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Structure of Amorphous Films Containing Tri-*p*-tolylamine and Bisphenol-A Polycarbonate As Determined by High-Resolution ^{13}C NMR of Partially Deuterated Samples in the Solid State

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ABSTRACT: Polymer properties can be dramatically modified when polymers are blended with various small molecules. This work explores the usefulness of high-resolution solid-state NMR to probe the short-range ordering and specific interactions of tri-*p*-tolylamine and bisphenol-A polycarbonate in amorphous films. The technique involves intermolecular cross polarization from species containing protons to completely deuterated species. Resonances from carbons in completely deuterated molecules are visible in the cross-polarized spectrum only as a result of cross polarization from protons in neighboring molecules. The transfer of magnetization, which is dependent on the dipolar coupling between the protons and the carbon, is explored as a probe of site-specific interactions and spatial arrangements in the film.

Introduction

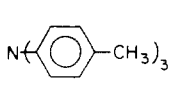
New techniques developed in recent years have made solid-state ^{13}C NMR spectroscopy a powerful analytical tool. Problems that have been overcome include (1) long relaxation times for ^{13}C nuclei in solids, (2) low sensitivity, and (3) broadening of resonances from dipolar couplings of carbons to protons and from chemical shift anisotropies.[1]

The effects of both long relaxation times and low sensitivity of the ^{13}C nuclei in solids are alleviated by cross polarization of carbon nuclei through the protons.[2] In the cross-polarization procedure, the proton spin–lattice relaxation time T_1 controls the rate at which the experiment can be repeated. This is usually much shorter than the T_1 of the ^{13}C nuclei themselves. In addition, the carbons benefit from some of the inherent sensitivity of the protons in the cross-polarization procedure.

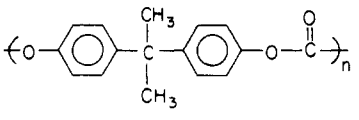
Broadening of several kilohertz from dipolar coupling interactions and chemical shift anisotropy are removed by (1) application of proton decoupling irradiation fields of 1.5 mT or more (this strong irradiation narrows the resonances by collapsing the carbon–proton dipolar interactions[1]) and (2) use of magic-angle spinning to remove broadening due to the anisotropy of the chemical shift.[3] In this paper we will explore the usefulness of solid-state NMR as a probe of the structure of systems consisting of small molecules in solid polymer matrices. Such composites have application in a variety of systems such as photoresists, charge-generation and -transport layers, and optical storage devices. The structure and morphology of composites affect their physical, mechanical, and chemical properties. Tools that elucidate their structural details enable us to optimize the desirable properties.

Various ways to use solid-state NMR to study interactions between molecules have been published. Crystal-packing effects on the chemical shift in the NMR spectrum are one source of information.[4] Special techniques to allow observation of intermolecular cross polarization in samples containing mixtures of deuterated and protonated species are also useful, but the limitations and applicability of this approach have not been fully explored.[5]

We report here the application of solid-state NMR to the elucidation of the structure and morphology of a blend of tri-*p*-tolylamine in a bisphenol-A polycarbonate (BPAPC) matrix.



TRI-p-TOLYLAMINE



BISPHENOL-A-POLYCARBONATE

Blends composed of certain amines in a polycarbonate are of intrinsic interest because of their photoconductive properties.[6] Information regarding the spatial orientation of the amine with respect to the polycarbonate in the blend will be presented, based on data obtained through the use of cross polarization from species containing protons (protonated) to those with no protons (deuterated).

Experimental Section

Solid-State NMR Spectra. Solid-state spectra were obtained on a spectrometer (constructed by S. Gross and N. Zumbulyadis) interfaced to a Nicolet 1180 minicomputer.[7] The resonant ^{13}C frequency was 50.29 MHz. The magic-angle spinning probe (Chemagnetics, Fort Collins, CO) had a 90° proton pulse width of 5 μs and used bullet-shaped spinners made of poly(oxymethylene). The spinning rate was ~4 kHz. The spinning angle was adjusted by observing the size of the spinning sidebands in the ^{79}Br spectrum of KBr, which was added routinely to every sample.[8] The Hartmann–Hahn match was adjusted frequently on an adamantane standard. We have found that our ability to cross-polarize deuterated carbons efficiently from nearby protons depends critically on how well the match is made. Cross-polarization times varied from 0.5 ms to more than 20 ms, depending upon the circumstances. Usually, 1000–2000 accumulations were required for each spectrum.

Relaxation measurements were made on a Bruker CXP-100 spectrometer with a ^{13}C resonance frequency of 25.18 MHz. Proton 90° pulse widths were 5 μs. Andrew–Beams-type poly(oxymethylene) spinners were used on this instrument. The spinning rate was 4.5 kHz.

Chemicals. Tri-*p*-tolylamine (Kodak Laboratory Chemicals) was recrystallized from hot ethanol and zone refined with 80 passes. Deuterated tri-*p*-tolylamine (Merck) was used without further purification. Bisphenol-A polycarbonate (Kodak Laboratory Chemicals) was used as received.

