

Structure and Thermodynamics of Weakly Segregated Rod–Coil Block Copolymers

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ABSTRACT: The self-assembly of a series of monodisperse rod–coil block copolymers is studied in the weak segregation limit. This unusual weakly segregated system consists of polyisoprene (PI) coil blocks and poly(alkoxyphenylene vinylene) (PPV) rod blocks solubilized with alkoxy side groups. The order to microphase disorder transition (ODT) and nematic isotropic (NI) transition are experimentally investigated to produce a rod–coil block copolymer phase diagram in a system that follows polymeric scaling relationships. Small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), polarized optical microscopy, depolarized light scattering, and wide-angle X-ray scattering (WAXS) are used to map the phase diagram. As the symmetric diblock copolymer is heated, a series of transitions from lamellar to nematic to isotropic phases are observed. The NI transition temperature decreases with increasing coil fraction, and at high coil fractions only an isotropic phase is observable. The phase behavior is in qualitative agreement with weak segregation calculations based on Landau expansions reported by other groups. Transmission electron microscopy (TEM) reveals unusual grain structures in the low-temperature lamellar phase. The high bending energy of the rod microdomains results in lamellae with long persistence lengths and grain boundaries defined by broken lamellae. Changes in domain spacing with temperature suggest rod rearrangements within the lamellar phase.

Introduction

Block copolymers have received a great deal of attention for their ability to self-assemble into a variety of nanophase structures;^{1,2} this nanometer scale structure creates many useful properties in rubbers, adhesives, thin films,³ and nanopatterned surfaces.⁴ Much of the work to date has focused on coil–coil block copolymers where the molecular shape closely matches Gaussian coil models. Nanoscale control and patterning of functional block copolymers presents a new challenge due to nonidealities in molecular conformation and mixing interactions that are present in these materials. In a large class of polymers the primary or secondary bonding structure reduces the ability of the chain to undergo conformational rearrangement such that the polymer exhibits rigid chain behavior; typical rodlike polymers include helical proteins and semiconducting polymers with rigid π -conjugated backbones. As a consequence of the highly functional nature of many rodlike polymers, rod–coil block copolymers containing a rod block and a model coil block are interesting for several applications. Rod–coil block copolymers with amino acid-based rod blocks have been suggested as models for membrane structural proteins or DNA gels^{5–9} and for use as artificial membranes.¹⁰ The structural and rheological properties of these rod–coil block copolypeptides¹¹ and their gels¹² are also being studied. There is also great interest in rod–coil block copolymers for use in organic electronics, where the importance of the interface between two materials with different work functions is becoming increasingly apparent.^{13,14} Controlling the active layer morphology and interfacial structure in multicomponent devices on the 10 nm length scale of an exciton diffusion length is critical to optimizing device performance.^{15–18} Rod–coil block

copolymers are promising for control on this length scale, and these materials are being explored as a possible route to influence the morphology of multicomponent active layers in LEDs^{19–21} and photovoltaics.²²

Although self-assembly of rod–coil block copolymers has potential as an elegant path to achieve the same type of nanoscale structural control exercised in coil–coil systems, the necessary predictive polymer thermodynamics of these materials remains largely unknown. In classical block copolymers, the conformational properties of both blocks are characterized by Gaussian chain statistics, and the microphase structure is a compromise between minimizing the interaction energy between unlike blocks and the stretching of the Gaussian coils.^{1,2} In rod–coil block copolymers the rod block has an effectively infinite persistence length, and a single orientational vector defines its conformation. The self-assembly of rod–coil systems is further complicated by the anisotropic interactions and liquid crystalline behavior of the rod block. The chain stretching, isotropic Flory–Huggins interaction, and anisotropic rod interactions all impact the free energy and equilibrium microphase structure, and the interplay between these effects creates equilibrium structure and thermodynamics that are distinct from coil–coil block copolymer systems.

Theoretical studies have predicted a diversity of structures in rod–coil diblock copolymers. The first theoretical investigations of these materials used analytical free energy calculations and scaling relationships to understand the microphase behavior and predicted transitions between nematic, smectic A and C, bilayer, and “puck” phases.^{23–27} Alternately, several works have treated rod–coil block copolymers in the weak segregation limit through the use of a Landau expansion for the free energy in terms of both compositional and orientational order parameters.^{28–30} A transition from isotropic to nematic was predicted at low coil fractions,

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whereas the block copolymer was predicted to transition directly to a microphase-separated structure at high coil fractions. Self-consistent-field theory (SCFT) has also been applied to rod-coil block copolymers.^{31–35} These studies predicted complex phase diagrams including isotropic, nematic, and lamellar structures for a wide range of compositions across the center of the phase diagram. Arrowhead and bilayer microphases were also predicted for rod-rich systems, while strip or puck morphologies were favored in coil-rich systems.

Experimentally, rod-coil diblock copolymer systems have been studied far less than their coil-coil counterparts. While these prior studies have demonstrated an intriguing structural diversity in rod-coil block copolymer systems, experimental phase diagrams are incomplete, and a solid understanding of thermodynamics in these systems is lacking. A major difficulty in addressing these problems is the preparation of a suitable model material. To make a comparison with simulations, a model rod-coil block copolymer must be mapped onto a coarse-grained theory that ignores molecular detail on a scale smaller than the statistical segment length. Both the rod and coil block must be chemically homogeneous on the length scale of a statistical segment, and the coil must be long enough to have Gaussian chain statistics. The rod should be nearly perfectly rigid: free of structural defects or the possibility of folding and conformational changes in the bulk. Both blocks should have low polydispersity for the material to be easily modeled, and it is also useful to have polymers with a low enough Flory-Huggins parameter and weak enough liquid crystalline interactions such that phase transitions can be experimentally accessed.

A variety of approaches have been employed for the preparation and study of rod-coil systems. Lamellar and hexagonal morphologies were observed in oligomeric polypeptides,^{36,37} whereas only lamellar structures were observed in higher molecular weight polymers.^{5–9} While the complex secondary and tertiary protein structures provide interesting structural behavior, block copolypeptide materials add extra complication beyond a fundamental rod-coil system. Rod-coil oligomers have received more attention as model materials since small-molecule chemistry can be used to produce monodisperse samples of oligomeric molecules, and the small size of the molecules may lead to weaker segregation in these systems. However, rod-coil oligomers may not self-assemble according to the same scaling behavior as their longer polymeric analogues; in particular, the coil block may be too short or fully extended and thus not follow Gaussian chain statistics. Radzilowski et al. observed strip and puck phases^{38–40} and that annealing led to a disruption of ordering.^{38,39} Li and co-workers observed a disordering transition with increasing temperature in oligomeric rod-coil materials.⁴¹ Other researchers have also observed smectic, hexagonal, nematic, and isotropic phases.^{42–46} However, they found domain sizes on the order of the contour length of the polymer, suggesting the coils were fully extended.^{42,43}

Polymeric rod-coil systems are more likely to scale as the theoretical predictions, and studies of high molecular weight systems have revealed novel and intriguing phase behavior.^{47–51} For solution self-assembled block copolymers with poly(hexyl isocyanate) (PHIC) rods, wavy lamellar, zigzag, and arrowhead morphologies were observed, and the molecular packing was identified as similar to smectic C and smectic O

type liquid crystals.⁴⁸ Because of the strongly segregated nature of this system and the kinetic structural trapping inherent in solvent casting, the equilibrium nature of these structures is unclear. Work on protein-based, oligomeric, and polymeric rod-coil systems has been the subject of several reviews,^{8,52–55} and while these previous experimental studies have illustrated the rich potential of rod-coil block copolymers for assembly into a variety of morphologies, the underlying thermodynamics remain largely unknown.

