Small-angle neutron scattering and neutron reflectometry study of a model graft copolymer

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A model graft copolymer material consisting of polystyrene (PS) chains grafted onto a poly(ethyl acrylate) backbone was studied by small-angle neutron scattering (SANS) and neutron reflectivity. This 28 wt% PS graft material exhibited a lamellar phase morphology; it also produced abnormal butterfly isointensity patterns in SANS when uniaxially strained. It is believed that the polydispersity in structure of the copolymers is critical in producing the unexpected lamellar morphology.

(Keywords: graft copolymer; SANS; neutron reflectivity)

The interfacial properties of block copolymers are of great interest because of their widespread use as compatibilizers in the production of polymer blends. In this application, their presence at the interface between incompatible polymers lowers the surface energy and enhances interfacial adhesion, thus stabilizing the mixture against phase separation. In industrial applications, block and graft copolymers are the most frequently used copolymer structures, owing to their effectiveness at relatively low concentration and, in the case of graft copolymers, their low cost and ease of synthesis[1]. However, fundamental experimental studies have focused almost exclusively on the more tractable diblock and triblock copolymers[2]. An earlier study on polyisoprene–polystyrene graft copolymers found a similar phase diagram, with possibly somewhat different phase boundaries, to that seen in diblocks[3]. While much can and has been learned about the compatibilization of blends by the study of these model materials, we expect that a study of the interfacial and phase behaviour of the more complicated, yet technologically more important, graft copolymer would yield new and useful information.

Graft copolymers are typically produced *in situ* by the addition of reactive materials, such as peroxides, to a mixture of incompatible polymers[4,5]. We synthesized our model graft copolymers by copolymerizing an anionically polymerized macromonomer of methacrylate-terminated polystyrene (PS) with ethylacrylate[6]. The partially deuterated ethylacrylate monomer was synthesized by the reaction of perdeutero-ethyl alcohol and acryloyl chloride. The copolymer used in the present work contained 28 wt% PS. Since the number-averaged molecular weight (M_n) of this material was about 150 000 g mol^{-1} and the M_n of the PS macromonomers was 14 600 g mol^{-1}, the copolymer had, on average, three PS grafts attached randomly on each poly(ethyl acrylate) (PEA) backbone.

For the small-angle neutron scattering (SANS) studies, we prepared thick (~0.5 mm) films of the copolymer by melt compression moulding. The films were formed in a conventional press and heated to 130°C for 3 min and were then annealed for 6 h at 130°C, again under pressure. We mounted the films on a stretching device that clamped opposite ends of the films and allowed the application of uniaxial strain by the use of a thumbscrew. The SANS measurements were performed on the SAD instrument at the Argonne National Laboratory Intense Pulsed Neutron Source (IPNS) and on the 30 m SANS camera at the National Institute of Standards and Technology Cold Neutron Research Facility.

For neutron reflectivity (NR) studies[7], thin (~1500–2000 Å) films of the copolymer were deposited onto silicon substrates by spin-coating from 3% toluene solution. The samples were then annealed in a vacuum oven for 24 h at 130°C. The reflectivity data were obtained on the POSYII reflectometer at IPNS[8].

The effect of annealing was to increase the apparent macrophase ordering. This was evidenced by an increase in height and decrease in width of the peaks in the SANS

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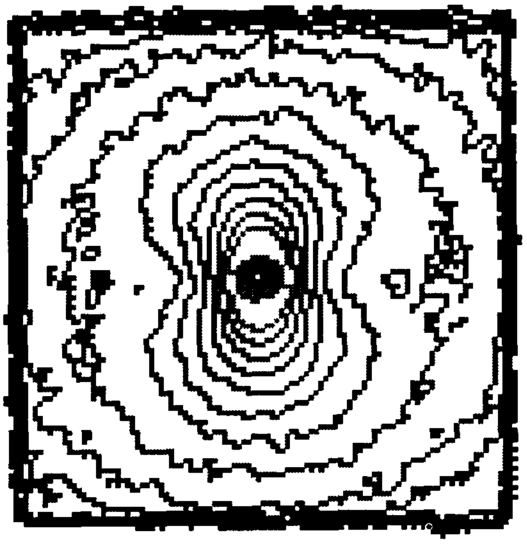

Figure 1 Two-dimensional SANS from 28% PS sample that had been annealed before stretching for 6 h at 130°C. The elongation ratio is 1.75; the maximum q shown here is $\sim 0.05\,\text{Å}^{-1}$

and NR spectra. This suggests that the domains within which the PS-rich regions are arranged periodically grow and/or coalesce as the samples are annealed. This interpretation is also consistent with mechanical measurements showing that annealed samples are stiffer and more brittle than 'quenched' samples[9].

Application of uniaxial strain produced anisotropic scattering patterns such as those shown in *Figure 1*. These patterns are similar to the 'abnormal butterfly' seen previously in strained gels and blends[10–13]. Our data exhibit a peak at $q \approx 0.02\,\text{Å}^{-1}$ ($q = (4\pi/\lambda)$ sin $(\theta/2)$, where θ is the scattering angle) and perhaps an additional peak at much lower q, below $0.001\,\text{Å}^{-1}$. This could be indicative of another phase separation occurring at much longer length scales, perhaps due to the small amount of ungrafted PEA homopolymer that may be present in the samples. In fact, the butterfly patterns may well originate at this macrodomain level of length scales, since the SANS patterns are more isotropic for $q \gtrsim 0.01\,\text{Å}^{-1}$. Since the anisotropy in the SANS is much more pronounced in the low q region, it is not surprising that similar butterfly-like patterns have been observed by light scattering in these samples[14].

