and after the NMR measurements would easily determine which crystalline phase is present.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

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Reply to the Letter of Perry, Grasso, Koenig, and Lando

Our recent observations[1] of poly(butylene terephthalate) (PBT) in the α and β phases by high-resolution, solid-state ^{13}C NMR prompted us to conclude that significant conformational changes in the tetramethylene portion of the PBT chains do not accompany the α to β transition. This conclusion was based on the nearly identical chemical shifts observed for the methylene carbons in both phases and on comparison to the chemical shifts observed by Grenier-Loustalot and Bocelli[2] for the single crystals of several PBT model compounds that crystallize with their tetramethylene segments (O–C–C–C–C–O) in the ttt, ttg, and gtg conformations, where t = trans and g = gauche. These authors found the resonances of the central methylene carbons in the model compounds with gauche bonds to appear 3 ppm upfield from those of the central methylene carbons in the ttt model compounds. Because the chemical shift observed for the central methylene carbons in both α and β PBT were nearly identical with each other and with those observed for the ttt model compound,[2] we concluded that both α and β PBT have nearly an all-t tetramethylene conformation.

It is not surprising that our ^{13}C NMR results disagree with those reported by Perry and Koenig,[3] because they recorded spectra at room temperature leading to broad resonances (4–5 ppm) probably resulting from contributions made by both the crystalline and amorphous carbons. By contrast, we observed much narrower resonances (1–2 ppm) for PBT when observing at $T > 100$ °C, which is well above the T_g of this polymer and prevents the efficient cross-polarization of the mobile amorphous carbon nuclei.

We do not agree that IR data demonstrate that the tetramethylene segments are in a crumpled conformation in the α phase and in an extended conformation in the β phase. All they show is that the methylene region of the IR spectrum is most sensitive to the presence of the α and β phases of PBT. In addition, we also mentioned that there are serious disagreements between the structures derived for α and β phase PBT from X-ray diffraction studies.

We agree that "solid-state NMR is a useful technique for studying conformational changes as evidenced by the γ-gauche effect observed in polymers", and we also believe it possible that "the chemical shift of two carbons in different conformational states may appear the same". However, the PBT model compound work[2] makes clear that the CH_2 carbons in a gauche conformation resonate 3 ppm upfield from those in the trans conformation of the tetramethylene glycol fragment.

The X-ray patterns we observed for our α- and β-phase PBT samples are not identical. The pattern for our β PBT sample does show evidence for the presence of some α phase, but judging from the relative intensities of the α and β reflections, we believe our sample to be predominantly of the β phase. Yokouchi et al.[4] have demonstrated that annealing PBT under tension at elevated temperatures enhances the formation of the β phase. Rapid MAS should increase the tension on our β sample, which would also oppose a β to α conversion.

We agree that recording an IR spectrum of our β sample before and after the NMR measurements would be worthwhile, but we have not yet figured out how to accomplish this. On the other hand, we feel that IR measurements performed on the PBT model compounds of Grenier-Loustalot and Bocelli[2] would be most useful in determining whether or not IR is diagnostic for folded, or crumpled, and extended conformations of the tetramethylene glycol fragment in PBT crystals.

In summary, on the basis of the comments of Perry, Grasso, Koenig, and Lando, we see no need to alter the conclusions reached in our ^{13}C NMR studies[1] of α and β PBT.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

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On the Phase Behavior and the Limits of Miscibility of Styrene-*co*-Vinylphenol Blends with Poly(alkyl methacrylates)

One of the more intriguing questions posed over the last decade by those working in the general field of polymer blends is "how many favorable intermolecular interactions are required in order to achieve miscibility"? To give an example relevent to this study, poly(methyl methacrylate) (PMMA) is immiscible with polystyrene (PS) but miscible with poly(vinylphenol) (PVPh). "How many vinyl phenol (VPh) units would we need to incorporate into PS to render it miscible with PMMA?" In other words, "what are the limits of miscibility for the PMMA–poly(styrene-*co*-vinylphenol) (STVPh) system"? Chen and Morawetz recently reported a seminal fluorescence study of blends of polymethacrylates with styrene copolymers containing

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hydrogen bond donors.[1] A number of findings of this work are germane to our study. It was determined that only 2% of VPh in PS was required to form a miscible blend with poly(butyl methacrylate) (PBMA), while even less (approximately 1%) was necessary in the case of PMMA and poly(ethyl methacrylate) (PEMA). Similar conclusions were reported in 1984 in an important paper by Pearce et al.,[2] who studied blends of polymethacrylates with hexafluoro-2-hydroxyisopropyl (HFHP) modified polystyrenes. For these systems, 4 and 2% of the HFHP units were found to be necessary to form miscible blends with PMMA and PBMA, respectively.