We report here a study of the structure and thermodynamics of a weakly segregated rod-coil block copolymer system with polymeric scaling properties. A model system of monodisperse poly(alkoxyphenylene vinylene) (PPV) rods and polyisoprene (PI) coils is prepared, and side-chain functionalization of the PPV is used to control the Flory-Huggins interaction parameter, liquid crystalline interactions, and rod-to-coil aspect ratio. The structure and thermodynamics of the weakly segregated rod-coil system are studied to produce an experimental phase diagram showing transitions between lamellar, nematic, and isotropic phases.

Experimental Methods

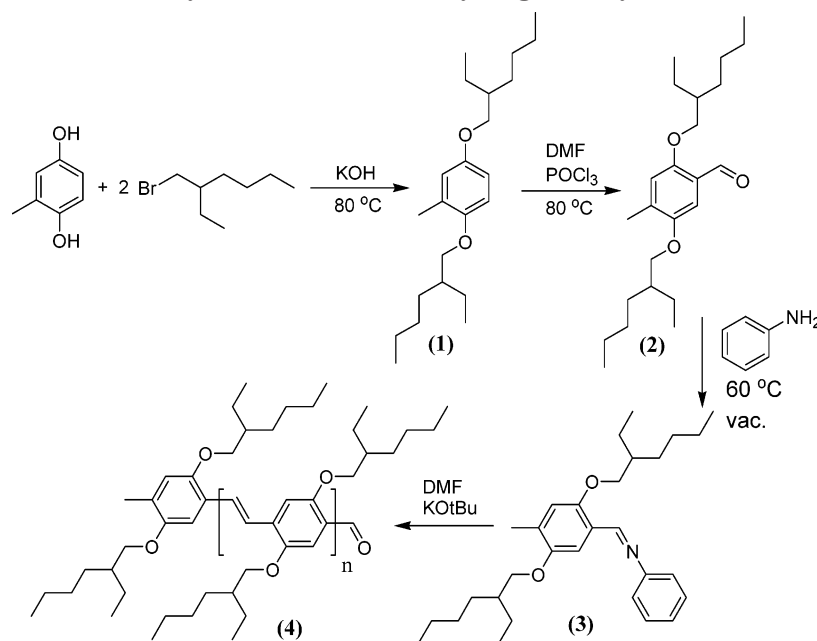
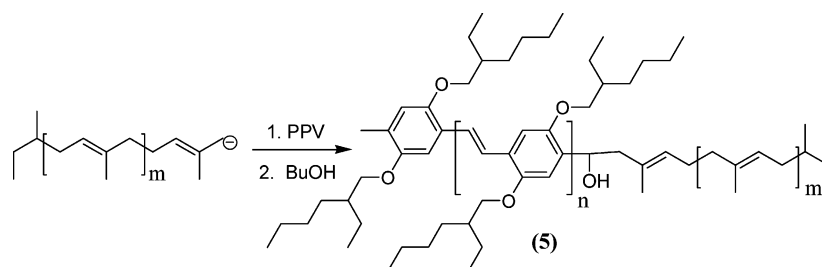
Materials. DMF was dried over 3 Å molecular sieves. Benzene was purified by sparging with dried nitrogen followed by passage through an activated alumina column (UOP A2 Alumina, 12–32 mesh). Isoprene was purified over CaH₂ followed by Bu₂Mg. Butanol was dried over CaH₂. All other reagents and solvents were used as received. For column chromatography, Merck grade 9385 silica gel (230–400 mesh, 60 Å) was used. NMR spectra were acquired on a Bruker AVB-300 magnet in CDCl₃ as solvent.

Synthesis of 2,5-Di(2'-ethylhexyloxy)toluene, 1. PPV monomer and polymer were synthesized according to Scheme 1. Etherification⁵⁶ of methylhydroquinone was achieved by dissolving 43.2 g of methylhydroquinone (0.341 mol) and 56 g of KOH (0.998 mol) in 500 mL of absolute ethanol and refluxing at 80 °C for 1 h. 177.5 mL of ethylhexyl bromide (192.8 g, 0.998 mol) was added dropwise, and the mixture was refluxed at 80 °C overnight. The reaction mixture was poured out onto water, and the product was extracted with ether. The product was cleaned using column chromatography. ¹H NMR δ: 0.89 (m, 12H, -CH₃), 1.30 (m, 16H, -CH₂-), 1.68 (m, 2H, -CH-), 2.20 (s, 3H, Ar-CH₃), 3.77 (t, 4H, -O-CH₂-), 6.70 (m, 3H, ArH).

Synthesis of 2,5-Di(2'-ethylhexyloxy)-4-methylbenzaldehyde, 2. Formylation, as described in a previously published procedure;⁵⁷ was performed by mixing 124.39 g of molecule 1 (0.357 mol) with 178.5 mL of anhydrous CHCl₃ (266.3 g, 2.231 mol) and 101.2 mL of dry DMF (95.5 g, 1.306 mol). Using a dropping funnel, 142.8 mL of POCl₃ (234.9 g, 1.532 mol) was added dropwise while keeping the mixture below 40 °C. The reaction was stirred for 1 h at ambient temperature and then refluxed at 80 °C for 48 h. The product was poured out onto ice, extracted into dichloromethane, and neutralized. The product was purified by column chromatography. Overall yield for the previous two steps was 79%, and no meta or ortho formylation products were observed. ¹H NMR δ: 0.88 (m, 12H, -CH₃), 1.32 (m, 16H, -CH₂-), 1.73 (m, 2H, -CH-), 2.27 (s, 3H, Ar-CH₃), 3.84 (d, 2H, -O-CH₂- meta to aldehyde), 3.91 (d, 2H, -O-CH₂- ortho to aldehyde), 6.81 (s, H, Ar-H meta to aldehyde), 7.23 (s, H, Ar-H ortho to aldehyde), 10.41 (s, H, -CH=O).

Synthesis of 2',5'-Di(2''-ethylhexyloxy)-4'-methyl-N-benzylideneaniline, 3. To produce the imine,⁵⁸ 7.23 g of aniline (77.6 mmol) was combined with 13.4 g of product 2 (35.6 mmol). The mixture was reacted at 60 °C under ~10 Torr vacuum for 2 h. This product was used without further purification. ¹H NMR δ: 0.80 (m, 12H, -CH₃), 1.23 (m, 16H, -CH₂-), 1.62 (m, 2H, -CH-), 2.17 (s, 3H, Ar-CH₃), 3.81 (m, 4H, -O-CH₂-), 6.69 (s, H, -N=CH-Ar-H meta), 7.09 (m,

Scheme 1. Synthesis of DEH-PPV by Seigrist Polycondensation

Scheme 2. Synthesis of PPV-*b*-PI Copolymer by Coupling of Anionically Grown PI with Aldehyde-Terminated PPV

3H, =N-Ar-*H* ortho and para), 7.25 (m, 2H, =N-Ar-*H* meta) 7.47 (s, H, -N=CH-Ar-*H* ortho), 8.78 (s, H, Ar-CH=N).

Synthesis of Poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylene vinylene) (DEH-PPV), 4. PPV was synthesized by Seigrist polycondensation, as previously described.^{22,58} This reaction allows for the preparation of PPV with a narrow molecular weight distribution. The reaction temperature determines the molecular weight of the polymer, and the product polymer has a well-defined chemical structure containing only trans-linked units. 3 equiv (14.25 g) of potassium *tert*-butoxide was added to 1.8 L of dry DMF and heated to 30 °C. Compound **3** was added dropwise and allowed to react for 30 min. The reaction was poured out onto acidified water and stirred for 48 h to hydrolyze the unreacted imines. Product was collected, neutralized, and fractionated with a chromatography column. The fractionated product was precipitated into methanol at -20 °C. The overall yield was 4.97 g (39.0%). Polarized optical microscopy and differential scanning calorimetry demonstrated that the homopolymer was solid below 59 °C, liquid crystalline until 225 °C, and isotropic above that temperature. ¹H NMR δ : 0.89 (m, 12(*n* + 1)H, -CH₃), 1.45 (m, 16(*n* + 1)H, -CH₂-), 1.81 (m, 2(*n* + 1)H, -CH-), 2.24 (s, 3H, Ar-CH₃), 3.96 (m, 4(*n* + 1)H, -O-CH₂-), 7.20 (s, 2nH, -CH=), 7.53 (s, 2(*n* + 1)H, Ar-*H*), 10.43 (s, H, -CH=O).