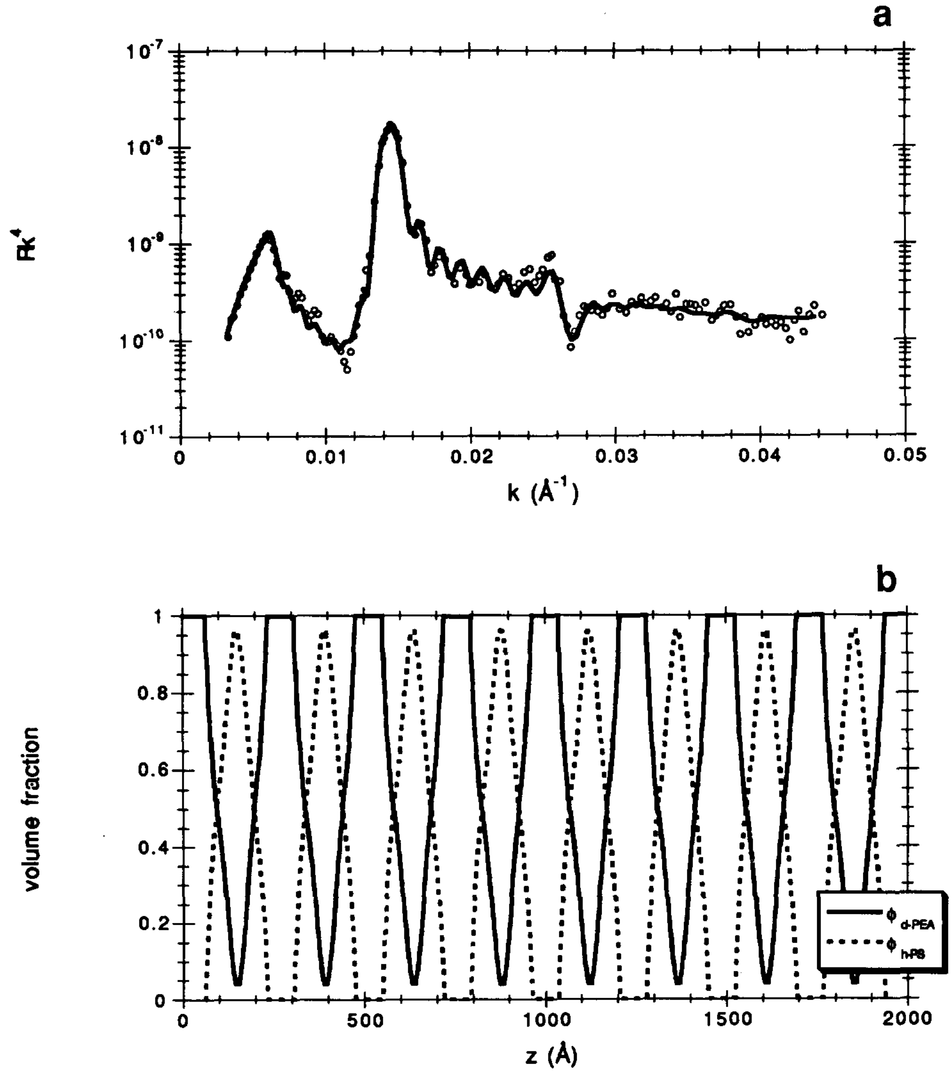

Figure 2 (a) Neutron reflectivity from 28% PS thin film sample annealed for 24 h at 130°C ($k = (\pi/\lambda)$ sin θ, where θ is the angle of reflection). (b) Real-space profile corresponding to fit in $R(k)$ plot (z = distance from sample/substrate interface)

We also observed evidence for periodic structure in the NR data, as shown in *Figure 2*. A Fourier series method was used in modelling the NR data[15]. The resulting profile has the correct average composition, though this has been allowed to vary. The flat-topped PEA regions are due to limiting the volume fraction of any component to be between zero and unity. The resulting profile has alternating layers of pure PEA and $\gtrsim 80\%$ PS. This lamellar phase morphology was later confirmed in a bulk sample by transmission electron microscopy[16].

In conclusion, we have performed SANS and NR measurements on a graft copolymer containing monodispersed PS grafts on a polydisperse elastomeric PEA backbone. Our results show that the system is strongly segregated into ordered microphases both in the bulk solid state and in thin films. A lamellar microphase was observed in the PEA-*g*-PS copolymer, which contained 28 wt% PS grafts. This is surprising and quite different from what is observed in diblock copolymers of similar composition and strength of segregation. For instance, polyisoprene–polystyrene diblocks at this composition would be expected to form cylinders or perhaps a bicontinuous structure. In fact, if one takes into account that the graft copolymer's structure forces twice as many backbone chains as graft chains to the interface, one would expect the interface to bend towards the graft component even for symmetric compositions[16,17].

There are several possible causes for this anomalous lamellar structure; the most important are probably the polydispersity in the backbone molecular weight and randomness of the grafts' position. These factors result in significant polydispersity in the backbone molecular weight per graft. This polydispersity should decrease the elastic energy on the PEA side of the interface[18]. Another result is the presence of many grafts that are attached quite close together on the backbone. This small piece of backbone could be micellized into the PS domains; in fact, the depth profile in *Figure 2* implies considerable phase mixing on the PS side of the interfaces.

These results are part of a comprehensive study that includes PEA-*g*-PS molecules having different compositions. Experiments are also underway on the behaviour of graft copolymers 'sandwiched' between their homopolymer constituents, i.e. compatibilization.

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