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Self-Organization of Graft Copolymers at Surfaces, Interfaces and in Bulk

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Self-Organization of Graft Copolymers at Surfaces, Interfaces and in Bulk

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The morphology in bulk and thin film of high-integrity graft copolymers has been investigated by small angle neutron and light scattering, neutron reflectivity, and transmission electron microscopy. The model graft copolymers are based on two chemically incompatible blocks composed of an elastomeric polyethylacrylate backbone onto which pendant monodisperse thermoplastic polystyrene are *statistically* placed. Two different levels of graft corresponding to an average of 1 and 3 per chain were investigated. In the bulk phase, the low graft level shows irregular fractal-like structures while the high graft level exhibits lamellar microdomains. In thin film, ordered structures were observed also in both compositions. The interphase adhesion between the polystyrene and the polyethylacrylate microdomain was investigated by uniaxially elongating the copolymer films. The low level graft material exhibits normal behavior characteristic of filler-reinforced rubber: the isotropic scattering pattern deforms in an anisotropic manner, i.e., ellipsoid-shaped with the long axis perpendicular to the stretching direction. An "abnormal Butterfly" pattern was observed with the high graft level. The butterfly pattern is attributed to the deformation of the lamellar morphology of the copolymer.

There is now a substantial literature on the equilibrium domain structure formed by diblock and triblock copolymers^(1, 2). In the bulk phase, the localized segregation of the chemically dissimilar block into ordered microdomains such as spheres, cylinders, double diamonds, lamellae, is now relatively well understood^(3, 4). In a thin film, a strong orientational aspect is additionally introduced due to the constraint imposed by the two interfaces (air/copolymer, copolymer/substrate), the surface energy difference between the blocks, the chemical affinity of one of the blocks with the substrate, etc.^(5, 6).

Compared to block copolymers, relatively few morphological studies have been carried out

on graft copolymers⁽⁷⁾. These materials are technologically important, particularly in their ability to compatibilize polymer blends⁽⁸⁾ and to form thermoplastic elastomers⁽⁹⁾. Indeed, they constitute the primary compatibilizers in commercial applications. Usually, the graft copolymers are produced *in situ* under controlled reactive processing conditions⁽¹⁰⁾. One well-known example is the esterification reactions between immiscible polyesters⁽¹¹⁾.

Graft copolymers, A_gB, are "macromolecular combs" composed of a linear backbone A onto which pendent side B block(s) are placed. The two blocks A and B are generally incompatible, therefore it is expected that these graft copolymers will exhibit mesoscopic structures which depend on a number of parameters such as the graft level and their distribution along the backbone, the relative molecular weight of the backbone and the pendent graft. The number of structural variables is large compared with conventional diblock and triblock copolymers. In addition, the synthesis of these materials (macromonomer techniques⁽¹²⁾, graft onto⁽⁸⁾ and graft from⁽⁸⁾ synthesis procedures) lead to a statistical placement of the graft onto the chain backbone. This random placement of the grafts endows these copolymers with a somewhat less defined molecular architecture as compared to anionically polymerized block copolymers. In the few studies that have been carried out, the separation of the domains in the di(tri)block copolymer systems and the domains appear in the

We report in this work an effort to explore the equilibrium domain structure formed by graft copolymers. The model graft copolymer is a thermoplastic elastomer based on a polymeric polydisperse backbone of polyethylacrylate (PEA) and monodisperse thermoplastic (PS) grafts.

EXPERIMENTAL

Synthesis of graft copolymers.

The macromonomer technique is a versatile and efficient method to produce graft copolymers⁽¹²⁾. The specific synthesis procedure is described by Milkovich et al.⁽¹³⁾. The methacrylate-terminated polystyrene macromonomers were synthesized by end capping anionically polymerized polystyrene anions with ethylene oxide, and subsequently, terminated the group with methacryloyl chloride. The macromonomer has an average molecular weight $M_w = 14,600$ g/mole with a polydispersity $M_w/M_n = 1.2$. The (acrylate)-polystyrene based macromonomers (reactivity ratios⁽¹²⁾ $r_2 \approx 0.7$) were prepared by dissolving partially deuterated ethylacrylate and the macromonomer in methyl ethyl ketone, degassing with nitrogen for 2 hours, while simultaneously heating the solution to 60°C for 24 hours. The polymerization was initiated with azobisisobutyronitrile. The copolymerization was carried out with two different feed ratios of the macromonomer (9 and 28wt% PS, denoted in the following text by M9 and M28). The product was precipitated in a large excess of n-butanol and then extracted with a 50/50