Synthesis of Poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylene vinylene)-*block*-poly(1,4-isoprene) (PPV-*b*-PI), 5. PPV-*b*-PI block copolymers were synthesized according to Scheme 2. Anionic polymerization of isoprene was performed in benzene using *sec*-butyllithium (1.4 M in cyclohexane) as initiator to produce predominantly 1,4 addition (~93%) of isoprene. The reaction was allowed to proceed at room temperature, and an aliquot of polyisoprene homopolymer was collected and terminated with dry butanol to measure molec-

ular weight and polydispersity. PPV (0.4 equiv) was dried under vacuum at room temperature overnight and then dissolved in benzene and injected to terminate the living polyisoprene.⁴¹ The polymers were allowed to react for 30 min, and then the remaining polyisoprene was terminated with butanol. The polymer was precipitated in methanol, and excess homopolymer was removed using column chromatography.

Gel Permeation Chromatography (GPC). The molecular weights of polyisoprene homopolymers were measured on a Waters 2690 GPC with a Viscotek refractive index detector and a low-angle light scattering detector using a 670 nm laser. Light scattering was used for absolute molecular weight determination without the use of calibration standards. The polystyrene equivalent molecular weights of the PPV homopolymer and PPV-*b*-PI block copolymers were measured on a Waters 150-CV GPC with a M486 tunable absorbance detector at 450 nm (near the absorbance peak of PPV) and a refractive index detector. GPC of one of the polymers and its precursor homopolymers is shown in Figure 1. The chromatograph of the polymer as-synthesized (not shown) has two peaks: one for excess polyisoprene homopolymer and one for the block copolymer. This homopolymer was removed in the following purification step. Standard-independent molecular weights and polydispersities for the PI block were calculated using refractive index and light scattering detectors, and the polydispersity of all PI samples was less than 1.05. The number-average molecular weight of the PPV block was determined using NMR end-group analysis by comparison of the aldehyde proton peak with the OCH₂ peak. Molecular weights for each block are shown in Table 1.

Because of the complex hydrodynamics of rodlike molecules^{59,60} and the lack of a suitable GPC standard, determination of the absolute molecular weight and polydispersity of

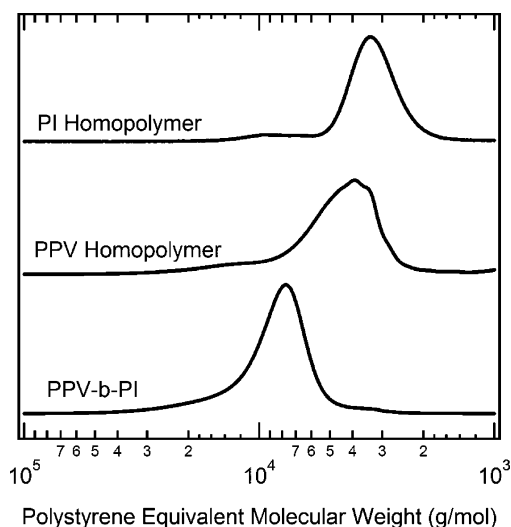


Figure 1. GPC of block copolymer PPVbPI-42 and its precursor polymers. PPV-*b*-PI was synthesized by linking a polyisoprene anion to PPV with low polydispersity. The increased molecular weight and low polydispersity of the block copolymer indicates the success of the coupling reaction.

PPV by GPC is difficult. The polystyrene (PS) equivalent PDI for the PPV block was measured to be 1.17. For rod polymers the PS equivalent PDI is a gross overestimate of the actual polydispersity because the hydrodynamic volume of the rod molecules increases much more rapidly with molecular weight than the hydrodynamic volume of coil polymers. This has an effect of stretching the high molecular weight tail of the distribution in rod polymers, increasing their polydispersity. Therefore, 1.17 is an upper limit on the true polydispersity of the rod block.

Density. The density of PPV was found to be 0.988 ± 0.001 g/cm³ using a density gradient column at 23 ± 0.1 °C with methanol and ethylene glycol as solvents. For PI, a density of 0.90 from the literature⁶¹ was used.

Small- and Wide-Angle X-ray Scattering (SAXS and WAXS). Samples for SAXS and WAXS were prepared by annealing polymers in a vacuum oven at 120 °C for 24 h to form 1 mm thick disks and then sealing the sample between Kapton windows. SAXS and WAXS experiments were performed on beamline 1-4 of the Stanford Synchrotron Radiation Laboratory (SSRL). The beamline was configured with an X-ray wavelength of 1.488 Å and focused to a spot size of ~0.5 mm diameter. A single quadrant of two-dimensional scattering patterns was collected on a CCD detector with a 100 mm diameter. The two-dimensional profiles were radially averaged and corrected for detector null signal, dark current, and empty cell scattering. SAXS profiles were converted to absolute intensities using a polyethylene standard calibrated at NIST, and WAXS profiles were left in arbitrary units.

Transmission Electron Microscopy (TEM). Samples for TEM were prepared by spin-coating films of ~100 nm thickness from 2% toluene solution onto silicon nitride windows. All samples were annealed under vacuum at 80 °C for 12 h and cooled slowly to room temperature. Polymers were stained by exposure to the vapor from a 2% OsO₄ solution for 4 h or the vapor of a 0.5% RuO₄ solution for 30 min. Bright-field images were taken within 3 days after staining on a JEOL 200CX microscope at the National Center for Electron Microscopy operating at an accelerating voltage of 200 kV.

Polarized Optical Microscopy (POM) and Depolarized Light Scattering (DPLS). 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 placed on an in situ argon-purged heat stage for optical imaging. Samples were annealed into the isotropic phase, cooled, and then heated at a rate of 0.2 °C/min to determine the temperature at which birefringence disappeared. Samples for DPLS were prepared by annealing a sample of polymer at 120 °C overnight in a vacuum oven to form a 0.3 mm thick disk. The disk of polymer was then sealed between two quartz windows and annealed for an additional 15 min at 120 °C under a nitrogen atmosphere. Depolarized light scattering was measured using a previously described instrument.⁶² The sample was heated and cooled three times, and data to determine transitions were taken from the first cooling and second heating pass. Reported values of I/I_0 were normalized by the transmission of the sample.

Differential Scanning Calorimetry (DSC). Samples were also characterized using a TA Instruments 2920 DSC to investigate thermal transitions. Samples were heated to 220 °C at 10 °C/min to erase any thermal history, then cooled to 20 °C at 10 °C/min, and reheated to 270 °C at 5 °C/min.

