Diluent effects on carbonate mobility in bisphenol-A polycarbonate in the solid state

L. A. Belfiore*, P. M. Henrichs† and S. L. Cooper
Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA

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The effect of miscible low molecular weight additives on the mobility of the carbonate group in bisphenol-A polycarbonate (BPAPC) has been studied using n.m.r. and dielectric relaxation experiments in the solid state. Proton-enhanced dipolar-decoupled carbon-13 n.m.r. spectra of BPAPC, isotopically enriched at the carbonate position, are obtained without magic-angle sample spinning. The resolved chemical shift anisotropy allows study of nuclear spin relaxation for the carbonate groups in the polymer that have different orientations relative to the static magnetic field in the laboratory frame. The spin–lattice relaxation time in the rotating frame ($T_{1\rho}$) is measured at a motional-probe frequency of 50 kHz for the undiluted polymer and for BPAPC–diluent blends containing either dibutylphthalate or dinitrobiphenyl. The $T_{1\rho}$ exhibits some dependence on orientation in all systems studied. In the blend containing dibutylphthalate (DBP), $T_{1\rho}$ is decreased by a factor of two for all orientations of the carbonate group. This implies that DBP substantially increases the spectral density of 50 kHz motions in the carbonate region of the polymer at ambient temperature. In contrast, dinitrobiphenyl does not significantly alter the Fourier component of thermal fluctuations at 50 kHz. Dielectric relaxation measurements at 10 kHz reveal that the primary (T_g) and secondary (β) motional processes in BPAPC are affected by low molecular weight additives. An intermediate relaxation process appears in the temperature interval between the glass transition temperature (T_g) and the sub-T_g β-relaxation (T_β) in the polymer–diluent blends. The n.m.r. spin–lattice relaxation rate in the rotating frame, $T_{1\rho}^{-1}$, correlates well with the relative magnitude of the dielectric dissipation factor ($\tan \delta_\varepsilon$) between T_g and T_β.

Keywords Polycarbonate; solid state n.m.r. relaxation; plasticization; antiplasticization; dielectric relaxation

INTRODUCTION

The macroscopic mechanical and thermal properties of bisphenol-A polycarbonate (BPAPC) in the glassy state are affected considerably by the addition of miscible low molecular weight diluents. In all cases, the glass transition temperature (T_g) of the blend decreases continuously as the diluent volume fraction is increased. In some systems, there is a composition region where the room-temperature tensile modulus of the blend exceeds that of the undiluted polymer. The term 'antiplasticization' is used to describe diluent-induced rigidity and brittleness in glassy polymer–diluent blends in contrast to the decrease in tensile moduli usually observed in plasticized systems[1-3].

Previous mechanisms that have been proposed to distinguish plasticization from antiplasticization have focused primarily on (a) the effect of the diluent on both the primary (T_g) and secondary (β) relaxation processes in the polymer determined using dynamic mechanical and dielectric spectroscopy[4-7], (b) the observation of a new relaxation process in polymer–diluent blends in a temperature region intermediate between the T_g and β-loss peaks[8], (c) the glass transition temperatures of the polymer and the diluent[2,9], (d) the deviation of the overall fractional free volume from linear additivity when the two components of the blend are intimately mixed at the molecular level[3,5,10,11], and (e) specific interactions between polymer and diluent due to secondary forces of attraction[3,12,13]. In a previous study[14], it has been suggested that the temperature dependence of the interaction free energy of mixing changes abruptly at the glass transition temperature when a polymer–diluent blend is cooled below its T_g from the molten state. This information has been used to predict the relative magnitudes of the Flory–Huggins interaction parameter (χ) for blends in the glassy state.

It is well known and understood that the presence of molecular motion is responsible for relaxation or decay of nuclear magnetization[15]. Schaefer *et al.*[16-18] have shown that high-resolution, solid-state n.m.r. spectroscopy can be used to study motions in glassy polymers. With the aid of techniques such as high-power dipolar decoupling (DD), magic-angle sample spinning (MASS), and cross polarization (CP), both high-resolution and high-sensitivity carbon-13 n.m.r. spectra of solid polymers have been obtained. From the site-specific nature of these spectra *via* the isotropic chemical shift interaction, a variety of spin relaxation experiments were carried out and interpreted in terms of motions in selected regions of the macromolecule. In a previous study[19], the ^{13}C spin–lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured for several BPAPC–diluent systems from high-resolution n.m.r. spectra. The relatively low-T_g additives, dibutylphthalate (DBP) and dibutylsuccinate (DBS), enhance the mid-kHz mobility of both the aromatic and aliphatic regions of the polymer at 25°C. In contrast,

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[*] Present Address: Dept. of Agricultural and Chemical Engineering, Colorado State University, Ft. Collins, Colorado 80523, USA

[†] Eastman Kodak Research Laboratories, Rochester, New York 14650, USA

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higher-T_g additives such as dinitrobiphenyl (DNB) and diphenylphthalate (DPP) produce no significant changes in the Fourier components of BPAPC chain mobility of the order of 50 kHz. Both DNB and DPP are classified as antiplasticizers for polycarbonate whereas DBP and DBS are conventional plasticizers. This classification was determined from a comparison of tensile moduli at ambient temperature when the diluent concentration in the blend exceeded 20 wt%[1].

