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Kinetics of formation of a surface enriched layer in an isotopic polymer blend

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ABSTRACT

The surfaces of blends of high-molecular-weight deuterated and protonated polystyrene, after annealing above the glass-transition temperature, are enriched in the deuterated component owing to a surface energy difference between the components of isotopic origin. We have measured the kinetics of growth of the enriched layer using forward-recoil spectrometry (FRES). Following a suggestion of Lipowski and Huse, we interpret our data by assuming that the growth of the layer is diffusion limited and that the non-equilibrium layer is in local equilibrium with the edge of that region just below the surface that is depleted in deuterated polystyrene. The concentration against depth profiles that are predicted by this model as a function of annealing time are in quantitative agreement with those measured by FRES.

§ 1. INTRODUCTION

In equilibrium a two-component mixture will in general have a different surface composition to the bulk; if the two components have different surface energies the system can save surface energy by having a higher volume fraction of the low-energy component at the surface. Such effects have been reported for polymer blends (Jones, Kramer, Rafailovich, Sokolov and Schwarz 1989a, Bhatia, Pan and Koberstein 1988); indeed simple theoretical considerations lead to the conclusion that such effects in polymer blends should be important and almost universal. However, as is usually the case with polymers, achieving equilibrium may not be easy, as relaxation times may be very long. In this paper we present experimental results showing how an enriched layer at the surface of a model polymer blend system builds up with time. The system is polystyrene (PS)/ deuterated polystyrene (d-PS). Such mixtures have recently been shown to be slightly non-ideal, with a tendency to phase separate at high molecular weight (Bates and Wignall 1986a, b). We have previously studied the equilibrium enrichment of the surface of such a mixture with the deuterated component (Jones *et al.* 1989a) and were able to interpret these equilibrium results with mean-field theory (Nakanishi and Pincus 1983, Schmidt and Binder 1985). In order to understand our present results we have constructed a simple diffusion-based model; quantitative agreement is found between our experimental results and these calculations.

§ 2. EXPERIMENTAL PROCEDURE AND RESULTS

The polymers used and methods of analysis have been presented before (Jones *et al.* 1989*a*). Briefly, films about 1 μm thick of blends of high molecular weight

