Macromolecules 1989, 22, 2157-2166

The Influence of Blending on the Local Motions of Polymers: Studies Involving Polycarbonate, Poly(methyl methacrylate), and a Polyester

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Received June 21, 1988; Revised Manuscript Received October 7, 1988

ABSTRACT: Blends of bisphenol A polycarbonate (BPA-PC) and poly(methyl methacrylate) (PMMA) exhibit a lower critical solution temperature (LCST) close to 200 °C and therefore can be prepared either as single-phase or two-phase blends simply by control of the sample preparation temperature. The single-phase blends have distinctly different sub-T_g relaxation spectra, as detected by dynamic mechanical spectroscopy, from those of the individual components or the corresponding two-phase blend. The β peak of BPA-PC is suppressed by the addition of PMMA when the two components are mixed on a molecular scale. Deuterium NMR spectroscopy also shows that local motions in the BPA-PC backbone are slower in the one-phase blends containing PMMA than they are in the pure polymer. In addition, BPA-PC motions are more inhibited in a one-phase blend containing poly(cyclohexylenedimethylene terephthalate) (PCHDMT) than they are in the pure polymer. Local motions in the PMMA chain were relatively unaffected by blending with BPA-PC. Only minor changes in the deuterium NMR spectra of samples containing deuterated PMMA or in the mechanical spectra were observed.

Introduction

The local backbone or side chain motions of polymers in miscible blends may be expected to differ from those of the pure components. A difference in the free volume of the blend, compared with that of the pure materials, would affect chain dynamics, for example. Significant volume contraction on mixing has been observed for miscible polymer–polymer blends as well as for polymers mixed with small amounts of low-molecular-weight compounds.[1-5] Specific effects of one blend component on the structure of the other may also affect the local chain dynamics. One of the polymers may induce a conformational change in the other. Mitchell and Windle found by X-ray scattering that the introduction of poly(phenylene oxide) (PPO) into polystyrene (PS) leads to a conformational change of the PS from a stacked arrangement of phenyl rings to one allowing for efficient packing of PS with PPO.[6]

Local chain motions show up experimentally as low-temperature (that is, sub-T_g) relaxations in either dynamic mechanical spectroscopy (DMS) or dielectric relaxation measurements (DE). When rapid enough, motion also narrows the broadline proton NMR spectrum of the polymer. The components of a polymer blend often give overlapping signals in DMS, DE, and proton NMR, however, making analysis of motion in the individual components difficult. Deuterium NMR spectroscopy is a powerful alternative tool for characterization of local motion in polymers because only the signals from specifically deuterated sites are observed.[7,8] The deuterium line shape gives important information about both the rate and geometry of reorientational motion at the chosen site.

Experimental results with DMS have shown that localized chain motions in polymer blends are indeed sometimes much less prominent than they are in pure polymers. In single-phase blends of PS and PPO, Yee observed that the low-temperature γ peak of PS, ascribed to the phenyl group rotation, was reduced by small amounts of added PPO.[9] The low-temperature transition of poly(vinyl chloride) is suppressed in blends with either poly(ϵ-caprolactone)[10,11] or acrylonitrile–butadiene copolymers.[12] The suppression of low-temperature transitions in polymer blends is reminiscent of a similar phenomenon that occurs when certain polymers are mixed with low-molecular-weight "antiplasticizers".[1,13,14] In a few polymer blends containing bisphenol A polycarbonate, the local motions of each component, detected by DMS, appear to be almost unaffected by the presence of the other,[15,16] but signal overlap for some of these systems makes interpretation of the experimental results difficult.

Because chain motion is a likely factor contributing to bulk polymer properties such as impact strength and ductility,[17-22] we have initiated research to clarify to what degree the chain dynamics of bisphenol A polycarbonate (BPA-PC) are modified when it is blended with either poly(methyl methacrylate) (PMMA) or poly(cyclohexylenedimethylene terephthalate) (PCHDMT). We have at the same time assessed some of the effects of blending on the dynamics of the PMMA. The structures of the polymers used in this study are shown in Figure 1.

The primary tools in the present research were DMS and deuterium NMR spectroscopy. As a basis for the discussion to follow about motion in the polymer blends, a summary of what is known about the dynamics of the pure polymers is provided in the next few paragraphs.

Cooperative movement of the carbonyl groups and the phenyl rings most probably contributes to the β process of BPA-PC detected with DMS at about −100 °C (1 Hz).[23] Strong dielectric relaxation at low temperature confirms that the dipolar carbonyl group is mobile.[24] Low-frequency measurements of phenomena such as creep, stress relaxation, DMS, and DE have resolved the low-temperature relaxation spectrum of BPA-PC into two components: a peak at higher temperature that has been assigned to the cooperative phenyl ring and carbonyl motions and a peak at lower temperature associated with the motion of the carbonyl group by itself.[25-27] Deuterium and carbon NMR spectroscopy show that the aromatic rings in BPA-PC undergo facile 180° flips.[8,28-35] Bulky groups on the aromatic rings of BPA-PC increase the temperature at which the mechanical relaxation is observed and raise its activation energy.[23,36,37] NMR spectroscopy shows that substituents such as chlorine or methyl groups on the ring near the carbonate group impede ring motion.[35,38-39]

The relaxation observed at low temperature by DMS in BPA-PC is depressed or even eliminated by the addition of dialkyl phthalates or chlorinated biphenyls and terphenyls.[13,40,41] The addition of dibutyl succinate or diphenyl phthalate to BPA-PC also increases the spin–lattice relaxation times, T_1, of nuclei in the aromatic and quaternary carbon sites.[42] Furthermore, the phenyl–carbonyl relaxation in the dielectric spectrum of BPA-PC (the higher temperature β transition) was found to be sup-

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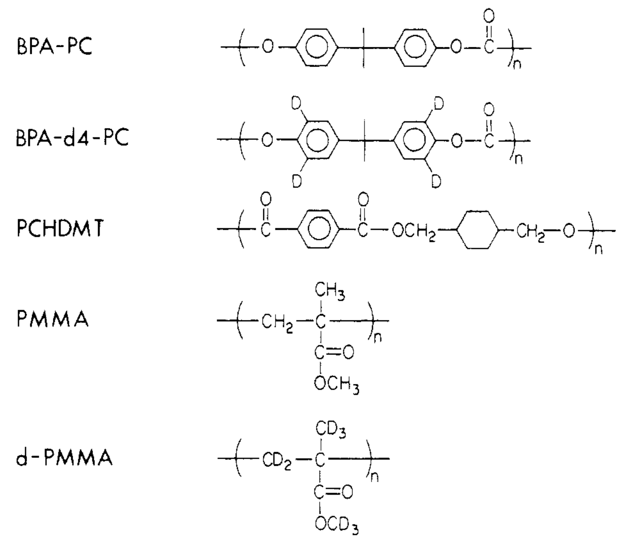

Figure 1. Structures of the polymers used.

pressed by small amounts of bisphenol A diphenyl carbonate.[43] Thus a consistent pattern of inhibition of motion by small amounts of low-molecular-weight additives emerges.