In the previous study[19], $T_{1\rho}$ for the carbonate carbon in BPAPC was not determined. This lack of information is primarily due to the fact that the carbonate carbon resonance is not well-resolved in the high-resolution natural-abundance ^{13}C CP-n.m.r. spectrum of BPAPC in the solid state[16]. In the present study, this difficulty is overcome by the use of isotopic labelling. Even in the absence of magic-angle sample spinning, the ^{13}C n.m.r. spectrum of polycarbonate, isotopically labelled at the carbonate position, retains its site-specific character because the resulting powder pattern is predominantly due to one type of carbon nucleus. Hence, the purpose of this study was to examine with the aid of isotopic enrichment whether the mobility of the carbonate group is affected by intermolecular interactions between polymer and diluent in the glassy state.

EXPERIMENTAL

N.m.r.

Proton-enhanced ^{13}C n.m.r. spectra of isotopically-enriched polymeric solids were obtained using a laboratory-constructed spectrometer (Eastman Kodak Co.) operating at 200 MHz for ^1H (50.3 MHz for ^{13}C) with an Oxford magnet[20]. The 90° pulse width for ^1H was 4.5 μs. Samples were inserted in the probe (purchased from Chemagnetics, Fort Collins, Colorado) in containers made from standard 10 mm glass tubing. Carbon-13 spin–lattice relaxation experiments in the rotating frame were carried out using the methodology of Schaefer *et al.*[16] without magic-angle sample spinning. The carbonate carbon powder spectrum was generated *via* cross polarization[21,22] at 50 kHz using a contact time of 3 ms. Following Stejskal and Schaefer[23], spin–temperature alternation in the rotating frame was used during cross polarization to suppress two types of artefacts which can occur in proton-enhanced spectra: (1) carbon signals generated by spin–lattice relaxation rather than cross polarization, and (2) voltage transients generated in the probe by long r.f. pulses in the carbon channel. The ^{13}C magnetization was allowed to decay in the presence of a 50 kHz effective magnetic field in the rotating frame after breaking thermal contact with the proton spin system. The technique for measuring the r.f. power in the carbon channel is described elsewhere[14]. The ^{13}C free induction decay was acquired with simultaneous high-power proton decoupling at 50 kHz. For each spectrum, 128 FID's were accumulated using quadrature detection with a pulse sequence delay time of 4 s. Each FID contained 512 time-domain data points prior to Fourier transformation. The spectral width was 20 kHz and the line broadening was 100 Hz. The temperature of the probe was not controlled and was assumed to be at ambient conditions.

Dielectric relaxation

Dielectric experiments on bisphenol-A polycarbonate and BPAPC–diluent blends in the solid state were carried out using an apparatus designed to operate in the a.c. steady-state mode. The sinusoidal frequency of the applied voltage was controlled using a Krohn-Hite Model 4100R oscillator. Conductive and capacitive balances were made with a General Radio 1615-A capacitance bridge equipped with a Princeton Applied Research Model 129A two-phase/vector lock-in amplifier for null detection. The sample temperature was controlled electronically by a Ransco cryogenic test chamber Model SD14-1 using liquid nitrogen as the coolant. Thermal equilibration was attained at each temperature before measurements were made. Data were taken in increments between 5° and 15°C with the closer measurement intervals in the regions of the dielectric loss maxima. The samples for dielectric testing were discs 7.6 cm (3.0 in) in diameter and approximately 0.50 mm (0.020 in) in thickness. The dielectric samples were placed between the two stainless-steel electrodes in a Balsbaugh Model LD-3 three-terminal condenser. The surface of the sample was gold-plated under vacuum to ensure good electrical contact between the sample and the electrodes.

Materials

Bisphenol-A polycarbonate, ^{13}C-enriched at the carbonate position, was synthesized for the n.m.r. experiments *via* the solution polymerization (methylene chloride/pyridine) of isotopically-labelled phosgene (Merck, 90% ^{13}C in benzene solvent) and bisphenol-A at ambient temperature. The intrinsic viscosity of the labelled polymer in methylene chloride was 0.215 dl g^{-1} at 25°C. This corresponds to a weight-average molecular weight ($\bar{M}_w$) of 8900 ± 800 using the data of Berry *et al.*[24] which were calibrated with results from light-scattering measurements. The glass transition temperature of the ^{13}C-labelled polycarbonate was 127°C (using the endpoint of the incremental change in specific heat) at a heating rate of 20°C min^{-1}. From the calorimetric data of Merrill and Petrie[25], the number-average molecular weight ($\bar{M}_n$) was estimated to be 3300 ± 200. This implies that the number-average degree of polymerization was ≈ 13.

