

Inter-Polymer Interaction of Polymer Blend in Solution as Studied by NMR: Polycarbonate/Poly(methyl methacrylate)

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ABSTRACT: The polymer–polymer interaction in solution of the miscible polymer blend of bisphenol A polycarbonate/poly(methyl methacrylate) (PC/PMMA) is investigated by NMR methods. The inter-polymer ^1H nuclear Overhauser effects (NOE) can be observed, suggesting that PC and PMMA are in close contact with each other in solution. The ^{13}C spin-lattice relaxation time ($^{13}\text{C}-T_1$) is measured for the mixture and pure polymers in solution. The temperature dependence of $^{13}\text{C}-T_1$ is affected by mixing only for the phenyl and the methoxy carbon resonances. It is concluded that the phenyl group of PC and the methoxy group of PMMA interact with each other in solution.

KEY WORDS High-Resolution NMR / Polycarbonate / Poly(methyl methacrylate) / Polymer Blend / Inter-Polymer Interaction / Nuclear Overhauser Effect / ^{13}C Spin-Lattice Relaxation /

For two or more different polymers to be miscible, a characteristic polymer–polymer interaction must be operative between the component polymers.¹ It is of particular interest to investigate how and to what extent component polymers in blend interact with each other. NMR spectroscopy provides information about such inter-polymer interaction, which reflects the ^1H dipole–dipole interaction.

The high-resolution achieved in solution enables us to investigate a specific region of interaction. In solution, the dipole–dipole interaction gives rise to the transient nuclear Overhauser effects (transient NOE) between two spins.² Since the strength of dipole–dipole interaction is proportional to the inverse sixth-power of the inter-proton distance, there occurs no appreciable NOE between protons separated by more than 5Å .^{2,3} NOE is,

therefore, a sensitive probe to investigate whether component polymers are in close contact on a microscopic scale. It is true that the structure of blend in solution may not be identical to that in solids. Nevertheless, the interacting region is probably identical in both solution and solids. Crowther *et al.*⁴ and Mirau *et al.*^{5,6} carried out the ^1H NOE experiment to study polystyrene/poly(vinyl methyl ether) (PS/PVME) blend. They showed that polystyrene and poly(vinyl methyl ether) are in close contact in toluene, but not in chloroform. Zhang *et al.*⁷ investigated the hydrogen-bonding interaction of polymer blend in solution by examining NOE.

Bisphenol A polycarbonate/poly(methyl methacrylate) (PC/PMMA) blend has been studied from various viewpoints.^{8–13} Gardlund studied the PC/PMMA blend prepared by the melt extruding method, and showed on

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the basis of dynamic mechanical analysis and scanning electron microscopic observation that the blend is partially miscible. The partial miscibility is ascribed to the $n-\pi$ complex formation between the ester group of PMMA and phenyl ring of PC.^{8,9} Differential scanning calorimetric (DSC) and cloud point experiments showed that PC/PMMA blend exhibits the lower critical solution temperature (LCST) behavior.¹⁰⁻¹² Furthermore, the molecular motion of PC/PMMA blend in the solid state was studied by ²H NMR.¹³

In this paper, we describe the high-resolution NMR study on the inter-polymer interaction of PC/PMMA blend in solution. ¹H NOE and ¹³C spin-lattice relaxation time (¹³C- T_1) experiments in solution are undertaken. Evidence of the $n-\pi$ interaction between the phenyl ring of PC and the methoxy group of PMMA is given. If such interaction exists, we expect that blending may alter molecular motion, which reflects ¹³C- T_1 . The temperature dependence of ¹³C- T_1 is examined, and mixing effects on molecular motion of PC and PMMA are discussed.

EXPERIMENTAL

Materials

PC and PMMA were obtained from ALDRICH Chemical Co., Inc. The weight averaged molecular weight/number averaged molecular weight (M_w/M_n) is 33,800/13,400 for PC and 93,300/46,400 for PMMA. Atactic PMMA is used. The triad tacticity was determined from the intensity of signals of the α -methyl proton, and the ratio of $mm:mr:rr$ is 13:40:47. PC and PMMA were dissolved in anhydrous tetrahydrofuran (THF) at concentrations of 2–4 wt/v%, and mixed at weight ratios of 5:5. Very thin and optically transparent films were obtained by casting the solutions on a glass plate at 58°C.¹³ The films were dried further under vacuum at 110°C for 5–6 days. The transparent 5:5 film was dissolved again in deuterated THF (THF- d_8)

at 5 wt/v% for the ¹H NOE and ¹³C- T_1 experiments.

NMR Measurements

All NMR spectra were obtained on a JEOL JNM-GX270 spectrometer operating at 67.5 MHz for ¹³C and 270 MHz for ¹H. The ¹³C- T_1 experiments in THF- d_8 solution at various temperatures were conducted by the conventional inversion recovery method. The free induction decays (FIDs) were stored in 8K data points. The number of accumulated FIDs was 48. The length of ¹³C 90° pulse was 8 μ s, and acquisition time + pulse delay time was 40 s. ¹H NOE difference spectra were obtained at -20°C by the truncated driven NOE technique.³ The ¹H radio frequency intensity for irradiation was 15 Hz. The FIDs were stored in 4K data points using ¹H 45° pulse of 8 μ s, and acquisition time + pulse delay time was 8 s. The number of accumulated FIDs was 256.