Carbon spin-exchange results for BPA-PC containing ^{13}C-labeled dibutyl phthalate have been interpreted in terms of preferential interaction of the additive with the carbonate region of BPA-PC.[44] It may be that the suppression of motion by small molecules is a direct consequence of the interaction with the carbonate unit. Interestingly, however, whereas bisphenol A diphenyl carbonate suppressed the phenyl–carbonyl combined relaxation in the dielectric spectrum, it had little effect on the carbonyl relaxation assigned to pure carbonyl motion.[43]

The β relaxation observed by DMS near room temperature for PMMA is generally assigned to hindered rotation of the ester side group about the C–C bond that links it to the backbone. The activation energy for this process, obtained from mechanical and dielectric data, is between 19 and 23 kcal/mol.[45] Molecular mechanics techniques yield, with reasonable constraints on the movements of adjacent side groups, activation energies that agree well with the experimental results.[46] Although far less experimental evidence exists for the effect of small molecules on the β relaxation of PMMA than for BPA-PC, it seems that low-molecular-weight additives do not suppress the β transition.[15]

Little is known specifically about chain motions in PCHDMT. A mechanically active β peak has been observed near −70 °C (1 Hz).[47] Poly(ethylene terephthalate) (PET), which has the same terephthalate structural unit as PCHDMT, also has a large β transition in the same temperature regime.[48-50] The aromatic rings in other polyesters of terephthalic acid undergo 180° flips.[51,52] At room temperature, however, the deuterium spectrum of polyesters with deuterated terephthalate groups is much less averaged by ring flipping than is that of deuterated BPA-PC.

Experimental Section

Polymers. The bisphenol A polycarbonate was LEXAN, from General Electric Co., and has a $\overline{M}_{\rm w}$ = 49 000 g/mol and a $\overline{M}_{\rm n}$ = 23 000 g/mol. The poly(methyl methacrylate) was Plexiglas V(811)-100, from Rohm and Haas Co., and has a $\overline{M}_{\rm w}$ = 79 000 g/mol and a $\overline{M}_{\rm n}$ = 44 000 g/mol. The synthesis of deuterated BPA-PC, specified herein as BPA-d4-PC, is described in a separate paper.[53] It has a $\overline{M}_{\rm w}$ = 377 000 g/mol and a $\overline{M}_{\rm n}$ = 82 000 g/mol. The completely deuterated PMMA, which will be referred to as d-PMMA, was obtained from Bruker Instruments as shavings from the preparation of deuterated spinners for ^{13}C NMR spectroscopy. It has a $\overline{M}_{\rm w}$ = 438 000 g/mol and a $\overline{M}_{\rm n}$ = 205 000 g/mol. All indicated molecular weights were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) and are in polystyrene-equivalent units. Poly(cyclohexylenedimethylene terephthalate) was obtained from the Tennessee Eastman Co. and has a $\overline{M}_{\rm w}$ of 47 000 g/mol and $\overline{M}_{\rm n}$ of 30 000 g/mol as indicated by size-exclusion chromatography in poly(ethylene terephthalate)-equivalent units.

Sample Preparation. The one-phase blends of protonated BPA-PC and PMMA were prepared by dissolving each polymer in THF at a 5 wt % level, mixing the solutions together in the desired proportions, and solution casting the blend, using a coating knife, onto a glass plate mounted on a heating block. Control of the temperature of the coating block to between 50 and 65 °C and restriction of the film thickness to no more between 1–2 mils assured that the films were optically clear and homogeneous. The films were dried under vacuum at 110 °C for 5–6 days.

The phase behavior of blends of BPA-PC and PMMA has been investigated by others.[54-57] The exact temperature range of the lower critical solution temperature (LCST) for PMMA/BPA-PC blends varies with PMMA specimen and with the molecular weight of the polymers.[54,55,57] For the protonated samples used herein, the LCST for a 50/50 wt % blend should occur in the temperature range between 180 and 200 °C.[56] Annealing of the one-phase blend between 200 and 270 °C for several hours under vacuum did give an opaque film with two glass transition temperatures, as evidenced by DSC and DMS. An annealing temperature of 250–270 °C was best for sample preparation because it resulted in amorphous, rather than partially crystalline, blends.

The above procedure used for preparation of one-phase samples of the nonlabeled polymers did not yield totally clear films for the blends of BPA-d4-PC and PMMA or BPA-PC and d-PMMA. This is probably because the molecular weights of the deuterated polymers were much higher than those of the protonated polymers. Single-phase blends of these deuterated polymers were therefore prepared by dropwise addition of a THF solution containing both polymers, at a total concentration of 2–5 wt %, into 10 parts of *n*-heptane. The resulting precipitate was dried under vacuum at 110 °C for 6 days.

A two-phase blend of BPA-d4-PC and PMMA was prepared by solution casting a 5% solution of the polymers in THF onto a glass plate with a coating knife. The coating block was not heated. The resulting film was opaque and was annealed at 250 °C subsequent to preparation for several hours.

A blend of BPA-d4-PC and PCHDMT in a weight ratio of 30/70 was obtained when a solution of the two polymers in dichloromethane containing just enough hexafluoro-2-propanol to dissolve the polyester was added dropwise to the nonsolvent methanol. The precipitate was dried between 70 and 80 °C for 2 days. A homogeneous blend resulted when the powder was pressed at 180 °C for 8–10 min. DSC analysis showed that it contained crystallized PCHDMT, however. To remove crystallinity, the film was then pressed at 280 °C for 8 min and quenched. Ester–ester interchange between the polyester and the polycarbonate does occur in melts of polyesters and polycarbonates, but independent studies on protonated material have shown that only a few percent of the polycarbonate groups undergo reaction in 8 min at 280 °C.[58]

Measurements. Differential scanning calorimetry was performed with a Du Pont 990 thermal analyzer equipped with a data-analysis program by Laboratory Micro Systems, Inc. The heating rate was 20 °C/min. All BPA-PC/PMMA samples were heated to 170 °C on a first run to provide a uniform sample history, were cooled under nitrogen, and then were subjected to a second scan for the actual analysis. The PCHDMT/BPA-d4-PC sample was heated to 120 °C in the DSC prior to analysis. The glass transition temperature, T_g, was taken as the midpoint between the onset and end point in the change in heat capacity.

Deuterium NMR spectra were obtained with a Bruker CXP-100 spectrometer equipped with a Bruker Aspect 3000 computer operating a home-built probe in a narrow-bore magnet at 41.45 MHz. The diameter of the sample tubes was 7 mm. Each spectrum contained 2K data points and spanned 1.67 MHz.

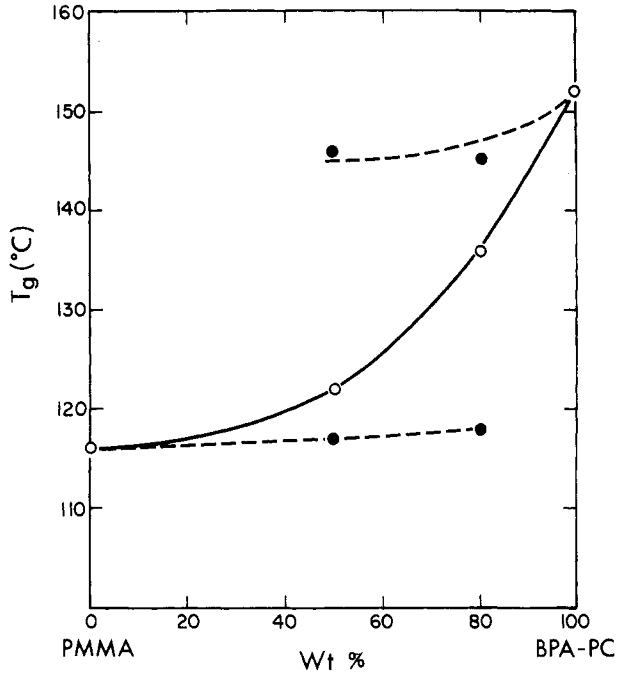

Figure 2. Composition dependence of the glass transition temperatures, taken as the midpoint of the change in heat capacity in the DSC curve obtained at a heating rate of 20 °C/min, for the (○) single-phase and (●) two-phase BPA-PC/PMMA blends.

Exponential weighting equivalent to 1000 Hz of line broadening was used prior to Fourier transformation.

