# Universalization of the Phase Diagram for a Model Rod-Coil Diblock Copolymer

## Bradley D. Olsen,<sup>†</sup> Manas Shah,<sup>‡</sup> Venkat Ganesan,<sup>‡</sup> and Rachel A. Segalman<sup>\*,†</sup>

Department of Chemical Engineering, University of California, Berkeley, California 94720, and Materials Science Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712

Received April 30, 2008; Revised Manuscript Received July 1, 2008

ABSTRACT: The Flory-Huggins interaction is measured for a model rod-coil block copolymer system, poly(alkoxyphenylenevinylene-*b*-isoprene), by fitting the interfacial segregation of block copolymer to a homopolymer interface and by using the random phase approximation (RPA) for block copolymers. The measured interfacial segregation of a block copolymer to the interface between homopolymers, fit with a self-consistent field theory (SCFT) simulation using  $\chi$  as a variable parameter, gives a functional form  $\chi = 34.8/T - 0.091$ . When RPA is applied to neutron scattering curves for the rod-coil system above the order-disorder transition, the theoretical structure factors are inconsistent with observed scattering curves due to complex aggregated structures formed in the nematic and isotropic states. Using the Flory-Huggins parameter and a previously measured value of the Maier-Saupe parameter, the PPV-*b*-PI phase diagram may be converted from system-specific variables to dimensionless parameters. Under the assumptions that the rods are ideal nematogens, interaction strengths are composition-independent, and rod-coil and rod-rod interactions are local, this yields the first quantitative universal phase diagram for rod-coil block copolymers.

#### Introduction

Rod-coil block copolymers have been widely investigated as a means to self-assemble 10-100 nm length scale structures from functional biological<sup>1-4</sup> or semiconducting polymers.<sup>5-12</sup> In these materials, the helical secondary structure or conjugated polymer backbone of the functional polymer gives rise to a rodlike chain shape, significantly altering the observed selfassembly of the block copolymer. The interplay between liquid crystalline ordering of the rod blocks and microphase separation of the rods and coils results in a number of phases not observed in traditional block copolymers, including the zigzag and arrowhead phases,13 hexagonal strip or puck phases with rectangular or cylindrical rod nanodomains,<sup>14</sup> and perforated lamellar phases with oriented rod layers.<sup>15</sup> An equilibrium phase diagram for these materials has also been charted using a system based on poly(alkoxyphenylenevinylene) (PPV) rods and polyisoprene (PI) coils, where the alkoxy side groups passivate the PPV rods and allow both order to microphase disorder transitions (ODTs) and liquid crystalline clearing transitions (LCTs) to be experimentally explored in a reversible manner.<sup>16-18</sup> Lamellar phases are preferred across most of the phase diagram, including all of the weak segregation limit, due to strong aligning interactions between the rods. When asymmetry in both the coil fraction of the block copolymer and the ratio of the characteristic length of the coil to the rod is increased, hexagonal arrays of rectangular rod nanodomains are also observed. A hexagonal to lamellar transition is found around 80% coil, with the lamellar phase stable closer to the ODT. Heating above the ODT results in transitions into intermediate nematic and high-temperature isotropic phases. A relatively wide nematic region is observed in weakly segregated, symmetric block copolymers, but it narrows with increasing coil fraction until it eventually terminates, resulting in a direct lamellar to isotropic transition at high coil fractions. At larger segregation strengths, the nematic region is narrower but persists for all coil fractions.

In order to generalize these studies of model materials and apply them to predict the self-assembly of other functional polymer systems, their phase behavior must be recast in terms of a set of universal parameters characterizing all block copolymers with a rod-coil molecular shape. Theoretical studies of rod-coil systems suggest that the self-assembly and liquid crystalline ordering of these molecules are governed by four universal parameters:<sup>19–25</sup> the Flory–Huggins interaction,  $\chi N$ ; the Maier–Saupe interaction,  $\mu N$ ; the coil fraction,  $\phi$ ; and the coil to rod length ratio,  $\nu$ . The Flory-Huggins interaction measures the local repulsion between rod and coil segments, and the Maier-Saupe parameter is an alignment parameter wellknown for small molecule liquid crystals.<sup>26</sup> The coil fraction measures the relative volume of the two segments. The coil to rod length ratio is represented in various forms in different theories, but all represent the same physical phenomenon: the mismatch in scaling dimension between the rod and coil that leads to a difference in their characteristic length or interfacial area occupied as a function of molecular weight. Therefore, this parameter,  $\nu$ , is a measure of the packing geometry of the molecules. Detailed exploration of this universal phase diagram in terms of all four parameters using Landau theories<sup>22,24</sup> or self-consistent field theory<sup>23</sup> shows complex phase behavior in this higher order space and that control of all four parameters is critical to achieving the desired nanoscale structure and molecular alignment.

Experimental measurement of these universal parameters for rod-coil systems has proven challenging. While the estimation of  $\phi$  and  $\nu$  can be performed with relative ease based on the densities of the homopolymers, the statistical segment length of the coil polymer, and the packing radius of the rod polymer (assuming equal coil and rod monomer volumes), quantification of  $\mu$  and  $\chi$  requires independent thermodynamic measurements. Maier–Saupe theories for small-molecule liquid crystals provide a basis for estimating  $\mu$  from the nematic–isotropic transition of a liquid crystalline material.<sup>26</sup> Previous work has shown that  $\mu$  may be estimated from the nematic–isotropic transition temperature as a function of molecular weight in a polymeric liquid crystalline system, providing a value for this parameter

<sup>\*</sup> Corresponding author: e-mail segalman@berkeley.edu.

<sup>&</sup>lt;sup>†</sup> University of California, Berkeley.

<sup>\*</sup> University of Texas at Austin.

in the PPV-b-PI system.<sup>27</sup> Several different techniques developed for measuring  $\chi$  in coil-coil polymer systems are also available for rod-coil systems; however, the limitations of rod-coil systems make these techniques difficult to apply. The random phase approximation (RPA) theory for miscible polymer blends<sup>28</sup> is one of the most common techniques used to estimate  $\chi$  for pairs of coil-shaped polymers, providing the detailed empirical temperature and composition dependence of this parameter.<sup>29</sup> Alternately,  $\chi$  may be estimated from the miscibility-immiscibility transition in polymer blends, with changing molecular weights or compositions used to establish the temperature dependence. However, because of strong segregation between most rod and coil polymers, it is extremely difficult to find blend systems in which miscibility can be accessed. Even relatively low molecular weight blends of the weakly segregated PPV/PI system show  $q^{-4}$  scaling at high temperatures in small-angle scattering, suggesting immiscibility throughout the experimentally accessible region.