Deuterated Polycarbonate. To a three-neck round-bottom flask equipped with stirrer, dropping funnel, and gas inlet tube was added a methylene chloride solution of deuterated bisphenol-A (Merck) and pyridine. The appropriate amount of phosgene was condensed into cold methylene chloride and placed in the funnel. The phosgene solution was added dropwise at room temperature with constant stirring. As the polymerization progressed, the viscosity increased markedly; therefore, the rates of stirring and of phosgene addition were decreased. The product was isolated by precipitation into methanol, filtered, and washed. The white solid was oven dried under vacuum at 40 °C for 24 h. The product had an intrinsic viscosity of 0.95 dL/g in methylene chloride, an average molecular weight of 112000, and a single glass-transition temperature of 147 °C.

Cross-polarization studies on the pure deuterated amine and deuterated polycarbonate showed that few residual protons were present. However, it was possible, under exacting Hartmann–Hahn conditions and long delay and mixing times, to observe a weak ^{13}C spectrum for the amine. The amine spectrum was very

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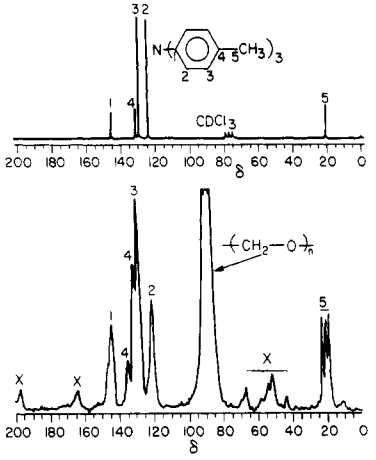

Figure 1. Upper spectrum: ^{13}C NMR spectrum of tri-*p*-tolylamine in $CDCl_3$. Lower spectrum: CP MAS ^{13}C NMR spectrum of tri-*p*-tolylamine in the solid state. The large resonance at 90 ppm is due to the sample container of poly(oxymethylene). Spinning sidebands are marked by ×.

sensitive to the Hartmann–Hahn match. With deuterated polycarbonate, no carbon resonances were ever observed during the cross-polarization experiment. ^1H NMR solution spectra showed that both the amine and the polycarbonate contained <1% protons.

A mixture of 160 mg of the deuterated amine and 150 mg of the nondeuterated amine was precipitated from methylene chloride. This mixture contained equimolar amounts of the two species.

Film Coatings. Films were prepared by hand coating methylene chloride solutions of the amine/polycarbonate (10% solids) on a nickel-coated Estar support with a 0.010-mil coating blade at a block temperature of 24 °C. The films were then cut into ~2 × 2 cm squares, which were cured in an oven at 60 °C for 15 h. The squares were removed from the support and stacked about four high; a punch was used to form circular film samples. A few hundred of these circular film samples were stacked in the spinner and, to improve stability and give a reference signal for adjustment of the spinning angle, were surrounded with KBr.

Differential Scanning Calorimetry. Differential scanning calorimetry results were obtained on a Du Pont Model 990 thermal analyzer equipped with a Model 910 cell base and DSC cell. The sample temperature was varied at 10 °C/min in a nitrogen atmosphere. T_g values were determined from the midpoints in the heat-capaity shifts. Samples were ~10 mg.

Results

Tri-*p*-tolylamine. The solid-state ^{13}C NMR spectrum of crystalline tri-*p*-tolylamine is shown in Figure 1 along with the spectrum of a $CDCl_3$ solution. The most striking difference between the two spectra is the increased number of the resonances in the solid-state spectrum. In the solid there are three methyl resonances around 21 ppm separated by 2 ppm, whereas there is only one resolved resonance in the solution spectrum.

Figure 2 shows a spectrum of the solid acquired by a technique that includes a short period between cross polarization and data acquisition during which the proton decoupler is turned off. This technique, which we will refer to as interrupted decoupling, allows suppression of signals from monoprotonated and diprotonated carbons as a result of their strong dipolar interaction with the proton reservoir.[9] The spectrum taken with interrupted decoupling shows three signals for the methyl-substituted aromatic carbon resonance, separated by about 3 ppm, near 131 ppm. The interfering signals from the protonated aromatic carbons have been suppressed. The spinner signal at 90 ppm persists, owing to its large initial intensity. Fast internal rotation of the amine methyl groups allows their signals to remain in spite of three attached protons.

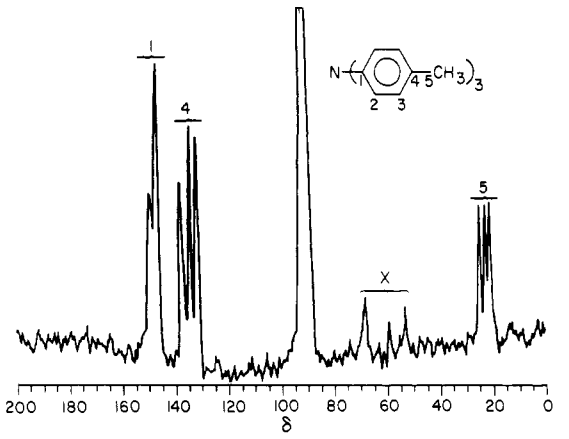

Figure 2. CP MAS ^{13}C NMR spectrum similar to the lower spectrum of Figure 1, except an 80-μs interrupted decoupling delay was used.