Most spectra were generated from quadrupole echos formed by two 90° pulses of 3.2 μs. In some cases spectra were also obtained from the echo formed by three pulses. In the three-pulse experiment the first 90° pulse creates transverse magnetization. The transverse magnetization evolves freely for a short period of time and then is partially converted into quadrupole order or "spin alignment" by a 45° pulse.[59] The spin alignment is relatively long-lived. After periods as long as several milliseconds it can still be reconverted into transverse magnetization by another 45° pulse. An echo then forms in a time following the third pulse equal to the delay between the first and second pulse. The intensity of the echo and its shape are affected by reorientational motion that has occurred during the course of the experiment. Because the delay between the second and third pulses is relatively long, the spin-alignment experiment is sensitive to motions taking place at rates much slower than those that affect the two-pulse experiment.[59] Typically, the delay between the first two pulses in the spin-alignment experiments was 80 μs so as to provide for full separation of the alignment echo and the "feed-through" signal that inevitably follows the third pulse.[60] The delay between the second and third pulses was 2 ms. For analysis, the echo was Fourier transformed to give an "alignment" spectrum.

Spin-lattice relaxation times were measured by following the recovery of longitudinal magnetization after a saturating pulse train. A quadrupole echo was created with two 90° pulses after the recovery period for observation of the signal. The height of the echo at the point of maximum refocusing was then analyzed as a function of the recovery time. Curve fitting was accomplished with programs written for the SAS statistical package (SAS Institute, Inc., Box 8000, Cary, NC 27511) on an IBM 3090 computer.

Dynamic mechanical measurements were obtained by using a Rheovibron DDV-II dynamic tensile tester (Toyo Measuring Instruments, Ltd., Japan) automated by IMASS, Inc. The data were measured at frequencies of 1.1, 11.0, and 110.0 Hz from −150 °C to the glass transition temperature, using a heating rate of 1.5 °C/min.

Results

Differential Scanning Calorimetry. The results of DSC analysis of the polycarbonate/poly(methyl methacrylate) blends are shown in Table I and Figure 2. The clear films of BPA-PC/PMMA and the precipitated samples of BPA-d4-PC/PMMA and BPA-PC/d-PMMA showed only one endothermic transition, which is associated with the glass transition. This result verifies that only a single, mixed amorphous phase was present in each of these samples. The temperature of the transition for all these blends was a function of blend composition, as would be expected for a homogeneous blend. Figure 2 illustrates this for the protonated blends. No evidence of a crystal melting point below 300 °C was observed in any of the single-phase blends. The breadth of the DSC transition for the deuterated blends was somewhat broader than that for the corresponding protonated blends, suggesting that the former were slightly more heterogeneous.

Table I
Glass Transition Temperatures for Samples and Blends

sample	DSC, °C (20 °C/min, midpoint)	DMS, °C (tan δ, 110 Hz)
BPA-PC	152	167
BPA-d4-PC	160	
PMMA	116	145
d-PMMA	120	
PCHDMT	92	114
BPA-PC/PMMA 50/50 cast	122	148
BPA-PC/PMMA 50/50 anneal 200 °C	118/145[a]	
BPA-PC/PMMA 50/50 anneal 270 °C	117/146	135/160
BPA-PC/PMMA 80/20 cast	136	152
BPA-PC/PMMA 80/20 anneal 250 °C	118/145[a]	131/162
BPA-d4-PC/PMMA 50/50 pptd	131	
BPA-d4-PC/PMMA 50/50 anneal 250 °C	119/147	
BPA-d4-PC/PMMA 80/20 pptd	147	
BPA-PC/d-PMMA 50/50 pptd	131	
BPA-PC/d-PMMA 80/20 pptd	139	
BPA-d4-PC/PCHDMT 30/70 molded	110	130

[a] Presence of small melting peak.

The DSC results for the BPA-PC/PMMA and BPA-d4-PC/PMMA samples that were annealed above their LCST revealed two distinct glass transitions at temperatures very close to the glass transition temperatures of the individual components. This is consistent with the presence of two phases in these materials. The T_g corresponding to the BPA-PC-rich phase is slightly depressed relative to that of pure BPA-PC. Partial miscibility of PMMA and BPA-PC has previously been observed in melt extruded blends.[61,62] A small melting peak was observed for a few of these samples, as indicated in Table I, demonstrating that some crystallization of BPA-PC, as well as phase separation, had occurred during sample preparation. The DMS results were not visibly altered by the presence of small amounts of crystallinity. The DSC results for the PCHDMT/BPA-d4-PC blend are also shown in Table I. A single, composition dependent T_g was obtained, indicating a single-phase blend. The DSC results also revealed this blend to be amorphous.

Deuterium NMR Spectroscopy. Figure 3 shows deuterium NMR spectra taken at 32 and −23 °C for pure BPA-d4-PC, the one-phase 50/50 blend of BPA-d4-PC with PMMA, and the one-phase 30/70 blend of BPA-d4-PC and PCHDMT. The spectra of BPA-d4-PC are essentially identical with those published by Fischer et al.[15]

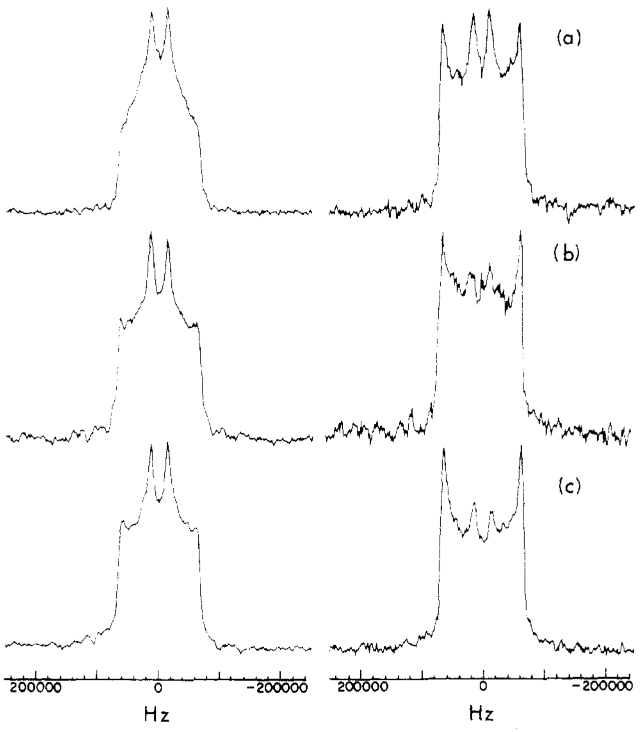

Figure 3. Deuterium NMR spectra measured for (a) pure BPA-d4-PC, (b) the one-phase, 50/50 blend of BPA-d4-PC and PMMA, and (c) the 30/70 blend of BPA-d4-PC and PCHDMT. Spectra on the left are for a sample temperature of 32 °C and those on the right are for a sample temperature of −23 °C. All spectra were obtained with a delay between the echo-forming pulses of 25 μs. The delay between experiments was 2 s for all spectra except that of the PMMA blend at −23 °C, for which the delay was 5 s.

At both 32 and −23 °C the edges of the spectra of the blends are more pronounced than are those of the spectrum of the pure polymer although the differences in the spectra are fairly subtle.

Spiess and co-workers found that there is a distribution of ring-flipping rates for BPA-d4-PC at room-temperature spanning several orders of magnitude. The Arrhenius activation energy derived from the temperature dependence of the center of the rate distribution was about 9 kcal/mol.[30] We successfully simulated the spectra of BPA-d4-PC taken at −23 and 32 °C by assuming a log-normal distribution of flipping rates with a standard deviation in ln (k) of 2 and an activation energy of 9 kcal/mol. The central flipping rate at room temperature was 8×10^6 s^{-1}.