The random phase approximation has also been applied by Leibler to traditional block copolymers, where miscible systems may be achieved at higher values of  $\chi N$ .<sup>30</sup> This work allows  $\chi$ to be estimated from the form factor of the block copolymer molecule above the ODT. Several authors have adapted this formalism to rod-coil block copolymers, allowing the form factor for these molecules to be calculated and providing a theoretical basis for the use of block copolymer form factors to estimate  $\chi$  in rod-coil systems.<sup>22,31,32</sup> The interaction parameter might also be estimated from the location of the ODT in rod-coil systems; however, the breakdown of mean field theories due to fluctuations near the order-disorder transition and difficulties in estimating the parameter from a system that also microphase separates complicate this determination. Measurements of interfacial segregation of a block copolymer to the interface between two homopolymer phases provide a fifth technique for the estimation of  $\chi$ .<sup>33–35</sup> A number of theoretical<sup>36,37</sup> and experimental<sup>38</sup> works have explored the effects of classical block copolymers at a homopolymer interface, demonstrating a decrease in interfacial tension due to selective segregation of the block copolymer that is linear in the block copolymer content at low concentrations. Leibler also developed an analytical theory for block copolymer brushes at a homopolymer interface, and the effects of homopolymer and block copolymer molecular weight on the surface excess and interfacial tension have been explored, showing agreement with the theoretical predictions.<sup>39-41</sup> The interfacial segregation technique has been shown for coil-coil systems to produce estimates of  $\chi$  that are in quantitative agreement with measurements made by scattering techniques.41,42

In this work, we apply both the RPA theory for rod-coil block copolymers and the interfacial segregation of rod-coil block copolymers to a rod/coil homopolymer interface to measure the Flory-Huggins interaction parameter,  $\chi$ . We show that although our weakly segregated rod-coil system has an accessible order-disorder transition, the structure in the nematic and isotropic microphase disordered regions does not follow the RPA structure predictions. Using our estimate of  $\chi$  from temperature-dependent interfacial segregation, we universalize the rod-coil block copolymer phase diagram, providing the first experimentally generated phase diagram that can be quantitatively compared with theories for rod-coil block copolymer self-assembly and has predictive capacity for application to functional systems.

#### **Experimental Methods**

**Synthesis.** Synthesis of poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene) (DEH-PPV) was carried out as described previously.<sup>16</sup> Siegrist polycondensation<sup>43,44</sup> of poly(phenylenevinylene) Scheme 1. Structure of PPV-b-PI Rod-Coil Block Copolymers



Table 1. Molecular Parameters for Block Copolymers and Homopolymers

block copolymer	PPV M <sub>n</sub> (g/mol)	PPV PDI	PI M <sub>n</sub> (g/mol)	PI PDI	Ν	$\phi$	ν
PPV-hp	5300	1.6			138		
PI-hp			84300	1.01	197		
PPVbPI-52	3500	1.16	3500	1.04	98	0.52	0.298
PPVbPI-72	3500	1.16	7800	1.02	159	0.70	0.442
PPVbPI-83	3500	1.16	15300	1.02	272	0.83	0.626

was chosen as the polymerization route because it allows lowpolydispersity PPV to be produced with few chemical defects in the polymer backbone. Poly(1,4-isoprene) (PI) was synthesized anionically in a nonpolar solvent to achieve 93% 1,4-addition and quenched with anhydrous butanol to form PI homopolymer. To form PPV-b-PI block copolymer, living PI chains were quenched with aldehyde-terminated DEH-PPV in benzene, as described previously.<sup>16</sup> Deuterated PI blocks were synthesized from perdeuterated isoprene monomer (purchased from Polymer Source, 98% isotopic enrichment) to give  $\sim 65\%$  1,4-addition, as determined by <sup>2</sup>H NMR. Scheme 1 illustrates the chemical structure of the final block copolymers. Molecular weights of the PI blocks and homopolymers were measured on a Waters 2690 gel permeation chromatograph (GPC) with a Viscotek refractive index detector calibrated using PI standards. The polydispersity of all PI blocks was less than 1.05. The number-average molecular weights of the PPV blocks and homopolymers were measured by NMR end-group analysis. Using GPC calibrated with polystyrene standards, the polydispersity of the PPV rod blocks was estimated to be 1.16 and the polydispersity of the PPV homopolymer was 1.60. Molecular weights and dimensionless parameters characterizing the block copolymers and homopolymers are given in Table 1. N is the number of volumetric repeat units in each block copolymer based on a PI repeat unit reference volume, and  $\phi$  is the volume fraction of PI. The coil to rod length ratio,  $\nu$ , is related to the geometric parameter used in self-consistent field theories<sup>21,23</sup> and is calculated from homopolymer density data as described previously.<sup>16</sup>

Small-Angle Neutron Scattering (SANS). SANS samples of PPV-b-PI block copolymers were prepared by annealing samples under vacuum at 140 °C overnight and then sealing between two optical grade quartz windows. Samples were further annealed under nitrogen at 140 °C for 15 min to remove any shear stress induced during sample preparation, and then the samples were slowly cooled to room temperature. SANS experiments were conducted on the NG3 and NG7 beamlines at the National Institute of Standards and Technology cold neutron source in Gaithersburg, MD.45 The raw data were converted to absolute coherent scattering intensities, I, as a function of  $q (q = 4\pi \sin(\theta/2)/\lambda)$ , where  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of the incident beam) using corrections for detector sensitivity, background, empty cell, and incoherent scattering intensity according to standard procedures.<sup>46</sup> An incoherent scattering intensity standard for deuterated PI was prepared from a sample of deuterated PI homopolymer with a molecular weight of 6600 g/mol and a polydispersity of 1.03, and an incoherent intensity standard for PPV was prepared using a hydrogenated DEH-PPV sample with a molecular weight of 3500 g/mol and a polydispersity of 1.17. The upper limit of the SANS sample holder was 200 °C. Experiments were conducted at 1, 4, and 13 m sample to detector spacings and combined to produce



**Figure 1.** Schematic of DSIMS sample geometry. DSIMS samples are fabricated by casting PPV layers onto  $SiO_2$  surfaces and then sequentially adding a PI layer containing block copolymer, a PCHE capping layer to prevent dewetting, a deuterated PI layer to serve as a concentration calibration, and a PS layer to serve as a thickness calibration.

scattering curves over more than 2 decades in q. Error bars are included on all data, but for most of the data in this paper the error in I is less than the size of the data points.

