SHORT COMMUNICATIONS

Short-Range Order in a Miscible Polymer Blend

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It is well known that the miscibility of dissimilar polymers with high molecular weights arises from specific interactions between them, such as hydrogen bonding and weak charge transfer complex.¹ The presence of specific interactions has been confirmed by Fourier-transform infrared and NMR spectroscopies.^{2,3} Specific interactions are expected to induce some conformational changes of individual chains with mixing. The situation may be characteristic to a polymer–polymer mixture and different from that in polymer–solvent system. The difference may originate from the connectivity in chain molecules of both components in the former system. Conceivable alignments of dissimilar chains should be parallel to each other and the chains would be locally stretched (compared with random coil chains). It reminds us of the classic meander model by Pechhold *et al.*⁴ as an extreme case. Anyhow, one may expect some ordering in chain packing in the miscible polymer–polymer mixture.

In order to verify the ordering in the miscible polymer–polymer mixture, we carried out depolarized light scattering experiments. The miscible system used in this communication is poly(methyl methacrylate) (PMMA)/poly-

(vinylidene fluoride) (PVDF). As a reference system, we employed PVDF/methyl ethyl ketone (MEK) solution.

The polymer specimens used in this study are commercial polymers. PVDF was supplied by Kureha Chemical Industry Co., Ltd.; KF1100, $\bar{M}_w = 7 \times 10^4$. PMMA was supplied by Mitsubishi Rayon Co., Ltd.; Acrypet VH001, $\bar{M}_w = 8.6 \times 10^4$, $\bar{M}_n = 4.8 \times 10^4$. The blend composition of PMMA/PVDF was limited in a range of 100/0—70/30. When PVDF content is higher, crystallization takes place.⁵

A rod specimen of 8 mm diameter and 25 mm length was prepared by injection-molding using a miniature molder, Mini-Max Molder (CS-183 MMX, Custom Scientific Instruments, Inc.), set at 220°C. The as-molded specimen was held and annealed in the mold for 5 min to relax the macroscopic chain orientation and the annealed specimen was detached from the molder. Further it was set in a hot chamber and slowly cooled in order to keep it away from frozen stress. The cooling procedure is shown in Figure 1. Zero birefringence in the annealed specimen was confirmed by a polarizing microscope fitted with a sensitive tint plate. No crystallization was confirmed by differential scanning calorimetry

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Figure 1. Cooling procedure. The interval between the first cooling and second one has no significant meaning. It is simply due to the safety requirement at our laboratory. The third cooling is carried out in the oil bath of the light scattering apparatus.

(910 DSC, du Pont Instruments Co., Ltd.). PVDF/MEK solution was made up in a NMR tube with the inner diameter 8 mm. The basic design of the apparatus for the depolarized light scattering is similar to that of Flory *et al.*⁶ A 632.8 nm He-Ne laser (5 mW; LHR-151, Melles Griot Co., Ltd.) was used as a light source. The incident light was polarized by a Glan-Thomson prism and was intercepted by a light chopper driven at 500 Hz. The specimen was put into a quartz cell of inner diameter 38 mm filled with liquid paraffine in order to prevent anomalous reflection due to the small curvature of the rod specimen. The analyzer was also a Glan-Thomson prism. Polarizer and analyzer axes crossed at 90°, *i.e.*, the H_v geometry. The H_v scattered light was detected by a photomultiplier (R268, Hamamatsu Photonics Co., Ltd.). The photocurrent was converted to EMF and measured with a single phase lock-in amplifier (5600, NF Electronic Instrument Co., Ltd.). Measurement was carried out at 20°C.