These observations also impinge on the much larger question concerning the role of "copolymers" in the free energy of mixing and phase behavior of polymer blends. Mean-field binary interaction models[3-5] are popular and have been employed to explain miscibility in a number of copolymer blends, especially those involving relatively weak intermolecular interactions. We have come from the other direction in our work and have emphasized the role of relatively strong, directionally specific intermolecular interactions (hydrogen bonds) in phase behavior.[6-15] A theory describing the free energy of mixing based upon a simple association model has been presented[7] and extended to include the calculation of spinodal phase diagrams.[11,12] Such phase diagrams have been calculated for several different binary polymer blend systems, including PVPh blends with various polyacrylates, polyacetates, and polyesters;[13] amorphous polyurethane blends (APU) with different polyethers;[14] and ethylene-*co*-methacrylic acid copolymer (EMAA) blends with a series of polyalkyl and poly(vinyl alkyl) ethers.[15] The theoretical predictions of the gross phase behavior were found to compare well with experimental observations of the miscibility of these systems.

In this paper we will build on our previous studies of PVPh blends. We will demonstrate that we can predict the broad phase behavior of PVPh blends with a series of polymethacrylates. We will further demonstrate that we can employ data derived from these "pure homopolymer" blends to calculate the free energy of mixing of hypothetical STVPh copolymer–polymethacrylate blends and predict miscibility limits that are in remarkable agreement with the experimental data of Chen and Morawetz.

The poly(4-vinylphenol) (PVPh) employed in this study has been described previously.[13,15] Amorphous poly(alkyl methacrylates) having number-average molecular weights in the range 10–40 000 with relatively narrow molecular weight distributions ($M_w/M_n < 1.5$) were synthesized in our laboratories by the technique of group-transfer polymerization.[16] The polymethacrylates were polymerized in tetrahydrofuran between 25 and 50 °C with 1-methoxy-1-(trimethylsiloxy)-2-methylpropene as an initiator and tris(dimethylamino)sulfonium bifluoride as the catalyst.[17] Those synthesized include poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PPMA), poly(isopropyl methacrylate) (PiPMA), and poly(*n*-butyl methacrylate) (PBMA). Poly(*tert*-butyl methacrylate) (PtBMA) was purchased from Polysciences, Inc.

The interpretation of infrared spectra and the quantitative measurement of "free" and hydrogen-bonded carbonyl groups in PVPh blends with polymers containing carbonyl groups is now firmly established.[18,19] Details of the preparation of the blend samples for infrared analysis have also been presented before.[13] Moreover, we have recently reported theoretical calculations for a series of PVPh blends with polyacrylates, polyacetates, and polyesters and compared the results to experimental observations.[13] Quantitative data of the fraction of "free" carbonyls were obtained at 150 °C for all the PVPh–poly(alkyl methacrylate) systems and show very similar trends to the analogous polyacrylate blends containing the same number of aliphatic carbons.[13] Accordingly, we present in Table I only the results of the PVPh–PEMA system which were used to confirm the magnitude of K_A (see later).