**Polarized Optical Microscopy (POM).** An Olympus BX51 microscope with crossed polarizers and an Instec HCS302 heat stage was used to image samples. Samples were pressed between two glass slides and into the isotropic phase, cooled, and then heated at a rate of 0.2 °C/min to locate phase transitions. The nematic—isotropic transition was identified as the temperature at which all birefringence disappeared.

Dynamic Secondary Ion Mass Spectrometry (DSIMS). Samples for DSIMS were prepared by spin-casting a 300 nm thick layer of DEH-PPV homopolymer onto a 300 nm thick layer of thermal oxide on a Si wafer to insulate the film from electrical charging during ion etching.47 PPV homopolymer was not fractionated, and the films were cast from CHCl<sub>3</sub> to produce smoother films.<sup>27</sup> A 600 nm thick layer of PI homopolymer blended with PPVbPI-83 block copolymer containing a deuterated isoprene block was spin-cast onto mica from toluene and transferred onto the PPV film through use of the mica transfer technique.<sup>42</sup> Milli-Q water was used in order to minimize residual salt contamination, though trace chlorine was still detectable. A 150 nm layer of poly(cyclohexylethylene) (PCHE) was transferred onto the PI layer by the mica transfer technique to cap the PI layer, preventing dewetting during annealing. Samples were then annealed in ultrahigh vacuum  $(<10^{-6}$  Torr) for 96 h to allow an equilibrium surface excess of block copolymer at the PPV/PI homopolymer interface to be reached. After cooling to room temperature, a 100 nm layer of deuterated PI and a 150 nm layer of hydrogenated polystyrene were added onto the film to serve as concentration and etch rate calibration layers, respectively. The final sample geometry is illustrated in Figure 1. Depth profiles were acquired using a Physical Electronics 6650 dynamic SIMS. A 2 kV, 40 nA beam of O<sub>2</sub><sup>+</sup> ions was rastered over the sample to etch a 200  $\mu$ m  $\times$  200  $\mu$ m crater. Charge neutralization was maintained with a 0.6 eV defocused electron beam. The etch rate was converted to a quantitative depth scale using the precise polystyrene layer thickness measured by ellipsometry, and the deuterated PI coil block fraction was calculated by normalizing to the deuterium ion signal in the deuterated PI homopolymer layer. The bulk concentrations of PI coil block in the PPV and PI homopolymer layers were calculated by averaging over the center of each layer. The surface excess was calculated as the integral of the experimental concentration less the bulk concentration for the corresponding phase, using the peak coil block concentration to identify the position of the interface.

**Self-Consistent Field Theory (SCFT) Simulation.** SCFT simulation of the rod–coil/rod/coil blend system was performed using a previously developed model for rod–coil block copolymer blends with rod and coil homopolymers.<sup>48</sup> The SCFT equations were solved in real space using a pseudodynamical steepest descent algorithm developed by Fredrickson and co-workers.<sup>49</sup> Simulations were performed in one dimension to match the symmetry of the

experimental geometry, and the modified diffusion equation was solved using finite difference. To give the chain axis steps and the spatial discretization approximately equal sizes, a simulation box of 187.7 nm was discretized into 200 lattice points, and the block copolymer of  $\sim$ 272 repeat units was discretized into 47 lattice points. The number of lattice points used for rod and coil homopolymers was scaled proportionally to the number of repeat units. The configurational integral over rod orientation was evaluated using Gaussian quadrature with 10 points in  $\theta$  and 32 points in  $\varphi$ . Simulations were initialized with periodic w fields, random  $\pi$  fields, and fully oriented **M** fields to mimic the layered film structure. For the purposes of the simulation, the rod and coil homopolymer fractions were set equal, and a sufficiently large simulation volume was used so that bulk solubility levels of the block copolymer in each homopolymer phase could be determined. Degrees of polymerization based on a PI repeat unit reference volume for the homopolymers and PPVbPI-83 (Table 1) were used to calculate all of the geometric parameters for the molecules. The Maier-Saupe parameter as a function of temperature was calculated from previously reported data,<sup>27</sup> with a fit to additional polymers giving an improved estimate of  $\mu = 183/T - 0.236$ . Simulations were performed for  $\chi$  increments of 0.001 or smaller for all temperatures, and the  $\chi$  that resulted in the minimum mean-square error from the experimental data was chosen as the best fit.

#### **Results and Analysis**

Interfacial Segregation Measurement of  $\chi$  Segregation of a block copolymer to the interface between two homopolymers is a powerful technique to measure the Flory-Huggins interaction between two polymers. The technique relies on the selective segregation of an AB diblock copolymer to the interface between A and B homopolymers in order to minimize the total number of unfavorable A-B contacts in the system. The interfacial excess of the block copolymer depends strongly on both the block copolymer concentration and  $\chi$ , allowing  $\chi$  to be quantitatively estimated by comparison of the experimental interfacial segregation as a function of bulk concentration with that calculated theoretically using SCFT simulations. This technique is particularly useful in strongly segregated systems where the RPA theory may not be applied due to immiscibility of the two blocks. The interfacial segregation technique is also useful in systems that tend to form aggregates because it may be performed at low block copolymer concentrations.

Since rod-coil block copolymers show strongly nonideal interactions and tend to be very strongly segregated, the interfacial segregation technique is ideally suited for the measurement of  $\chi$  in these systems. Even in the relatively weakly segregated PPV-b-PI system, annealing of the films at elevated temperatures leads to an easily quantified interfacial excess of block copolymer. Figure 2 shows the ion counts as a function of DSIMS etch depth within the polymer multilayer films for a nominal loading of 5% block copolymer in the PI layer. The interfaces between each of the polymer layers are marked by large peaks in the Cl or Si ion intensity due to the presence of residual salts from the water used to fabricate the film assemblies. Segregation of the PPV-b-PI block copolymer to the interface between the PI and PPV homopolymers is clearly indicated by the large increase in the deuterium signal at this interface. The constant deuterium signal throughout the majority of the PI and PPV layers indicates that the sample has been annealed for sufficiently long to reach an equilibrium concentration of block copolymer in both phases. Increasing the initial loading in the coil phase results in increased surface excess peak as well as higher concentration in the coil phase, while the relatively large coil fraction of the block copolymer used results in a very low solubility in the rod phase.