The polycarbonate used for dielectric testing was obtained from the General Electric Co. as Lexan® pellets. Analysis by gel-permeation chromatography calibrated for polystyrene gave a number-average molecular weight of 2.7×10^4 and a polydispersity index ($\bar{M}_w/\bar{M}_n$) of 2.2.

The low molecular weight additives used in this study were dibutylphthalate (DBP), 2,2′-dinitrobiphenyl (DNB), and methylabietate (MA). DBP and DNB were obtained courtesy of Eastman Chemical Products. MA (trade name Abalyn) was kindly supplied by Hercules Inc.

Sample preparation

Bisphenol-A polycarbonate is known to crystallize in the presence of certain low molecular weight additives that induce plasticization[26]. This process occurs in a limited temperature range above the depressed T_g of the polymer–diluent blend and below the melting point. The sample preparation technique was designed to avoid this complication. Amorphous BPAPC–diluent blends for the solid-state n.m.r. and dielectric relaxation experiments

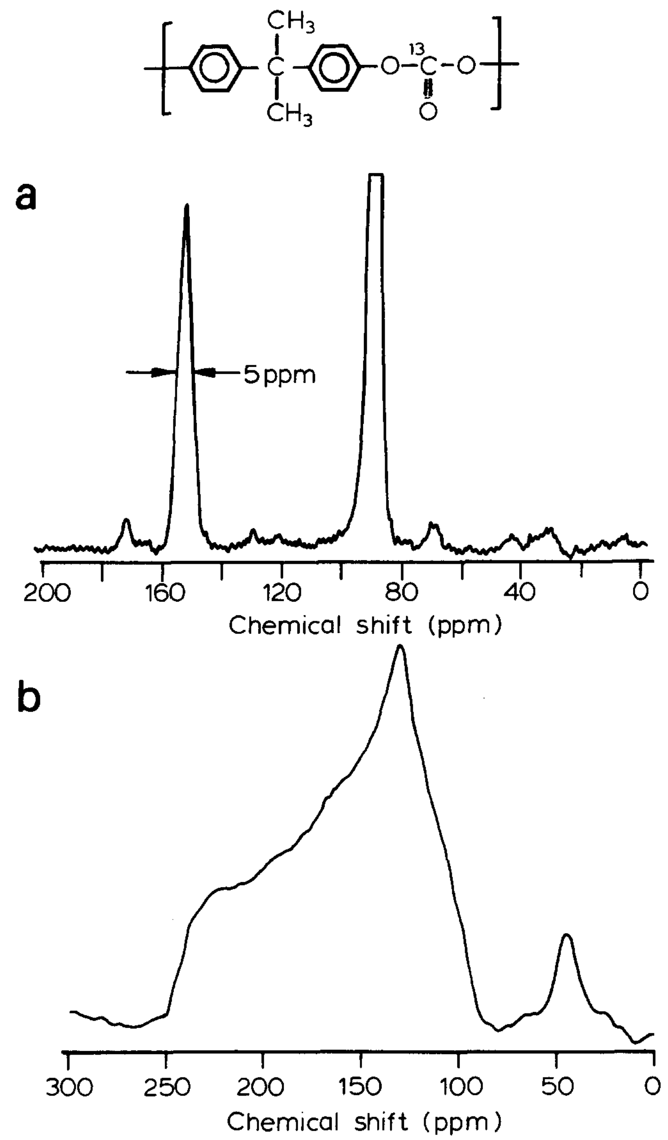

Figure 1 Proton-enhanced dipolar-decoupled ^{13}C n.m.r. spectra of bisphenol-A polycarbonate labelled at the carbonate position. (a) With magic-angle sample spinning at 4100 Hz. The strong signal at 90 ppm is due to the Delrin rotor. Spectral parameters: cross-polarization contact time, 4 ms; 32 FID's; 4096 time-domain data points; line broadening, 25 Hz; pulse sequence delay, 3 s. (b) Without magic-angle sample spinning. The spectral parameters are given in the Experimental

were prepared in the following manner: (a) the polymer was dried under vacuum at elevated temperature to remove any traces of moisture, (b) the components of the blend were dissolved in dichloromethane and intimately mixed for at least 24 h, (c) the solvent was removed by room temperature evaporation in a fume hood, (d) the inhomogeneous polymer film was removed from the casting surface and further solvent removal was carried out at ≈75°C for 10 h, (e) the resulting material was compression moulded at 230°C for 5 min under a load of 2 MPa to produce a homogeneous blend composition, and (f) the material was quenched in an ice bath at slightly above atmospheric pressure. The same procedure was followed in preparing test samples of the undiluted polymer. In a previous study of diluents in polycarbonate[19], wide-angle X-ray diffraction patterns of representative blends prepared according to the procedure described showed no indication of BPAPC crystallinity.

