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Intermolecular Cross-Polarization Studies of the Miscibility Enhancement of PS/PMMA Blends through Ionic Interactions

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ABSTRACT: The CP/MAS ^{13}C NMR technique is employed in this study to probe the bulk structures of deuteriated PS/protonated PMMA blends containing ionically interacting groups. Deuteriated PS does not show a ^{13}C NMR signal in CP/MAS experiments since the magnetization of ^{13}C is primarily polarized by protons. However, if protons of the PMMA chains can be found within a few angstroms of the deuteriated PS, then the ^{13}C NMR signals of PS can be observed, with the intensity of PS signals depending upon the proximity of deuteriated PS to the PMMA. The present results show that the PS/PMMA pair is immiscible. However, when PS is lightly sulfonated (3.3 mol % of $-SO_3H$) and PMMA is copolymerized with 2.3 mol % 4-vinylpyridine (4VP), the miscibility of the blend is enhanced, due to proton transfer from the $-SO_3H$ to the 4VP with the formation of ionically interacting sites on the deuteriated PS and the PMMA. By the introduction of about 9.5 mol % of interacting groups ($-SO_3H$ and 4VP), the blend shows much greater enhancement in miscibility. When the $-SO_3H$ on the deuteriated PS is neutralized with $N(CH_3)_4OH$ and the 4VP is quaternized with CH_3I, the blends exhibit similar or even better miscibility compared with the proton-transfer blends. This is attributed to the direct ion–ion interactions in the blends. Blend recovery methods affect the chain proximity in the blend.

Introduction

In recent years, polymer blends have been the subject of extensive investigations.[1-3] In many instances, the properties of the blends are superior to those of the individual components. Since most polymer pairs are not miscible, one of the important features of polymer research is the investigation of miscibility enhancement techniques since control of miscibility allows one to control the final properties.

Many miscibility enhancement strategies have been explored in the past. These include copolymerization, either in the form of random copolymers or preferably in the form of blocks used as emulsifiers,[4] utilization of hydrogen bonding between the dissimilar chains,[5,6] formation of donor–acceptor complexes,[7] and, in addition, dipole–dopole,[8] ion–dipole,[9] and ion–ion interactions.[10]

Miscibility enhancement by ionic interactions has been the subject of extensive studies in this laboratory. For example, the immiscible polymer pair poly(ethyl acrylate) (PEA)/polystyrene (PS) can be made miscible by the incorporations of ca. 5 mol % 4-vinylpyridine into the PEA and a comparable amount of sulfonic acid in the PS.[10] In the process of mixing, proton transfer occurs from the sulfonic acid to the pyridine, which results in the formation of opposite charges on the different chains and leads to strong coulombic interactions which hold the chains together. A wide range of other systems has been treated in a similar manner, including the pair poly(tetrafluoroethylene)/poly(ethyl acrylate).[11] Ion–dipole interactions are another way for improving misci-

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Table I
Blend Preparation Methods

sample no.	blends	content of SSA[a]/4VP[b]	blending ratio	recovery methods	RI[c]
I	PS/PMMA	0/0	50/50	A	0
II	PSSSA/PMMA4VP	3.3/2.3	50/50	A	0.48
III	PSSSA/PMMA4VP	9.5/9.6	50/50	A	1.00
IV	PSSSN/PMMA4VPQ	3.3/2.3	50/50	A	0.44
V	PSSSN/PMMA4VPQ	9.5/9.6	50/50	A	1.31
VI	PSSSN/PMMA4VPQ	9.5/9.6	50/50	B	1.72

[a] Styrenesulfonic acid. [b] 4-Vinylpyridine. [c] Relative intensity.

bility of polymer systems, illustrated by the case of poly(ethylene oxide) and poly(styrene-*co*-lithium methacrylate) blends.[9]

Many techniques are available for the study of miscibility in polymers. Light scattering, for example, can probe the domain sizes of the order of the wavelength of light (ca. 1000–10 000 Å). Dynamic mechanical measurements are sensitive to the dimensions of ca. 100 Å, but they require a T_g difference of at least 30 °C between the individual components. Other methods include FTIR, UV, fluorescence spectroscopy, dielectric measurements, and optical and electron microscopy, among many others. Recently, high-resolution solid-state NMR spectroscopy has become available and has been utilized to explore the microstructures of polymer blends on a molecular level. A variety of techniques have been developed in this field in recent years. Relaxation time measurements,[12] spin diffusion determinations,[13,14] signal attenuation in fluorine-containing systems,[15] and different delay and decoupling methods[16] are a few examples.