decalin/petroleum ether mixture to remove unreacted macromonomer. The styrene/ethylacrylate composition was determined by elemental analysis and ^1H -NMR. The graft efficiency is about 97% as determined from GPC measurements using a combination of refractive index and ultraviolet detectors and extraction results. The number average molecular weight of each graft copolymer as determined by GPC yielded a $M_n \sim 150,000$ g/mole. The M9 and M28 wt% PS correspond to an average of 1 and 3 grafts per chain, respectively. Due to the statistical nature of the grafting processes⁽¹²⁾, drift in composition, and the polydispersity of the backbone, the precise determination of the molecular architecture of these graft copolymers is difficult (although estimation based on the initial feed ratios and the reactivity of the macromonomer is possible). No attempt is therefore made to molecularly characterize the graft copolymers.

Small Angle Scattering.

Thick films (≈ 0.5 mm) were prepared by melt compression molding and annealed at 130°C (above the glass transition of the graft copolymers) for 6 hours prior to measurement. Small angle neutron scattering measurement (SANS) were performed on the SAD instrument at the Argonne National Laboratory's (ANL) Intense Pulsed Neutron Source (IPNS) and on the NG7 SANS instrument located at the National Institute of Standards and Technology's Cold Neutron Research Facility. Small angle light scattering (SALS) experiments were performed using a two-dimensional 16-bit charge-couple device (CCD) detector (Princeton Instrument). The incident light was a He-Ne laser ($\lambda = 6328\text{\AA}$). The scattered light impinges on a diffusive screen and is collected by the CCD. The length scale that can be studied with this instrument extends from $2\pi/q = 20\text{ }\mu\text{m}$ to $0.95\text{ }\mu\text{m}$.

Neutron Reflectivity.

Thin films ($\approx 1200\text{-}2000\text{\AA}$) of the graft copolymers were deposited onto silicon substrates by spin-coating from 2-3% toluene solution at 2000 rpm. Prior to film deposition, the substrate were cleaned by soaking overnight in chromic-sulfuric acid, and then rinsed with toluene just before spinning on the film. No attempt was made to strip the native silicon oxides. The sample were then annealed at 130°C in a vacuum oven for 24 hours prior to measurement. Neutron reflectivity experiments were performed on the POSY II instrument at ANL Intense Pulsed Neutron Source (IPNS)⁽¹⁴⁾. The detail of the NR technique have been considered elsewhere⁽¹⁵⁾. Briefly, a well collimated beam of neutrons is reflected from a thin film sample at grazing incidence ($0.3^\circ < \theta < 3^\circ$). The reflectivity R as a function of the momentum transfer $k = 2\pi/\lambda \sin \vartheta$ (λ is the neutron wavelength and ϑ is the angle of incidence (reflection)), is a nonlinear optical transform of the contrast in the direction normal to the substrate. Inversion of the phaseless $R(k)$ directly to the depth profile is not mathematically possible, so data are typically fitted to a model profile. Specular neutron reflection spectra were collected at three reflection angles (nominally 0.5° , 1.1° , 1.7°), and

the data from each angle were treated separately to allow variation in instrumental resolution with angle.

RESULTS AND DISCUSSIONS

I. Bulk Structure.

Shown in Fig. 1a and 1b are electron micrographs of ultra-thin sections of M9 and M28. The materials were stained with ruthenium tetroxide (RuO_4). Light regions indicate polyethylacrylate and dark regions polystyrene. The morphology of M9 (Fig. 1a) is an irregular, fractal-like structure with a diffuse boundary. This is not surprising because the complex architecture of the copolymer chain does not allow complete phase separation to occur (although non equilibrium structures cannot be ruled out). From the micrograph a correlation on the order $300\text{\AA}$ can be obtained by fast Fourier transform (FFT) of the image. The morphology of M28 (Fig. 1b) exhibits a rather surprising lamellar morphology; tilting the graft copolymer does not show any indication of cylindrical morphology. Given the architecture of the graft copolymers, one would expect the PEA-PS interface to bend strongly toward the PS graft even for composition higher than 50%. The origin of this lamellar phase can be associated with the polydispersity of the backbone molecular weight between grafts which leads to a less than expected curvature of the interface toward the PS graft component. In addition to this effect, due to the difference in the reactivity ratios of the reactants ($r_2 \approx 0.7$), there are probably many attachments where the molecular weight between grafts is very small, especially, toward the end of the chain. This situation will lead to more phase mixing on the PS side of PEA-PS interface (see the neutron reflectivity of the next section).