Spectra in Figure 4 derived at 32 °C from the "alignment" echo show the differences among the three samples more clearly than do the spectra in Figure 3. This is because the echo in the spin-alignment experiment is formed over a much longer time period than is the echo in the standard two-pulse experiment. Slow motions have a much stronger effect on the spin-alignment spectrum than on the standard spectrum.

The edges of a deuterium spectrum of the two-phase blend of BPA-d4-PC and PMMA were only slightly more pronounced than are the edges for the spectrum of pure BPA-d4-PC, shown in Figure 3. This result is consistent with the DSC results, indicating BPA-PC in two-phase blends is essentially independent of the PMMA.

Figure 5 shows spectra taken at 142 and 162 °C of samples containing deuterated PMMA (d-PMMA). At the lower temperature the spectrum is dominated by the signal of the methyl groups, which is reduced in width by rapid methyl rotation. The signals of the backbone methylene

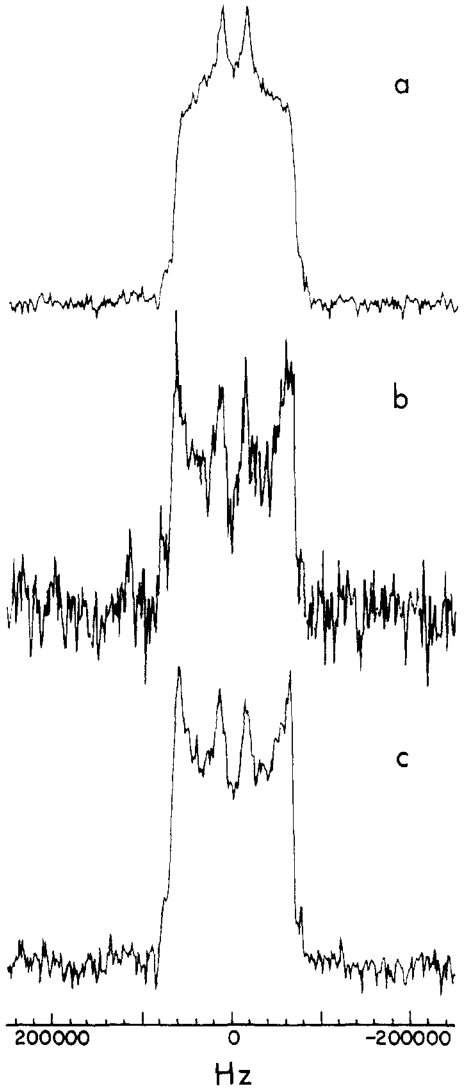

Figure 4. Deuterium NMR spectra of the blends used for Figure 3 obtained at 32 °C from the alignment echo. Following an initial 90° pulse, quadrupole order was created after 80 μs with a 45° pulse. After 2 ms, transverse magnetization was recreated with another 90° pulse, and data acquisition was begun at the top of the echo formed 80 μs after the third pulse. The total delay between experiments was 1 s.

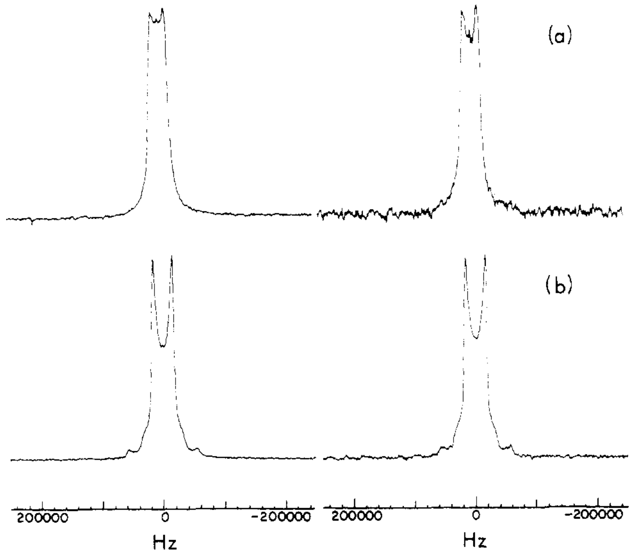

Figure 5. Deuterium spectra of d-PMMA (left) and the 50/50 blend of d-PMMA and BPA-PC (right) taken at (a) 162 °C and (b) 142 °C.

Table II
Deuterium Spin-Lattice Relaxation Times[a]

		component 1		component 2	
sample	temp, °C	weight	T_1, ms	weight	T_1, ms
BPA-d4-PC	32	0.69 ± 0.04	7.6 ± 1.0	0.31 ± 0.04	143 ± 39
BPA-d4-PC/PMMA					
50/50 one-phase	32	0.62 ± 0.02	13.4 ± 1.7	0.38 ± 0.02	406 ± 98
80/20 one-phase	32	0.71 ± 0.02	10.2 ± 0.9	0.29 ± 0.02	287 ± 69
50/50 two-phase	32	0.69 ± 0.03	9.3 ± 1.0	0.31 ± 0.03	228 ± 56
BPA-d4-PC/PCHDMT					
30/70 one-phase	32	0.63 ± 0.02	11.2 ± 1.0	0.37 ± 0.02	284 ± 48
BPA-d4-PC	−23	0.35 ± 0.02	13.4 ± 2.1	0.65 ± 0.02	814 ± 64
BPA-d4-PC/PMMA					
50/50 one-phase	−23	0.25 ± 0.02	14.3 ± 3.9	0.75 ± 0.02	1480 ± 147
80/20 one-phase	−23	0.34 ± 0.02	19.5 ± 4.3	0.66 ± 0.02	1180 ± 140
BPA-d4-PC/PCHDMT					
30/70 one-phase	−23	0.25 ± 0.02	26.2 ± 4.4	0.75 ± 0.02	1202 ± 80
d-PMMA	32	0.40 ± 0.01	4.9 ± 0.3	0.60 ± 0.01	451 ± 22
d-PMMA/BPA-PC					
50/50 one-phase	32	0.42 ± 0.01	5.0 ± 0.5	0.58 ± 0.02	471 ± 36
20/80 one-phase	32	0.42 ± 0.01	5.3 ± 0.5	0.58 ± 0.02	527 ± 44
d-PMMA	100	0.39 ± 0.01	9.7 ± 0.8	0.61 ± 0.01	373 ± 22
d-PMMA/BPA-PC					
50/50 one-phase	100	0.41 ± 0.01	10.0 ± 1.1	0.59 ± 0.02	428 ± 39
20/80 one-phase	100	0.43 ± 0.02	11.3 ± 1.8	0.57 ± 0.03	439 ± 64

[a] From fitting of the relaxation curve in terms of two exponential components.

group form a much broader pattern underlying the signal of the methyls. The spectra of pure, amorphous d-PMMA and the 50/50 blend of d-PMMA and BPA-PC are essentially identical.

An increase of the temperature from 142 to 162 °C resulted in a reduction in the width of the methyl pattern and a general decrease of the signal for the backbone carbons. In addition, the center of the spectrum was filled in. The central intensity was somewhat greater for the blend than for the pure d-PMMA.

We will assume that the distribution of ring-flipping rates that appears to occur in BPA-d4-PC reflects a distribution of local packing arrangements for the chains in the amorphous samples. Although rings at different sites flip at different rates, the parameters used for the spectral simulations show that essentially all the rings flip at a rate that is slow compared with the deuterium Larmor frequency measured in angular frequency units (260.5×10^6 rad/s). Standard NMR relaxation theory[63] shows that, in this circumstance, the rate of nuclear relaxation resulting from ring flipping is directly proportional to the ring-flipping rate. The width of the distribution of spin-lattice relaxation times should thus be a measure of the width of the distribution of correlation times for ring flipping.