The experimental coil block fraction depth profiles show much broader surface excess peaks than the SCFT simulation



Figure 2. DSIMS depth profile of multilayer film for measuring interfacial segregation. The upper PS layer is indicated by strong hydrogen and carbon signals, while the transition to the perdeuterated PI layer is marked by a sharp drop in the H signal and an increase in the D signal. Upon etching into the PCHE layer, the D signal once again drops and the H signal increases. In the PI/PPV-b-dPI layer there is a moderately strong D signal due to the equilibrium solubility of the block copolymer, and the peak near the PPV interface indicates interfacial segregation. The solubility of the block copolymer is much lower in the PPV homopolymer, resulting in a sharp drop in the D signal upon etching into this layer. The interfaces between each pair of polymer layers are marked by peaks in Cl or Si due to residual salts from the Milli-Q water used in making the multilayer films, and a very large increase in the Si signal also marks the boundary between the polymers and the SiO<sub>2</sub> coating. The nominal weight fraction of the block copolymer in the PI layer is 5%.



**Figure 3.** Coil block concentration at the PPV/PI interface. SCFT simulations of PPV-*b*-PI segregation to the PPV/PI interface are able to match the equilibrium concentration in the PI region, but they slightly underestimate the solubility of the block copolymer in the PPV phase. The experimental profile has a larger peak width than the simulation due to interfacial roughening of the experimental interface when the surface energy is lowered by the block copolymer. The nominal weight fraction of the block copolymer in the PI layer is 2.5%.

results. Figure 3 shows the concentration of coil block in the polymer layers (converted to a quantitative coil fraction using the deuterated PI layer signal as a calibration) plotted as a function of depth within the layered sample for a nominal block copolymer loading of 2.5% in the PI phase. An SCFT simulation condition closely matching the experimental condition is overlaid, showing that the predicted peak width is much narrower than that observed experimentally. The width of the experimental peak vastly exceeds the instrumental resolution of the SIMS and therefore is due almost entirely to the structure



**Figure 4.** SCFT fits to experimental block copolymer surface excess at 90 °C. Using  $\chi$  as a fitting parameter, the simulated block copolymer surface excess as a function of block copolymer concentration in the coil homopolymer phase can be fit to experimental data. At low concentration the experimental data are linear, but at higher concentration they show a sharp increase in slope, presumably due to aggregate formation. The fit is only performed using low concentration data (filled points), giving an estimated  $\chi$  of 0.005  $\pm$  0.001 at 90 °C. Representative theoretical curves are shown to illustrate the impact of changing  $\chi$  on the SCFT predicted surface excess.

of the sample. Studies of coil-coil systems have shown that the addition of block copolymer can promote interfacial roughening due to the lowering of the surface energy of the homopolymer interface,<sup>50</sup> and it is likely that such an effect is responsible for much of the interfacial width observed in these systems. By examining the chlorine concentration at interfaces due to trace contamination from the water used to put down the polymer layers, a measurement of interfacial width may be obtained. The PS/dPI interface near the top of the film did not undergo annealing and therefore provides a good measure of interfacial width due to the layer deposition technique. While this upper interface chlorine peak has a Gaussian peak width of 18 nm, the annealed PPV/PI interface has a peak width of 86 nm. Although solid PPV films have been demonstrated to have some roughness,<sup>27</sup> this interfacial width is much larger than the rms roughness of  $\sim 4$  nm of the PPV layer as determined by scanning force microscopy. At high concentrations, the surface excess peak also broadens due to aggregation of the block copolymers that may result in multiple layers of micelles at the interface.<sup>34</sup> It is noteworthy that the simulation slightly underestimates the block copolymer solubility in the PPV layer; this may arise from errors in quantifying the molecular weight of the PPV homopolymer due to its polydispersity or due to collapse or extension of the PI coil in the PPV rod homopolymer. In order to minimize the impact of these complex effects on the measurement of  $\chi$ , the rod homopolymer molecular weight and rod-coil block copolymer coil fraction were chosen so as to minimize the solubility of the block copolymer in the rod homopolymer.

The total surface excess of coil block may be used to provide an estimate for  $\chi$  in these systems regardless of interfacial broadening. Plots of the surface excess as a function of the coil block concentration in the coil phase are shown in Figure 4. The experimental data show a linear increase in the surface excess at low concentration, but at higher concentrations the surface excess increases more rapidly than expected based on the initial linear slope. This sharp change in slope is indicative of aggregation effects in the polymers. However, it is opposite that observed in coil–coil block copolymers, where increasing block copolymer concentration results in a decrease in the slope of the surface excess curve.<sup>34</sup> In the coil–coil system, micelles tend to form at the air/polymer interface due to their surface



**Figure 5.** Temperature dependence of  $\chi$  in a rod-coil block copolymer. Using a series of interfacial segregation experiments, the temperature dependence of  $\chi$  may be extracted. A fit to three data points over the range 90–110 °C gives an estimate  $\chi = 34.8/T - 0.091$ .

energy; however, in the rod—coil system the only evidence of block copolymer segregation is at the homopolymer interface. Micelles that segregate to this interface would be counted as coil block surface excess, potentially resulting in the large increase in slope at higher concentrations of block copolymer. Extrapolating the linear trend at low concentration to zero shows that the lines do not pass through the origin, indicating that there is finite solubility of the block copolymer in the coil homopolymer even with no interfacial segregation. This solubility increases with increasing temperature. The simulated curves fail to capture this effect, nearly passing through the origin. The simulated surface excess curves also show the opposite curvature of the experimental behavior, exhibiting a convex shape similar to the behavior in a traditional block copolymer system.

At low concentrations the fit between the experiment and the theory is quite good, allowing  $\chi$  to be estimated. As expected for a weakly segregated system, the values of  $\chi$  are relatively close to 0. The empirical form of  $\chi \sim A/T + B$  found to work in most aliphatic and aromatic hydrocarbon polymers is used here to give a best fit of  $\chi = 34.8/T - 0.091$ , as shown in Figure 5. There is a large disparity between the magnitudes of  $\mu$  and  $\chi$ ;  $\mu$  is roughly 50 times greater than  $\chi$  in the experimental temperature range where ordered phases are observed. This suggests that rod alignment interactions are relatively strong compared to the rod-coil repulsive interactions and accounts for the large nematic phase observed above the order-disorder transition. In contrast, Pryamitsyn et al. plot the simulated phase diagram for a ratio  $\mu/\chi = 4$ , much below that in our system, and observed only a narrow nematic region.