Results and Analysis

Microphase Structure. Nondimensionalization of the free energy expression in a rod-coil block copolymer system yields four independent thermodynamic quantities that parametrize phase space:^{31,35} χN , the Flory-Huggins interaction parameter; μN , the Maier-Saupe parameter; ϕ , the coil volume fraction; and ν , the relative block size. The relative coil-to-rod block size is defined as $bN^{1/2}/Na$, where b is the statistical segment length of the coil block and N is the number of volumetric units. For the calculation of N , ϕ , and a , the volumetric unit is defined as the volume of a single isoprene unit, making the number of volumetric units in the coil block equal to its number-average degree of polymerization. The rod's segment length, a , is defined as the length of rod that will fit into a volumetric unit, so a is much shorter than both the contour length and the Kuhn length of the rod. The number of volumetric units, the coil fraction, and the relative block size are estimated on the basis of molecular weights and homopolymer densities for each block. Using the density of PPV, average bond lengths from the literature,⁶³ and assuming a cylindrical PPV shape, the effective molecular diameter is calculated to be 1.09 nm. The contour length of a PPV rod is 6.61 nm, and a is 0.135 nm. The statistical segment length of polyisoprene, b , is 0.652 nm,⁶⁴ and this value is used to calculate the radius of gyration for the coil and ν . The contour lengths of the block copolymers are estimated in Table 1 for a predominantly *cis*-PI with 93% 1,4 addition. Calculated values of all molecular parameters are tabulated in Table 1.

Thermodynamic repulsion between rod and coil blocks leads to microphase separation in rod-coil copolymers analogous to the classical phase behavior of coil-coil block copolymers. The model rod-coil block copolymers are investigated with X-ray scattering and electron

Table 1. PPV-*b*-PI Block Copolymers

block copolymer	PPV M_n (g/mol)	PI M_n (g/mol)	N	ϕ	ν	rod length (nm)	coil R_g (nm)	block copolymer contour length (nm)
PPVbPI-42	3545	2367	82	0.42	0.533	6.61	1.57	22.3
PPVbPI-59	3545	4938	116	0.59	0.448	6.61	2.21	37.5
PPVbPI-72	3545	8129	166	0.72	0.374	6.61	2.90	59.8
PPVbPI-89	3545	25483	421	0.89	0.235	6.61	5.15	173.8

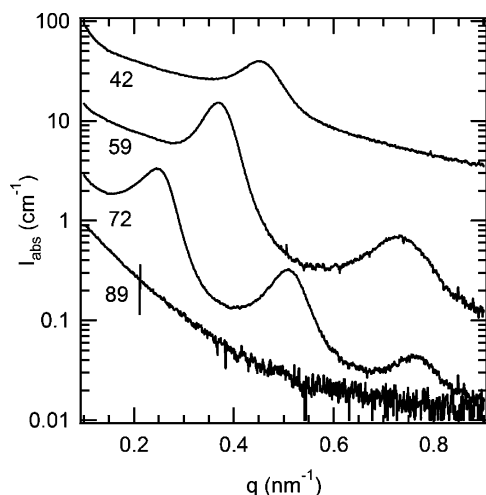


Figure 2. SAXS of all block copolymers at 40 °C. PPVbPI-89 is microphase disordered, showing no peaks. The three block copolymers with smaller coil volume fractions are microphase separated with peaks at integer multiples of their respective q^* , indicating lamellar structure. In the case of PPVbPI-42, higher order peaks are outside of the experimentally accessible q range, but the lamellar structure is confirmed by electron microscopy.

microscopy to establish the microphase structure and structural transitions. SAXS curves for each polymer at 40 °C are shown in Figure 2; the polymers organize into lamellae as indicated by peaks occurring at integer multiples of q^* . Peaks remain at integer multiples of q^* upon heating, demonstrating that the lamellar structure persists throughout the microphase-separated region. The lamellar region is surprisingly wide, extending to a coil volume fraction approaching 0.85. Above a

coil fraction of 0.85, the polymer shows no scattering peaks throughout the accessible q range.

TEM yields additional information about the morphology of these lamellae. Samples stained with OsO_4 show dark polyisoprene block microdomains and light PPV block lamellae, as shown in Figure 3a–c. The micrographs clearly indicate qualitative variations in lamellar structure as the composition of the block copolymer is changed. The approximately symmetric block copolymer PPVbPI-42 has grains of lamellae oriented parallel and perpendicular to the plane of view. Lamellae oriented perpendicular to the surface appear as alternating light and dark stripes whereas lamellae oriented parallel to the surface appear as solid gray regions. Imaging with a large tilt angle reveals lamellar edges near the boundary of the parallel regions, and examination of several grains of parallel lamellae shows many of them have visible defect structures where a single lamellar layer is oriented perpendicular to the surface in the middle of the grain. These structures both indicate the lamellar nature of the gray regions. The orientation of perpendicular lamellae is correlated across 3–10 rod microphases, and rod microphases have a very long persistence length. In contrast, the lamellae in coil-coil block copolymers show a great deal of curvature.¹⁴ Because of the preferential alignment of the rod block directors, grains of rodlike mesogens have a large elastic energy of bending. In rod-coil block copolymers this elasticity will impart rigidity to the rod microphase, resulting in a free energy penalty for bending a lamellae and creating structures with a long persistence length. TEM also illustrates that defects and grain boundaries are characterized by discontinuities in the rod microphase. Lamellar structures break at

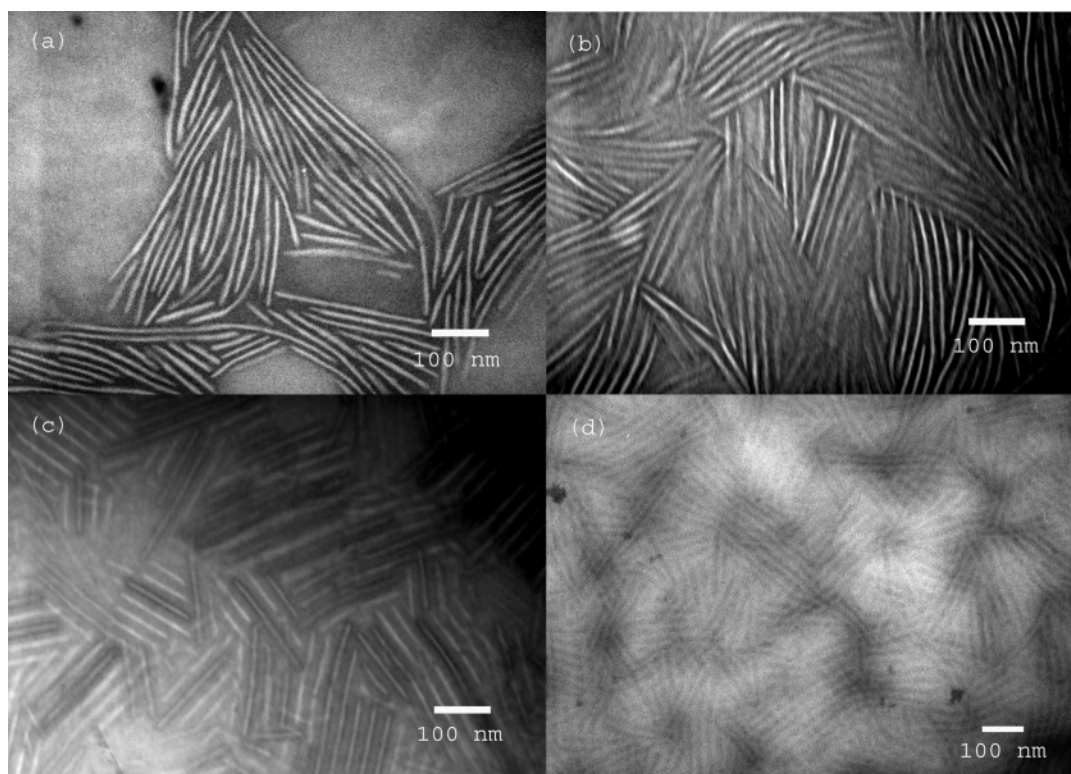


Figure 3. TEM of block copolymer films on silicon nitride windows. Staining with OsO_4 reveals the lamellar structure of PPVbPI-42 (a), PPVbPI-59 (b), and PPVbPI-72 (c). Regions with little or no phase contrast are a result of lamellar orientation parallel or nearly parallel to the substrate. The lamellar structures have remarkably high persistence lengths and orientational correlations, and grain boundaries are characterized by the breaking of lamellar structures. PPVbPI-72 stained with RuO_4 (d) provides a complementary picture of the lamellar structures in this polymer.

grain boundaries, and Y-shaped dislocations are only observed in the coil-rich regions. Most defects in coil-coil copolymer lamellar structure involve curvature or junctions between individual microphases, and these types of defects carry a large penalty due to bending elasticity in rod-coil block copolymers. Breaking a lamellae and generating additional interface is favored in a rod-coil system over the curvature imposed by a defect, resulting in broken rod microphases at grain boundaries. It should be noted that the domain spacing in this polymer was too small to allow for detection of higher order SAXS peaks within the experimental q range (Figure 2), but TEM confirms the lamellar morphology.