Methyl rotation in d-PMMA probably occurs at a rate comparable to the deuterium Larmor frequency. Furthermore, there are several different kinds of deuterium nuclei in d-PMMA. The relation between the distribution of deuterium spin-lattice relaxation rates and the distribution of motional rates is likely to be much more complicated for d-PMMA than for BPA-d4-PC.

The recovery of longitudinal magnetization following a saturating pulse train was, in fact, highly nonexponential for all of the blend samples. The observed curve in each case was a composite of a wide range of curves decaying at different rates. For simplicity in our analysis, we approximated the measured relaxation curve as a sum of two exponential functions. In some cases the fit could have been improved with the use of three exponential functions, but this would not have aided in the analysis of the data. We will find it convenient to refer later in the paper to the "fast relaxing" and the "slow relaxing" components of the blends. The reader should recognize that this nomenclature is a semantic convenience and is not meant to imply that there are only two dynamic populations of rings in the polymers. The results of spin-lattice relaxation measurements on a variety of the deuterated samples are summarized in Table II.

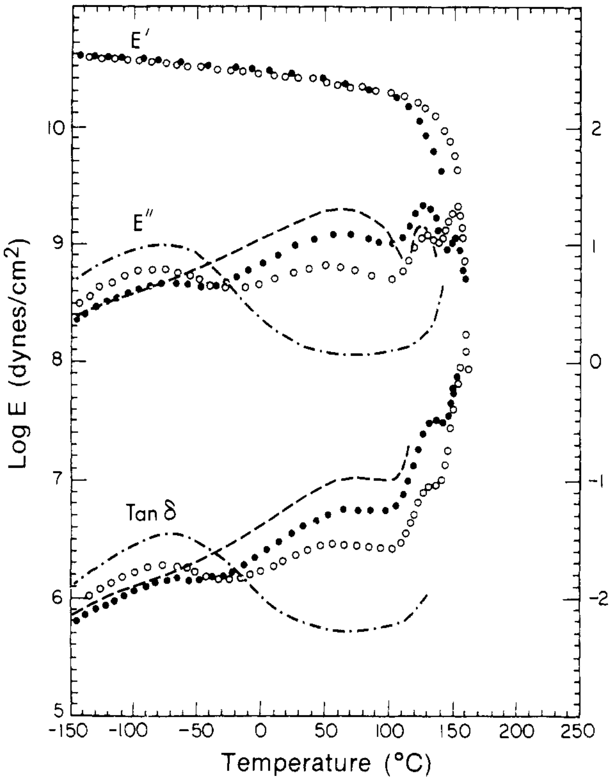

Figure 6. Dynamic mechanical spectra, at 110 Hz, of the two-phase blends of BPA-PC and PMMA with compositions: (●) 50/50 and (○) 80/20. Spectra of the pure components are shown for reference: (---) PMMA and (-·-) BPA-PC.

Dynamic Mechanical Spectroscopy. The dynamic mechanical properties of the two-phase and the one-phase blends of BPA-PC and PMMA, obtained at 110 Hz, are presented in Figures 6 and 7. Also presented in these figures are tan δ and log (E'') curves for pure PMMA and pure BPA-PC.

Figure 6 shows that the low-temperature DMS spectra of the two-phase blends are essentially superpositions of

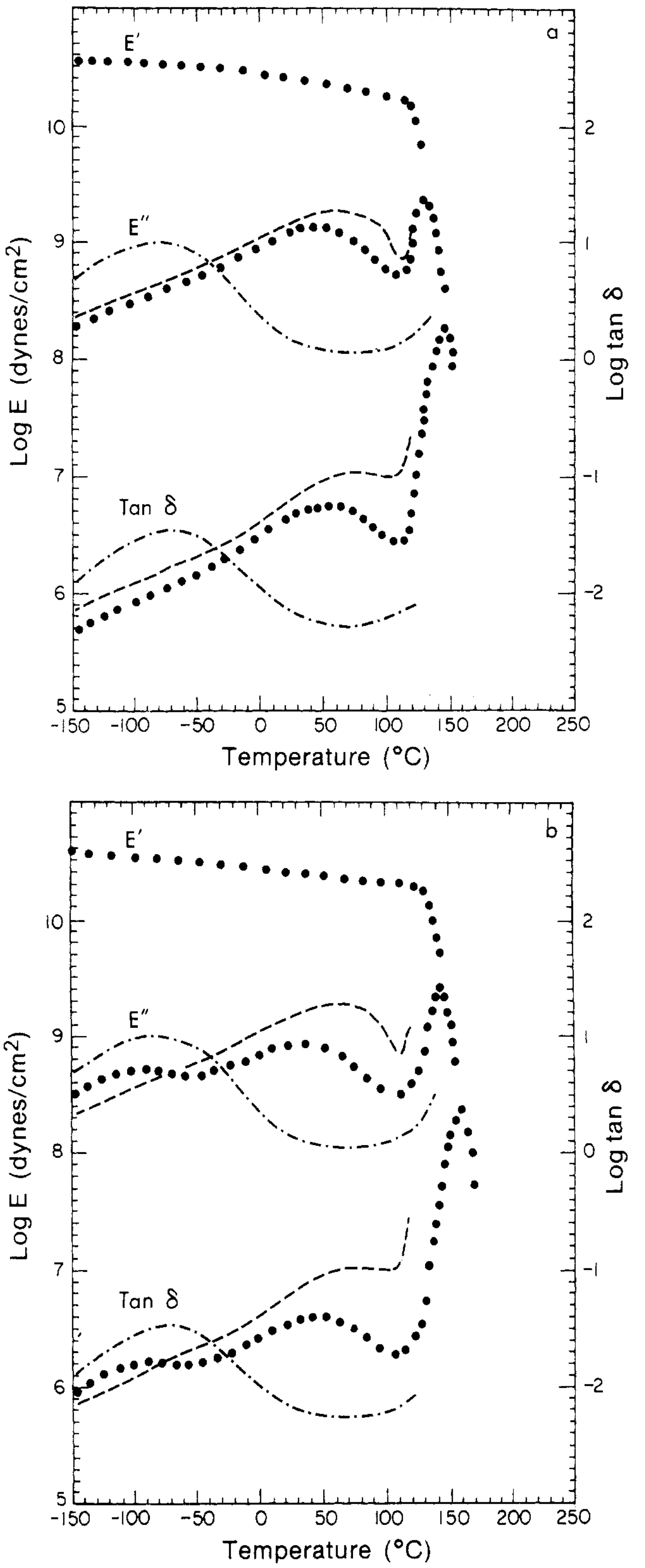

Figure 7. Dynamic mechanical spectra, at 110 Hz, of (a) the one-phase 50/50 blend of BPA-PC with PMMA and (b) the one-phase 80/20 blend of BPA-PC and PMMA. Spectra of the pure components are shown for reference (same symbols as in Figure 7).

those of the individual components. The curve shapes and the temperatures of the maxima in the β peaks for the blends are very close to those for the pure polymers; the relative peak heights are proportional to the blend composition, although the BPA-PC β peak height is somewhat lower than expected, especially for the blend that contains 80 wt % BPA-PC. This effect is perhaps due to partial miscibility of BPA-PC with PMMA.

Table III
Activation Energies Obtained from DMS for the β Transitions

sample	E_a,[a] kcal/mol
BPA-PC	10.0
PMMA	22.5
BPA-PC/PMMA 50/50 single-phase	17.9
BPA-PC/PMMA 50/50 two-phase	11.6 and 22.6
BPA-PC/PMMA 80/20 single-phase	11.6 and 14.6
BPA-PC/PMMA 80/20 two-phase	13.0 and 17.4
PCHDMT	13.1
BPA-d4-PC/PCHDMT 30/70	12.6

[a] Average of values obtained from tan δ and E''.