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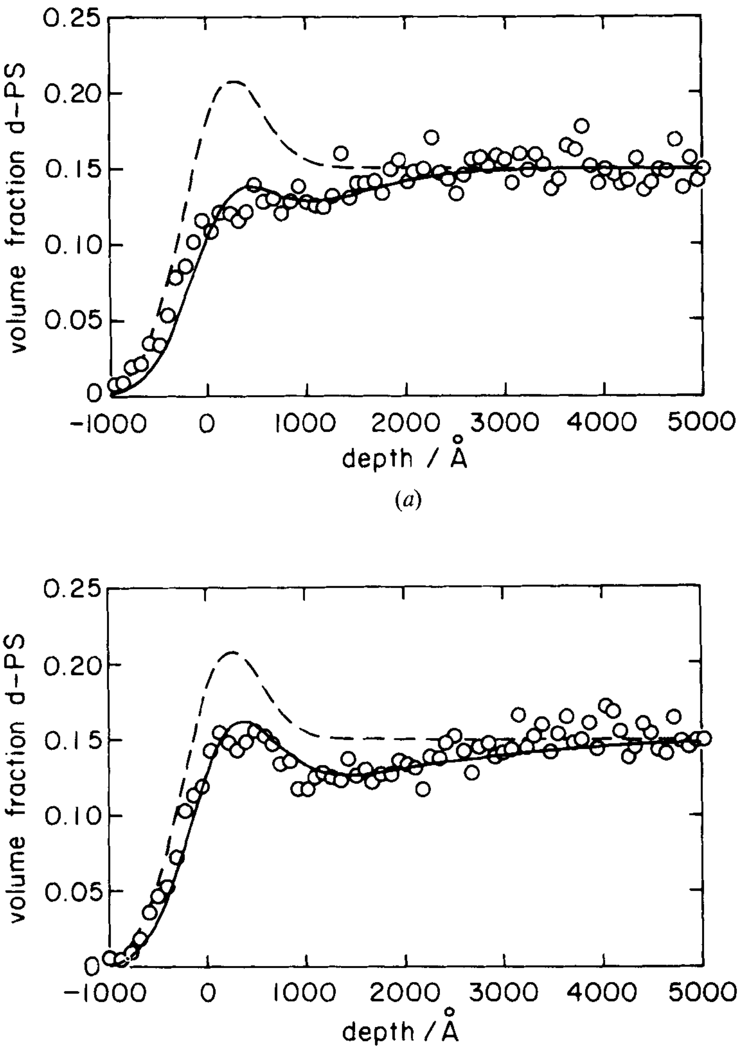
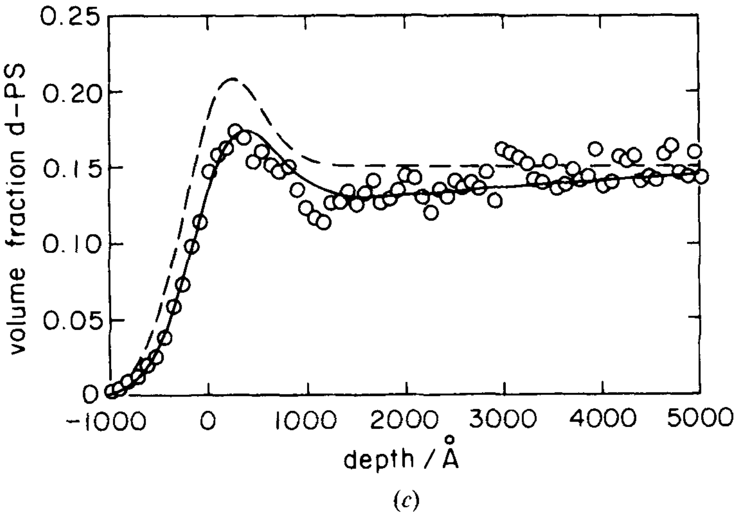
polystyrene (1·8 M, Pressure Chemicals) and deuterated polystyrene (1.03 M, Polymer Laboratories) are prepared by spin coating from toluene solution onto silicon substrates. The films are annealed under vacuum for various times, and their near surface deuterium depth profiles are measured using forward recoil spectrometry (FRES) (Mills, Green, Palmstrøm, Mayer and Kramer 1984). Figure 1 shows a series of forward recoil depth profiles for a 10% d-PS blend after varying annealing times. The dashed line on each profile is the equilibrium profile, convoluted with the instrumental resolution factor; profiles were considered to be at equilibrium when the amount of surface segregated material ceased to change with annealing time. The solid lines are the predictions of the model which is discussed below.

Fig. 1

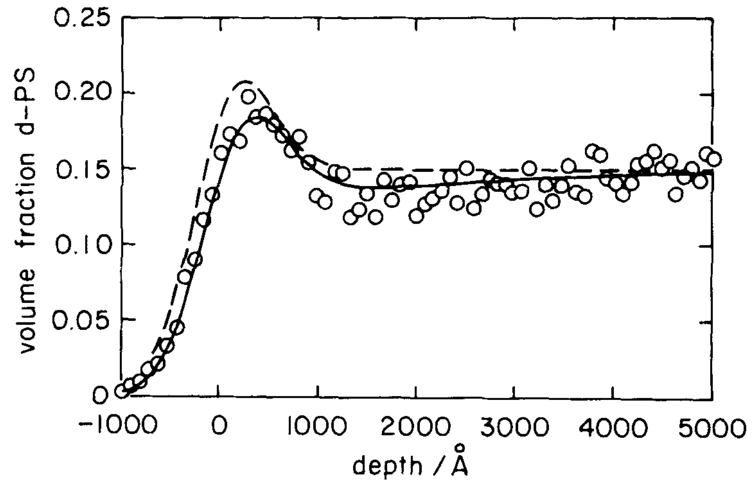


(a)