Table I
Quantitative Infrared Data

PVPh:PEMA comp, vol fractn	fractn of hydrogen-bonded carbon groups	PVPh:PEMA comp, vol fractn	fractn of hydrogen-bonded carbon groups
0.21:0.79	0.266	0.61:0.39	0.483
0.41:0.59	0.391	0.81:0.19	0.547
0.51:0.49	0.424		

Table II
PVPh Blend Parameters

polymer	molar vol, cm^3/mol	solubil param, $(cal\ cm^3)^{1/2}$	interaction param, χ^{PVPh}
PVPh	100.5	10.89	
PS	98.0	9.20	
PMMA	86.5	9.07	0.559
PEMA	102.4	8.95	0.624
PPMA	118.2	8.86	0.686
PBMA	134.1	8.80	0.732
PiPMA	119.9	8.49	0.953
PtBMA	138.9	8.00	1.390

The theoretical equations developed to describe the stoichiometry, free energy changes, and phase behavior of hydrogen-bonded polymer blends have been discussed in detail.[7,11,12] Calculations of theoretical spinodal phase diagrams for blends of PVPh containing various poly(alkyl methacrylates) were performed in precisely the same manner as described previously[13] by using the parameters listed in Table II.

Molar volumes were calculated by using the glassy molar group contributions listed in Table 4.6 of Van Krevelen's book.[20] Solubility parameters were calculated in a consistent manner by using the molar attraction constants of Hoy.[21] The interaction parameters, χ, were calculated[22] by using the simple relationship $\chi = (V_B/RT)[\delta_A - \delta_B]^2$. The molar volume of PVPh was used as a reference volume V_B and values of χ calculated in this manner are labeled χ^{PVPh} in Table II. The degree of polymerization for both polymers was assumed to be 500.

K_2 and K_B, the equilibrium constants describing the self-association of PVPh in the dimer and "chain-like" structures, respectively, were determined as described previously[11,13,23] and values of 20.9 and 66.5 were employed.[24] K_A, the equilibrium constant describing the association of PVPh with polymethacrylates, was determined experimentally from the miscible PVPh–PEMA system.[25] A value of $K_A = 5.6$ was obtained from quantitative infrared measurements (Table I) by using the least-squares fitting procedure described in ref 13 for this blend system at 150 °C (a temperature well above the T_g of the system to minimize nonequilibrium effects). With the assumption that the van't Hoff relationship is valid over the temperature range considered and the use of the enthalpies listed in Table III of ref 13, K_A was determined to be 47.6 at 25 °C. This is in excellent accord with the K_A value obtained previously for the PVPh–polyacrylates blends and an average value of $K_A = 50$ was used in our calculations.

The results of the spinodal calculations are displayed in Figure 1. Again, we emphasize that we are primarily