As the coil fraction is increased, the grain structure qualitatively changes. A slightly coil-rich sample (PPVb-PI-59) is characterized by smaller grains of lamellae that appear intertwined with one another. Regions of lower and higher contrast indicate lamellae oriented at different angles to the surface. Tilting the sample accentuates some structures while blurring others as lamellae are rotated through a variety of angles with respect to the plane of view. Lamellar orientation is correlated across groups of 3–5 lamellae, and intersections between lamellae are again characterized by breaks in the PPV phase. With a further increase in coil fraction (PPVbPI-72), the lamellar orientation becomes more strongly correlated and grain size grows, producing grains as wide as 15–20 parallel lamellae. The lamellae show very little bending over several hundred nanometers and always break at grain boundaries, demonstrating the large bending modulus associated with liquid crystalline order in the rod microphase. RuO₄ staining provides a complementary image of PPVbPI-72 by preferentially staining the PPV phase. RuO₄ has a complicated staining chemistry,⁶⁵ but test samples of blended PPV and PI suggest that the PPV phase is stained more rapidly, appearing as the dark phase in Figure 3d. Under these staining conditions contrast is much lower and the overlap of lamellae becomes visible. The pattern of overlapping lamellae indicates that the width of the lamellae is less than the sample thickness and that the same breaking of rod microphases at grain boundaries observed in the plane of view also occurs throughout the depth of the sample.

As the block copolymers are heated, they undergo a transition from an ordered lamellar phase into a microphase disordered regime, as shown in SAXS intensity plots for a representative polymer in Figure 4. The order-disorder microphase transition (ODT) is characterized by a drop in intensity of the primary scattering peak and the disappearance of higher order peaks with increasing temperature. This transition temperature can be further quantified through a discontinuity in the plot of inverse primary peak intensity vs inverse temperature, as shown in Figure 5. This discontinuity occurs at the same temperature as the disappearance of higher order peaks and is shown in Table 2. The chemical link between blocks should generate weak concentration correlations, and the polymer should show a weak primary peak due to this correlation even in the disordered regime.⁶⁶ In this case the PPV and PI blocks have low contrast, so the peak intensity decreases to such an extent that it is lost in the baseline noise at high temperatures. As a result, the number of intensity measurements that can be extracted above the ODT is limited.

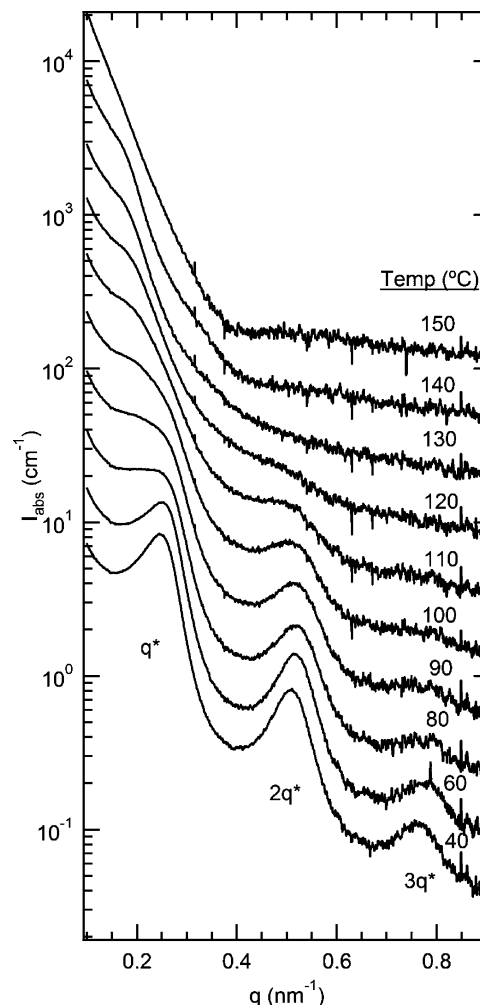


Figure 4. Small-angle X-ray scattering curves for PPVbPI-72 in the vicinity of the order-disorder transition. Curves are offset along the vertical axis for clarity. The spacing of peaks at integer multiples of q^* indicates a lamellar structure. Higher order peaks disappear above 120 °C, indicating the order-disorder transition.

In the case of a rod-coil block copolymer, the nature of the ODT is different than in a coil-coil copolymer. In a coil-coil material the disordered phase is spatially homogeneous and liquidlike, with no possibility of orientational order.⁶⁷ Although density fluctuations or micelles may persist, the ensemble average density is spatially invariant. In a rod-coil block copolymer, the ODT is still a transition from an ordered to a spatially homogeneous phase, but orientational order may persist in the disordered state as driven by rod-rod interactions, implying that there may be multiple disordered phases. More succinctly, in coil-coil materials the ODT breaks both orientational and positional symmetry, but in rod-coil materials the ODT need only break positional symmetry.

Liquid Crystalline Order. Above the ODT, it is possible for the rod-coil block copolymer to be in multiple disordered states: a nematic (oriented) or an isotropic (unoriented) phase, as illustrated in Figure 6. Optical techniques provide complementary information to SAXS that allows this shorter scale order to be investigated. Optically anisotropic phases, such as the nematic and lamellar phases, exhibit birefringence whereas the isotropic phase does not, and these techniques have been widely used to provide information regarding liquid crystalline phases and phase transi-

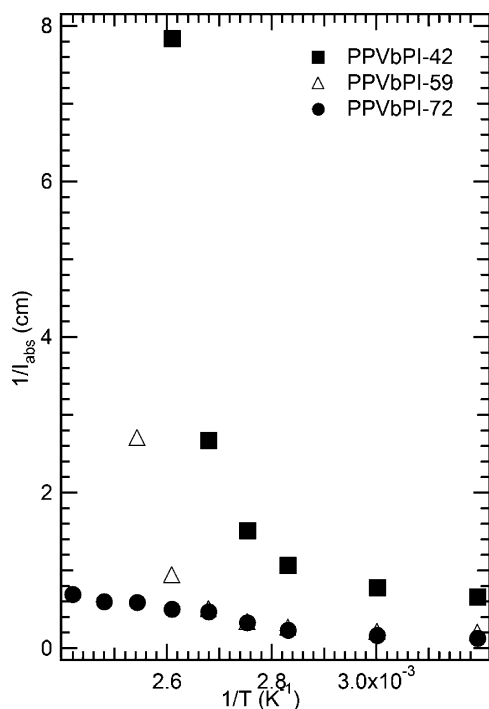


Figure 5. Inverse intensity of peak heights in the vicinity of the order-disorder transition. The discontinuity in slope of the inverse I vs inverse T curve indicates the order-disorder transition (ODT). Above the ODT the curve is linear, and extrapolation to zero inverse intensity gives the spinodal temperature.