(b)



(*c*)



(*d*)

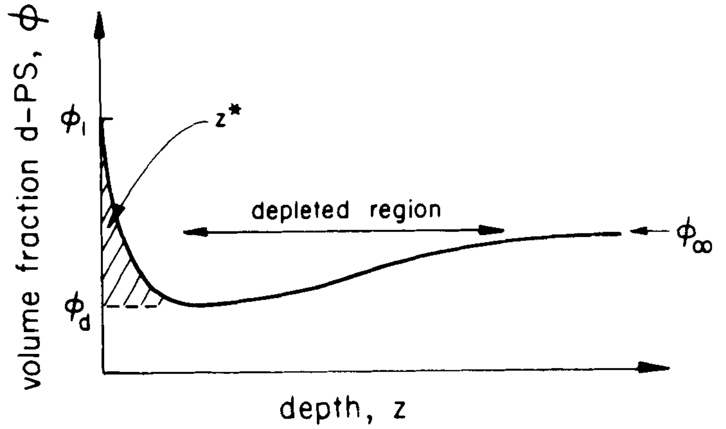
Depth profiles of d-PS in a blend with PS with an initial uniform volume fraction of d-PS of 0·10, after annealing times of (*a*) 3 h, (*b*) 12 h, (*c*) 1 day and (*d*) 2 days. The dashed line represents the equilbrium enrichment; the solid line is the fit from the model discussed in the text.

§ 3. DISCUSSION

Equilibrium surface enrichment in this system can be understood in terms of a mean-field model which has been described before (Nakanishi and Pincus 1983, Schmidt and Binder 1985, Jones *et al.* 1989a). Essentially the equilibrium surface profile is determined by competition between the free energy gain of having the lower surface energy component at the surface and the free energy costs (*a*) of having a region at a different composition than the bulk and (*b*) of sustaining a composition gradient between the bulk and the surface layers. In the case of an isotopic mixture such as polystyrene/d-polystyrene a small surface energy difference due to differences in bond polarizability between C–D and C–H bonds (Bartell and Roskos 1966) favours the deuterated component at the surface; the bulk thermodynamics of mixing may be approximated by the Flory–Huggins expression with a small positive (unfavourable) segment–segment interaction parameter, which has been measured previously by small-angle neutron scattering for this system (Bates and Wignall 1986a, b). The cost in free energy of sustaining a gradient may be expressed by way of the familiar gradient squared term in the free energy, as derived from the random-phase approximation (Binder 1983, de Gennes 1979). In our system such a theory predicts an approximately exponential decrease of the d-PS volume fraction from a higher surface value to its bulk value, with a decay length of the order of the bulk correlation length for concentration fluctuations. Measurements of the surface excess coverage of d-PS as a function of bulk blend composition by forward recoil spectrometry allow us to extract a physically reasonable value for the difference in surface energy between the species (Jones *et al.* 1989a), and measurements by dynamic secondary-ion mass spectrometry (Jones, Kramer, Rafailovich, Sokolov and Schwarz 1989b), high-resolution forward-recoil spectrometry (Sokolov, Rafailovich, Jones and Kramer 1989) and neutron reflectivity (Composto *et al.* 1989, Jones *et al.* 1990) have shown reasonable agreement with the predictions for the detailed shape of the near-surface profile.