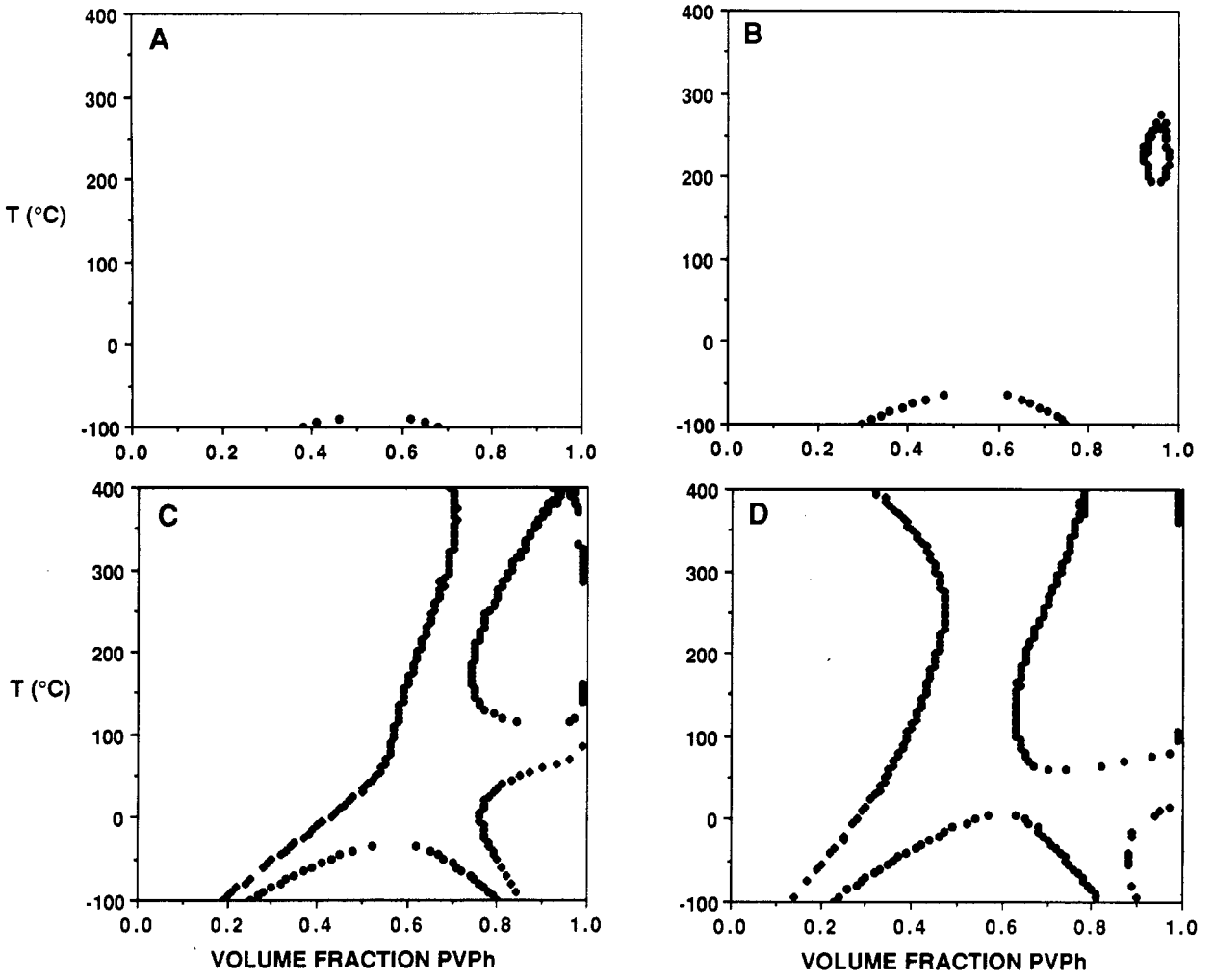
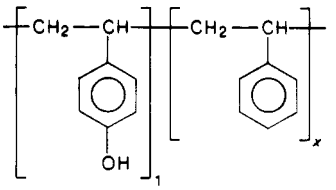


Figure 1. Calculated spinodal phase diagrams for PVPh–poly(alkyl methacrylate) blends: (A) (●) PMMA; (B) (●) PEMA; (C) (●) PPMA and (◆) PiPMA; (D) (●) PBMA and (◆) PtBMA.

concerned with trends rather than the specifics of the phase diagrams. As one might anticipate, the broad general features of the phase diagrams calculated for the PVPh blends with polymethacrylates are very similar to those described previously for the analogous polyacrylates.[13] PMMA (Figure 1A) and PEMA (Figure 1B) are predicted to be *essentially* miscible from above −50 °C to well above their degradation temperatures. As we increase the molar volume of the methacrylate unit and proceed to the PPMA (Figure 1C) and PBMA (Figure 1D) blends, the small closed immiscibility loop calculated at about 200 °C for the PEMA blend at extreme PVPh compositions becomes progressively larger. Concurrently, the size of the lower phase boundary increases. These two regions merge in the case of the PiPMA (Figure 1C) and PtBMA (Figure 1D) blends, forming a large two-phase area for PVPh-rich blends extending throughout the entire temperature range. While the PPMA blend is predicted to be miscible at ambient temperature, PVPh-rich blends of this polymer would be expected to phase separate at moderately elevated temperatures. Both PBMA and PiPMA blends are on the edge of miscibility at room temperature and can be described as "partially miscible" systems. Finally, PVPh–PtBMA blends are predicted to be essentially immiscible, except in blends very rich in PtBMA. We will not dwell on these results, since they are very similar to those described previously, except to state that the trends predicted theoretically are in good agreement with our infrared studies and in reasonable accord with the thermal studies of Goh and Siow.[25]

Assuming that styrene is an inert diluent, we can readily estimate the equilibrium constants K_2 and K_B for hypothetical STVPh copolymers of varying composition by computing an average chemical repeat that contains one VPh unit and scaling according to the ratio of the molar volumes.[11]