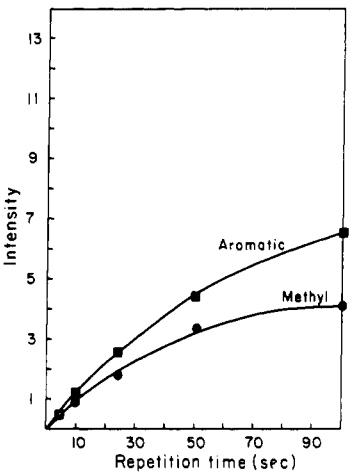

Figure 3. Relaxation data for the aromatic (C2, see Figure 1) and methyl protons of the crystalline amine. The intensity of carbon resonances is plotted vs. the overall delay between data acquisitions.

Figure 3 shows a plot of the intensity of selected amine carbon resonances vs. the delay between data acquisitions. This technique effectively measures the spin–lattice relaxation time of the protons, which cross polarize the carbon magnetizations, by the progressive-saturation method. Such plots show that the T_1 values of the protons of the crystalline amine are >60 s. Only a single value for the relaxation time was found for the protons, whether the observed carbons were methyl or aromatic, because rapid spin diffusion leads to a uniform T_1 for all the different types of protons.[10] The relaxation curves were well fitted with an exponential function.

Tri-*p*-tolylamine/Polycarbonate. Figure 4a shows the solid-state ^{13}C spectrum of bisphenol-A polycarbonate. A comparison with Figure 1 shows that some of the polycarbonate aromatic resonances occur at frequencies similar to those of the amine. Fortunately, many of the potentially overlapped signals of the polymer can be removed by a judicious choice of interrupted decoupling delay. Parts a and b of Figure 4 show this clearly. The resonances resulting from the aromatic carbons with a proton attached are effectively suppressed by use of an interrupted decoupling delay of 80 μs.

Parts c and d of Figure 4 show the spectra of a blend of 20% of the amine in the polycarbonate matrix under the same conditions used in parts a and b of Figure 4, respectively. Figure 5 shows the aromatic and aliphatic resonances of the amine (with interrupted decoupling) as

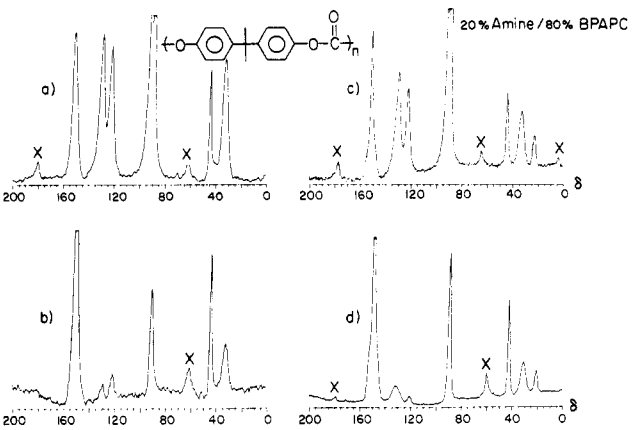

Figure 4. CP MAS ^{13}C NMR spectra acquired under normal CP (a, c) and with 80-μs interrupted decoupling delay (b, d). (a) Bisphenol-A polycarbonate, (b) bisphenol-A polycarbonate (interrupted decoupling), (c) 20% tri-*p*-tolylamine/80% bisphenol-A polycarbonate, (d) 20% tri-*p*-tolylamine/80% bisphenol-A polycarbonate (interrupted decoupling). Spinning sidebands are marked by ×.

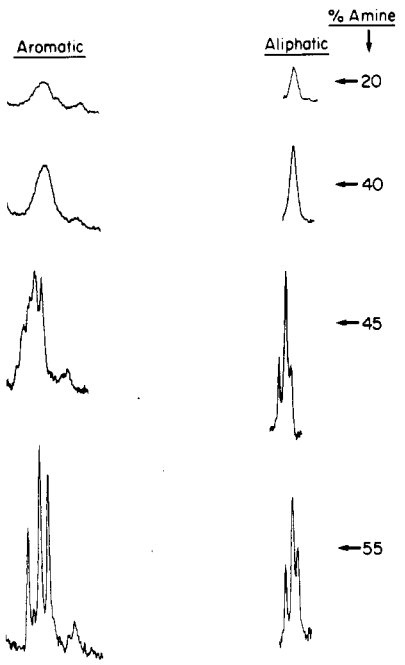

Figure 5. Methyl-substituted aromatic carbon resonance and the methyl resonances of the amine as a function of amine concentrations in blends with bisphenol-A polycarbonate.

a function of the amine concentration in the polycarbonate. Multiple resonances for the methyls and the aromatic carbon (C4) are clearly apparent when the amine concentration is >40%. Below this concentration, the methyl and aromatic signals are only single broad resonances.

Figure 6 shows a proton relaxation plot obtained from the methyl carbon of the amine. Owing to the short relaxation times observed, it was necessary to determine these values by using a saturation–recovery sequence prior to cross polarization. The protons relax exponentially with a time constant of 0.25 s, which is more than an order of magnitude smaller than that for the protons in the pure amine. Relaxation studies on the pure polycarbonate show its proton T_1's to be ~200 ms.

The 50% amine/polycarbonate blend showed two different proton relaxation times associated with the aliphatic carbons of the blend. The relaxation time associated with the amine was the longest (1 s). A shorter time (0.4 s) is associated with the methyl protons in BPAPC.