Universalization of the Phase Diagram. Combining the temperature dependence of  $\chi$  with that previously measured for  $\mu$  allows the PPV-*b*-PI phase diagram to be translated into a universal phase diagram for all molecules with a rod-coil molecular shape. This translation provides the first universal phase diagram for rod-coil block copolymers and generalizes the specific results for the PPV-*b*-PI system to make them predictive for any system that can be characterized in terms of  $\chi N$ ,  $\mu N$ ,  $\nu$ , and  $\phi$ . This phase diagram is shown in Figure 6, plotted once to show the transition dependence on  $\chi N$  and once to show the dependence on  $\mu N$ . The phase diagram is inverted relative to that as a function of temperature due to the upper critical solution temperature (UCST) type behavior displayed by the PPV/PI system.

This phase diagram shows strong qualitative similarities with theoretical predictions based on Landau theories<sup>22</sup> and self-consistent field theory.<sup>23</sup> The isotropic phase is the most stable

at low  $\chi N$  and  $\mu N$ , and in all cases lamellar phases occupy a very large region of the phase diagram. The hexagonal phases calculated by Pryamitsyn and Ganesan<sup>23</sup> are also observed experimentally, although only in the moderate segregation limit. In the weakly segregated limit, a broad nematic region that narrows with increasing coil fraction and eventually pinches off is observed both experimentally and in the phase diagram of Holyst and Schick.<sup>22</sup> For both Landau theory and SCFT, the theoretical phase diagram shows the same strong asymmetry in the  $\chi N$  and  $\mu N$  at which the OTD and liquid crystalline clearing transition occur, consistent with the experimental result that the transitions are at lower values of these interaction strengths for rod-rich systems. Since the full phase diagram for rod-coil systems is theoretically predicted to be four dimensional, we suggest that quantitative improvements in the agreement between the theory and experiment might be obtained by recalculating the theoretical prediction for the specific conditions used in these experiments.

Application of this phase diagram to predicting the behavior of rod-coil block copolymer systems must proceed cautiously and with a full understanding of the approximations inherent in its development. Theories of rod-coil polymers that parametrize the system in terms of only four parameters treat the rods as ideal nematogens, where the most ordered phase the rod homopolymer may achieve is nematic. However, in many rod systems, including DEH-PPV, crystalline or smectic phases may be observed at low temperatures. While in DEH-PPV the interactions leading to these phases are relatively weak, in many cases these additional interactions may have a large effect on the self-assembly behavior. Furthermore, the estimates of  $\chi$  and  $\mu$  were made assuming purely local rod-rod and rod-coil interactions as is common for many polymer models.49,51 Nonlocal interactions between rod and coil molecules may impact their observed self-assembly behavior and are not captured by these treatments. Finally, the assumed form of  $\chi$ that has been fit with the interfacial segregation data does not include concentration-dependent terms that have been shown to be important in some polymer systems.<sup>29</sup>

**Comparison of Polymer Structure with RPA Calculations.** The random phase approximation provides a complementary means to measure the Flory–Huggins interaction in a block copolymer system through measurements of the polymer structure factor in the disordered state. The ideal structure factor of noninteracting block copolymer molecules shows a single peak due to the correlations between the two chemically bonded blocks, and for interacting systems the shape and intensity of this peak may be used to estimate the interaction parameter.

Regardless of the coil fraction, the structure factors observed in weakly segregated PPV-b-PI block copolymers do not correspond to the predictions of RPA theory, as shown in Figure 7. Upon heating, the polymers transition from the lamellar ordered state into either an intermediate nematic state followed by a high-temperature isotropic state or directly into the isotropic state depending on the coil fraction of the polymers. In the lamellar phase, the polymers exhibit a series of evenly spaced peaks indicative of the lamellar morphology superimposed on a power law background that appears to be approximately continuous through the region with the scattering peaks. For all of the polymers investigated, this slope is in the range of 2.3-3.1. Heating results in a slow decrease in these peak intensities, and a broad shoulder begins to appear at high q just below the order-disorder transition (ODT). The ODT is identified by SAXS as the temperature at which the higher order scattering peaks disappear and the primary scattering peak drops sharply in intensity,<sup>17</sup> and values of the ODT for all three polymers are shown in Table 2. The primary peak position is also shifted to lower q upon heating, as observed previously in



**Figure 6.** Universal phase diagram for weakly segregated rod-coil block copolymers. The universal phase diagram, where the temperature axis has been replaced by either  $\chi N$  or  $\mu N$ , is applicable to any system with a rod-coil molecular shape and can be used in a predictive capacity for functional rod coil systems. The phase diagram shows that increasing  $\chi N$  or  $\mu N$  results in the formation of nanostructured phases and liquid crystalline ordering, respectively. Phases are identified as lamellar (L), nematic (N), and isotropic (I).



**Figure 7.** SANS of PPV-*b*-PI block copolymers at elevated temperatures. Heating of PPV-*b*-PI block copolymers results in disordering of the lamellar morphology, marked by a decrease in the primary peak intensity and disappearance of higher order scattering peaks. At the order—disorder transition (ODT) a high-*q* shoulder appears, and this shoulder grows in intensity as the polymers are heated past the ODT. Further heating results in the eventual disappearance of the primary scattering peak. Power law low-*q* scattering persists during heating and increases in intensity upon cooling of the polymers.