The SANS patterns from M9 and M28 are shown in Fig. 2a and 2b. Both copolymers produce interference peaks in their scattering profile. This is consistent with the micrograph in Fig. 1a and 1b. In order to characterize the scattering patterns, the data are fitted with a modified Ornstein-Zernike structure factor:

$$S(q) \propto \frac{1}{q^a} \frac{1}{1 + \xi^2(q - q_0)^2}, \quad (1)$$

where $q = 4\pi/\lambda \sin(\theta/2)$ is the scattering wave vector, λ is the neutron wavelength and θ is the scattering angle. This functional form was chosen simply because it has the necessary features of a quadratic maximum for the peak intensity and fits the data well from medium to high q . In addition, Eq. 1 allows the determination of the correlation length ξ , the peak position q_0 , and the exponent describing the high- q decay. The resulting parameters are given in Table 1. It is difficult to accurately determine the high- q exponent with SANS, because of the incoherent background of the hydrogenous component of the graft copolymers. In fitting the data, the resulting exponent

appear to be slightly larger than 3 which, if correct, would indicate rough interfaces between the domains.

Graft copolymer	ϕ_{PS}	$q_0, \text{\AA}^{-1}$	$L \approx 2\pi/q_0, \text{\AA}$	$\xi, \text{\AA}$
M9	0.09	0.019	330	200
M28	0.28	0.0213	295	155

Table 1. Results from SANS. ϕ_{PS} is the weight fraction of PS graft. The other quantities are defined in the text (Eq. 1).

II. Thin Film.

The specular neutron reflectivity from M9 and M28 are shown in Fig. 3 (a, d) along with the model profiles used to produce the fitted curves (Fig. 3 (c, d)). The fitted curves shown are calculated by modeling the depth profile of each film with a Fourier series of the form⁽¹⁶⁾:

$$\phi(z) = \phi_0 + (e^{-z/\xi} + e^{(z-z_0)/\xi}) \sum_i \langle a_i \cos(\frac{2\pi z}{L}) + b_i \sin(\frac{2\pi z}{L}) \rangle, \quad (2)$$

where ϕ is the volume fraction of the minor PS component, z_0 is the total film thickness and ξ is the characteristic length from the surface (sample-air and sample-substrate) of the film over which ordering persists. This model makes a few assumptions about the structure that may or may not be accurate. It assumes that the periodic structure is: strongest at the interface, homogeneous throughout the film (except for the exponential damping), damped in the identical way at both interfaces. Due to the available range in k space in the data, we were able to fit only the first 3 or 4 orders in the series. Some of the parameters from the fits are given in Table 2. Note that the domain spacing in the thin film and bulk sample differ approximately by 10 to 20%.

Graft Copolymer	ϕ_{PS}	$L, \text{\AA}$	$\xi, \text{\AA}$	L_{NR}/L_{SANS}
M9	0.09	295	540	0.89
M28	0.28	243	∞	0.82

Table 2. Results from neutron reflectivity. ϕ_{PS} is the weight fraction of PS grafts. The other parameters are defined in the text (Eq. 2).

The profile from M9 shows clearly periodic structure that propagates throughout the film (Fig

3b). The maximum PS volume fraction is only about 0.3. This result is consistent with the fractal like structure of the morphology in Fig. 1a (i.e., correlated clusters). The neutron reflectivity data from M28 can only be successfully modeled with a lamellar profile, composed of alternating layers of 100% PEA and nearly > 80% PS. The PS layers never quite reach the pure PS level and the mixing is more pronounced at the boundaries. Also the alternating layers are nearly equal in thickness. This result is entirely consistent with the micrograph in Fig. 1b.

III. Interphase adhesion

1. Tensile Stress-Strain Behavior.

Figure 4 shows the stress-strain relation of a 0.1mm thick film of graft copolymer M9 and M28. The graft copolymer was uniaxially elongated at a constant rate of 0.5 cm/min at room temperature. The M9 curve shows the sigmoid shape characteristic of filler-reinforced (or cross-linked) rubber with an upward curvature (hardening) at a strain greater than 200%⁽¹⁷⁾. The material exhibits a remarkable recovery even close to the breaking point.