Table 2. Phase Transition Temperatures ($^{\circ}\text{C}$) in PPV-*b*-PI Copolymers

block copolymer	optical clarity (DPLS)	NI transition (microscopy)	ODT
PPVbPI-42	131	225	110
PPVbPI-59	149	195	120
PPVbPI-72	123	134	120

tions⁶⁸ as well as block copolymer microphase and grain structure.⁶²

Below the ODT the rod-coil block copolymers exhibit a smectic-like pattern through polarized optical microscopy, while slightly above the ODT the polymers display a nematic texture, as shown in Figure 7. Further heating results in complete loss of birefringence, indicating the transition to the optically inactive isotropic phase. The nematic-isotropic (NI) transition temperature, given in Table 2, depends strongly on coil volume fraction. For symmetric block copolymers, the nematic region is wide. As coil fraction decreases toward rod-rich copolymers, the NI transition temperature increases rapidly, approaching the transition temperature

of pure PPV. Around a coil fraction of 0.72 the NI transition and ODT converge, suggesting the possibility of two regions in the phase diagram: one region where the isotropic phase transitions to the nematic phase and a second region where the isotropic phase transitions directly to an ordered phase. Very coil-rich block copolymers are isotropic throughout the accessible temperature range.

Depolarized light scattering is used to further quantify these transitions, and a representative curve, shown in Figure 8, exhibits two temperature-dependent transitions. At low temperatures, the sample is characterized by extremely low transmission due to strong scattering (opacity) but strong birefringence. Although the DPLS signal is still strong in this region, the error in the quantitative value is large due to errors inherent in accurately normalizing a small signal to account for the transmission through a strongly scattering sample. The strong birefringence, polarized optical microscopy texture, and SAXS structure all confirm a smectic-like morphology at low temperatures. As the sample is heated, the polymer reaches a lower temperature transition at approximately the same temperature as the ODT observed in SAXS, as shown in Table 2. At the lower temperature transition, transmission increases rapidly to a high level. There is still strong birefringence above this transition, and the samples show all the optical characteristics of a nematic phase.⁶⁸ The DPLS signal drops with further increasing temperature until a higher temperature transition point is reached at which the birefringence disappears entirely. This higher temperature transition occurs at the same temperature as the NI transition identified from polarized optical microscopy. Above the second transition, the sample is characterized by high transmission and low birefringence, indicative of an isotropic disordered phase. For coil volume fractions greater than 0.85, the sample shows isotropic characteristics throughout the entire experimentally accessible range. The observed sequence of transitions from smectic-like to nematic to isotropic represents characteristic behavior for a mesogenic system, and hysteresis observed in the DPLS curve suggests that both transitions are weakly first order, consistent with results on other polymeric¹ and mesogenic⁶⁸ systems. DSC was also used to probe transitions in the block copolymers. Unfortunately, the changes in enthalpy and heat capacity associated with these transitions are relatively subtle. As a result, the DSC data are far less illustrative than the combination of scattering and microscopy.

WAXS probes the molecular spacing between rods within a lamellar layer. Representative WAXS profiles as a function of temperature are shown in Figure 9. The

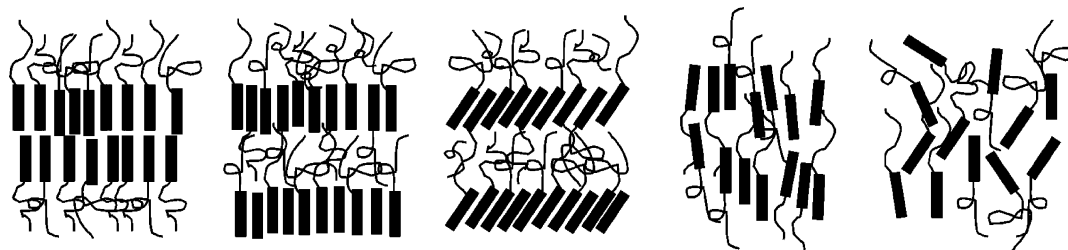


Figure 6. Illustration of molecular packing in possible rod-coil block copolymer microphases. From left to right the phases are bilayer, smectic A-like monolayer, smectic C-like monolayer, nematic, and isotropic. While regions of the lamellar, nematic, and isotropic phases can be clearly demarcated on the phase diagram, discerning between the lamellar structures is more difficult. On the basis of domain spacing, the two monolayer phases are the most probable lamellar morphologies, with transitions in rod tilt and chain stretching occurring as the polymers are heated through the order-disorder transition.

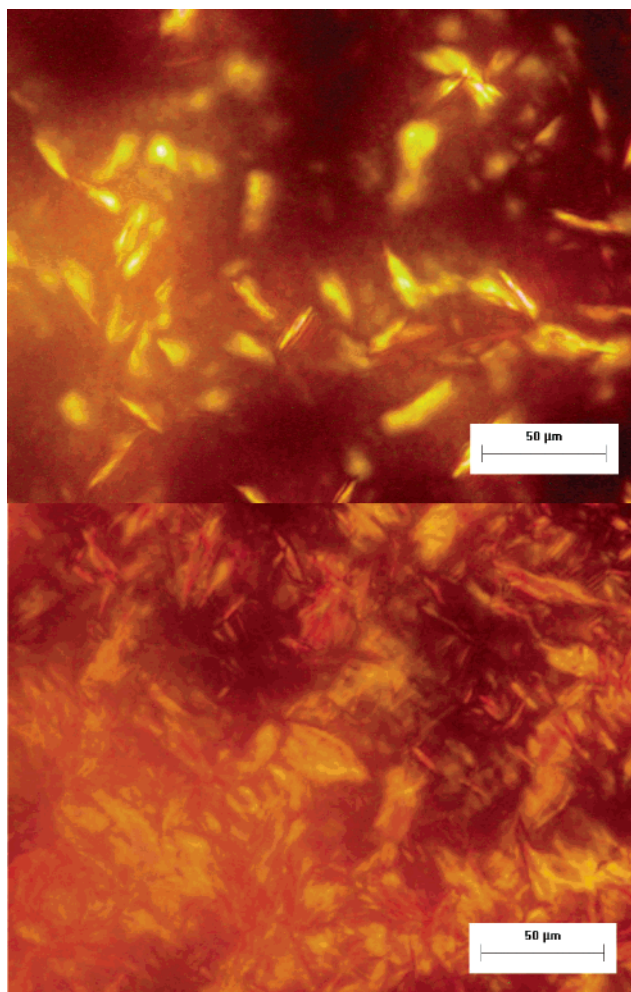


Figure 7. Optical micrographs of liquid crystalline textures in PPVbPI-42. At 120 °C (top) a nematic phase is observed, while at 80 °C (bottom) the material exhibits a smectic phase. Heating above the nematic region results in the disappearance of all optical texture, indicating the isotropic region.

large peak at 6 nm^{-1} corresponds to lateral rod-rod spacing of 1.05 nm, in reasonable agreement with the value of 1.09 nm calculated on the basis of bond length and density arguments. The slight decrease in q from 6.13 to 5.81 nm^{-1} over a range of 160 °C corresponds to a change in intermolecular spacing from 1.02 to 1.08 nm, and this small change is attributed to thermal expansion. Unlike the other three materials, PPVbPI-89 shows only a weak peak at ambient temperatures that decreases in intensity upon heating, consistent with its disordered and isotropic nature throughout the experimentally accessible temperature region.