Table 2. SANS Fits and Phase Transitions in PPV-b-PI Block Copolymers

polymer	coil $R_{\rm g}$ (Å)	rod $R_{\rm g}$ (Å)	correlation length (Å)	low-q scaling	high-q scaling	ODT (°C)	LCT (°C)
PPVbPI-51	19.0	18.5	$8.65\pm0.02$	$3.05\pm0.02$	$2.74\pm0.01$	$140 \pm 10$	$199 \pm 3$
PPVbPI-70	28.2	18.5	$9.02 \pm 0.02$	$2.98\pm0.01$	$2.75 \pm 0.01$	$140 \pm 10$	$194 \pm 2$
PPVbPI-83	39.9	18.5	$9.64 \pm 0.03$	$3.52 \pm 0.01$	$2.61 \pm 0.01$	$140 \pm 10$	$142 \pm 2$

PPV-b-PI polymers.<sup>16</sup> The high-q shoulder also becomes significantly more pronounced with increasing temperature. Further heating results in the gradual disappearance of all scattering peaks, and the high-q shoulder becomes extremely pronounced by the highest accessible temperature of 200 °C. The slope at low q also increases slightly, especially in the polymers at low coil fractions. The liquid crystalline transition temperatures above the ODT are identified by POM and given in Table 2. In PPVbPI-52 and -70 the liquid crystalline clearing temperature occurs above the order-disorder transition, indicating that the polymers have an intermediate nematic phase between the ordered lamellar and high-temperature isotropic phases. For PPVbPI-83, the liquid crystalline clearing temperature coincides with the ODT, indicating a direct transition from the lamellar to the isotropic phase. Both the appearance of the scattering peaks and the high-q shoulder are consistent regardless of whether the ODT marks a transition into an intermediate nematic phase or an isotropic phase.

Cooling of all three polymers results in qualitatively reversible phase transitions, although quantitative changes in the intensity of the low-q scattering are observed. As shown by the curves in Figure 7, recooling of the polymers at all coil fractions results in the reappearance of weak primary scattering peaks, with the primary peaks growing in intensity and higher order peaks eventually appearing below the ODT. The positions of the peaks on cooling below the ODT are identical to those of the original structure, indicating that the formation of the microphaseseparated structure is reversible. However, irreversible changes are observed in the low-q scattering. Upon cooling from 200 to 170 °C, an increase in the low-q scattering is observed in all samples. Figure 8 shows plots of the scattering on heating and cooling in PPVbPI-70 in absolute intensity, providing a quantitative illustration of the large magnitude of the increase in low-q intensity. This low-q feature is unusual, in that it cannot be represented as additive contributions from short and long length scale features due to the fact that the extrapolation of



Figure 8. Absolute neutron scattering intensity of PPVbPI-70. SANS curves for PPVbPI-70 plotted in absolute intensity show that on heating there is little change in the low-q scattering but an increase in the high-q scattering due to the appearance of the high-q shoulder. On cooling, there is a large increase in the low-q scattering and a small decrease in the high-q scattering as the shoulder disappears.

the low-q power law scaling exceeds the experimentally observed scattering intensity. We note that the shoulder that appears is observable for a single detector configuration and thus is not an artifact of the time series of acquisitions used to span the large q range. On further cooling below the ODT, the intensity of this low-q power law scattering increases at higher q values as well, resulting in a uniform power law background throughout the entire q range. While the increase in low-q scattering upon cooling is perplexing, the thermal reversibility of the order—disorder transition is clearly demonstrated by the reappearance of evenly spaced Bragg reflections at the same spacing as the original lamellar structure.

These observations are not consistent with predicted RPA structure factors. RPA structure factor calculations by Holyst and Schick,<sup>22</sup> Hammouda,<sup>31</sup> and Borsali et al.<sup>32</sup> all predict that the rod-coil block copolymer structure factor should qualitatively resemble that of a coil-coil block copolymer. The materials are predicted to show a primary scattering peak at all temperatures due to positional correlations between the two blocks induced by the chemical bond between them, and a finite scattering intensity is predicted at low q. The observation of power law scattering at low q and disappearance of the primary peak are both contraindicative of the RPA structure. Although neutron scattering provides much stronger contrast due to deuteration of the PI block, similar structural features are also observed in X-ray scattering of higher molecular weight PPVb-PI block copolymers. The lack of applicability of the RPA in the melt does not invalidate the use of mean-field treatments of rod-coil systems in all instances. In aqueous solution, Crespo et al. show that rod-coil block copolymers do have a structure factor consistent with the RPA, suggesting that the non-meanfield behavior may be specific to high concentrations or melts.<sup>60</sup>

Since the polymers do not follow the RPA, some association or aggregation between the polymers that results in correlations between the positions of neighboring rods or coils that are not accounted for by the assumptions of the RPA calculation is likely. These types of associations are well-known in coil-coil block copolymers above the ODT, where liquid micellar phases may be observed in highly asymmetric polymers.52,53 While it is experimentally difficult to definitively determine the nature of these non-RPA association or aggregation effects, fitting of the data with various model scattering functions can provide insight into the most likely structures. Fitting of the data with structure factors for micellar aggregates of various shapes (cylinders, etc.) produces extremely poor fits. The micelles would have to be extremely large to account for the low-qscattering, and there is no sign of the Guinier scattering regime even below 0.002 1/Å. The shoulder at high q does not fit to a

form factor or structure factor oscillation from micellar structures due to the lack of higher or lower order oscillations on comparable length scales. Scattering curves that qualitatively resemble those of our rod-coil systems have been observed by a number of different authors in systems with multiscale or fractal structures. Often, two disparate length scales of structures lead to this type of scattering, where the large length scale structure is too large to be fully probed by the scattering technique and therefore appears as only a power law decay of the scattering intensity at low q. The shorter length scale demonstrates both a Guinier regime and a power law decay of scattering in the high-q region. Beaucage and co-workers have developed a unified approximation that is able to reliably fit these dual length scale structures independent of the exact shape of either the small or large length scale structure,<sup>54,55</sup> and this equation has been successfully applied to polymeric systems with a fractal dimension deviating from 2, that of a Gaussian coil that can be easily modeled by the Debye function.<sup>56</sup> The Beaucage form factor has been applied to mass fractals from aggregated anionic chains in solution<sup>57</sup> and aggregates of core-shell dendrimers in solution.<sup>58</sup> This type of two-regime structure is commonly observed in fractal aggregates of polymeric materials, including semiconducting polymers.<sup>59</sup> Alternately, Hammouda and co-workers have developed a fit function used to fit similarly shaped fractal aggregates formed by the clustering of PEO chains in solution.<sup>61</sup> When applied to the PPV-b-PI scattering curves, the Beaucage function provides a relatively poor fit and the Hammouda function provides an excellent fit, as shown in Figure 9. The scaling of the power law regions and the characteristic length scale of the shoulder in the curves are given in Table 2. The scaling in both regions is in the range of 2.6–3.5, intermediate between Porod scattering from interfaces between phases and the scattering of lowdimensional fractal aggregates such as disks, coils, or rods. The characteristic length scale of the high-q structures ranges from 8.65 to 9.64 Å, increasing with increasing coil fraction. As shown in Table 2, these length scales are much shorter than the radius of gyration of either the rod or coil of the block copolymer. The high-q feature also corresponds to a length scale smaller than that given by the Debye function of the corresponding PI block, suggesting that this feature is submolecular. Fits with the Beaucage function, although unable to fit the data as quantitatively as the Hammouda function, produce similar results for the scaling powers and the characteristic length scale of the short length scale structures. Fitting the scattering curves with the Hammouda function in the nematic region, excluding the primary peak from the fit, shows that only the intensity of the low-q scattering feature has a strong and systematic