The M28 curve shows behavior characteristic of ductile polymers. First, the initial stress increases sharply up to λ (final length/initial length) = 1.1 (elastic regime). Then a yielding process, i.e., plastic deformation, takes place at about $\lambda = 1.2$. This is followed by an elastic deformation of cold drawing under nearly constant load over $\lambda = 1.3$ -2.1. Above $\lambda = 2.1$, the deformation exhibits the characteristic of strain hardening and ultimately the material ruptures at $\lambda = 2.5$.

2. Small angle scattering.

The two-dimensional SANS patterns of the copolymer M9 recorded at room temperature during the elongation process, i.e., transversing the strain-stress curve, are shown in Figure 5. The elongation direction is vertical. In its unstretched state ($\lambda = 1$), M9 gives a fully isotropic, circular pattern with a characteristic length $\approx 330\text{\AA}$. Upon extension above $\lambda > 1.5$, the pattern of M9 transforms to an ellipsoid shape with the long axis perpendicular to the stretching direction. Shown in Fig. 6 (a,b) are curves representing data parallel and normal to the elongation direction by averaging the data in $\pm 25^\circ$ sector about these axis. The positions and widths of the scattering peaks in these curves are shown in Fig. 7 (a, b). The particle spacing corresponding to the peak increases linearly with the applied strain in the parallel direction and stays relatively constant in the normal direction. This suggests an affine deformation of the arrangement of the PS domain. The order, as measured by the reciprocal of the width of the scattering peak, decreases in all direction as the strain increases, but is destroyed more quickly parallel to the strain. A fit to the curve with a scaling law of the form $(\Delta q)^{-1} \propto \lambda^\omega$ results in a value of $\omega = -0.31$. Above $\lambda = 2$, "two-point" scattering pattern develops upon hardening of the sample (i.e., in the upward curvature section on the stress-strain curve). The behavior is similar to the behavior observed in strained semi-

crystalline polymers⁽¹¹⁾. This finding is expected since the PS hard phase (correlation length $\sim 300\text{\AA}$) acts essentially as a physical crosslink between the PEA rubber matrix with a corresponding strong interphase adhesion. The affine deformation indicates that an uniform distribution of the internal strain within the system. This is consistent with the fractal-like nature of the morphology of M9.

The two-dimensional SANS patterns of the copolymer M28 recorded at room temperature during the elongation process are shown in Figure 8. The elongation direction is vertical. In its unstretched state ($\lambda = 1$), M28 gives a fully isotropic, circular pattern with a characteristic length $\approx 300\text{\AA}$. Above $\lambda \approx 1.2$, the scattering patterns of M28 is anisotropic with the now familiar double-winged "butterfly patterns"⁽¹⁹⁻²²⁾. The origin of the butterfly can be attributed to the lamellar morphology of the copolymer. The lamellae are initially *randomly oriented*. Therefore, the initial stress increases sharply at low elongation due to the high load bearing of the hard PS microdomains. At the yielding point ($\lambda \approx 1.2$) which corresponds to the appearance of the butterfly, the PS domains are disrupted and the initial correlation length ξ vanishes. As the elongation increases, a distribution of correlations develops along the stretching direction. This enhances the scattering intensity in the wings of the butterfly pattern.

While there have been some theoretical effort to explain this kind of pattern, the resulting expression for the scattered intensity $I(q)$ does not agree with the present data. Our data exhibits a peak at $q \approx 0.02\text{\AA}^{-1}$ and Porod-like behavior at high q ; neither of the cited treatment can include these characteristics. The modified Ornstein-Zernike structure factor (Eq. 1) does fit the IPNS ($0.005\text{\AA}^{-1} < q < 0.3\text{\AA}^{-1}$) SANS data well. The resulting values for the fitted parameters are shown in Table 3. The anisotropy is all in q_0 and the same correlation length ξ can be used for both the parallel and perpendicular data sets. The peak position, $q_{0\parallel}$, parallel to the stretching direction decreases with λ with a nearly linear dependence, while $q_{0\perp}$, stays almost constant. This behavior is similar to that seen in the M9 material and could mean that, as observed in gels, the butterfly pattern crosses over to a more conventional elliptical pattern at high q ⁽²¹⁾. Another point to notice from the fitted parameters is that the exponent α increases as the sample is stretched until $\lambda = 2.35$, the high q scattering is nearly Porod-like.