In the present work, intermolecular cross-polarization technique will be used to study the phase structure of deuteriopolystyrene (PS)/poly(methyl methacrylate) (PMMA) blends containing ionic groups. Generally, in CP/MAS ^{13}C NMR measurements, the deuteriated polymer chains will not show NMR resonance lines since the polarization of carbon-13 magnetization originates primarily from the proton reservoir. However, if the deuteriated component forms an intimate mixture with a protonated component and the distance between the deuteriated chains and the protonated chains is within a few angstroms, then the deuteriated component may get polarized by the nearby protonated chains so that a partial or full spectrum of the deuteriated component can be detected. Since the cross-polarization only occurs if the interacting atoms are within a very short range, this method can give a good estimate of chain proximity. The applicability of this technique in polymer blends has been studied recently with a well-known miscible polymer pair PS/PVME and an immiscible polymer pair PS/PMMA.[17,18] The results show that the technique is an effective tool in characterizing the miscibility of polymer blends as well as interface interdiffusions.

Although it is known that the blend of PS/PMMA is immiscible,[19] a recent solution NMR study revealed that when PMMA was copolymerized with a small amount of 4-vinylpyridine and PS was lightly sulfonated, the mixture of poly(methyl methacrylate-*co*-4-vinylpyridine) (PMMA4VP) and poly(styrene-*co*-styrenesulfonic acid) (PSSSA) in DMSO resulted in a close proximity of the chains of the two components.[20] The driving force for miscibility enhancement in this polymer pair is the formation of the pyridinium sulfonate ion pair by proton transfer from the PSSSA to the PMMA4VP. Obviously, it is of great interest to study such blends in the solid state, since in solutions the effect of solvent on the miscibility can be crucial. Furthermore, in most cases, polymers, as well as their blends and composites, are used in solid form. An understanding of the bulk structures of polymer systems gives a better base for property design. Due to the small difference in the T_g's of the two blending components, this system cannot be effectively studied with dynamic mechanical methods. The present work, therefore, uses the CP/MAS ^{13}C NMR technique to study the miscibility enhancement of the blends of PMMA and PS with different contents of interacting groups in various forms.

Experimental Section

Materials. Deuteriated polystyrene with a molecular weight of approximately 180 000 was made by anionic polymerization (deuteriated styrene: Cambridge Isotope Laboratory; $d > 98\%$). The polymer was purified by precipitation, using benzene and methanol as the solvent and the nonsolvent. Sulfonation was conducted in 1,2-dichloroethane (American Chemicals; reagent) at 50 °C using a procedure similar to that described elsewhere.[21] The polymer was recovered by steam stripping, washed with deionized water, dried, dissolved in benzene/methanol (90/10, v/v), and precipitated in methanol. The final polymer was vacuum dried at 50 °C until constant weight was obtained. The degree of sulfonation was determined by dissolving an adequate amount of PSSSA in benzene/methanol (90/10) and titrating the solution with either standardized NaOH/methanol solution or N(CH$_3$)$_4$OH/methanol solution. Neutralization of PSSSA was carried out by dropping the appropriate amount of a N(CH$_3$)$_4$OH/methanol solution to PSSSA in benzene/methanol with stirring. The composition of benzene/methanol mixture was varied so that a clear PSSSA solution was obtained. The neutralized PSSSA (PSSSN) was freeze-dried followed by vacuum drying at 60 °C to constant weight. NMR measurements of PSSSN showed that the degree of sulfonation was in good agreement with the titration data.

Poly(methyl methacrylate-*co*-4-vinylpyridine) was prepared by free radical polymerization as described elsewhere.[22] The conversion was kept at about 30% so that good homogeneity of the unit distribution in the polymer chains can be obtained. 4VP contents were determined by titration with a perchloric acid/acetic acid solution. Quaternization was performed by adding excess methyl iodide (Aldrich; 99.5%, fractionally distilled before use) to a PMMA4VP solution in benzene/ethanol (90/10) at reflux temperature for 2 h. The resultant polymer (PMMA4VPQ) was first freeze-dried and then vacuum dried.