**Figure 9.** Fits of SANS curves at 200 °C. Fitting of the block copolymer scattering curves for all coil fractions with the Hammouda function results in excellent agreement with the experimental data across the entire q range. These fits suggest that the polymers form a mass fractal aggregate structure above the order—disorder transition, where the short length scale is submolecular, ~8–9 Å.

temperature dependence, indicating that on heating the primary structural rearrangement is an increase in the high-*q* scattering intensity.

On the basis of these results, we hypothesize that the melting of these rod-coil block copolymers out of the ordered state results in the formation of mass fractal aggregates. The short length scale characterizing the structures is submolecular, while the large length scale is extremely large, suggesting that distinct micellar objects are not formed. The large length scale structure is present in both ordered and disordered samples, although its fractal dimension changes on disordering of the block copolymer. Depending on the temperature and the coil fraction, these mass fractal structures may show either nematic or isotropic liquid crystalline structure. Although identifying the source of this large length scale structure is very difficult, one hypothesis might be that the unique defect structures at grain boundaries, favoring continuity of the coil block, leads to large length scale connectivity and fractal structure in these materials. On the basis of the relative contribution of the high- and low-q scattering features to the invariant, the low-q feature represents a negligible fraction of the total scattering power except upon recooling the sample, when the low-q contribution to the invariant increases significantly. This suggests that the low-q scattering is somehow related to disorder in the lamellar structure of the sample. While the samples on heating form extremely well-ordered lamellae due to thermal annealing below the ODT after drying from solvent, the lamellae that re-form on cooling show significantly less intense lamellar reflections and a higher low-q intensity. This is consistent with a disordered large length scale connectivity or fractal disorder.

#### Conclusions

Experimental measurements of parameters governing rod alignment and rod-coil repulsion in a rod-coil diblock copolymer allow a universal phase diagram for this class of molecules to be prepared. Two separate techniques are applied to estimate the Flory-Huggins interaction parameter in a rod-coil block copolymer system. The segregation of block copolymers to the interface between two homopolymers is used to estimate  $\chi$  by comparison with SCFT theory. The experimental surface excess profiles are significantly broadened due to the low surface energy of the compatibilized interface, but comparison of the total surface excess between experiment and theory allows  $\chi$  to be calculated by fitting the experimental data with the theory at a variety of temperatures. In our experimental range,  $\gamma N$  is found to be relatively small, consistent with the weakly segregated nature of the system, and it is more than an order of magnitude smaller than the Maier-Saupe parameter  $(\mu N)$ . Using these parameters allows the phase diagram for the PPV-b-PI system to be universalized under the assumptions of ideal nematic rods, composition-independent  $\chi$  and  $\mu$ , and local rod-rod and rod-coil interactions, providing the first quantitative experimental phase diagram that applies to the general class of rod-coil block copolymers. In the isotropic state, the scattering of these rod-coil materials is inconsistent with RPA calculations at all coil fractions, suggesting that they form aggregated or associated structures inconsistent with the basic structural assumptions of the RPA. Curve fits to the scattering profiles indicate that these structures are most consistent with fractal aggregates commonly observed in many polymer systems.

Acknowledgment. We gratefully acknowledge support from an NSF CAREER Award. This work made use of the Materials Research Laboratory Central Facilities at the University of California Santa Barbara supported by the National Science Foundation under Award DMR00-80034. We thank Tom Mates for assistance with DSIMS experiments. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. We also thank Man-Ho Kim and Boualem Hammouda for experimental assistance and helpful discussions. B.D.O. gratefully acknowledges the Fannie and John Hertz Foundation for a graduate fellowship. V.G. acknowledges partial support by a grant from the Welch Foundation and the Petroleum Research Fund of the American Chemical Society.

### **References and Notes**

- Minich, E. A.; Nowak, A. P.; Deming, T. J.; Pochan, D. J. Polymer 2004, 45, 1951–1957.
- (2) Lecommandoux, S.; Achard, M. F.; Langenwalter, J. F.; Klok, H. A. Macromolecules 2001, 34, 9100–9111.
- (3) Losik, M.; Kubowicz, S.; Smarsly, B.; Schlaad, H. Eur. Phys. J. E 2004, 15, 407–411.
- (4) Gallot, B. Prog. Polym. Sci. 1996, 21, 1035–1088.
- (5) Ball, Z. T.; Sivula, K.; Frechet, J. M. J. *Macromolecules* **2006**, *39*, 70–72.
- (6) Lu, S.; Liu, T. X.; Ke, L.; Ma, D. G.; Chua, S. J.; Huang, W. Macromolecules 2005, 38, 8494–8502.
- (7) Van De Wetering, K.; Brochon, C.; Ngov, C.; Hadziioannou, G. Macromolecules 2006, 39, 4289–4297.
- (8) Yu, W. L.; Meng, H.; Pei, J.; Huang, W.; Li, Y. F.; Heeger, A. J. Macromolecules 1998, 31, 4838–4844.
- (9) Chochos, C. L.; Kallitsis, J. K.; Gregoriou, V. G. J. Phys. Chem. B 2005, 109, 8755–8760.
- (10) Tzanetos, N. P.; Kallitsis, J. K. Chem. Mater. 2004, 16, 2648–2655.
- (11) Sary, N.; Rubatat, L.; Brochon, C.; Hadziioannou, G.; Ruokolainen, J.; Mezzenga, R. *Macromolecules* **2007**, *40*, 6990–6997.
- (12) Dai, C. A.; Yen, W. C.; Lee, Y. H.; Ho, C. C.; Su, W. F. J. Am. Chem. Soc. 2007, 129, 11036–11038.
- (13) Chen, J. T.; Thomas, E. L.; Ober, C. K.; Mao, G. P. Science 1996, 273, 343–346.
- (14) Radzilowski, L. H.; Carragher, B. O.; Stupp, S. I. *Macromolecules* **1997**, *30*, 2110–2119.
- (15) Tenneti, K. K.; Chen, X. F.; Li, C. Y.; Tu, Y. F.; Wan, X. H.; Zhou, Q. F.; Sics, I.; Hsiao, B. S. J. Am. Chem. Soc. 2005, 127, 15481– 15490.
- (16) Olsen, B. D.; Segalman, R. A. Macromolecules 2005, 38, 10127– 10137.
- (17) Olsen, B. D.; Segalman, R. A. Macromolecules 2006, 39, 7078-7083.
- (18) Olsen, B. D.; Segalman, R. A. Macromolecules 2007, 40, 6922-6929.