RESULTS AND DISCUSSION

Nuclear magnetic resonance

Carbonate ^{13}C powder spectrum. The proton-enhanced dipolar-decoupled ^{13}C n.m.r. spectrum of bisphenol-A polycarbonate, isotopically enriched at the carbonate position, is shown in *Figure 1* with and without magic-angle sample spinning. The isotropic chemical shift of 152 ppm for the carbonate carbon using MASS at 4100 Hz is in agreement with the value found in deuterated chloroform solution[14,27]. The spectrum in *Figure 1b* illustrates the absorption lineshape under non-spinning conditions for a chemical shielding tensor without axial symmetry. The width of the resonance pattern is attributed primarily to the chemical shift anisotropy (CSA). Each orientation of the carbonate group relative to the static magnetic field in the laboratory frame results in a resonance at a different chemical shift. In principle, more information is available from a n.m.r. spectrum obtained without MASS. This is true in the present study because the CSA lineshape is primarily due to one type of carbon nucleus in the polymer.

The proton-decoupled CP–MASS ^{13}C n.m.r. spectrum which includes 25 Hz of artificial line broadening (*Figure 1a*) reveals an isotropic lineshape approximately 350 Hz wide (at half height) for the carbonate carbon. This suggests that both intermolecular and intramolecular homonuclear dipolar interactions between ^{13}C-labelled nuclei are negligible. However, it should be emphasized that both CSA and dipolar line broadening will be reduced by MASS if the strengths of the interactions are less than the spinning frequency.

From *Figure 1b*, the principal values of the chemical shielding tensor for the carbonate carbon nucleus in BPAPC are approximately 100 ppm, 127 ppm, and 230 ppm relative to liquid tetramethylsilane. Hence, the CSA is ≈7 kHz at the high field condition. The orientation of the principal axis system in the macromolecule was assigned by analogy with other compounds[28].

The relatively small signal centered at ≈40 ppm in *Figure 1b* is assigned to the natural abundance aliphatic ^{13}C nuclei in the polymer. There are at least two factors which contribute to the intensity of this resonance. First, the signal is comprised of two types of carbons (two methyls and one quaternary) in the BPAPC repeat unit. Secondly, the smaller CSA of aliphatic carbons relative to that for aromatic and carbonate carbons results in a narrower lineshape and, therefore, a considerable signal intensity.

The ^{13}C powder spectra of the two samples containing the low molecular weight additives are almost identical to the spectrum of the undiluted polymer. In the blend of polycarbonate and dibutylphthalate, the natural abundance aliphatic ^{13}C resonances of the diluent contribute noticeably to the polymer spectrum only in the region between 10 and 50 ppm. Diluent-induced changes in carbonate mobility in BPAPC are not apparent from a comparison of the CSA lineshapes.

Spin–lattice relaxation in the rotating frame. Carbon-13 n.m.r. powder spectra from the spin–lattice relaxation experiment in the rotating frame at 50 kHz are shown in *Figure 2* for polycarbonate and a blend of polycarbonate and dibutylphthalate. The time τ corresponds to the duration of the spin–lattice relaxation interval. It is evident that the rate of decay of the lineshape is not

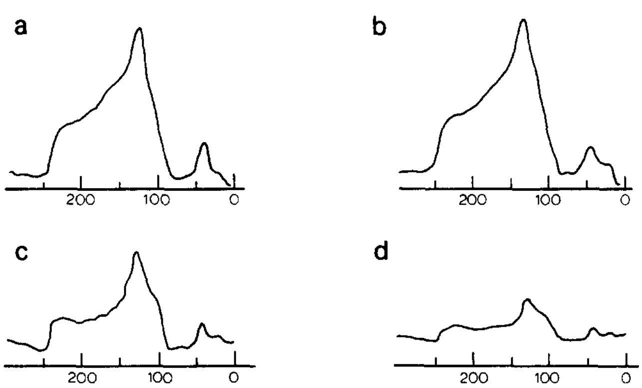

Figure 2 ^{13}C n.m.r. powder spectra of the carbonate carbon in isotopically enriched polycarbonate illustrating spin–lattice relaxation in the rotating frame at 50 kHz. The time allotted for the decay of the magnetization is designated by τ. (a) and (c) BPAPC and (b) and (d) blend of BPAPC (71%) and dibutylphthalate (29%). (a) and (b): τ, 1 μs; (c) and (d): τ, 18 ms

isotropic in each system. More importantly, the lineshape decays faster in the blend containing dibutylphthalate relative to the undiluted polymer.

