined Hydroxyl Groups: A Chemically Versatile, Model Hydroxylated Surface

The chemistry of surface-confined hydroxyl groups is central to a wide range of adhesives technologies. Glass, mineral, and most metal (in the ambient) surfaces contain hydroxyl groups that are routinely exploited with coupling agents to prepare composite materials,[1,2] modified electrodes,[3] and chromatography supports.[4] For the purpose of studying hydroxylated-surface chemistry, these inorganic surfaces are often not suitable substrates: Their high surface energies cause spontaneous hydration and adsorption of atmospheric contaminants. These materials are opaque in much of the spectrum lucid to hydroxyl group chemistry, and transmission spectroscopies are not useful analytical techniques. They can dissolve in acidic and basic solution (the metal–oxygen bonds are labile); thus the surfaces are not stable to the reaction conditions of many hydroxyl group transformations. The density of hydroxyl groups (number of hydroxyl groups per cubic centimeter of surface area) on these surfaces cannot be controlled. These problems do not prevent practical applications of chemistry at these surfaces; however they do impede its fundamental study. We have been studying surface modification of chemically resistant polymers[5-7] with the objective of preparing materials with a reactive surface functionality and inert bulk. These materials obviate the problems of inorganic surfaces; their advantages as surface chemistry substrates have been discussed.[7]

We have reported[8] the independent introductions of carboxylic acid, aldehyde, and alcohol functional groups to the surface of poly(chlorotrifluoroethylene) (PCTFE) film using two step modification sequences: Lithium reagents containing the protected functional groups react with PCTFE film surfaces via a reduction–addition–elimination sequence; deprotection of the functional groups renders PCTFE–COOH, PCTFE–CHO and PCTFE–OH. Equation 1 summarizes the synthesis of PCTFE–OH; the



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