The gradual decrease in the intensity of the rod-rod spacing peak is consistent with the preservation of short-range order in the block copolymers across the ODT and NI transitions. It is expected that nematic liquid crystals show short-range smectic-like order, and the arrangement of rodlike molecules in an isotropic fluid is still governed by anisotropic short-range packing constraints.⁶⁸ As the block copolymer becomes disordered, the increased mixing of the rod and coil blocks disrupts the regularity of the rod-rod spacing. The presence of a rod-rod spacing peak indicates the persistence of short-range correlations between rods above the ODT and NI transition. As the correlations gradually decay with increasing temperature, the intensity of the peak continuously decreases. At high coil

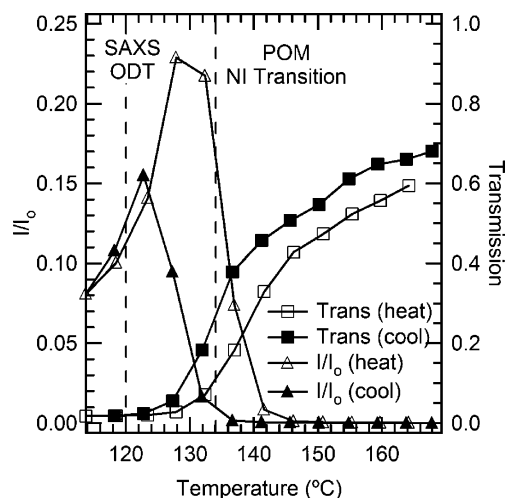


Figure 8. Depolarized light scattering and transmission of PPVbPI-72. Calculated values of I/I_0 are normalized by transmission. The polymer exhibits three phases: a birefringent phase with low transmission at low temperatures, a birefringent phase with moderate transmission from 123 to 137 °C, and a nonbirefringent phase at high temperatures. The low-temperature phase corresponds to the lamellar region identified by SAXS and TEM, the middle phase is nematic, and the high-temperature phase is isotropic.

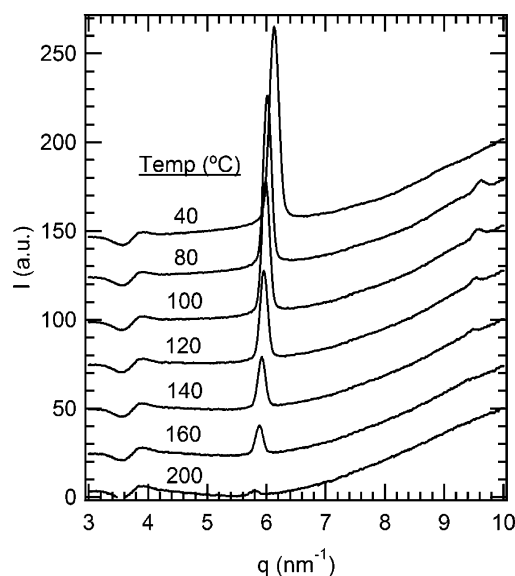


Figure 9. Wide-angle X-ray scattering of PPVbPI-72. The primary peak around 6 nm^{-1} corresponds to the spacing between rod blocks. The intensity of this peak decreases with increasing temperature but shows no discontinuity at the transition temperatures identified by SAXS, optical microscopy, or depolarized light scattering. The dip and rise at 3.6 nm^{-1} are a result of error in the empty cell scattering subtraction, as the Kapton windows of the empty cell show a large feature at that q value.

volume fractions the disordering effect of mixing rod and coil blocks dominates to such an extent that the rod-rod spacing is disrupted even at low temperatures.

Transitions in the Ordered Phase. As with coil-coil block copolymers, the domain spacing of rod-coil copolymers is expected to be a function of the polymer's radius of gyration and temperature, and the domain spacing provides clues as to the relative stability of different ordered phases. In rod-coil block copolymers, the lamellar phase may consist of several different rod arrangements. Rods may form bilayers or monolayers, as shown in Figure 6. Furthermore, the rods may be

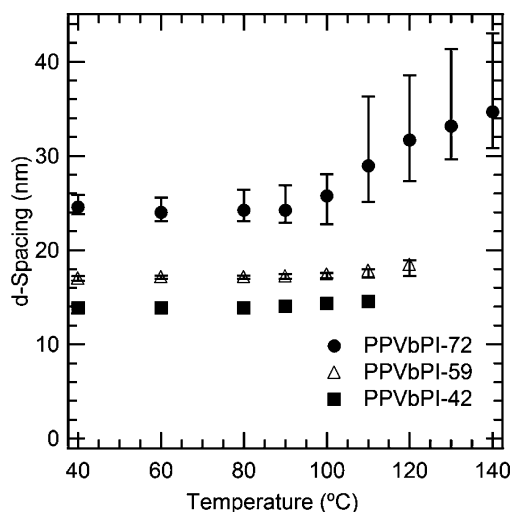


Figure 10. Lamellar layer spacings in ordered block copolymers. The increase in domain spacing with temperature suggests a transition in lamellar morphologies.

oriented perpendicular to the rod-coil interface or tilted at some angle off of perpendicular.

The relative stability of these lamellar phases is the subject of several theoretical predictions. Bilayers minimize the unfavorable interaction between the blocks and may be preferred in highly segregated regimes.⁴¹ Semenov and co-workers predict, however, that since the bilayer phase affords less interfacial area to the coil, the chain must stretch more to adopt this configuration.^{23,24} For this reason, the bilayer is not predicted to occur in the weakly segregated limit or in block copolymers with large coil fractions.^{23,31} Experimentally, it is difficult to ascertain exact thicknesses of individual PPV lamellae from our TEM images due to broadened interfaces, which may result from both staining and interpenetration in this weakly segregated regime. Comparison of the lamellar spacing (obtained from SAXS) to block copolymer dimensions (Table 1) indicates that either the rods are arranged in greatly tilted bilayers or in monolayers. In either monolayers or bilayers, the contour length of the block copolymer is greater than the domain spacing, so the coils are never fully extended. No transition between bilayer and monolayer arrangements (as would be indicated by a discontinuity in domain spacings observed in X-ray scattering or a transition in DSC) was observed.

Within the lamellar phase, the rod blocks may also assume tilted or perpendicular orientations. In fact, several theoretical works suggest rods tilted relative to the lamellar normal (smectic C) will reorient parallel to the normal (smectic A) as temperature is increased.^{31,35} This reorientation will result in changes in domain spacing as the lamellar distance increases to accommodate the rod's length, and the coil rearranges to accommodate a loss in interfacial area. As seen in Figure 10, PPVbPI-42 and PPVbPI-59 domains do not appear to change in size with temperature below the microphase disorder temperature. From the scattering spectra of PSbPPV-72 (Figure 4), however, the first- and second-order peak positions appear to be temperature dependent, as shown in Figure 11. As the microphase disorder transition is approached, the intensity of the first-order peak dramatically decreases, and errors in background subtraction become substantial, as reflected in the error bars for the data from PSbPPV-72. In particular, the low q side of the peak appears to be more

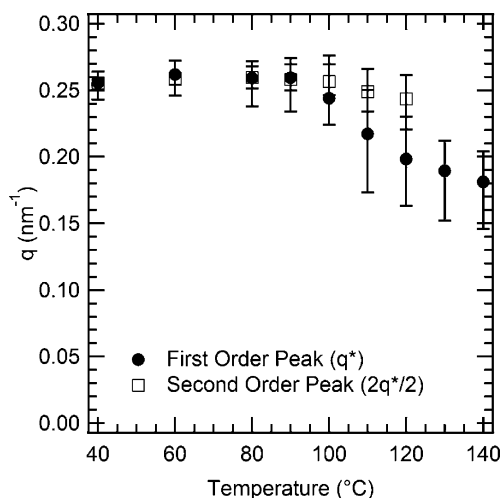


Figure 11. Peak positions for first- and second-order scattering in PSbPPV-72. Error bars reflect uncertainty in background subtraction in these weakly scattering samples. An obvious decrease in domain spacing is seen and may be attributed to subtle changes in liquid crystalline structure.

affected by background scattering, so the error bars reflect more uncertainty in this direction. Ideally, the first- and second-order peaks ought to track exactly with temperature, and as shown in Figure 11, the error bars overlap, but complete agreement is not present. At this early stage, we do not understand the origin of this discrepancy. Conservative comparisons of the shifts in the first- and second-order peaks as a function of temperature, however, result in an estimate of domain spacing changes of at least 5 nm. A better understanding of the detailed structure of the lamellae and the chain shape as a function of temperature is the subject of ongoing work.