Diluent effects on the ^{13}C $T_{1\rho}$ relaxation curves at 50 kHz are shown in *Figure 3* for the carbonate group orientation in BPAPC which results in a resonance at 127 ppm. The logarithm of the resonance intensity at 127 ppm is plotted against the time τ that the ^{13}C magnetization was held (spin-locked) in the rotating frame at 50 kHz after breaking thermal contact with the proton spin system. The absolute magnitude of the resonance intensity, $I(\tau)$ shown in *Figure 3*, is arbitrary. A linear least squares fit of the relaxation data between $\tau = 10$ ms and $\tau = 50$ ms was obtained using the following equation:

$$\ln\{I(\tau)\} = \ln\{I(0)\} - \frac{\tau}{T_{1\rho}}$$

where $T_{1\rho}^{-1}$ characterizes the relaxation rate of the magnetization in the rotating frame. In contrast to the MASS $T_{1\rho}$ studies on the other nonequivalent carbons in the polycarbonate repeat unit[16,17,19,29], where the relaxation behaviour was described best by a distribution of n.m.r. relaxation times, the rate of decay of the ^{13}C magnetization in the carbonate powder spectrum is adequately characterized by one relaxation time constant.

It is assumed that transient oscillations in the carbon spin system following removal of the ^{1}H r.f. field at $\tau = 0$ do not affect the $T_{1\rho}$ relaxation curves. The persistence of such oscillations is controlled by the lifetime of dipolar order in the proton nuclear system. For 75% crystalline polyethylene, the oscillations last for $\approx 70\,\mu s$[30]. The conclusions here are based on the rate of decay of the carbonate magnetization between 10 and 50 ms, by which time it is assumed that the proton dipolar order will have disappeared.

Later discussions of $T_{1\rho}$ as a source of information about polymer motion require that the mechanisms for decay of the ^{13}C magnetization in the rotating frame are understood. For most carbons, the decay results from modulation of the carbon–proton dipolar interactions at frequencies similar to the carbon precession frequency about its effective field in the rotating frame. In the spin–lattice mechanism, the modulation is the result of the reorientational motion of the polymer itself, whereas in the spin–spin mechanism, the modulation results from the internuclear interactions among the protons. Schaefer and coworkers[17,31] have measured ^{13}C $T_{1\rho}$ relaxations for several glassy polymers, including polycarbonate, spinning at the magic angle. They conclude that at room temperature the protonated aromatic carbons in BPAPC relax primarily by a spin–lattice mechanism. It is considered here unlikely that the carbonate carbon relaxation is primarily spin–spin in nature if the relaxation of the protonated aromatic carbons is spin–lattice in nature.

It is possible, however, that the carbonate carbon relaxes through a chemical-shift anisotropy mechanism rather than a dipolar mechanism. It has been observed recently in studies not yet published that there is nuclear Overhauser enhancement greater than 2 over the entire carbonate powder pattern. Schaefer[16] also observed a large NOE on the small portion of the carbonate band resolvable in unenriched samples, albeit at a lower magnetic field strength. These results demonstrate that spin–lattice relaxation in the laboratory frame is largely dipolar in nature. There would have to be a large low-frequency contribution to the spectral density function controlling $T_{1\rho}$ relaxation which does not contribute at high frequency to the spectral density function controlling T_1 relaxation in order that $T_{1\rho}$ relaxation proceeds by a

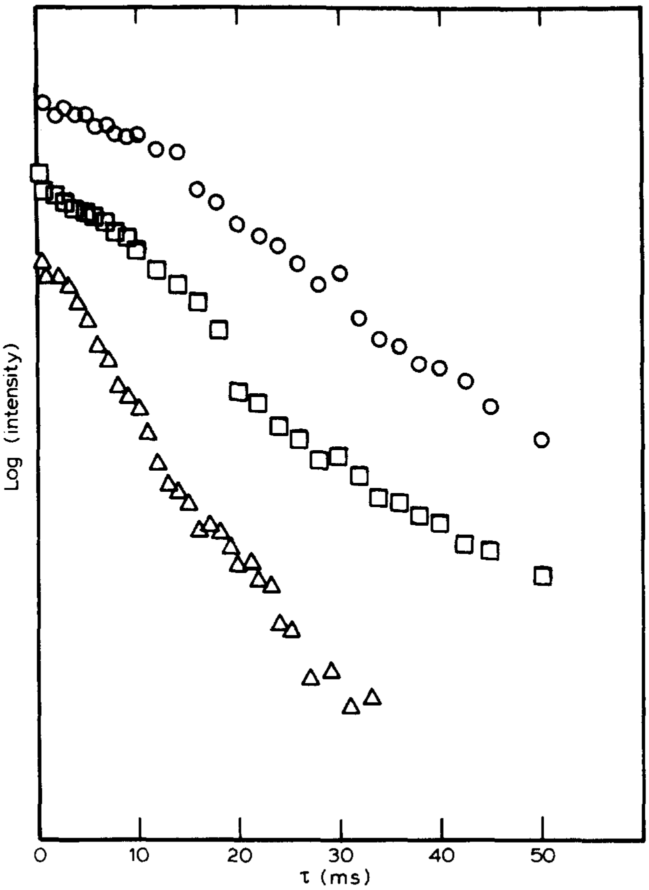

Figure 3 $T_{1\rho}$ curves at 50 kHz for the carbonate carbon resonance at 127 ppm in ^{13}C-labelled polycarbonate. The logarithm of the resonance intensity is plotted as a function of the time that the ^{13}C magnetization was held in the rotating frame without cross-polarization contact with the protons. The materials are: ○, BPAPC; □, 69% BPAPC-31% dinitrobiphenyl; and △, 71% BPAPC-29% dibutylphthalate