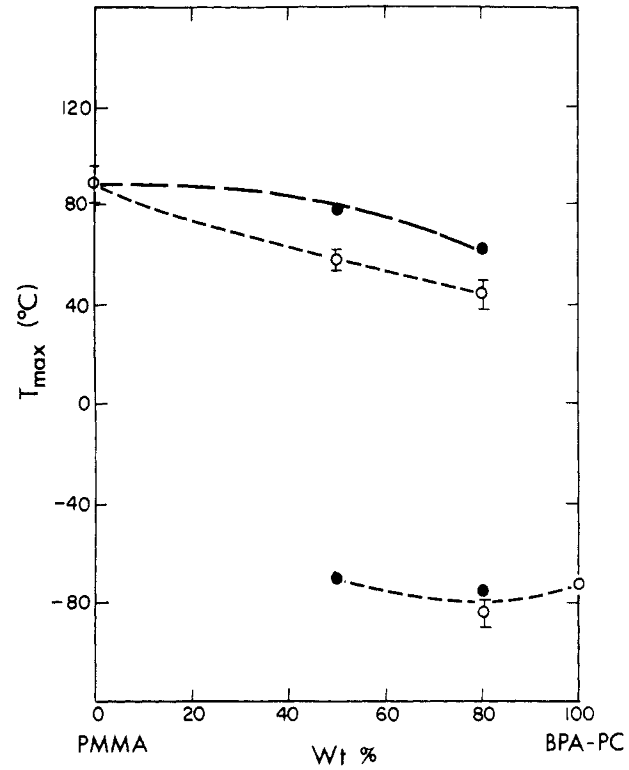

Figure 8. Plot of T_{max} for the β transition in the tan δ curve, at 110 Hz, versus weight % BPA-PC for the blends with PMMA: (○) single-phase blends; (●) two-phase blends.

On the other hand, parts a and b of Figure 7 reveal that the low-temperature spectra of the one-phase blends are fundamentally different from those of the pure components. In the spectrum for the 50/50 blend of BPA-PC with PMMA there is no evidence of the relaxation peak found for pure BPA-PC. In the spectrum of the 20/80 blend the β peak associated with the BPA-PC component is just visible (see Figure 7b), and its maximum occurs at a slightly lower temperature than that for pure BPA-PC. The location of the maximum of the β peak near ambient temperature for the one-phase blends of BPA-PC and PMMA does not coincide with that found for pure PMMA and seems to be a function of the blend composition.

Values for activation energies, E_a, determined from the Arrhenius equation

$$f = f_0 e^{(-E_a/RT_{max})} \tag{1}$$

where f is the measurement frequency and R is the gas constant, are tabulated for each system in Table III. The reported values for E_a are averages of those obtained from the maxima in the β peaks, T_{max}, in the E'' and tan δ spectra; these do not differ by more than 2 kcal/mol. The values obtained for the E_a associated with the PMMA β peak vary with composition, analogous to the temperatures of the peak maxima. This is shown in Figure 8.

The DMS spectra for the BPA-d4-PC/PCHDMT blend and the spectra for the individual components are shown in Figure 9. Since the β transitions of BPA-PC and PCHDMT are extremely overlapped, it is difficult to assess the effect of polymer blending on the transitions of the individual polymers, but it does appear that the position of the β peak and the shape of the E' curve for the blend are very similar to those of the pure PCHDMT polymer.

Discussion

DMS and deuterium NMR spectroscopy provide complementary information about polymer dynamics. The strength of deuterium NMR is that it is highly selective, giving information about motion only in those moieties that have been selectively deuterated. However, it is most sensitive to 180° flips of aromatic rings. Such flips are not by themselves mechanically active, but ring flips can serve as a "reporter" function, indirectly reflecting the rate of mechanically active motions to which they are coupled.

DMS directly detects dynamic processes contributing to the mechanical properties of a polymeric sample. Sub-T_g loss peaks of polymers observed by DMS are usually quite broad, however. Application of DMS to polymeric blends is complicated because overlap of the broad transitions from the individual components often occurs.

Both DMS and NMR show that local motion of the BPA-PC chain is inhibited in the one-phase blends of BPA-PC with PMMA. For the sample containing equal weights of the two polymers, the DMS transition was almost completely suppressed. The shoulders of the deuterium NMR spectra, which reflect in part the overall rigidity of the chain fragments, were more pronounced for the blend than for pure BPA-d4-PC. Although there was no evidence of a low-temperature β relaxation peak associated with BPA-PC in the tan δ and E'' curves for the 50/50 single-phase blend, the averaging in the deuterium spectrum that does occur shows that local motion is not completely quenched. Examination of the storage modulus, E', as a function of temperature shows also that some mechanical relaxations occur at low temperature. Figure 10 shows the temperature dependence of the storage modulus of the blend as compared to that of the pure components. If no relaxations occurred at low temperature, the initial slope of E' for the blend would be identical with that for pure PMMA. Clearly some change in the modulus with temperature does take place. The number of chain fragments moving rapidly at these temperatures is small, however.

A more detailed understanding of the effect of blending on the local chain motion in BPA-PC requires some analysis of the distribution of correlation times for motion. The deuterium spin-lattice relaxation times allow us to make such an analysis. To provide a basis for discussion of the results for the blend, we will first discuss the data for pure BPA-d4-PC (see Table II).

The observed relaxation curves for BPA-d4-PC are adequately fit by sums of two exponentials. The reader should keep in mind that the two exponentials only approximate the actual decay curve, which is the result of a broad distribution of correlation times. The apparent relaxation times for the two exponential functions are simply approximations to the collective relaxation behavior of many different kinds of nuclei. Most of the deuterium nuclei in BPA-d4-PC relax rapidly at 32 °C; the shorter collective relaxation time is 8 ms. A significant portion of the sample relaxes much more slowly, however, with a collective relaxation time of about 140 ms. We may also surmise that there is a component that relaxes in much less than 8 ms, but we do not directly detect this component. Overall, the distribution of relaxation times, and