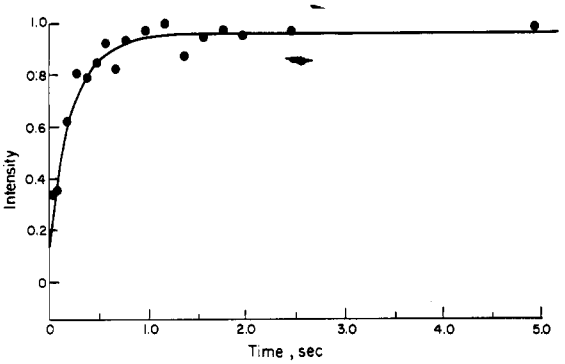

Figure 6. Relaxation data for the methyl carbon resonance of amine in 30% amine/70% bisphenol-A polycarbonate. Intensity of the carbon resonances vs. a delay after saturation was applied to the protons in the system. All other carbon resonances in the spectrum showed similar relaxation behavior.

Table I
DSC Results

% amine	T_g, °C	mp, °C
0	145	250
10	111	
20	84	205
30	66	199
40	50	115 (weak), 194
45	41	110, 193
50	36	87, 191
55	30	95, 118
60	25	85, 120
100		114

Differential scanning calorimetry results on the samples used in Figure 5 are summarized in Table I.

Tri-*p*-tolylamine/Polycarbonate (Deuterated). As mentioned before, it is possible to probe intermolecular interactions through the use of mixtures of deuterated and nondeuterated species. In the cross-polarization experiment, deuterated species will not give rise to an NMR signal unless they are in intimate contact with protons in adjacent molecules. To provide background information on the method, we applied it first to a mixture of deuterated tri-*p*-tolylamine with nondeuterated (protonated) tri-*p*-tolylamine. These results provided a basis for a study of the amine/polycarbonate blend.

A physical 1:1 mixture of the deuterated and protonated amine resulted in a spectrum, obtained under interrupted decoupling conditions, that was almost the same as that from the protonated amine alone. This mixture was simply prepared by mixing equimolar amounts of the normal amine, the species with hydrogens, and the completely deuterated amine, which contained essentially no hydrogens. By contrast, the interrupted decoupling spectrum of the 1:1 mixture precipitated from methylene chloride (Figure 7) did show resonances from the deuterated amine, which were easily differentiated from those of the normal amine because their signals persisted under interrupted decoupling conditions whereas some of those of the normal amine did not.

Noticeable in Figure 7 is only a single broad signal for the methyls instead of the three resonances for the nondeuterated material. An isotope effect apparently shifts the resonances of the deuterated material so that they cannot be resolved from those of the nondeuterated compound.[11]

Figure 8a shows the spectrum of 40% deuterated amine in BPAPC acquired without interrupted decoupling, and Figure 8b shows the spectrum acquired under interrupted decoupling conditions. Two resonances for the deuterated amine can be resolved in Figure 8, those of the methyl and

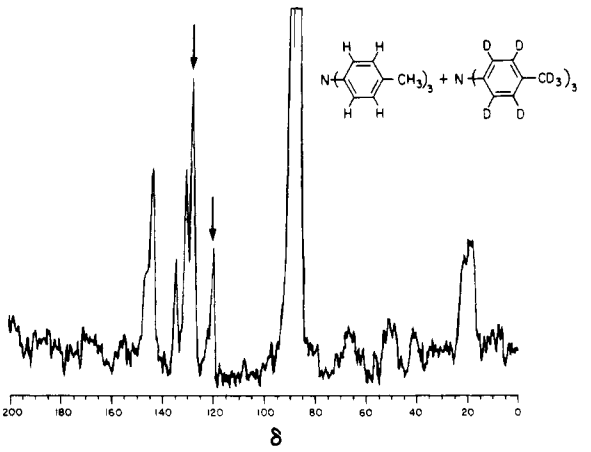

Figure 7. Spectrum of a 1:1 mixture of the amine and completely deuterated amine after precipitation from methylene chloride. Resonances due to deuterated aromatic carbons are shown with an arrow. Other resonances from carbons in the deuterated species are overlapped with resonances from the proton-bearing species. The spectrum was acquired with 10-ms CP time and 80-μs interrupted decoupling.

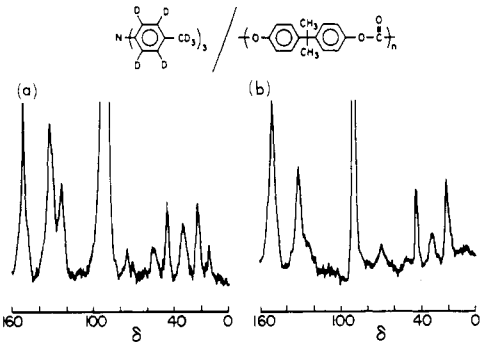

Figure 8. (a) Normal CP spectrum of 40% deuterated amine/60% bisphenol-A polycarbonate. (b) Spectrum of above acquired with an 80-μs interrupted decoupling delay. Both spectra were acquired with a 10-ms cross-polarization time.

the methyl-substituted aromatic carbons. The deuterated aromatic carbons are not readily visible but may give rise to at least part of the broad resonance upon which the resonance for the methyl-substituted aromatic carbons is found.

Relaxation times for the protons, again obtained with a saturation–recovery sequence measured through the carbons, were ~0.2 s for all the observable carbon resonances.