- (19) Semenov, A. N. Mol. Cryst. Liq. Cryst. 1991, 209, 191-199.
- (20) Semenov, A. N.; Vasilenko, S. V. Zh. Eksp. Teor. Fiz. 1986, 90, 124– 140.
- (21) Matsen, M. W.; Barrett, C. J. Chem. Phys. 1998, 109, 4108-4118.
- (22) Holyst, R.; Schick, M. J. Chem. Phys. 1992, 96, 730-740.
- (23) Pryamitsyn, V.; Ganesan, V. J. Chem. Phys. 2004, 120, 5824-5838.
- (24) Reenders, M.; ten Brinke, G. Macromolecules 2002, 35, 3266-3280.
- (25) Williams, D. R. M.; Fredrickson, G. H. Macromolecules 1992, 25, 3561–3568.
- (26) Singh, S. Phys. Rep. 2000, 324, 108-269.
- (27) Olsen, B. D.; Jang, S. Y.; Luning, J. M.; Segalman, R. A. Macromolecules 2006, 39, 4469–4479.
- (28) de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.
- (29) Nedoma, A. J.; Robertson, M. L.; Wanakule, N. S.; Balsara, N. P. Ind. Eng. Chem. Res. 2008, 47, 3551–3553.
- (30) Leibler, L. Macromolecules 1980, 13, 1602-1617.
- (31) Hammouda, B. J. Chem. Phys. 1993, 98, 3439-3444.
- (32) Borsali, R.; Lecommandoux, S.; Pecora, R.; Benoit, H. *Macromolecules* 2001, *34*, 4229–4234.
- (33) Shull, K. R.; Kramer, E. J. Macromolecules 1990, 23, 4769-4779.
- (34) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. Macromolecules 1990, 23, 4780–4787.
- (35) Dai, K. H.; Kramer, E. J. Polymer 1994, 35, 157-161.
- (36) Noolandi, J.; Hong, K. M. Macromolecules 1982, 15, 482-492.
- (37) Noolandi, J.; Hong, K. M. Macromolecules 1984, 17, 1531-1537.
- (38) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* 1989, 22, 1449–1453.
- (39) Dai, K. H.; Kramer, E. J. J. Polym. Sci., Part B: Polym. Phys. 1994, 32, 1943–1950.
- (40) Dai, K. H.; Kramer, E. J.; Shull, K. R. *Macromolecules* **1992**, *25*, 220–225.
- (41) Green, P. F.; Russell, T. P. Macromolecules 1991, 24, 2931-2935.
- (42) Reynolds, B. J.; Ruegg, M. L.; Mates, T. E.; Radke, C. J.; Balsara, N. P. *Macromolecules* **2005**, *38*, 3872–3882.

- (43) de Boer, B.; Stalmach, U.; van Hutten, P. F.; Melzer, C.; Krasnikov, V. V.; Hadziioannou, G. *Polymer* **2001**, *42*, 9097–9109.
- (44) Kretzschmann, H.; Meier, H. Tetrahedron Lett. 1991, 32, 5059-5062.
- (45) Glinka, C. J.; Barker, J. G.; Hammouda, B.; Krueger, S.; Moyer, J. J.; Orts, W. J. J. Appl. Crystallogr. 1998, 31, 430–445.
- (46) Kline, S. NIST Center for Neutron Research, 2001.
- (47) Segalman, R. A.; Hexemer, A.; Hayward, R. C.; Kramer, E. J. Macromolecules 2003, 36, 3272–3288.
- (48) Tao, Y. F.; Olsen, B. D.; Ganesan, V.; Segalman, R. A. Macromolecules 2007, 40, 3320–3327.
- (49) Fredrickson, G. H.; Ganesan, V.; Drolet, F. *Macromolecules* **2002**, *35*, 16–39.
- (50) Dai, K. H.; Norton, L. J.; Kramer, E. J. Macromolecules 1994, 27, 1949–1956.
- (51) Fredrickson, G. H. *The Equilibrium Theory of Inhomogeneous Polymers*; Oxford University Press: New York, 2006.
- (52) Wang, X. H.; Dormidontova, E. E.; Lodge, T. P. *Macromolecules* 2002, 35, 9687–9697.
- (53) Sakamoto, N.; Hashimoto, T.; Han, C. D.; Kim, D.; Vaidya, N. Y. *Macromolecules* **1997**, *30*, 1621–1632.
- (54) Beaucage, G. J. Appl. Crystallogr. 1995, 28, 717-728.
- (55) Beaucage, G.; Schaefer, D. W. J. Non-Cryst. Solids 1994, 172, 797-805.
- (56) Beaucage, G. J. Appl. Crystallogr. 1996, 29, 134-146.
- (57) Stellbrink, J.; Willner, L.; Richter, D.; Lindner, P.; Fetters, L. J.; Huang, J. S. Macromolecules 1999, 32, 5321–5329.
- (58) Stancik, C. M.; Pople, J. A.; Trollsas, M.; Lindner, P.; Hedrick, J. L.; Gast, A. P. *Macromolecules* **2003**, *36*, 5765–5775.
- (59) Li, Y. C.; Chen, K. B.; Chen, H. L.; Hsu, C. S.; Tsao, C. S.; Chen, J. H.; Chen, S. A. *Langmuir* **2006**, *22*, 11009–11015.
- (60) Crespo, J. S.; Lecommandoux, S.; Borsali, R.; Klok, H. A.; Soldi, V. Macromolecules 2003, 36, 1253–1256.
- (61) Hammouda, B.; Ho, D. L.; Kline, S. *Macromolecules* **2004**, *37*, 6932–6937.

MA800978C