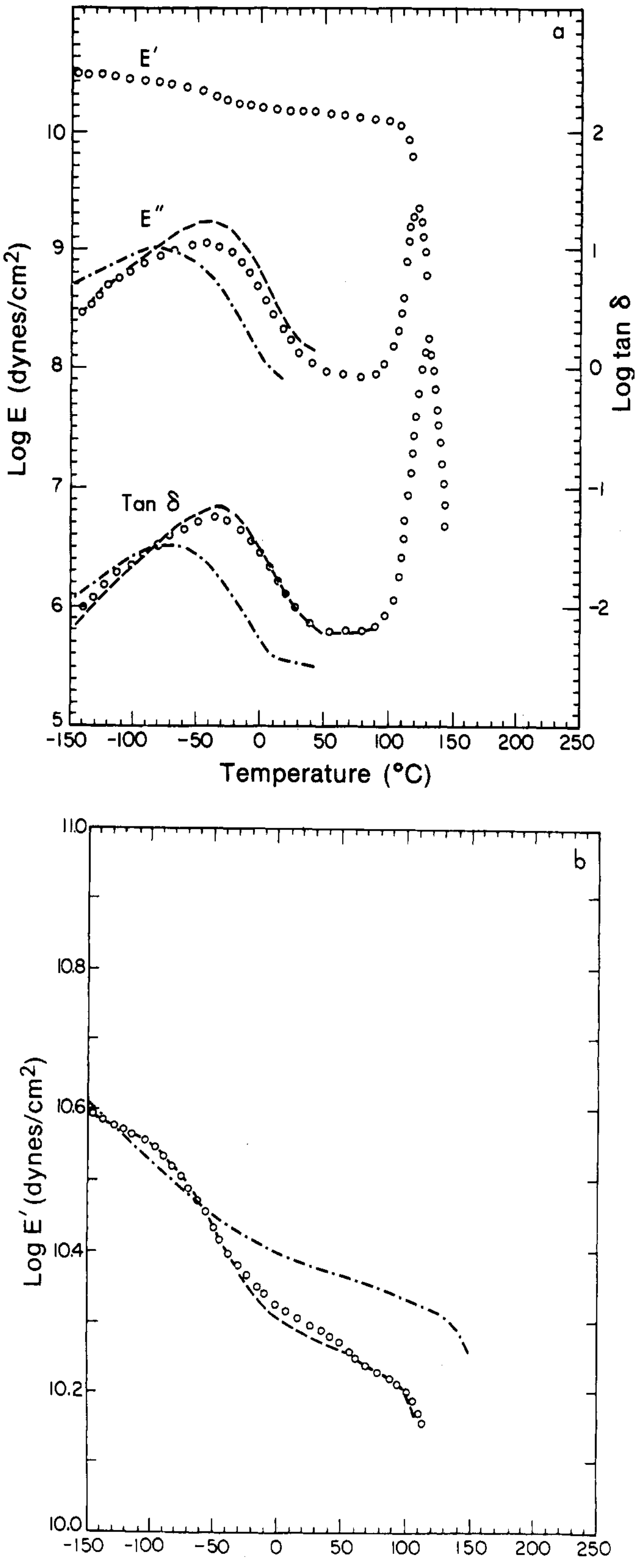

Figure 9. (a) Dynamic mechanical spectra of (○) the 30/70 blend of BPA-d4-PC and PCHDMT obtained at 110 Hz. (b) Temperature dependence of the storage modulus, E', for (○) the 30/70 blend of BPA-d4-PC and PCHDMT, at 110 Hz. Spectra of the pure components are shown for reference: (- - -) PCHDMT and (- · -) BPA-PC.

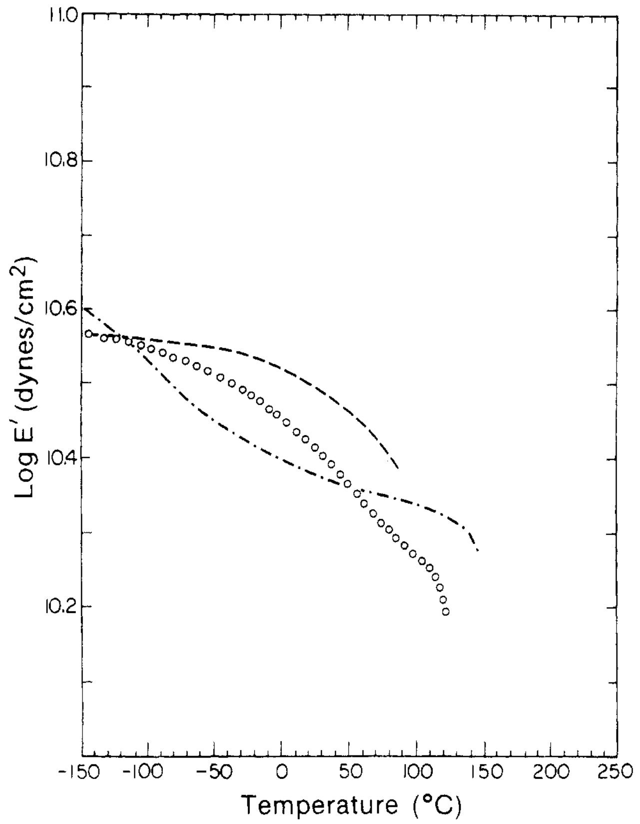

Figure 10. Temperature dependence of E' for the single-phase 50/50 blend of BPA-PC and PMMA, at 110 Hz. Modulus curves for the pure components are shown for reference (same symbols as in Figure 7).

consequently the distribution of correlation times for chain motion, appears to span roughly 2 orders of magnitude, in line with the conclusions of Schmidt, Kuhn, and Spiess.[30] At −23 °C most of the deuterium nuclei have a collective T_1 value of only about 800 ms. A smaller number of nuclei have a collective T_1 value of about 11 ms. There probably also are nuclei relaxing in a time much longer than 800 ms, but the relaxation of these nuclei would be detected only if the magnetization decay were followed for much longer times than were practical. The total span of the distribution of relaxation rates (in orders of magnitude) is slightly larger for BPA-d4-PC at −23 °C than at 32 °C.

For the one-phase, 50/50 blend of BPA-d4-PC and PMMA at 32 °C, both the slow- and fast-relaxing groups of deuterium nuclei recover more slowly from saturation than do the corresponding groups of nuclei in pure BPA-d4-PC. At −23 °C, however, the fast-relaxing component of the BPA-d4-PC/PMMA blend has almost the same collective spin–lattice relaxation time as does that of the pure polymer; the bulk of the BPA-d4-PC in the blend has a much longer relaxation time. Apparently the distribution of correlation times for ring motion in BPA-PC is broader for the blend than it is for the pure polymer. But the short-correlation-time edge of the distribution for the blend more or less coincides with that of the pure polymer.

We may use the temperature shift in the relaxation time for the major relaxation component of both the pure polymer and the blend as a basis for calculation of activation energies. Interestingly, the activation energy for ring flipping in the blend is exactly the same as that for the pure polymer (13.0 kcal/mol), in spite of the fact that the relaxation times at each temperature for the blend are longer than those for the pure polymer.

DMS shows clearly for the single-phase blend containing 80 wt % BPA-PC and 20 wt % PMMA that part of the BPA-PC undergoes relatively rapid motion even though much of the low-temperature transition of BPA-PC is suppressed. Blending affects the high-temperature side of the loss peak most strongly, and, as a result, there is an apparent shift of the observed peak maximum to lower temperature. Previous workers have found for other polymer blends that the high-temperature sides of the loss peaks are selectively suppressed in the DMS spectrum.[10,11,15]

The deuterium relaxation times obtained for the 80/20 blend at 32 °C were intermediate to those for the pure polymer and the 50/50 blend. For blends that are mixed at the molecular level, we would expect that the dynamic properties would change in a smooth fashion as a function of composition. At −23 °C the relaxation time of the major component of the 80/20 is also intermediate to those for the pure BPA-d4-PC and the 50/50 blend. The fast relaxation time appears to be slightly longer than those for either of the other two samples but is within experimental error of the fast relaxation time of the pure polymer.

All the results taken together suggest that blending of PMMA with BPA-PC results in inhibition of local motion in the latter. At the same time some chain motions are just as fast in the blend as in the pure polymer. The net result is a broadening of the distribution of correlation times for BPA-PC motion while the fast edge of the distribution remains situated at approximately the same place in the blend as in the pure polymer. The change in the distribution of correlation times is in part only a statistical phenomenon, however. A certain proportion of the BPA-PC chains in the blend is largely surrounded on the basis of chance by other BPA-PC chains, even when there is a significant amount of PMMA in the blend. The motion of these chains is at least as fast as are the motions in pure BPA-PC. Naturally, the fraction of the mobile BPA-PC units increases with increasing concentration of BPA-PC in the blend. Thus the low-temperature peak in DMS is visible in the single-phase 80/20 blend even though it cannot be detected in the 50/50 blend.