Varying the cross-polarization times between 0.5 and 20 ms had no noticeable effect on the relative intensities of the resonances resulting from the deuterated carbons. The intensities of these resonances indicated that methyl and nonprotonated aromatic carbons from a large majority of the deuterated molecules were being cross polarized.

Figure 9 shows the spectrum of 40% tri-*p*-tolylamine in deuterated bisphenol-A polycarbonate. All of the deuterated polycarbonate resonances are clearly visible, and their relative intensities do not vary as a function of the cross-polarization time. The relaxation time for the proton reservoir in this film was ~1 s.

Table II summarizes the proton relaxation data for all the species discussed in the previous sections.

Discussion

In this section we will discuss several topics: (1) crystal packing in pure tri-*p*-tolylamine, (2) how crystal packing effects can be used to monitor the crystallinity of the amine in a polycarbonate matrix, (3) general aspects of the in-

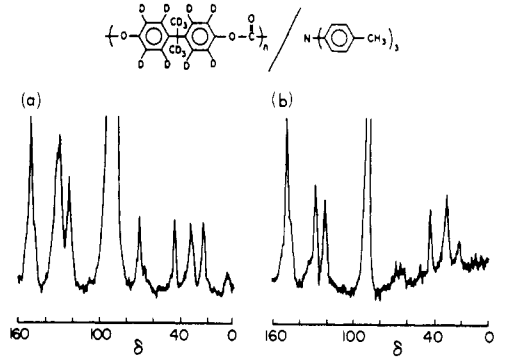

Figure 9. (a) Normal CP spectrum of 40% amine/60% deuterated bisphenol-A polycarbonate. (b) Spectrum of above acquired with an 80-μs interrupted decoupling delay. Both spectra were acquired with a 10-ms cross-polarization time.

Table II
Observed Proton Relaxation Times

sample	T_1, s
amine	>60
polycarbonate	>0.2
30% amine/polycarbonate	0.25
50% amine/polycarbonate	0.4–1.0
40% deuterated amine/polycarbonate	0.2
40% amine/deuterated polycarbonate	1.0

termolecular cross polarization of carbons in deuterated molecules by protons in adjacent molecules, (4) the use of intermolecular cross polarization to study spatial order in a system containing tri-*p*-tolylamine and polycarbonate, and (5) the relaxation properties of the above systems.

Crystal Packing in Tri-*p*-tolylamine. The crystal structure of the amine has been determined by X-ray analysis[12] and provides a basis for the interpretation of the crystal-packing effects evident in the NMR spectrum shown in Figure 1. The three separate resonances observed for the methyl and the methyl-substituted aromatic carbons can be understood only after careful consideration of the information derived from the X-ray analysis. The compound crystallizes in the triclinic group $P\bar{1}$ with two nonequivalent molecules per unit cell. Strictly speaking, this implies that there are six nonequivalent tolyl rings. However, the cell displays strong monoclinic pseudosymmetry, which is reflected in both the packing and the molecular structure of the individual molecules. Hence, for practical purposes, there are only three distinct tolyl groups in the structure. Moreover, two of these are related by an approximately twofold molecular axis of symmetry. The third tolyl group has a much larger twist angle than the other two. It seems unlikely that the differences in twist angles in the structure would result in multiple methyl signals in the NMR spectrum, especially since in the absence of intermolecular interactions (packing effects) we would expect, at most, two signals for the methyls.

The X-ray results show that each of the rings has a unique crystalline environment as a result of crystal packing. These different environments could be sufficient to cause the methyls to have different chemical shifts. Previous studies have shown that the methyl groups in hexaethylbenzene are magnetically inequivalent,[13] and intermolecular effects have been invoked as an important contribution to line widths in the carbon spectra of samples spinning at the magic angle.[14]

It is interesting that the nonequivalence of the aromatic rings is reflected even more strongly in the resonances of the carbons attached to the methyls than in those for the methyls themselves. The methyl resonances are ~2 ppm apart, whereas the resonances of the aromatic carbons to

which the methyls are attached are ~3 ppm apart.

Presumably, the protonated carbons in the three rings are also nonequivalent, but the width of the resonances from these carbons does not allow resolution of separate signals. The carbons attached directly to nitrogen are expected to give rise to additional splittings and broadening as a result of incomplete averaging of the dipolar coupling of the carbons to the quadrupolar nitrogen nucleus.[15]

Tri-*p*-tolylamine in Bisphenol-A Polycarbonate. The pure amine showed multiple methyl resonances. In contrast, the blend containing less than 40% tri-*p*-tolylamine in the polycarbonate gave a single, albeit broadened, methyl amine resonance and a single resonance for the attached amine ring carbon (see Figures 4 and 5). It is clear that the local environment of the amine molecules, at least in blends of low amine concentration, does not resemble that of the amine in the pure crystal. In fact, the breadth of the resonances suggests that there are a number of different local environments accessible to the amine molecules; each local environment causes carbons in that particular region to have a slightly different chemical shift.

Partial crystallinity of the amine could be observed when its concentration in the polycarbonate matrix was greater than about 40%. This phase separation was also apparent from visual examination of the samples, the ones with a high amine concentration being cloudy. Other evidence of the onset of crystallinity or phase separation comes from the differential scanning calorimetry results. In samples with phase separation there were two distinct melting points, one at the melting point of the pure amine and another higher one, which we assign to the amine–polymer mixture. The glass-transition temperature changed smoothly throughout the entire range of compositions.