The instrumental resolution of FRES, at 800 Å full width half maximum, is too large to resolve the structure in detail; however the general features are clear. The amount of material at the surface monotonically rises to the equilibrium value with annealing time, and below the surface there is a region depleted of d-PS. These observations lead us to propose a physical picture for the build up of the surface-enriched layer (schematically illustrated in fig. 2). Below the growing surface layer there is a depletion zone from which material to make the layer has been taken; d-PS from the bulk diffuses down the concentration gradient in the depletion zone to provide the material for the continued growth of the layer. It is clear that the size of the depletion zone must be controlled by the diffusion distance, $(Dt)^{1/2}$, where D is a mutual diffusion coefficient and t is the annealing time. If the diffusion distance is larger than the characteristic size of the enriched layer (which is of order the polymer

Fig. 2



A schematic sketch of a model for the build-up of a surface layer in a polymer blend.

radius of gyration) the rate-limiting factor controlling the growth of the layer will be the diffusive transport of material from the bulk to the surface rather than the internal equilibration of the surface layer. The volume fraction at the edge of the depleted zone nearest to the surface will vary rather slowly over the lengths characteristic of the surface enriched layer, and thus we can consider the enriched layer to be in local equilibrium with this volume fraction as suggested by Lipowski and Huse (1986).

Using this condition of local equilibrium we can construct a boundary condition for the diffusion equation which governs the supply of material to the surface enriched layer. This assumption implies that the relation between the surface excess after an annealing time t, $z^*(t)$, and the volume fraction at the edge of the depleted layer, $\phi_d(t)$, is

$$z^*(t) = f(\phi_d(t)), \tag{1a}$$

where f is simply the function relating the equilibrium surface excess z^* to the bulk volume fraction ϕ_∞ at equilibrium, that is

$$z^* = f(\phi_\infty). \tag{1b}$$

We have already stipulated that the diffusion distance must be large compared to the size of the surface layer, so we can make the approximation that the surface enriched layer is localised at the surface. Then the diffusion flux J in the depleted zone to the surface yields that rate of growth of the surface layer dz^*/dt,

$$\frac{dz^*}{dt} = -J. \tag{2}$$

This condition may be rewritten using Fick's first law and eqn. (1) as

$$D\frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial t}\frac{df}{d\phi}, \tag{3}$$

which, using Fick's second law, may be recast as

$$\frac{\partial \phi}{\partial x} = \frac{df}{d\phi}\frac{\partial^2 \phi}{\partial x^2}. \tag{4}$$

In our case the relation $z^* = f(\phi_\infty)$ has already been measured experimentally (Jones *et al.* 1989a), and is shown in fig. 3, together with a theoretical fit. It is well approximated by the linear expression $z^* = K\phi_\infty$ where K is 720 Å.

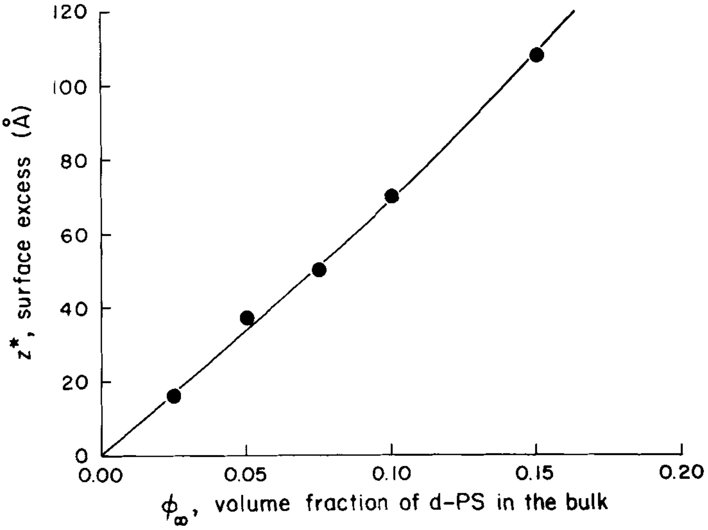
Before we discuss the detailed numerical solution of the diffusion equation with this boundary condition and the comparison of the results of this calculation with experiment, it is instructive to consider a simple approximate solution for the growth of the layer. Conservation of mass dictates that the amount of material removed from the depleted zone is the same as the surface excess; since the size of the depleted zone is of order $(Dt)^{1/2}$ this condition gives the following approximate equality