The reduction in mobility of the BPA unit in BPA-PC blends with PMMA suggests the pesence of strong intermolecular interactions between the two polymers. Gardlund has discussed a possible n–π complex formation between the n electrons of the ester group of PMMA and the π electrons of the BPA-PC rings.[62] Alternatively, the suppression of motion may simply result from steric interactions resulting from a loss of free volume in the blend as compared with the pure polymers.

Suppression of BPA-PC motion from blending with PMMA suggests that there should be a comparable suppression of mobility in the PMMA from blending with BPA-PC, especially if strong intermolecular interactions take place. The shift of the DMS β peak for the PMMA in the one-phase blends to lower temperature (Figure 7) and the corresponding decrease in activation energies (Table III), however, suggest that PMMA motion may actually be facilitated by the presence of BPA-PC.

Since the β peak of PMMA is very close to the α peak, the two are not perfectly resolved, and the exact shape of the β peak depends on sample annealing conditions. Annealing the one-phase blends near T_g raises the magnitude of tan δ and E'' in the temperature region near the onset of the α transition, as it does for the pure PMMA. This can result in an apparent shift of the PMMA β peak maximum to higher temperature. The magnitude of the change in the temperature of the PMMA β peak maximum with annealing is illustrated by the error bars in Figure 8. Our analysis shows that the effect of annealing does lead to an uncertainty of 2 kcal/mol in the values of E_a. On the other hand, the E_a values obtained from the PMMA β peak in the blend differ from those for pure PMMA by more than the estimated error of 2 kcal/mol, so the apparent effect of blending on PMMA motion may be real.

In principle, deuterium NMR spectroscopy might clarify the effect of polymer blending on the local motions of PMMA.[64,65] The spectrum of the 50/50 blend of d-PMMA and BPA-PC does appear to be slightly less averaged at 162 °C than is the spectrum of pure d-PMMA (Figure 5). The spectral differences may simply reflect the fact that the glass transition temperature of the blend is higher than that of the pure polymer, but NMR spectroscopy would suggest that PMMA chains in the blends are less mobile than those in the pure polymer. Deuterium spin–lattice relaxation times for d-PMMA observed for the pure polymer and for the polymer blends differ by less than the experimental error at a given temperature (Table II). There is a consistent shift of the relaxation times to higher values for increasing concentrations of BPA-PC, however. To the extent that the differences in the relaxation times are meaningful, they suggest that BPA-PC inhibits PMMA motion. BPA-PC has a much more subtle effect on local motions of PMMA than PMMA has on the local motions of BPA-PC. Unfortunately, our results do not completely clarify the situation.

The DMS results for blends that have been annealed above their LCST are consistent with the conclusion that these blends consist of more than one phase. Likewise, the deuterium NMR spectra are essentially those of pure BPA-d4-PC, as would be expected for a phase separated material. Nevertheless, the activation energies calculated from DMS data, shown in Table III, are not identical with those of the pure polymers, although those associated with the BPA-PC in the blends are the same as for pure BPA-PC to within the experimental error. The E_a values associated with PMMA decrease somewhat with the addition of BPA-PC but are not lowered as much as they are in the single-phase blends. Some degree of mixing may persist in the two-phase blends. A small amount of mixing would have a negligible effect on the NMR results.

Deuterium NMR shows that ring flips of BPA-d4-PC are inhibited in blends of BPA-d4-PC and PCHDMT. Suppression of ring flipping comparable to that observed for the 50/50 blend of BPA-d4-PC with PMMA appears to require a higher concentration of PCHDMT, however. Table II shows that blending of only 20% PMMA with BPA-d4-PC has about as much effect on the deuterium relaxation times as blending of 70% of PCHDMT with the polycarbonate. The temperature dependence of the relaxation times for the PCHDMT blend again leads to an activation energy of 13.0 kcal/mol, the same as that found for pure BPA-d4-PC and the PMMA blend. DMS is inconclusive about the effect of PCHDMT on the motions of BPA-PC.

Careful examination of the DMS results of Fischer and co-workers[15] on the miscible blend of BPA-PC and tetramethyl bisphenol A polycarbonate, TMBPA-PC, shows that the high-temperature portion of the β peak for BPA-PC is selectively suppressed. Complete suppression of the β peak in the blend does not occur, however, even for samples containing 80% by volume TMBPA-PC. Also, the shape of the TMBPA-PC β transition is not altered from that of pure TMBPA-PC. Both β transition heights vary in proportion to blend composition. In ternary blends of polystyrene (PS), BPA-PC, and TMBPA-PC, the shape and peak maximum of the BPA-PC β transition are not changed from those of the pure polymer.[66] It may be that polymers that are themselves capable of undergoing aromatic ring flips are less effective at suppressing motions in BPA-PC than are polymers that do not contain aromatic rings, such as PMMA.

Conclusions

Both DMS and deuterium NMR show that local motions in the BPA-PC backbone are inhibited by the presence of PMMA or PCHDMT in a miscible blend. DMS suggests that the motions of the side chains of PMMA may also be affected by blending with BPA-PC. We do not have any experimental evidence about the effect of blending with BPA-PC on the motions of PCHDMT.

The large changes in the local mobility in BPA-PC may have significant effects on the ultimate properties of these blend materials. It has been seen that for poly(2,2-bis-(3,5-dichloro-4-hydroxyphenyl)propane carbonate) (Cl_4-PC), where the β transition is shifted from −100 to about +100 °C, there is a loss of toughness.[23,36,67] The effect on the mobility of BPA-PC produced by blending with other polymers is very reminiscent of the antiplasticization phenomenon.[1,13,14,40,41] Antiplasticization of BPA-PC results in a significant increase in the polymer modulus. Modifications of the BPA-PC repeat unit that result in changes in the mechanical spectrum similar to those that we have observed also decrease the impact strength; the impact strength of a modified polycarbonate, with methyl group substitution ortho to the ester linkage, was lower than that of pure BPA-PC by a factor of 4.[68] Overall, we expect that the phenomena that we have observed will have important ramifications as to the mechanical properties of polymer blends produced from BPA-PC and other materials.

Acknowledgment. We are very grateful to Dr. David Teegarden for making the deuterated BPA-PC. We also thank Dr. Hsinjin Yang for his preparation of the blend of BPA-d4-PC and PCHDMT. Many conversations with Dr. Dennis Massa were very helpful in the development of the ideas presented in this paper.

Registry No. BPA-PC (SRU), 24936-68-3; BPA-PC (copolymer), 25037-45-0; PCHDMT (SRU), 24936-69-4; PCHDMT (copolymer), 25037-99-4; d-PMMA, 63541-79-7.

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Intramolecular Excimer Formation Dynamics of *meso*-Bis[1-(2-pyrenyl)ethyl] Ether Studied by Single-Photon Timing with Simultaneous Analysis

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Received July 19, 1988

ABSTRACT: The excited-state kinetics of *meso*-bis[1-(2-pyrenyl)ethyl] ether is reinvestigated in isooctane. With the use of nonstationary fluorescence techniques, kinetic and thermodynamic parameters of intramolecular excimer formation are obtained, and the existence of two conformers in the ground state of this compound is demonstrated.

Introduction

The photophysics of 2,4-diarylpentanes[1-4] and bis(1-arylethyl) ethers[5,6] as first-order model compounds for vinyl polymers[7] elucidated a number of features of the behavior of these compounds in solution. A more detailed knowledge of the molecular dynamics of these systems, in the ground and excited states, is being acquired.

The distribution of the possible conformers in the ground state has been intensively investigated by means of ^{1}H NMR spectroscopy.[8-10] In the case of *meso*- and *rac*-2,4-di(2-pyrenyl)pentane (D2PP), one can obtain information about the ground-state distribution of the con-

0024-9297/89/2222-2166$01.50/0