Intermolecular Cross Polarization. One purpose of our study was to explore the use of intermolecular cross polarization to probe the spatial orientation of molecules in the solid state. In the cross-polarization experiment only carbons that are dipolar coupled to protons give rise to ^{13}C resonances. Thus, signals from carbons in completely deuterated molecules cannot normally be observed. However, in mixtures of protonated and deuterated species, carbons in the deuterated molecules give rise to signals if they are dipolar coupled to protons in nearby protonated molecules. The strength of the dipolar coupling is inversely proportional to the cube of the distance between the two nuclei. The rate of cross polarization depends strongly on this coupling.[16] The appearance of deuterated carbon resonances in an intermolecularly cross-polarized system will then signify that the deuterated carbons have neighboring hydrogens only a few angstroms away. The efficiency of this transfer to individual resonances may provide information about the spatial orientation of the nuclei.

The resonances of the deuterated carbons that are cross polarized from nearby protons are easily discernible from those of monoprotonated or diprotonated carbon resonances by the use of an interrupted decoupling delay. The protonated carbon resonances are suppressed, but the deuterated carbon resonances are only slightly affected. The resonance of deuterated carbons may appear slightly shifted from the resonances of their protonated counterparts as a result of a small (usually <1 ppm) deuterium isotope effect.[11]

To test this potentially useful technique, we first studied mixtures containing tri-*p*-tolylamine and deuterated tri-*p*-tolylamine. The interrupted decoupling spectrum of the simple 1:1 mixture of both protonated and deuterated amine showed no evidence of resonances resulting from the deuterated amine. Thus, in this simple mixture, the hydrogens in the protonated amine were not close enough to the deuterated carbons for cross polarization to occur. The sample prepared by precipitation of the mixture from methylene chloride showed resonances resulting from both the deuterated and protonated species. The methyl resonances at 21 ppm showed a deuterium isotope effect on the ^{13}C chemical shift. These resonances are actually overlapped resonance lines resulting from both protonated and deuterated methyls. Deuterated resonances in the aromatic region, marked by arrows in Figure 7, persist even under the effect of an interrupted decoupling delay, while their protonated counterparts have been suppressed.

Deuterated Tri-*p*-tolylamine in Polycarbonate. The spatial information available from NMR is not nearly as detailed as that derived from X-ray analysis. However, NMR can be applied in systems for which X-ray analysis is difficult, such as amorphous films. The solid-state NMR spectra of films containing 40% deuterated tri-*p*-tolylamine in a polycarbonate matrix showed two signals from the deuterated amine—those from the methyl and the methyl-substituted aromatic carbon. Resonances from the other amine carbons (the deuterated aromatic carbons) are not obvious in Figure 8. They may be present as part of the broad hump at 125–130 ppm, but these results suggest that at least the methyl and the methyl-substituted amine carbons are in intimate contact with the protons of BPAPC, whereas the other carbons may be more isolated.

Furthermore, a single-exponential relaxation process for all the protons coupled to observable carbon resonances in the blend implies that there is a single reservoir of proton magnetization. This single relaxation time is consistent with a compatible blend, while at the same time, the cross-polarization results indicate that at least some of the aromatic carbons of the amine are being shielded from the protons of BPAPC.

Tri-*p*-tolylamine in Deuterated Polycarbonate. To be able to project a possible solid-state environment for the interaction of the amine and polycarbonate, we must also examine the interaction of the amine with deuterated polycarbonate. In contrast to the system of deuterated amine in polycarbonate, all carbon resonances from the deuterated species, in this case deuterated polymer, are visible in the interrupted decoupling spectrum. These deuterated carbon resonances resulted from cross polarization between the protons in the amine to the deuterated carbons of the polycarbonate. Similar proton spin–lattice relaxation times in this system measured through the carbon signals for the amine and polycarbonate again indicate that there is a single proton reservoir.

In the two blends containing deuterated species discussed above, variable cross-polarization times had no noticeable effect on the relative intensities of the resonances from carbons in the deuterated species. We might have expected a rather dramatic effect because of the strong dependence of the cross-polarization rate on the distance between the carbon and the protons to which it is dipolar coupled. Cross polarization is effective only when the distance between the protons and the deuterated carbon is a few angstroms. We can conclude that the average distances between the deuterated carbons whose resonances we observe and the protons to which they are dipolar coupled must be similar, whereas the deuterated carbons whose resonances we do not observe are some greater distance away from hydrogens in the neighboring molecules. However, it is important to consider briefly

under what other circumstances the deuterated carbons in this system will not give rise to observable resonances. It is possible that these deuterated carbons could have very short $T_{1\rho}$ relaxations, and as a result their magnetizations could actually be decaying during the cross-polarization time. Schaefer[5] and Stejskal[17] have shown how $T_{1\rho}$ could be contributing to our inability to observe these resonances, but we have no indication of short $T_{1\rho}$ relaxations.

To summarize, the two resonances observed for the amine suggest that only the methyl and the methyl-substituted aromatic carbons of the amine are in close contact with the protons of BPAPC. However, this assumes that the other amine carbons are not responsible for the broad resonances observed in the aromatic region of Figure 8b. The resonances resulting from the interaction of deuterated BPAPC with protonated amine indicate that all of the deuterated BPAPC carbons have similar dipolar couplings to the amine protons and that distances between any carbon of the polycarbonate and the amine protons are a few angstroms.