Table 1 Spin–lattice relaxation times in the rotating frame at 50 kHz for the principal values of the carbonate ^{13}C chemical shielding tensor in isotopically-labelled polycarbonate[a]

	$T_{1\rho}$ (ms)		
System	100 ppm	127 ppm	230 ppm
Polycarbonate	29, 31	27, 29	27, 31
69% Polycarbonate 31% Dinitrobiphenyl	25, 26	24, 27	26, 29
71% Polycarbonate 29% Dibutylphthalate	15, 16	15, 18	15, 16

[a] Results are presented from two experiments on each material

chemical shift anisotropy mechanism at the same time that T_1 relaxation proceeds by a dipolar mechanism. In work also to be published, it has been established that the bandshape of the carbonate carbon undergoes only modest changes when the temperature is decreased to as low as 18 K. Thus, the chemical shift of the carbonate group appears to be modulated only slightly by motion, and is unlikely to be able to contribute to relaxation processes.

Even if the carbonate carbon relaxes primarily by a dipolar process, it is possible that the detailed process involves transfer of magnetization from the carbonate carbon to the unenriched protonated carbons by spin diffusion. If the protonated carbons relax much faster than the carbonate carbon directly, spin diffusion then provides an indirect route for relaxation of the carbonate carbon. Normally, fast carbon–carbon spin diffusion can be ignored because of the low natural abundance of the ^{13}C nucleus, but for enriched samples it should be considered. For the unenriched carbons to be able to relax the labelled carbonate group effectively, however, their own relaxation times must be several-fold faster than that of the carbonate carbon to compensate for the differences in abundance. The relaxation times of the carbonate carbons (20–30 ms) are similar to those found previously for other carbons in polycarbonate samples spinning at the magic angle[19]. The apparent difference in relaxation behaviour of carbonate groups at different orientations also suggests that communication between the carbonate carbons is not rapid on the time scale of the relaxation experiment. In summary, it is assumed that the rotating frame spin–lattice relaxation of the carbonate carbon occurs by a dipolar mechanism and is motional in character.

In BPAPC, it is necessarily the protons of the aromatic rings which lead to dipolar relaxation of the carbonate carbon. As a result, the relaxation may reflect motion of either the carbonate group or the aromatic rings. The dielectric data given later indicate that the carbonate group in BPAPC is not static at ambient temperature. Most likely, motion of both groups contribute to the carbonate carbon relaxation, possibly in a co-operative manner.

Values for $T_{1\rho}$ at 100, 127 and 230 ppm are given in *Table 1* for polycarbonate and the two BPAPC–diluent blends which contain either 31% dinitrobiphenyl or 29% dibutylphthalate. The differing effects of the two low molecular weight additives on the carbonate ^{13}C $T_{1\rho}$'s in BPAPC are evident. At the three principal values of the chemical shielding tensor, the lower-T_g diluent, dibutylphthalate, substantially decreases $T_{1\rho}$ at 50 kHz relative to that for the undiluted polymer. In contrast, the higher-T_g diluent, dinitrobiphenyl, does not appreciably alter $T_{1\rho}$. In *Figure 4*, $T_{1\rho}$ is plotted as a function of chemical shift position in the powder spectrum for the three systems studied. The data points represent average $T_{1\rho}$'s from two experiments on each material carried out under identical conditions. In the undiluted polymer, $T_{1\rho}$ varies from 20 ms at chemical shifts of 140 and 160 ppm to 30 ms at 100 and 230 ppm. The anisotropy in the relaxation behaviour of the carbonate carbon in BPAPC persists when the polymer is blended with either of the two low molecular weight additives. The dependence of $T_{1\rho}$ on orientation may be due to anisotropic motions of the carbonate group in the macromolecule. Gibby *et al.*[32] have reported an example of anisotropic nuclear spin relaxation of ^{13}C in solid benzene. Good agreement was found between relaxation theory and experiment for a chemical shielding tensor with axial symmetry.

Compared to its value in the undiluted polymer, $T_{1\rho}$ is decreased by approximately a factor of two in the blend containing dibutylphthalate for all orientations of the carbonate group in BPAPC. This implies that DBP increases the spectral density of carbonate group motions on the order of 50 kHz. This is consistent with the $T_{1\rho}$ results of a previous study of diluents in polycarbonate obtained using high-resolution (CP-DD-MASS) ^{13}C n.m.r. spectra[19]. That all carbon $T_{1\rho}$'s in the BPAPC repeat unit are affected similarly by dibutylphthalate suggests that the lower-T_g diluents perturb macromolecular motions in a co-operative manner. However, it is possible to argue for a solvent-like alteration of the polymer matrix. $T_{1\rho}$ is not changed significantly by the higher-T_g diluent, dinitrobiphenyl, however, suggesting