For example, K_B for a STVPh copolymer containing x% of styrene would be determined from

$$K_B^{\mathrm{STVPh}[x]} = K_B^{\mathrm{PVPh}} \frac{V_B^{\mathrm{PVPh}}}{V_B^{\mathrm{STVPh}[x]}}$$

Alternatively, we could simply calculate the contribution of hydrogen-bonding interactions to the free energy by considering the styrene units to be an inert diluent and calculating the concentration of PVPh units in each blend. Either method can be used, but for various reasons (see below) it is more convenient to calculate an average repeat.

The magnitudes of K_2 and K_B vary with the composition of the STVPh copolymer, but the ratio of these two equilibrium constants to K_A is theoretically predicted to be constant.[11] This is because all the equilibrium constants

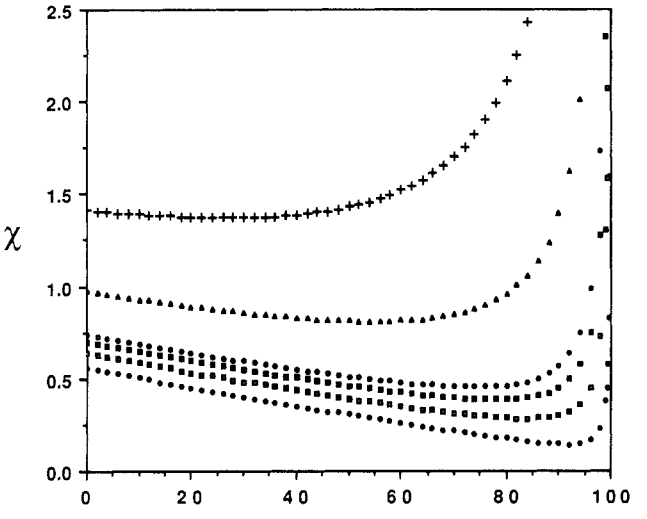


Figure 2. Graph of the calculated values of χ for STVPh–poly(alkyl methacrylate) blends as a function of the STVPh copolymer composition. From bottom to top: PMMA, PEMA, PPMA, PBMA, PiPMA, and PtBMA.

are defined in terms of chemical repeat units and are related to the equivalent equilibrium constants in terms of the self-associating *interacting unit* used to define the lattice cell size. The adjustment for the different size of the chemical repeat units enters through the factor $r = V_A/V_B$. Accordingly, having determined the values of equilibrium constants for polymethacrylate–PVPh blends, it is a straightforward matter to calculate the new values of the equilibrium constants for polymethacrylate–STVPh blends.

The solubility parameters of the STVPh copolymers, which change in an essentially linear fashion with copolymer composition, were estimated from the corresponding values of the pure polymers (PVPh = 10.89 and PS = 9.20 (cal cm^3)$^{1/2}$) by using the relationship of Scott:[24]

$$\bar{\delta}_B = \delta_B^{STVPh[x]} = \Phi_{PS}\delta_{PS} + \Phi_{PVPh}\delta_{PVPh}$$

Estimates of the value of χ for the STVPh–polymethacrylate blends may now be determined as before by using the relationship $\chi = (V_B/RT)[\delta_A - \bar{\delta}_B]^2$, where the molar volume of the STVPh repeat is employed as the reference volume, V_B. The results are summarized in Figure 2. Other things being equal, the closer χ is to zero the better the chance for molecular mixing. The value of χ *as defined here* is determined by two factors: (i) the size of the reference volume V_B, which increases with increasing styrene content in the STVPh copolymer and (ii) the difference in the solubility parameter of STVPh, $\bar{\delta}_B$, and its value relative to δ_A, the solubility parameter of the polymethacrylate. For the specific case of STVPh–polymethacrylate blends, these two factors tend to offset one another over a wide range of STVPh copolymer composition. With decreasing concentration of VPh in the STVPh copolymer, however, a point is reached where the value of χ rises rapidly. This occurs at the lowest concentration of VPh for PMMA and follows the trend PMMA < PEMA < PPMA < PBMA < PiPMA < PtBMA. This is an observation that has obvious implications for the calculated miscibility limits, especially in the absence of relatively strong intermolecular interactions. But, in our case, due consideration must also be given to the hydrogen-bonding contribution to the free energy of mixing, since this can radically effect the breadth of such windows.