Blending. About 0.1 g of an accurately weighed sample was dissolved in benzene/methanol (90/10) mixture to yield a clear solution with a concentration of 1% (w/v). This solution was then added dropwise to a similar solution of the other component with vigorous stirring at room temperature, followed by continued stirring for about 10–20 min. Since the solutions were very dilute, this procedure should yield an equilibrium mixture in solution. For both blends of PSSSA/PMMA4VP and PSSSN/PMMA4VPQ with higher concentrations of interacting groups (above 3 mol %), a gel was formed as soon as the first drop of the other solution was added, showing that a very rapid interaction is involved. The blended polymers were recovered in two ways:

A. The mixtures were freeze-dried and then vacuum dried at 60 °C to constant weight.

B. Only the gel part, which precipitated in blending, was taken out of the solution and then pressed between Teflon films

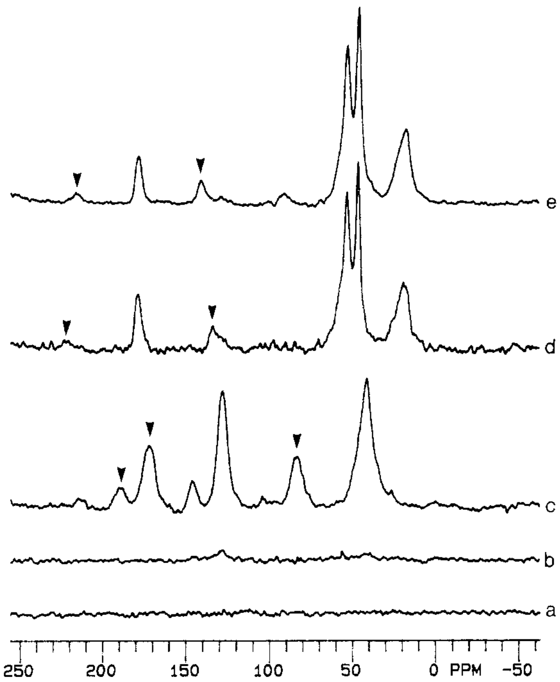


Figure 1. CP/MAS ^{13}C NMR spectra of deuteriated PS (a), deuteriated PSSSN with 9.5 mol % ions (b), protonated PS (c), PMMA (d), and PMMA4VPQ with 5 mol % ions (e).

at room temperature into a thin film followed by vacuum drying to constant weight.

The samples presented for this study are listed in Table I for convenience. Samples II and III illustrate the effect of increasing interacting group content for the systems in which the ion pairs are generated by proton transfer; samples IV and V illustrate the same effect for the systems in which the ions are already present on the chains, and samples V and VI show the effect of the different isolation methods. The data in the last column will be discussed later.

NMR Measurements. All of the CP/MAS ^{13}C NMR spectra were recorded at room temperature on a Varian XL-200 instrument, using a Macor rotor and Kel-F cap with a spinning rate ranging from 2 to 3.5 kHz. A cross-polarization pulse sequence was used with a contact time of 1.0 ms. The delay times between pulses were 10 s for PS and 4 s for PMMA4VP and for all the blends. Longer delay times did not have a discernible effect on the spectra of the blends. A total of 2000 transients were accumulated for each spectrum.

Results and Discussions

Under the present experimental conditions, deuteriated polystyrene is transparent in the ^{13}C NMR spectrum (Figure 1a,b) whether with or without ionic groups. On the other hand, protonated polystyrene gives three peaks at 146 ppm (quaternary carbon), 128 ppm (the remaining aromatic carbons), and 40 ppm (carbons on backbone) (Figure 1c). The peaks indicated by arrows are spinning sidebands, which can be identified by total sideband supression measurements. the CP/MAS ^{13}C NMR spectrum of PMMA is shown in Figure 1d. The peaks at 178, 52, 45, and 17 ppm represent resonances of a carbonyl group, methoxy group, quaternary carbon, and methyl group, respectively. The line for the –CH2– on the backbone (56 ppm) is engulfed by the intense methoxy peak. A quaternized PMMA4VP copolymer shows similar resonances as that of pure PMMA (Figure 1e).