RESULTS AND DISCUSSION

¹H NOE Experiments

Figure 1 shows the ¹H NOE difference spectra at -20°C. The methoxy (OCH₃) protons of PMMA at 3.4 ppm were irradiated. The irradiation time is indicated on the right-hand side in the figure. Both the intramolecular (\star) and inter-polymer (\ast) NOE are observed, which are all negative NOEs. Observation of the inter-polymer NOE indicates that the closest distance between PC and PMMA is less than 5 Å.

The relative intensity of NOE was estimated by the Lorentzian curve fitting. The NOE intensity is plotted against irradiation time in Figure 2. It is worthy of noting that the build-up rate is much faster for the phenyl protons than for the methyl protons of PC.

The initial build-up rate of NOE (cross-relaxation rate σ_{ij}) can be written by^{3,4}:

$$\sigma_{ij} = 1/10\gamma_H^4 \hbar^2 r_{ij}^{-6} \{ -J(0) + 6J(2\omega_H) \} \quad (1)$$

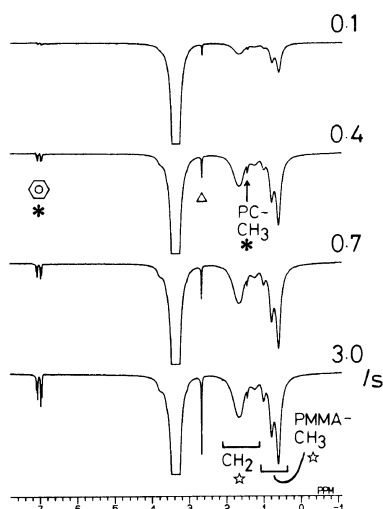


Figure 1. ^1H NOE difference spectra of PC/PMMA = 5:5 mixture in $\text{THF-}d_8$ at -20°C . The methoxy protons of PMMA are irradiated for the period shown in each spectrum. A symbol Δ denotes the residual water peak in $\text{THF-}d_8$ solution.

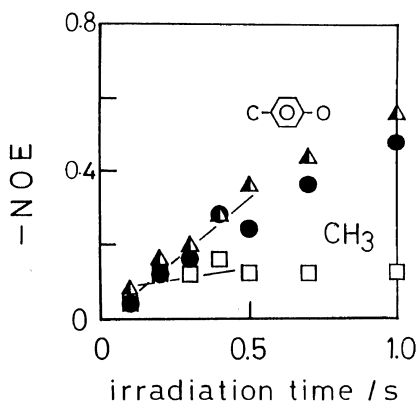


Figure 2. Irradiation time dependence of the inter-polymer ^1H NOE at -20°C when the methoxy protons of PMMA are irradiated. Relative NOE is plotted: the phenyl ring protons at carbon side (\bullet) and oxygen side (\blacktriangle), and the methyl protons of PC (\square). The solid lines show the initial slope from which relative distances are deduced. The ordinate is in arbitrary units.

where γ_{H} is the ^1H magnetogyric ratio, \hbar is Planck's constant divided by 2π , r_{ij} is the distance between proton i and proton j , $J(0)$ and $J(2\omega_{\text{H}})$ are spectral densities of motion of the interproton distance r_{ij} , and ω_{H} is the ^1H Larmor frequency.

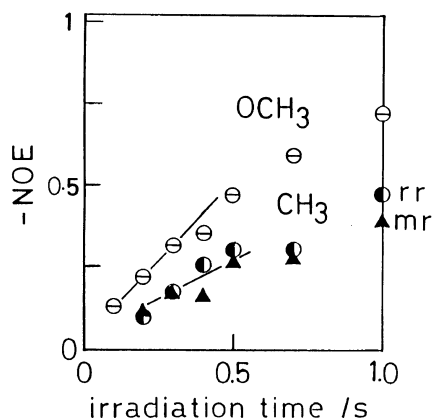


Figure 3. Irradiation time dependence of the inter-polymer ^1H NOE at -20°C when the phenyl ring protons of PC are irradiated: the protons of methoxy protons (\ominus), rr (\bullet) and mr (\blacktriangle) triad α -methyl protons of PMMA. The solid lines show the initial slope from which relative distances are deduced. The ordinate is in arbitrary units.

As can be seen in eq 1, $(\sigma_{ij}/\sigma_{ik})^{1/6}$ is equal to (r_{ik}/r_{ij}) , if we assume that the spectral density is the same for all proton pairs. We can estimate the ratio of the distance between the methoxy group of PMMA and phenyl group of PC and the distance between the methoxy group of PMMA and methyl group of PC. The initial rate of the phenyl ring protons of PC is four times greater than that of the methyl protons of PC. Thus, the distance between the methoxy group of PMMA and the phenyl ring of PC is about 20% shorter than the distance between the methoxy group and the methyl group. This provides evidence of intimate closeness between the methoxy group of PMMA and the phenyl group of PC.