Relaxation Times. We will consider here the implication of the relaxation times with regard to mobility in the blends.

The spin–lattice relaxation times of the protons in the crystalline amine were long enough to make accumulation of the carbon spectrum tedious. It is not unusual for rigid, crystalline solids to have proton T_1 values >100 s.[18] The rotation of the methyl groups in tri-p-tolylamine might have been expected to reduce this value, but the barrier for rotation of the methyl groups attached to aromatic rings is small and rotation is rapid at room temperature.[18] At room temperature, the proton spin–lattice relaxation time of thymine, which also has a rotating methyl group,[18] is comparable to what we found for the amine.

The decrease in the proton relaxation time of the amine from >60 to ~0.3 s upon blending with BPAPC has two reasonable sources. One is an increase in the overall mobility of the amine in comparison with its crystalline form. The other possibility is spin diffusion to the protons of the amine from the rapidly relaxing protons of BPAPC (relaxation time 0.2 s). Careful consideration of the relaxation times presented in Table II shows that both of these effects are important.

The proton relaxation time of 1.0 s for the amine in deuterated BPAPC is more than an order of magnitude smaller than the value for the pure material. Since the possibility of spin diffusion has been removed, this reduction is due entirely to the increased mobility of the amine in the BPAPC blend. If the datum from the 30% amine/BPAPC blend is now considered, the further reduction in the amine relaxation time from 1.0 s, observed in the deuterated blend, to ~0.3 s in the protonated spectrum is due to spin diffusion from BPAPC to the amine. This leads to the conclusion that both increased molecular motion and spin diffusion are responsible for the reduced relaxation times of the amine in the blends. If any domains of amine are formed in BPAPC, they must be small enough to allow complete spin diffusion from the amine to the polymer protons in a time period comparable to T_1.

Further changes in relaxation times are observed in comparing the blends of 30% and 50% amine with BPAPC. The only slightly longer relaxation time observed for the amine in the 50% amine/BPAPC sample is surprising since both NMR and DSC results show the crystalline nature of the 50% amine/50% BPAPC blend. It seems reasonable to expect that the relaxation time of the amine should increase dramatically with the onset of crystallization. This lack of increase can be understood if we assume that the crystalline domains of amine are small enough to allow spin diffusion from the polymer to the amine during the relaxation time. This type of process could lead to the slightly longer relaxation time that is observed.

It is obvious from the information given here that the amine/BPAPC system, at least for 40% amine/60% BPAPC, does on a molecular scale show evidence of both compatibility and a single proton reservoir and at the same time exhibit shielding of some of the aromatic carbons of the amine from the protons of BPAPC. Unfortunately, it has not been possible to determine the exact form of the ordering of the two species involved. Still, it is clear, from intensity considerations in the spectra of the deuterated species and the proton T_1's, that a large majority of the amine molecules are interacting with BPAPC. We have seen how the methyl and methyl-substituted aromatic carbons of the amine are close to BPAPC, whereas all the carbons of BPAPC seem to be close to protons of the amine. However, if the other aromatic carbons of the amine are cross polarized and appear simply as broad resonances, we are then dealing with a compatible system in which the NMR studies show no preferential ordering. We will, for the present, assume that the two clearly observed amine resonances are the *only* two deuterated amine carbons to be cross polarized and that the broad resonance at 125–130 ppm is not due to C2 and C3 of the deuterated amine. These results would then be consistent with planar stacks of amine molecules with BPAPC entwined about these stacks. These ordered regions would have to be small to be consistent with the compatibility observed.

It is possible, in this amine/polycarbonate system, that the polycarbonate acts only as a binder and that the unique photoconductive properties of the film are based solely on amine–amine interactions. To test this possibility, work is under way on a system containing both deuterated and protonated amine in a deuterated polycarbonate matrix. This study will also help to answer the questions which surround the apparent shielding of only certain amine carbons from BPAPC.

Conclusion

We studied in detail tri-p-tolylamine and its interaction in the solid state with itself and with a bisphenol-A polycarbonate matrix. The spectra of the pure crystalline amine were consistent with its X-ray analysis and showed clearly the often dramatic spectral peculiarities due to crystal-packing effects. The crystallization of the amine in the polymer matrix was followed in some detail by ^{13}C solid-state NMR spectroscopy. We observed pronounced spectral changes with the onset of crystallinity at the higher concentrations, a result confirmed by DSC.

The main emphasis of the work, however, was the use of deuterated species to probe the relative spatial orientation of the amine in a polycarbonate matrix. Our results show that the amine and the polymer do interact on a molecular basis, and the data are consistent with a compatible blend.