The CP/MAS ^{13}C NMR spectrum for the blend of PS and PMMA homopolymers (Figure 2a) resembles that for pure PMMA, indicating that the blend is completely phase separated under the present mixing procedure, since even insufficient interfacial mixing can give rise to observable intermolecular cross-polarization.[17] For the blend of PSSSA/PMMA4VP containing 3.3 mol % SSA and 2.3 mol % 4VP, however, a recognizable peak at 128 ppm, representing resonances of aromatic carbons in PS, is seen in the CP/MAS ^{13}C NMR spectrum (Figure 2b). This implies that at least some of the heterochains must be close to each other at the molecular level (within 10 Å). Since the peak is weak, the two components do not appear to be well mixed.

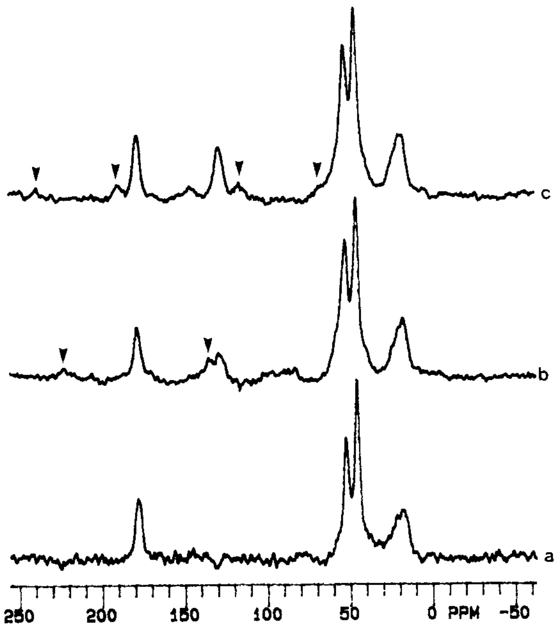


Figure 2. CP/MAS ^{13}C NMR spectra of the blends. a–c correspond to samples I–III, respectively.

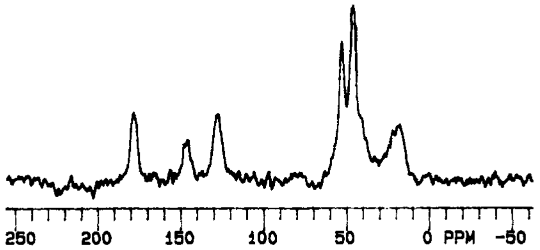


Figure 3. Addition results of 20% PS spectrum and 80% PMMA spectrum with spinning sideband suppression.

With 9.5 mol % interacting groups, the blend of PSSSA/PMMA4VP shows a much more intense peak at 128 ppm (Figure 2c), when compared with the 3 mol % blend. The relative intensities (RI) of the peaks at 128 ppm in the blends to those of the carbonyl peaks (178 ppm) in PMMA are listed in the last column of Table I. The data indicate that an enhanced chain proximity, and thus enhanced miscibility, is a direct consequence of the higher ion content. However, the efficiency of intermolecular cross-polarization is still not significant under the experimental conditions. In the normalized mode and on the same vertical scale for the most intense peak of each spectrum, the addition of about 20% of the pure PS spectrum to 80% of the PMMA spectrum with comparable sample weight gives a spectrum resembling that of the PSSSA/PMMA4VP blend with 9.5 mol % ions (Figure 3). This, however, does not imply that the blend is not completely miscible, since the experimental conditions were chosen so as to optimize the whole spectrum, not just the aromatic ring resonances. Longer contact times might be needed for the maximum intermolecular cross-polarization signals. The difference spectrum of the blend minus that of PMMA4VP shows that only the aromatic carbons of PSSSA are significantly polarized (Figure 4).

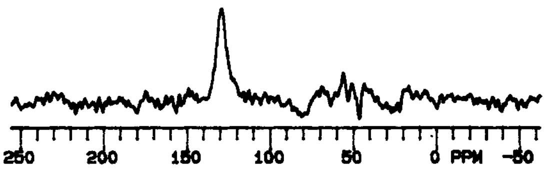


Figure 4. Difference spectrum of PSSSA/PMMA4VP with 9.5% ions minus that of PMMA4VP with spinning sideband suppression.

