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William MacKnight, *University of Massachusetts Amherst*

W. Wenig

F. E. Karasz

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**Small-Angle X-ray Investigation of Morphological
Order in the System Isotactic
Polystyrene-Poly(2,6-dimethylphenylene oxide)**

W. WENIG,[†] W. J. MACKNIGHT, and F. E. KARASZ*

*Polymer Science and Engineering Department, University
of Massachusetts, Amherst, Massachusetts 01003.
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Blends of isotactic polystyrene and poly(2,6-dimethylphenylene oxide) (PPO) can be crystallized by thermal treatment for PPO contents lower than 40%. The samples reveal crystallinities which vary from below 20% to just over 30%.^{1,2}

Wide-angle X-ray diffraction results show curves typical for partially crystallized isotactic polystyrene, which suggests that the blends consist of a homogeneous amorphous phase and a discrete crystalline phase. It is concluded from the appearance of a long period in the small-angle X-ray scattering (SAXS) curves of the blends that the crystals are arranged in a partially ordered manner. In an earlier

[†]Laboratorium für Angewandte Physik, Universität Duisburg, 4100 Duisburg, West Germany.

paper² we showed that the SAXS curves of these blends can be calculated theoretically by use of Hosemann's model of the linear paracrystal.³⁻⁵ This model proves to be a good approximation for systems with high correlation numbers ($N \geq 10$); however, for low correlation, as in the present iPS/PPO blends ($N \approx 2$), it may lead to false results. As was recently shown, the amorphous density as well as the mean sample density plays an important role.⁶

In this paper we present theoretical calculations using a model which recognizes the density contrast⁶ and compare the calculated morphological parameters to those that had been derived from Hosemann's black-white model.

Results

We first present results needed⁶ for this analysis. Let ρ_c be the electron density of the crystals, ρ_a the electron density of the amorphous layers, and ρ_u the mean sample density. The intensity as a function of s ($s = (2 \sin \theta)/\lambda$) is then given by

$$I(s) = \frac{1}{2\pi^2 s^2} \operatorname{Re} \left\{ \Delta \rho_i^2 \left[N \frac{(1-f_x)(1-f_y)}{1-f_z} + f_y \frac{(1-f_x)^2}{(1-f_z)^2} (1-f_z N) \right] + \Delta \rho_u^2 (1-f_z N) - \Delta \rho_i \Delta \rho_u \frac{1-f_x}{1-f_z} (1-f_z N) \right\} \quad (1)$$

where $\Delta \rho_i = \rho_c - \rho_a$, $\Delta \rho_u = \rho_u - \rho_a$, and f_x and f_y are the normalized thickness-distribution functions of the crystals and the amorphous layers:

$$f_x = \int_0^\infty H(x) e^{-2\pi i s x} dx$$

with a corresponding term for f_y , and

$$f_z = f_x f_y$$

Hosemann's "black-white" model results⁶ from (1) by using the approximation

$$\Delta \rho_i = 1; \quad \Delta \rho_u = 0 \quad (\rho_c = 1, \rho_a = \rho_u = 0)$$

$$I(s) = \frac{1}{2\pi^2 s^2} \operatorname{Re} \left\{ N \frac{(1-f_x)(1-f_y)}{1-f_z} + f_y \frac{(1-f_x)^2}{(1-f_z)^2} (1-f_z N) \right\} \quad (2)$$

Gaussian distribution functions had been used for both the lamellar and interlamellar thickness distributions. Mean sample densities of the partially crystallized and the amorphous samples have been measured by the density gradient method.

In Figure 1 the experimental SAXS curves for the blends of denoted composition are displayed together with various theoretical curves: the curves calculated by eq 1 and 2, respectively, and a curve calculated from eq 1 taking the best fit parameters obtained by using eq 2. A comparison of this curve with those calculated to give the best agreement with the experimental curves should provide an estimate of the validity of the "black-white" approximation. As Figure 1 shows, the black-white model is reasonably satisfactory for pure iPS but becomes more incorrect as the PPO content increases. Concurrently the correlation parameter (see below, Figure 4) decreases. This is in good agreement with earlier findings which state that the black-white model becomes increasingly invalid when the correlation of crystal lamellae decreases.

The crystal thicknesses (Figure 2), as well as the interlamellar distances (Figure 3), calculated from eq 1, appear lower than those calculated with eq 2. It has been questioned whether these small differences of the calculated values can be determined significantly. However, the

Figure 1. Small-angle X-ray scattering curves (Lorentz corrected) of pure iPS and a representative blend with composition as shown: (—) experimental curve; (---) best fit of the calculated curve using Hosemann's model; (···) best fit using the improved model; (-·-) curve calculated by use of the density model using the best fit parameters obtained with the Hosemann model. The mismatch of this curve shows the deviation between the two models.

Figure 2. Mean thickness of crystal lamellae, $\bar{x}$. The solid curve is calculated from the improved model, the broken curve from Hosemann's model.

decrease of the values of the crystal thickness in the pure iPS amounts to 40%, which is a considerable difference. Furthermore, it has to be considered that the scattering curve is most sensitive to variations for N values between 1 and 2, because the scattering curve then changes from a gas scattering curve (diffuse scattering) to one which is produced by interparticle interference. As for low corre-

Figure 3. Mean thickness of the amorphous layers, $\bar{y}$. The solid curve is calculated from the improved model, the broken curve from Hosemann's model.

Figure 4. Average number of crystals in a stack calculated for both models (solid curve, improved model; broken curve, Hosemann's model).

lation of the crystals, clusters of crystal lamellae as well as crystals with no correlated neighbors will occur in the sample.

For crystallinities below 50% the shape of the scattering curve is determined primarily by the fluctuation of the interlamellar distance distribution function. To what extent lamellar twisting or similar dislocations of the supermolecular lattice leads to erroneous determinations of

structure parameters cannot be concluded from these experiments alone. Evaluations of crystal size parameters from wide-angle X-ray scattering curves¹ yield values of the lamellar thicknesses of the same order of magnitude as the present results, and since there is no reason to assume the two models deal differently with the problem, we feel justified in discussing the parameters obtained at least qualitatively. Lamellar twisting, however, would primarily affect the correlation parameter N . Electron micrographs of iPS/PPO blends, obtained by the defocusing method,⁷ show bundles of 3–4 lamellae per cluster. It is difficult to compare morphological parameters derived from electron micrographs to those calculated with a one-dimensional model; it seems, however, that the statistical parameter N does not exactly define the number of the lamellae stacked in a cluster. However, the results do indicate that in this system of imperfectly formed crystalline aggregates both models show, albeit somewhat qualitatively, that blending further lowers the apparent lamellar correlation.

The calculations show that for both models the correlation decreases with increasing PPO content (Figure 4). This is confirmed by electron microscopy, which seems to show an even steeper decrease of this parameter.⁷ The results show that the lamellar cluster model has to be used carefully when systems with a very low orientation correlation of the lamellae are investigated. Although the order of magnitude of the correlation parameters and their variation with sample composition can be obtained with some accuracy, no absolute values can be given.

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