$$z^*(t) = [\phi_\infty - \phi_d(t)](Dt)^{1/2}. \tag{5}$$

The relation between $z^*(t)$ and $\phi_d(t)$ given by the local equilibrium assumption, eqn. (1), allows us to rewrite this as

$$z^*(t) = \frac{z^*_{eq}\phi_\infty(Dt)^{1/2}}{z^*_{eq} + \phi_\infty(Dt)^{1/2}}. \tag{6}$$

Fig. 3



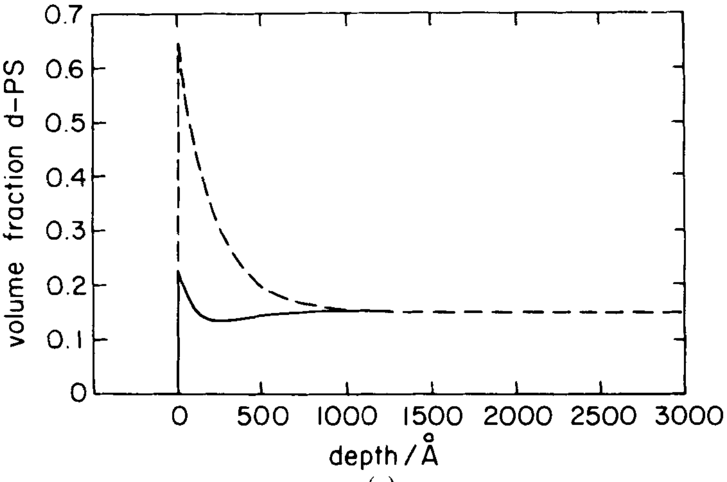
The surface excess of d-PS as a function of bulk volume fraction of d-PS, from Jones *et al.* (1989a). The solid line is a theoretical fit based on the mean field theory described Schmidt and Binder (1985), using the bare surface-energy parameters $\mu_1 = 0{\cdot}024$ Å and $g = -0{\cdot}0046$ Å, and the Flory–Huggins interaction parameter $\chi = 1{\cdot}48 \times 10^{-4}$ (Bates and Wignall 1986a, b).

From this relation we can see that the enriched layer starts to grow as $\sqrt{t}$, later slowing down as at the equilibrium surface excess z^*_{eq} is approached. The characteristic time for the approach to equilibrium is given by