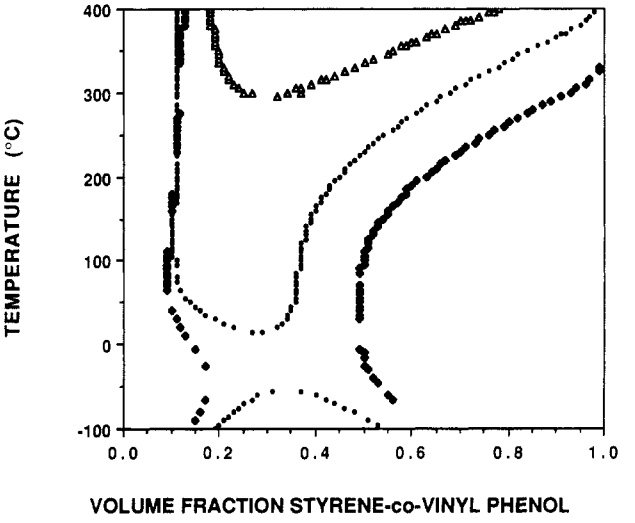


Figure 3. Calculated spinodal phase diagrams for PBMA blends with STVPh copolymers containing (△) 1.0, (●) 1.5, and (◆) 2.0 wt % VPh units.

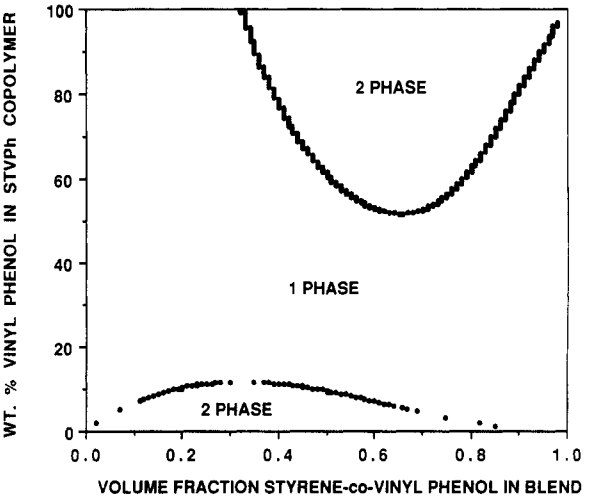


Figure 4. Calculated limits of miscibility for STVPh–PtBMA blends at 25 °C.

One final adjustment, which effects the contribution from combinatorial entropy, and then we have all the necessary input to calculate theoretical free energies of mixing and spinodal diagrams for the various STVPh–polymethacrylate blends. Since we wish to compare the free energy of mixing blends of comparable *molecular weight*, we must also adjust the values of N_A and N_B in the STVPh blends to reflect the increased molar volume of the average repeat of the STVPh copolymer, which we use to define a reference volume. This we do by multiplying N_A and N_B by the factor $V_B^{PVPh}/V_B^{STVPh[x]}$.

Figure 3 show the result of a typical calculation for PBMA blends with STVPh[x] copolymers, where [x] refers to the weight percent VPh in the copolymer. For the PMMA, PEMA, PPMA, and PBMA blends it was determined that roughly 0.1, 0.5, 1, and 2%, respectively, of VPh units in PS are required to produce a single phase over the entire range blend composition at ambient temperature. In other words, for these polymethacrylate blends, the limit of miscibility extends from pure PVPh to PS containing less than 2% VPh. The overall concurrence between these calculations and the experimental results of Chen and Morawetz[1] exceeds our wildest expectations. The corresponding lower limits calculated for the PiPMA and PtBMA blends are approximately 5 and 14% VPh, respectively. Neither PiPMA nor PtBMA blends are truely

miscible with PVPh (single phase over the entire blend composition range) at ambient temperature (Figure 2) and the upper limits of miscibility were determined for these two blends. We predict that about 10% of styrene must be incorporated into PVPh to render it miscible with PiPMA, while as much as 50% is necessary for the corresponding PtBMA blend. A typical diagram depicting the limits of miscibility for the latter blend at 25 °C is shown in Figure 4. We intend to experimentally test these predictions in the near future.