$\lambda (L/L_0)$	$q_{0\parallel}, \text{\AA}^{-1}$	$q_{0\perp}, \text{\AA}^{-1}$	$\xi, \text{\AA}$	α
1	0.0218	0.0218	145.9	1.26
1.08	0.0213	0.0209	126.1	1.38
1.28	0.0204	0.0216	120.1	1.54
2.35	0.0096	0.0206	80.39	1.65

Table 3. Fitting parameters for the IPNS SANS data from uniaxially stretched M28.

Shown in Fig. 10 is the 2-dimensional SALS pattern for M28 in the elastic regime above the yielding point. No light scattering was detected below the yielding point. Above $\lambda > 1.2$, a "Superbutterfly" appears whose extra feature is the appearance of a streak perpendicular to the elongation direction. At this moment we can give only some speculative remarks. The structural part most easily deformed is of course the rubbery PEA matrix. In the elastic regime, the deformation must be accompanied by a decrease in the segment density of the matrix along the stretching direction (graft poor domains due to PEA deficient in graft (7a)). The lower density regions in the matrix may not be uniformly distributed between the domains at high elongation. An inhomogeneous deformation composed of the lower density and the relatively undisturbed region (graft rich domains) may be the origin of the superbutterfly. The streak perpendicular to the stretching is probably due to the hyperextension of the PEA chain. The macrostructure which yields this phenomenon is still under investigation.

CONCLUSION

The development of new polymeric material with novel structure/properties involves new arrangement of monomers rather than the preparation of a new monomers. A large amount of scientific effort is focused toward this goal. From these efforts have arisen a family of new polymeric materials. It is quite obvious that a random arrangement of monomers situated along a chain backbone possesses different properties than diblocks, triblocks or graft copolymers of identical overall monomer composition. Graft copolymers, as noted previously, are both scientifically interesting and technologically important because of their useful in blend compatibilization and the breadth of potential structures that can be produced.

In this work, we briefly described some of the unique structure of graft copolymers and their behavior in bulk and thin film. Although we have examined one specific family of graft copolymers having an elastomeric backbone and thermoplastic grafts, the results may be general to graft copolymers. The underlying structural rearrangements of the phase separated entities can be examined and qualitatively understood through a combination of scattering methods and microscopy. The response of macrostructure and microstructure to the imposed stress and strain leads to a better understanding of the behavior of these technologically important copolymers. This work is continuing as well as the development of new graft structures containing other thermoplastic polymers, elastomers and semicrystalline polymers.

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FIGURES CAPTIONS

- Figure 1. Transmission electron micrograph of a) M9 (9wt% polystyrene graft) and b) M28 (28wt% Polystyrene graft). The PS domains appear dark.
- Figure 2. SANS data for a) M9 and b) M28. The open symbols are NIST data and the filled symbols are IPNS data.
- Figure 3. Specular neutron reflectivities data and fitted real-space profiles for a) and b) M9; c) and d) M28. In the depth profile, the solid line represents the PEA and the dashed lines the PS domains.
- Figure 4. Stress-Strain curve for M9 (filled circle) and M28 (open square).
- Figure 5. Two-dimensional SANS pattern for uniaxially stretched M9 at a) $\lambda=1$; b) $\lambda=1.5$; c) $\lambda=2.0$, d) $\lambda=3.0$. Range of scattering-vector amplitude is $0.005 \text{ \AA}^{-1} < q < 0.1 \text{ \AA}^{-1}$. The stretching direction is vertical.
- Figure 6. Wedged-averaged intensity data for M9, in direction a) parallel to, b) perpendicular to the stretching direction at different elongation (λ).
- Figure 7. The a) position and b) width of the scattering peak in the SANS data for M9 as a function of elongation λ .
- Figure 8. Two-Dimensional SANS from uniaxially strain M28 at elongation a) $\lambda=1$; b) $\lambda=1.08$; c) $\lambda=1.28$; d) $\lambda=1.75$. Range of scattering-vector amplitude is $0.005 \text{ \AA}^{-1} < q < 0.1 \text{ \AA}^{-1}$. The stretching direction is vertical.
- Figure 9. Wedged-averaged intensity data for M28, in direction a) parallel to, b) perpendicular to the stretching direction at different elongation (λ).
- Figure 10. Two-dimensional SALS pattern for uniaxially stretched M28 showing a "Superbutterfly" pattern above $\lambda>1.2$. Range of scattering-vector amplitude is $0.1 \mu\text{m}^{-1} < q < 5 \mu\text{m}^{-1}$.

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