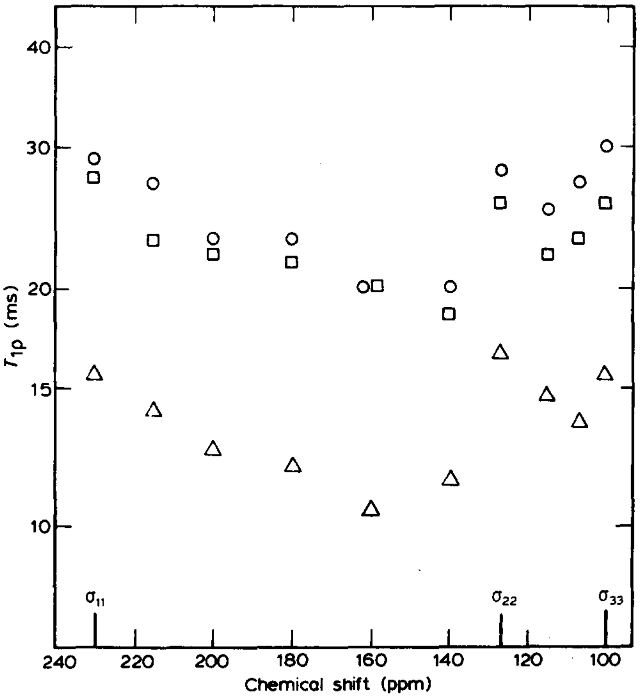

Figure 4 $T_{1\rho}$ at 50 kHz for the carbonate carbon in ^{13}C-labelled polycarbonate as a function of chemical shift in the powder spectrum. The principal values of the chemical shielding tensor are indicated on the horizontal axis. The materials are: ○, BPAPC; □, 69% BPAPC-31% dinitrobiphenyl; and △, 71% BPAPC-29% dibutylphthalate

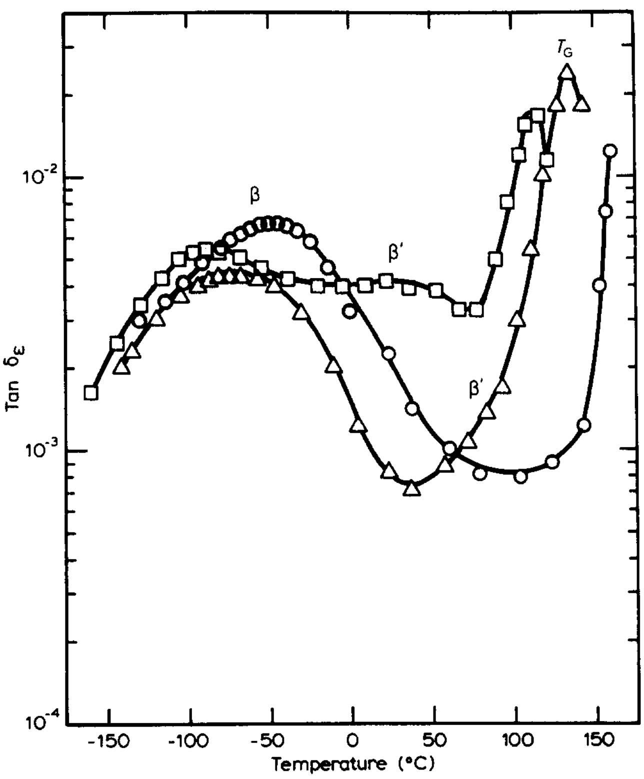

Figure 5 Temperature dependence of the dielectric dissipation factor at 10 kHz for: ○, BPAPC; □, 90% BPAPC-10% dibutylphthalate; and △, 90% BPAPC-10% methylabietate

that the Fourier component of micro-Brownian motions at 50 kHz for the carbonate groups in the macromolecule is not perturbed appreciably by DNB. This result is rationalized later where diluent effects on the dielectric relaxation behaviour of the polymer are discussed.

Dielectric spectroscopy

It is well known that motions of the electric dipoles in the polymer result in loss peaks in the spectrum of the dielectric dissipation factor. In BPAPC, the major β-relaxation process below T_g is attributed primarily to motions of the carbonate group[33,34]. However, the mobility of the carbonate group and, therefore, the magnitude and temperature position of the sub-T_g dielectric loss peaks are influenced by strong couplings to motions in other regions of the macromolecule. The dielectric relaxation results of Locati and Tobolsky[35] for the secondary transition in substituted polycarbonates strongly support the concept of co-operative chain dynamics.

In *Figure 5*, the temperature dependence of the dielectric dissipation factor is shown for high molecular weight polycarbonate and two BPAPC–diluent blends containing 10 wt% of the low molecular weight component. The temperature interval between $-160°$ and 160°C encompasses the two motional processes that occur in BPAPC at a probe frequency of 10 kHz. It is evident that the diluents, dibutylphthalate and methylabietate, shift the primary (T_g) and secondary (β) relaxation processes in the polymer to lower temperature. This type of behaviour in polycarbonate–diluent systems has been observed previously by investigators using both dynamic mechanical and dielectric relaxation experiments[4,7,11].