The NOE difference spectra of the phenyl protons of PC irradiated were also examined. The irradiation time dependence of the relative intensity of the inter-polymer NOE is shown in Figure 3. The build-up rate of NOE is larger for the methoxy peak of PMMA than for the mr triad and rr triad α -methyl peaks of PMMA. NOE is not remarkable for the mm triad α -methyl and the methylene peaks (not shown in the figure). Accurate estimation for the former peak may not be possible because of

the small peak intensity. This NOE result also gives proof of the proximity of the methoxy group of PMMA and the phenyl ring group of PC. To conclude, the phenyl group of PC and the methoxy group of PMMA interact with each other in THF solution.

It was found that the inter-polymer NOE can be observed only below -20°C . At higher temperatures above -20°C , the correlation time is presumably in a region where NOE is ineffective.^{2,14} A sharp peak showing negative NOE near 2.7 ppm in Figure 1 is due to residual water in THF- d_8 . NOE was not observed for the water peak, when the phenyl protons of PC were irradiated. The interaction between the methoxy group and the water molecule may give rise to the negative NOE.

$^{13}\text{C}-T_1$ Measurements

If a specific inter-polymer interaction exists between PC and PMMA, the molecular motion of polymer chain in the mixture in particular of the interacting region, is expected to be different from that of the pure polymer. In solution, fluctuation of the $^{13}\text{C}-^1\text{H}$ dipole interaction determines the ^{13}C spin-lattice relaxation time ($^{13}\text{C}-T_1$). The molecular motion can be detected by observing $^{13}\text{C}-T_1$.

Figure 4 shows the observed temperature dependence of $^{13}\text{C}-T_1$ of the methoxy carbon of PMMA in pure and mixed states. The results of the phenyl carbons of PC are shown in Figure 5. $^{13}\text{C}-T_1$ values of other carbons of the mixtures are almost identical to those of the pure polymers (not shown in the figures). The solid lines through the data points in Figures 4 and 5 are drawn only for reference.

It is of interest to note that the temperature of T_1 minimum of the methoxy carbon of PMMA is about 25°C higher for the mixture than for pure PMMA (Figure 4). This indicates that the correlation time of motion τ_c is larger in the mixture than in the pure polymer. The molecular motion becomes slower by mixing.

The T_1 curve of the phenyl carbons of PC in the mixture shifts to high temperatures

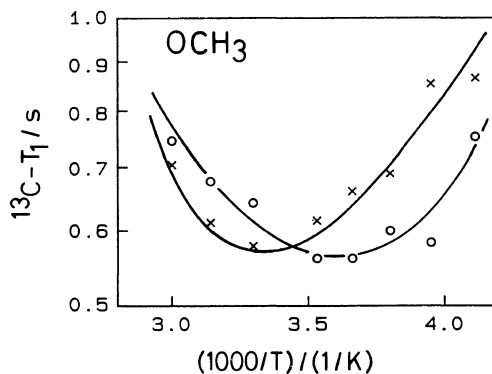


Figure 4. $^{13}\text{C}-T_1$ curves of the methoxy carbon of pure PMMA (O) and PC/PMMA=5:5 mixture (x) in THF- d_8 . The solid lines are written to guide reader's eyes.

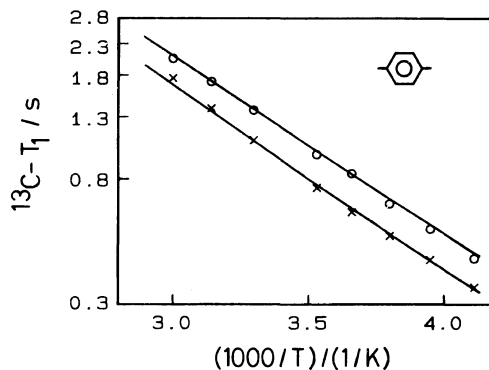


Figure 5. $^{13}\text{C}-T_1$ curves of the phenyl carbons of pure PC (O) and PC/PMMA=5:5 mixture (x) in THF- d_8 . The solid lines are written to guide reader's eyes.

compared to that of pure PC (Figure 5), indicating that the motion of the phenyl rings of PC is restricted by mixing. $^{13}\text{C}-T_1$ s of other carbons are not influenced by mixing. Since the molecular motion of only interacting region is affected, it is evident that change of $^{13}\text{C}-T_1$ curve proves the presence of interaction between the methoxy group of PMMA and phenyl group of PC.

CONCLUSIONS

It is concluded that the phenyl group of PC interacts with the methoxy group of PMMA in THF solution of PC/PMMA mixture. The

interaction manifests itself in reduction of the mobility of these groups.

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