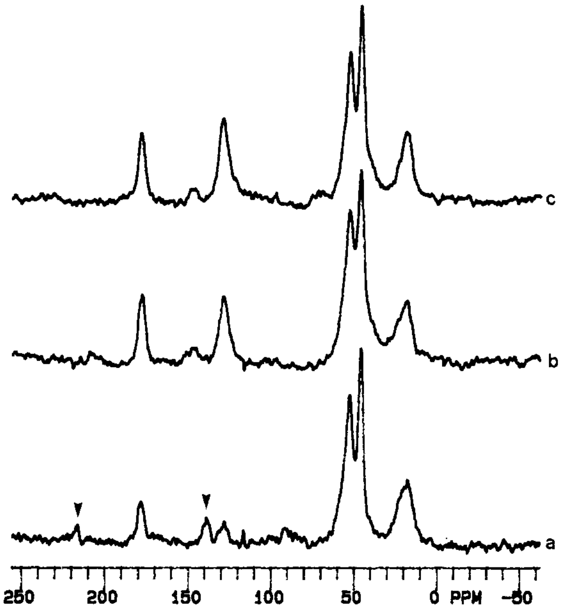
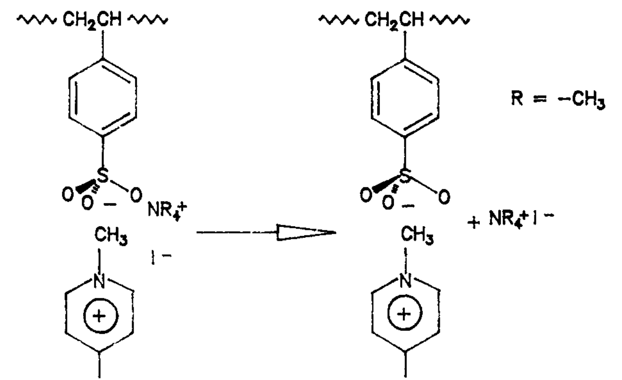


Figure 5. CP/MAS ^{13}C NMR spectra of PSSSN/PMMA4VPQ blends with different ion concentrations (a and b) and different recovery methods (b and c).

Scheme I



This means that the aromatic rings are closer to the PMMA chains or parts of them than the main chain of PSSSA. The bulky phenyl rings provide an effective spacer between the polystyrene backbone and the protons of the PMMA.

The blend of neutralized PSSSA and quaternized PMMA4VP (PSSSN/PMMA4VPQ, sample IV) containing exactly the same concentration of functional groups as sample II gives a similar result as that obtained from sample II (Figure 5a), indicating that, at the lower ionic group concentration, both ionomer/ionomer and proton-transfer blends show a weak miscibility enhancement effect. The miscibility enhancement in the PSSSN/PMMA4VPQ blend may result either from ion pair/ion pair association or from direct ionic interaction by the elimination of microions (Scheme I). The similar degree of miscibility enhancement for the blend PSSSN/PMMA4VPQ compared with the blend PSSSA/PMMA4VP implies the existence of comparable interactions in these two systems. For the blend of PSSSA/PMMA4VP, it had been demonstrated that strong ionic interactions due to proton transfer from PSSSA to PMMA4VP were involved.[20] Thus, it is reasonable to assume that, in the PSSSN/PMMA4VPQ blends, ionic interaction is predominant rather than ion pair/ion pair association. This idea is supported by the following observations: when the blend of PSSSN/PMMA4VPQ was prepared in DMSO at room temperature, the polymers precipitated from the solution as a gel. The supernatant DMSO solution shows a strong signal of $^+N(CH_3)_4$ by NMR while the polymer signals are at a noise level. This shows that the microions are eliminated from the polymer chains and remain in solution. If the same experiment is performed in a benzene/methanol (90/10) mixture, the polymers also precipitate. The salt $[^+N(CH_3)_4I^-]$ is only slightly soluble in that solvent. However, when the gel is removed and the supernatant liquid is shaken with water, the aqueous solution does show a strong $^+N(CH_3)_4$ signal. This suggests that upon blending the $^+N(CH_3)_4I^-$, perhaps in the form of microcrystals, is at least partly separated from the polymer matrix. Then the macroion pairs are formed, which leads to the miscibility enhancement at a strength comparable to that seen in the proton-transfer blends.

The ionomer/ionomer blend PSSSN/PMMA4VPQ containing 9.5 mol % interacting groups shows an even stronger aromatic ring resonance than the 3 mol % system (Figure 5b and Table I). This indicates that, in the ionomer/ionomer blends, heterochain proximity can also be improved with increasing ionic concentration, just as in the proton-transfer blends. If the blend is compared with proton-transfer blend containing the same concentration of interacting groups, it can be seen from Table I that an even closer chain proximity is found in ionomer/ionomer blend. This further miscibility enhancement is the result of the purely ionic interactions between the two polymer chains, uncomplicated by the presence of hydrogen and the possibility of directional hydrogen bonding.