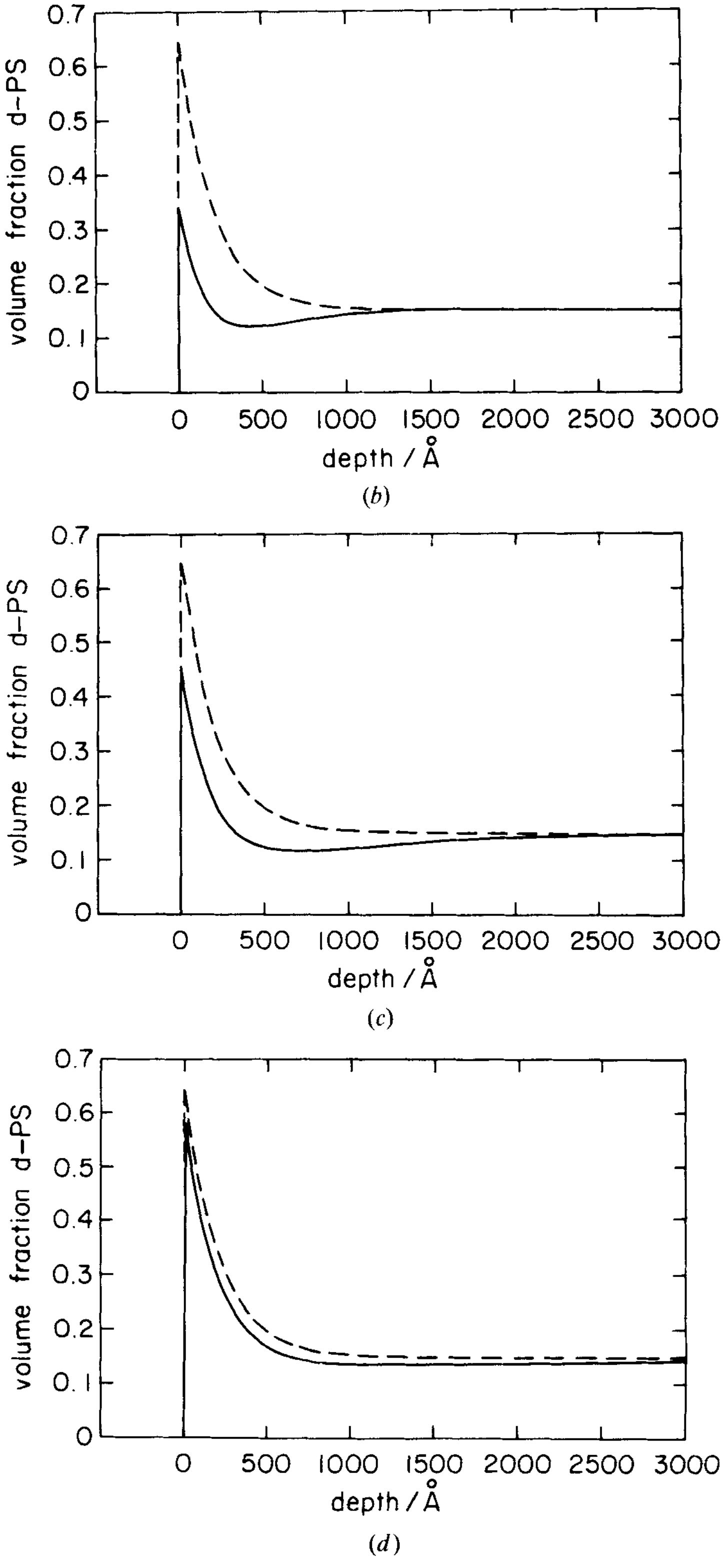
$$t_{\mathrm{eq}} = \left(\frac{z^*_{\mathrm{eq}}}{\phi_\infty}\right)^2 \frac{1}{D}. \tag{7}$$

Although these approximate results are instructive, we cannot directly compare

Fig. 4



(*a*)



The growth of the surface segregated layer of d-PS, as predicted by the model described in the text. In each case the dashed line shows the equilibrium profile, and the solid line the depth profile after times corresponding to values of the diffusion length $(Dt)^{1/2}$ of (*a*) 200 Å, (*b*) 400 Å, (*c*) 800 Å and (*d*) 3200 Å.

them with our experimental results. The 800 Å instrumental resolution of FRES prevents us from accurately measuring the time-dependent surface excess as defined here. Thus to compare the diffusion model with experiment we must compute the entire predicted profile and then convolute it with the known instrumental resolution function. We solved the diffusion equation numerically assuming a concentration-independent diffusion coefficient (in fact the mutual diffusion coefficient varies with composition owing both to the difference in chain lengths between the two species and to thermodynamic slowing down (Green and Doyle 1986); however over the restricted concentration range that we consider the error introduced by assuming the diffusion coefficient to be constant is small). We used a first-order finite-difference method, together with a mesh size in space that increased with time to compute the diffusion profile. Figure 4 shows results for a series of increasing times; a surface layer with an interface excess $z^*(t)$ from eqn. (1) has been added to the diffusion profile. Again, this procedure is only valid when the diffusion distance is large compared to the size of the enriched layer. In order to compare such profiles to the experimentally observed ones it is necessary to convolute them with the known instrumental resolution function; such convoluted curves are shown as solid lines on fig. 1; in these calculations we have used a diffusion coefficient of $5 \times 10^{-15} \mathrm{cm}^2 \mathrm{s}^{-1}$ and the experimental annealing times. The value for the mutual diffusion coefficient taken from the literature (Green and Doyle 1986) and extrapolated slightly to the correct temperature and molecular weights is $7 \times 10^{-15} \mathrm{cm}^2 \mathrm{s}^{-1}$; thus we find excellent qualitative and quantitative agreement between our model and the experimental results.