Weak Segregation Limit (WSL) Phase Diagram.

Using the aggregate data from scattering, TEM, DPLS, optical microscopy, and accompanying analysis, a phase diagram for weakly segregated rod-coil block copolymers is assembled, as shown in Figure 12. At low temperatures, the polymers form lamellar phases. Upon heating, the lamellae disorder into a nematic phase. The nematic region is widest for large rod fractions, and it appears to pinch off as the coil fraction is increased. After further heating the liquid crystalline clearing temperature is reached and the polymers transition into the isotropic phase. Polymers with the largest rod fractions have a broad nematic region and high liquid crystalline clearing temperature, consistent with the behavior of the PPV homopolymer. The polymer with the largest coil fraction is isotropic throughout the experimentally observable range, consistent with the PI homopolymer behavior.

The phase diagram for this PPV-*b*-PI system compares favorably with theoretical calculations by Landau expansions and SCFT. The Landau expansion calculations, valid in the weak segregation limit, predict transitions from isotropic to nematic at lower coil fractions and transitions directly to a microphase-separated structure at higher coil fractions.^{28,29} The theory also predicts a wide nematic region at low coil fractions and a broad isotropic region at high coil regions, in good agreement with experimental results. The experimentally observed pinching off of the nematic region with increasing coil fraction suggests that the theoretically predicted direct isotropic to lamellar tran-

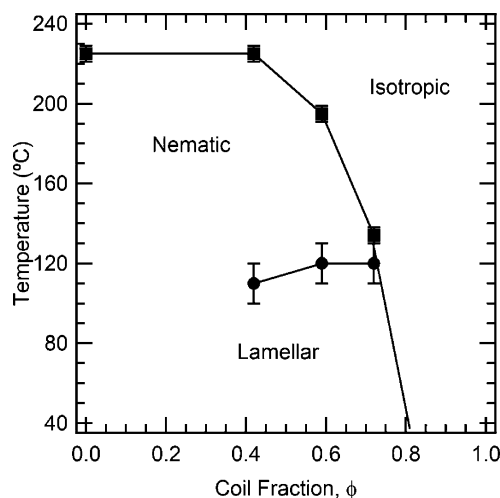


Figure 12. Experimental phase diagram for rod-coil block copolymers in the weak segregation limit. In the above phase diagram, rod length is kept constant while the coil length is changed. As a result, the geometrical factor, ν , ranges from 0.3 to 0.7 in the above plot. For coil fractions below ~ 0.85 , polymers transition from an isotropic to nematic to lamellar structure upon cooling, and with increasing coil fraction the nematic region becomes increasingly narrow. For coil fractions above 0.85, the isotropic phase spans the entire experimentally accessible range. The lamellar region potentially contains a variety of layered structures, including smectic A-like and smectic C-like regions.

sition would be observed in a more strongly segregated system. These results indicate that above the ODT anisotropic interactions between rods dominate the free energy, creating a nematic phase. Sufficiently large coil fractions modulate this rod-rod interaction, lowering the NI transition temperature, and for coil fractions greater than 0.85, the isotropic phase is the only experimentally accessible one. Considering the highly miscible nature of this system, agreement between experiment and the WSL calculations is not surprising.

These experimental results also agree qualitatively with the results of one-dimensional self-consistent-field theory. The calculations of Matsen and Barrett³¹ and Pryamitsyn and Ganesan³⁵ qualitatively predict the shape of the isotropic, nematic, and lamellar regions. The experimental result bears less resemblance to the 2D calculations performed on systems with lower values of ν (higher rod aspect ratio)³⁵ in which Pryamitsyn and Ganesan predicted strip or puck phases at high coil fractions, lamellar structures for more symmetric polymers, and bilayer or arrowhead structures for low coil fractions. These more complex phases were not experimentally observed, possibly due to the weakly segregated nature of our system or the difference in ν between the experiment and simulation.

The PPV-*b*-PI system showed some similar structures to those previously observed in high molecular weight rod-coil systems. Polymeric polypeptide-coil copolymers were⁵⁻⁹ observed to form only lamellar morphologies across a range of coil fractions similar to this study. In addition, our smectic-like lamellar phases are similar to those seen in mesogen jacketed block copolymers⁵¹ and solution self-assembled high molecular weight rod-coil systems;^{47,48} both are characterized by the formation of layers, rod tilting, and locally planar interfaces between the microdomains. However, we do not observe the more unusual phases seen in the solution self-assembled systems. The difference may be

due to the highly segregated nature of these systems or to the effect of lyotropic as opposed to thermotropic self-assembly.

Most importantly, the phase behavior of our weakly segregated polymeric system differs from previous thermodynamic observations, all of which were conducted on shorter rod-coil systems. Li et al. observed lamellae across a wide range of coil fractions in a lower molecular weight system based on PPV and PI. Their material also exhibited an ODT, but this temperature corresponded to the liquid crystalline clearing temperature and a separate nematic region was not observed.⁴¹ Radzilowski and Stupp synthesized a rod-coil block copolymer with an oligomeric rod attached by a flexible spacer to a short coil.³⁸⁻⁴⁰ They found thermodynamic transitions between an ordered and disordered state similar to those observed here; however, they saw a wide region of puck and strip structures across the same range of volume fractions where lamellae and disordered phases were observed in this study. These differences may be due to the length or aspect ratio of the rod block. Microphases of larger rod blocks are expected to have a higher bending energy, making them less able to accommodate curvature and reduce chain crowding in a puck or strip phase. The impact of aspect ratio on phase behavior can be understood on a scaling law basis^{25,27} by the greater interfacial area per chain allowed in the DEH-PPV system, resulting in a reduced force for chain contraction. Since the formation of pucks and strips is theoretically driven by reducing the entropy of chain stretching, a high aspect ratio system is expected to favor pucks. In terms of molecular parameters,³⁵ Radzilowski and Stupp's polymers have a greater monomer unit length in the rod block (smaller rod diameter) than the side-chain functionalized PPV, giving them a smaller value of ν . Other authors have also observed nonlamellar and nonsmectic phases in short rod-coil block oligomers.⁴²⁻⁴⁵ A direct comparison with the oligomer studies to determine whether puck and strip phases are stable in polymeric materials would require producing PPV-*b*-PI polymers of higher molecular weight to match ν and obtain polymers that are ordered across the entire compositional range of interest; this is the subject of ongoing research.

Conclusions

A series of monodisperse rod-coil block copolymers were prepared that could be parametrized in terms of polymeric theories, making it useful for studying fundamental phase behavior in rod-coil systems. Because of thermodynamic compatibilization of the rods and coils, these polymers are in the weak segregation limit, and order-disorder and nematic-isotropic transitions could be accessed. The polymers were characterized by scattering and microscopy to identify the ordered structure and phase transitions. At high temperatures and coil fractions, the polymers exhibit an isotropic phase, with transitions to a broad nematic region followed by lamellar (smectic-like) phases with decreasing temperature. Lamellar grains are characterized by long persistence lengths and broken lamellae at grain boundaries due to the high elastic energy of bending in the rod microphase. At some volume fractions, there is a change in domain spacing with temperature which suggests a reorientation of the rods within the lamellae. The experimental phase diagram derived from these observations is in qualitative agreement with weak segregation limit theories of rod-coil block copolymers

and one-dimensional SCFT calculations. The results of this study are promising for the use of self-assembly in rod-coil systems. By employing weakly segregated materials, isotropic, nematic, and lamellar phases can be self-assembled from functional rodlike materials such as semiconducting polymers or biomaterials, offering a level of structural control that will be useful in their application.

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