All of the above blends are recovered by a freeze-drying method. When the gel part, which involved over 95 wt % of total polymers, was taken out from the mixture of the two polymer solutions and then directly dried in a vacuum oven (sample V, recovery method B), a further increase in aromatic carbon resonances was observed, possibly due to a still more efficient packing of the polymer chains.

Conclusions

The study on the efficiencies of intermolecular cross-polarization demonstrates that the miscibility enhancement, characterized by a heterochain distance of within 10 Å, can be achieved by introducing ionic interactions between the two polymer chains. The ionic interaction in ionomer/ionomer blends is obtained by the elimination of microions from the polymer chains. With increasing interacting group concentrations, heterochain proximity is improved in ionomer/ionomer blends, as well as in proton-transfer systems. The methods of blend isolation also have observable impact on the heterochain proximity, possibly due to the packing effect.

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Registry No. (PMMA)(4VP) (copolymer), 26100-41-4; (PMMA)(4VP)$\cdot$$CH_3I$ (copolymer), 110923-53-0; $N(CH_3)_4OH$, 75-59-2.

Hydrostatic Pressure Dependence of Molecular Motions in Polycarbonates

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ABSTRACT: The temperature dependence of the proton NMR line width of polycarbonate and of the phenoxy resin formed from bisphenol A and epichlorohydrin have been measured as a function of hydrostatic pressure. These measurements lead to the conclusion that for both polymers, ring motions are suppressed by the denser chain packing resulting from hydrostatic pressure. The magnitude of the NMR pressure dependence is comparable to the pressure variation of the γ mechanical loss peak in polycarbonate. The ^{1}H NMR results, together with those from a variety of cross-polarization magic-angle spinning ^{13}C NMR experiments performed at room temperature and atmospheric pressure, are interpreted in terms of a bundle model of chain packing in the glassy matrix. From the observed activation volumes, activation energies, and main-chain reorientation rates, the bundles are inferred to involve the correlated motions of just a few chains.

Introduction

Polycarbonate (PC) forms a glassy polymer that is remarkable for its high-impact resistance and ductility over a wide temperature range. Molecular motions occurring below T_g have long been believed to be at least partly responsible for PC's favorable mechanical properties.[1] Indeed, a substantial mechanical loss peak ("γ") observed in PC indicates the presence of 1-Hz motions (which are coupled to bulk and shear modes) 250 °C below T_g.

Nuclear magnetic resonance (NMR) has been used to assemble a picture of the motions present in polycarbonate. Deuterium NMR line shapes,[2] ^{13}C chemical shift anisotropy patterns,[3] and ^{13}C–^{1}H dipolar spectra[4] have yielded the most specific information. The most obvious motions in the NMR spectra are 180° flips of the phenylene groups about their C_2 axes and methyl rotations about the C_3 axes. Because these motions carry the molecule back into itself, they cannot be directly responsible for the mechanical loss and favorable mechanical properties of PC. However, the rate of phenylene 180° flips does appear on the same temperature-frequency relaxation line with the γ mechanical and dielectric loss peaks.[5] Closer examination of the ^{13}C–^{1}H dipolar spectra of phenylene and methyl carbons indicates that other motions are also present at room temperature:[6] these include approximately 30° oscillations of the phenylene groups about the C_2 axes and 15° main-chain reorientations ("wiggles"). It has been proposed[7] that the main-chain motions create sufficient volume to enable, or gate, the 180° ring flips. Thus, the ring flips are an indirect measure of the mechanically active main-chain motions.

In this paper, we establish a link between the NMR measurements and the mechanically active motions. The mechanically active motions (specifically, the bulk modes) necessarily produce volume fluctuations that can be probed by changing the conjugate variable, pressure.[8,9] Thus, we have measured the temperature and pressure dependence up to 1800 bars of the proton T_2 in PC and in the phenoxy resin of bisphenol A and epichlorohydrin (PK). Because proton NMR measurements often are unable to specify the exact nature of motions present, our interpretation of motion is based on the high-pressure proton

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