§4. Conclusion

These experiments show that the growth of a surface layer enriched in the lower surface energy component in a polymer blend can be understood in terms of a simple diffusion model. It is important to note that this approach is restricted in validity to later times, when the limiting factor to growth is not the dynamics within the layer but transport of material to the surface. The earlier stages of growth of the layer are likely to be more complicated, involving transport at length scales smaller than a coil dimension for which simple diffusion ideas are inadequate. For systems of high molecular weight these early stages of growth are experimentally accessible (indeed, for the shortest annealing time used in this study the diffusion distance $(Dt)^{1/2}$ is comparable to the characteristic length of the surface layer) and experiments to elucidate the growth of the layer in this regime will prove interesting. However, for practical purposes the simple diffusion process is likely to be the most important in determining the approach to equilibrium.

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REFERENCES

BARTELL, L. S., and ROSKOS, R. R., 1966, *J. Chem. Phys.*, **44**, 457.

BATES, F. S., and WIGNALL, G. D., 1986a, *Phys. Rev. Lett.*, **57**, 1429; 1986b, *Macromolecules*, **19**, 934.

BHATIA, Q. S., PAN, D. H., and KOBERSTEIN, J. T., 1988, *Macromolecules*, **21**, 2166.

BINDER, K., 1983, *J. chem. Phys.*, **79**, 6387.

COMPOSTO, R. C., STEIN, R. S., JONES, R. A. L., KRAMER, E. J., FELCHER, G .P., KARIM, A., and MANSOUR, A., 1989, *Physica* B, **156 & 157**, 434.

DE GENNES, P.-G., 1979, *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press), p. 245.

GREEN, P. F., and DOYLE, B., 1986, *Phys. Rev. Lett.*, **57**, 2407.

JONES, R. A. L., KRAMER, E. J., RAFAILOVICH, M. H., SOKOLOV, J., and SCHWARZ, S. A., 1989a, *Phys. Rev. Lett.*, **62**, 280; 1989b, *Interfaces between Polymers, Metals and Ceramics*, edited by B. M. DeKoven, A. J. Gellman and R. Rosenburg, Materials Research Society Symposium Proceedings, Vol. 153, p. 133.

JONES, R. A. L., NORTON, L., KRAMER, E. J., COMPOSTO, R. J., STEIN, R. S., RUSSELL, T. P., FELCHER, G. P., MANSOUR, A., KARIM, A., SCHWARZ, S. A., RAFAILOVICH, M. H., and SOKOLOV, J., 1990 *Europhys. Lett.* (in the press).

LIPOWSKY, R., and HUSE, D. A., 1986, *Phys. Rev. Lett.*, **57**, 353.

MILLS, P. J., GREEN, P. F., PALMSTRØM, C. J., MAYER, J. W., and KRAMER, E. J., 1984, *Appl. Phys. Lett.*, **45**, 957.

NAKANISHI, H., and PINCUS, P., 1983, *J. chem. Phys.*, **79**, 997.

SCHMIDT, I., and BINDER, K., 1985, *J. Phys., Paris*, **46**, 1631.

SOKOLOV, J., RAFAILOVICH, M. H., JONES, R. A. L., and KRAMER, E. J., 1989, *Appl. Phys. Lett.*, **54**, 590.