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Registry No. PVPh, 24979-70-2; PEMA, 9003-42-3; PS, 9003-53-6; PMMA, 9011-14-7; PPMA, 25609-74-9; PBMA, 9003-63-8; PiPMA, 26655-94-7; PtBMA, 25189-00-8; (ST)(VPh) (copolymer), 24979-74-6.

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Diffusion of Camphorquinone in Oriented Polycarbonate Films

Viscoelastic properties of polymers are affected by externally applied perturbations. The external perturbation, such as stretching, induces a preferred orientation of polymer chain segments along the deformation axis. Conventional techniques (such as radioactive tracer and pulsed gradient NMR, etc.) for measuring the translational diffusion coefficient are limited to about 10^{-10} cm^2/s. Diffusion of small molecules embedded in solid-state polymers in the vicinity of the glass transition temperature (T_g) occurs at a smaller rate, in the order of 10^{-13}–10^{-15} cm^2/s, depending on the size of the diffusants. As a result, very little systematic study of small-molecule transport in polymers has been carried out. By use of the technique of laser-induced holographic grating relaxation (LIHGR), it has been possible to investigate the diffusion coefficient as small as 10^{-15} cm^2/s.[1-3] Although the small molecules are not covalently bonded to the polymer chain, it is found that the diffusion coefficient of the probing dye molecules dissolved in the amorphous solid-state polymer is determined by the relaxation dynamics of the polymer chain.[1,2] It is thus anticipated that orientation of the polymer chain by stretching will also impose a pronounced effect on the diffusion coefficient of the probing molecules. The study of the anisotropic diffusion behavior of the probe molecules in the polymer solid is difficult by using the conventional technique.

In this communication, we report the first quantitative measurement of the diffusion behavior of camphorquinone in stretched polycarbonate films using the LIHGR technique.

Experimental Section. Polycarbonate (PC) film samples were prepared by dissolving the PC resin (purchased from Aldrich Chemical Co., M_w = 20 000–25 000, polydisperse) and camphorquinone (CQ, 0.5% by weight relative to PC) in CH_2Cl_2 and then filtering the solution to remove dust. The filtered solution was casted on a Teflon plate to produce a film about 0.3–0.4 mm thick. The film was then uniaxially stretched in a silicone oil bath at a temperature slightly above T_g (≈148 °C) at 153 °C with a manually operated puller. The drawn films were then quenched to room temperature. In addition to the unstretched film, five specimens with percent elongation equal to 50, 70, 95, 123, and 150 were also prepared for the LIHGR measurement.

The holographic grating is induced by crossing two equal-intensity coherent beams derived from an argon ion laser radiation. The laser wavelength is 488.0 nm, and the crossing angle θ is 14.6°, corresponding to a grid spacing of 1.92 μm. The film was mounted in a rotatory stage; the long axis of the film can be accurately rotated with respect to the laser beams (see Figure 1). The temperature of the films was controlled in an oven set at 118 ± 0.1 °C.

Results and Discussion. Shown in Figure 2 is the effective diffusion coefficient [$D(\alpha)$] of camphorquinone in stretched PC having a percent elongation equal to 123% at 118 °C as a function of the orientation angle α. Only the transverse motion with respect to the grating contributes to the diffraction intensity. At $\alpha = 0°$ the optical experiment samples only molecules diffusing along the direction of stretch ($D_\parallel$). On the other hand, at $\alpha = 90°$, it samples those diffusing along the direction perpendicular to stretch ($D_\perp$). The effective diffusion coefficient observed at angle α is found to be related to $D_\parallel$ and $D_\perp$ by the equation: $D(\alpha) = D_\parallel \cos^2 \alpha + D_\perp \sin^2 \alpha$. This angular dependence is consistent with the fact that the diffusion coefficient is proportional to $\langle |\mathbf{r}|^2 \rangle$; stretching the film

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