It is proposed that the diluent effects on the carbonate carbon $T_{1\rho}$ in BPAPC can be rationalized using the results obtained from dielectric spectroscopy. The attempt to correlate n.m.r. and dielectric relaxation measurements may not be completely justified, however, because the time-correlation functions which describe motional fluctuations of the observable quantity in each experiment (magnetic dipole moment *versus* electric dipole moment) are most likely different. Yee and Smith[36] have alluded to such differences between time-correlation functions for magnetization and strain in a comparison of relaxation measurements using n.m.r. and dynamic mechanical spectroscopies. In addition, the high molecular weight polycarbonate used for the dielectric tests has a glass transition temperature of 150°C compared to the T_g of 127°C for the ^{13}C-labelled material synthesized for the n.m.r. study. Nevertheless, the concerted mobility of the carbonate group in the polymer is primarily responsible for the relaxation phenomena observed in each experiment. In this respect, the results should complement each other to some extent.

It is informative to compare the relative magnitudes of the dielectric dissipation factor in the temperature region between the primary (T_g) and secondary (β) relaxation processes for the three materials tested. The data in *Figure 5* reveal that $\tan\delta_\varepsilon$ in this region is approximately four times larger in the blend of polycarbonate and dibutylphthalate relative to that in the undiluted polymer. This is due to a new type of relaxation process (referred to as β' in *Figure 5*) which appears in the temperature region intermediate between T_g (115°C) and T_β (-90°C) in the BPAPC–DBP blend. The work of Seymour *et al.*[8] provides further evidence to support the existence of intermediate (β') relaxation processes in a mechanical and dielectric study of plasticization/antiplasticization in cellulose esters. The molecular origin of the β'-relaxation process is not completely understood. Seymour attributed this mobility to a diluent-induced mode of interaction which is co-operative between the two components in the blend. In contrast, the dielectric dissipation factor for the blend containing the higher-T_g diluent, methylabietate, is not substantially different from $\tan\delta_\varepsilon$ for the undiluted polymer in the temperature region between T_g and T_β. In this case, the β' loss peak appears as a shoulder on the low-temperature side of the primary transition and it is overwhelmed by the strong T_g process. Hence, the strength of the β'-relaxation process in the blend of BPAPC and MA appears to be weaker than that in the blend of BPAPC and DBP.

The intensity of the dielectric dissipation factor at 10 kHz in the temperature region intermediate between T_g and T_β depends strongly on the location of the β'-relaxation process in polycarbonate–diluent blends. The mid-kHz mobility of the carbonate group in the vicinity of ambient temperature is a function of the magnitude of $\tan\delta_\varepsilon$ between T_g and T_β. In the n.m.r. rotating-frame spin–lattice relaxation experiment at 25°C, the rate of decay of the carbonate ^{13}C magnetization ($\approx T_{1\rho}^{-1}$) is essentially a measure of the spectral density of co-operative carbonate group motions at 50 kHz. This suggests that both motional parameters which characterize polymer mobility in the mid-kHz regime should show similar trends when polycarbonate is blended with the low molecular weight additives. The dielectric and n.m.r. results for the blend of polycarbonate and the lower-T_g diluent, dibutylphthalate, are consistent with this hypothesis. Relative to the undiluted polymer, $\tan\delta_\varepsilon$ increases four-fold and $T_{1\rho}^{-1}$ increases two-fold in the BPAPC–DBP blend. In contrast, both motional parameters remain unchanged at ≈25°C in the blends containing the higher-T_g diluents, dinitrobiphenyl and methylabietate.

CONCLUSIONS

The mid-kHz mobility of the carbonate group in bisphenol-A polycarbonate at 25°C is enhanced when the polymer is blended with the low molecular weight, low-T_g (flexible) additive, dibutylphthalate. This is attributed to the occurrence of a new diluent-induced relaxation process in the BPAPC–DBP blend in the vicinity of ambient temperature. The higher-T_g additives, dinitrobiphenyl and methylabietate, which are well-known antiplasticizers for BPAPC, do not significantly alter the mid-kHz mobility of the carbonate group in BPAPC at 25°C.

The results presented in this study are consistent with those from a previous investigation of the chain dynamics of BPAPC-diluent systems in the glassy state using high-resolution (CP-DD-MASS) n.m.r.[19]. At each carbon site in the macromolecule, $T_{1\rho}$ at 50 kHz is decreased by the lower-T_g additives. This suggests that the spectral density of mid-kHz motions for the entire BPAPC repeat unit is increased *via* chain co-operativity by the additives which plasticize the polymer at ambient temperature. A solvent-like alteration of the polymer matrix by the lower-T_g diluents might also explain the observed phenomena, and the fact that phenyl group motion necessarily contributes to the dipolar relaxation of the carbonate group must be recognized.

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