References and Notes

(1) Mehring, M. *NMR Basic Princ. Prog.* **1976**, *11*.
(2) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(3) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(4) (a) Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338. (b) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762. (c) Hays, G. R.; Huis, R.; Coleman, B.; Claugue, D.; Verhoeven, J. W.; Rob, F. *J. Am. Chem. Soc.* **1981**, *103*, 5140. (d) VanderHart, D. L. *J. Magn. Reson.* **1981**,

14, 117. (e) Balimann, G. E.; Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *Philos. Trans. R. Soc. London, Ser. A* **1981**, *299*, 643. (f) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *J. Chem. Soc., Chem. Commun.* **1981**, 15. (g) Zumbulyadis, N.; Gysling, H. J. *Inorg. Chem.* **1982**, *21*, 5641. (h) Richarz, R.; Sauter, H. *J. Magn. Reson.* **1983**, *52*, 308.
(5) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1981**, *14*, 188.
(6) (a) Dulmage, W. J.; Light, W. A.; Marino, S. J.; Salzberg, C. D.; Smith, D. L.; Staudenmayer, W. J. *J. Appl. Phys.* **1978**, *49*, 5543. (b) Borsenberger, P. M.; Chowdry, A.; Hoesterey, D. C.; Mey, J. W. *Ibid.* **1978**, *49*, 5555.
(7) Gross, S.; Zumbulyadis, N. *Rev. Sci. Instrum.* **1982**, *53*, 615.
(8) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(9) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(10) (a) McCall, D. W. *J. Elastomers Plast.* **1976**, *8*, 60. (b) McBrierty, V. J.; Douglass, D. C. *Phys. Rep.* **1980**, *63*, 61.
(11) Breitmaier, E.; Jung, G.; Voelter, W.; Pohl, L. *Tetrahedron* **1973**, *29*, 2485.
(12) Reynolds, S. L.; Scaringe, R. P. *Cryst. Struct. Commun.* **1982**, *11*, 1129.
(13) Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338.
(14) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361.
(15) (a) Hexem, J. G.; Frey, M. H.; Opella, S. J. *J. Chem. Phys.* **1982**, *77*, 3847. (b) Zumbulyadis, N.; Henrichs, P. M.; Young, R. H. *Ibid.* **1981**, *75*, 1603. (c) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Magn. Reson.* **1982**, *48*, 367.
(16) Demco, D. E.; Tegenfeldt, J.; Waugh, J. S. *Phys. Rev. B* **1975**, *11*, 4133.
(17) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.
(18) Andrew, E. R.; Green, T. J.; Hoch, M. J. R. *J. Magn. Reson.* **1979**, *29*, 331.

Studies of Chain Folding in Solution-Crystallized Poly(ethylene terephthalate)

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ABSTRACT: The relative conformer composition for poly(ethylene terephthalate) (PET) crystallized from a dilute solution in dimethyl phthalate as a function of temperature is studied with Fourier transform infrared spectroscopy. The trans isomer increases with crystallization temperature. Correlation of conformer composition and lamellar thickness for crystallized and annealed samples indicates that the fold structure contains between two and three gauche isomers and no trans contributions. These results are consistent with a regular adjacent reentry fold structure for solution-crystallized PET.

Introduction

Poly(ethylene terephthalate) (PET) crystallized from dilute solution is composed of aggregates of fibrillar crystals.[1,2,11] Fibrils radiate from a central nucleus and are composed of lamella-like structures. Wide-angle X-ray diffraction and electron microscopy have verified a chain-folded structure.[1] Infrared studies of the folding have been reported,[4] and more recently an infrared method has been described to measure the rotational composition in PET.[6] In this study the Fourier transform infrared (FTIR) and small-angle X-ray diffraction (SAXD) techniques are applied to solution-grown and annealed crystals with the goal of improving the present state of understanding of the disordered phase.

Background and Theory

Two parameters related to the fold structure are the long period and the relative conformer composition. For a given molecular weight and cilium length, a change in conformer composition alters the fold. In single crystals, where the amount of amorphous material is small, the magnitudes of the SAXD long period and the lamellar thickness become close. However, the quantities increasingly diverge as the intercrystalline regions become large. In poly(ethylene terephthalate), where the amorphous content is relatively high, the long period can be corrected to obtain the lamellar thickness. Illers and Hendus have developed such as relationship.[12] Assuming a two-phase structure (see Discussion) the lamellar thickness is related to the measured long period by the volume crystallinity as

$$\mathrm{LT} = L(\alpha)(\rho/\rho_c)$$

where L = long period, α = percent crystallinity, ρ = density, ρ_c = pure crystal density, and LT = lamellar thickness.

The interrelation of the lamellar thickness to the conformer composition depends on the morphological model chosen to describe the polymer structure. PET contains three conformational isomers: trans, gauche(+), and gauche(−). The two gauche conformers cannot be experimentally distinguished. The trans isomer is the major component in the crystalline phase. The gauche conformer is primarily contained in the folds and the amorphous phase as chain ends or tie molecules. We will derive the necessary equation to relate conformational composition to fold structure. Initially, we assume an ideal crystal model. Figure 1 defines useful parameters of the model. The total gauche can be represented by the degree of polymerization (DP) multiplied by the relative amount of gauche:

$$\text{total gauche} = (\mathrm{DP})(\%\ \text{gauche}) \qquad (1)$$

The gauche conformers are possibly located in the folds, tie molecules, and chain ends. The combination of these species equals the total gauche contents as

$$\text{total gauche} = \mathrm{TMG} + \mathrm{CEG} + \mathrm{FdG} \qquad (2)$$

where TMG = tie molecule gauche, CEG = chain end gauche, and FdG = fold gauche. The amount of fold gauche is equal to the number of crystal trans stems per molecule (i.e., the number of folds) times the number of gauche units per fold (n). The number of crystal trans segments per molecule is the crystal trans content, (DP)(% Txtal), divided by the number of trans molecules per stem (B).

$$\text{trans segments per molecule} = (\mathrm{DP})(\%\ \mathrm{Txtal})/B \qquad (3)$$

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