The intensity of scattered light under the H_v geometry is generally formulated by⁷

$$I_{H_v} = \frac{16\pi^4}{15\lambda_0^4} \left(\frac{n^2 + 2}{3} \right)^2 N \gamma_0^2 \int_0^\infty f(r) \frac{\sin hr}{hr} 4\pi r^2 dr \quad (1)$$

where λ_0 is the wavelength of the incident light, n is the refractive index, N is the number density of monomer units (in cm³), γ_0^2 is the

Figure 2. H_v scattering intensity versus scattering angle.

intrinsic mean-squared optical anisotropy of monomer unit, $f(r)$ is the orientation correlation function, defined for the angles between the optical axes of the scattering units located at a distance r apart, and $h = (4\pi/\lambda) \sin(\theta/2)$ is the scattering vector; λ being the wavelength in the medium and θ being the scattering angle between the incident and scattered rays. γ_0^2 is formulated by the polarizability difference of the monomer unit as⁸

$$\gamma_0^2 = 1/2[(\alpha_x - \alpha_y)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2] \quad (2)$$

where α_i is the principal polarizability of a monomer unit.

In Figure 2 is shown the H_v scattering intensity I_{H_v} of PMMA/PVDF mixtures as a function of θ . There is no angular dependence. This implies that the correlation length of orientation fluctuation is much smaller than λ . In this case ($hr \ll 1$), eq 1 is approximated as

$$I_{H_v} = \frac{16\pi^4}{15\lambda_0^4} \left(\frac{n^2 + 2}{3} \right)^2 N \gamma^2 \quad (3)$$

where γ^2 is the effective mean-squared optical anisotropy defined by

$$\gamma^2 = 4\pi N \gamma_0^2 \int_0^\infty f(r) r^2 dr = P \gamma_0^2 \quad (4)$$

P is the order parameter which formally describes the number of monomer units arranged parallel to each other, *i.e.*, $f(r) = 1$ within

Figure 3. Effective mean-squared optical anisotropy versus PVDF concentration. Broken line is based on simple additivity of polarizability for intrinsic mean-squared optical anisotropy.⁹

the orientation correlation volume with a fixed size.

In Figure 3 are shown the effective mean-squared optical anisotropy γ^2 as a function of PVDF concentration ϕ for both PMMA/PVDF and MEK/PVDF systems. The values of γ^2 are from I_{H_v} at $\theta = 90^\circ$, in other words, from the depolarized scattering intensity. Most interesting is the dramatic difference in the magnitude of γ^2 between the polymer-polymer and polymer-solvent systems; in the former system, γ^2 remarkably increases with ϕ . If we assume the simple additivity⁹ of the α_i in eq 2, i.e., $\alpha_i = \alpha_{i(\text{PVDF})}\phi + \alpha_{i(\text{PMMA})}(1 - \phi)$, the ϕ dependence of γ_0^2 is estimated to be such as shown by the broken line in Figure 3. The magnitude of γ_0^2 is very small. The observed value of γ^2 is much larger than that of γ_0^2 estimated and increases with ϕ . The dramatic deviation should be ascribed to the increase of the order parameters P in eq 4 with blending.¹⁰

Note here that the concave character of the broken line in Figure 3 is not important. It is simply due to the fact that our system consists of dissimilar polymers with different signs of optical anisotropy: the anisotropy of PMMA is negative while PVDF has positive anisotropy,

as discussed in our previous article.¹¹ The concave nature in γ_0^2 may result in the observed minimum in γ^2 .

Thus, the short-range ordering in the miscible polymer blend has been proved by polarized light scattering. We believe that the ordering requires two conditions: specific interactions and chain connectivity; i.e., ordering may be characteristic to the polymer-polymer mixture but not to the polymer-solvent system. We also believe that the ordering is not specific to our particular polymer pair but is a rather general phenomenon for some classes of miscible systems with specific interactions. This may be consistent with a recent argument based on the Monte Carlo simulation by Cifra *et al.*¹² Ordering should be taken into account for thermodynamic discussion of polymer-polymer miscibility, especially for unsolved problems such as the appearance of UCST (upper critical solution temperature) in mixtures of dissimilar polymers with high molecular weights.¹³⁻¹⁵ We believe that this communication provide a key evidence for this phenomenon.

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9. This additivity implies the parallel orientation of a pair of dissimilar monomer units.
10. Even if the estimated γ_0 is multiplied by a constant P , the calculated curve does not coincide with the

- observed curve. It probably suggests that P varies with ϕ ; *i.e.*, $P = P(\phi)$.
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