Monodisperse "Rodcoil" Copolymers

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Block copolymers of rigid, rodlike blocks coupled to flexible, coillike blocks offer the opportunity to study new aspects of microphase separation behavior. We term these polymers "rodcoil" in order to emphasize the difference in flexibility between the component blocks. This flexibility difference enriches the thermodynamic description of microphase separation, and unique phase behavior and microstructures may be discovered in experimental systems. As in coil–coil block copolymers, the chemical incompatibility between rod and coil blocks drives them to phase separate. However, the rigidity and prolate shape of rod blocks may allow them to assemble with orientational order. Theoretical work by Semenov and Vasilenko suggests that if the enthalpic and entropic penalties of having flexible segments intermixed with ordered rod segments are too great, then a layered, or smectic, ordering of the rods may occur.[1] Furthermore, this ordered packing of rods forces a higher density of coil chains at the rod–coil interface, and as a result much greater conformational stretching is required of the coil blocks than in analogous coil–coil block copolymers. Williams and Fredrickson have predicted that the amount of coil stretching at the rod–coil interface may influence the lateral dimensions of rod layers.[2] As coil length increases, chain stretching may be relieved if the lamellar structures separate into disklike fragments at the expense of increased surface energy. As another mechanism for relieving coil stretching, smectic layer structures may undergo a smectic A to smectic C transition, resulting in rods tilted with respect to the layer normal.[3,4]

Our objective here has been to initiate experimental work on the phase and scaling behavior of rod–coil systems. In this paper we report on the synthesis and preliminary characterization of the first monodisperse rodcoil copolymer in which both rod and coil segments are part of the molecular backbone. The effort described here was first reported earlier this year.[5] Figure 1 shows a representation by molecular graphics of an energy-minimized conformation of our rodcoil polymer. Also the rodlike segment when detached from the coil exhibits liquid crystalline behavior demonstrating the stiff segment's high aspect ratio in a condensed phase. The thermotropic behavior of the rod component may lead to the formation of various mesophases with changing temperature, and the long-range order may be influenced by external fields. The coils may also act to isolate liquid crystalline domains into discrete monolayers, forming nanoscale liquid crystals. As far as we know the only work reported so far involves "side-chain" liquid crystalline polymers coupled to polystyrene[6] and poly(methyl methacrylate),[7] but here the rod and coil components are not part of the same molecular backbone. Therefore, these systems lack an abrupt change in backbone rigidity along the chain's contour length. One of the groups working on side-chain systems[6] reported relatively uniform rod and coil regions in the microphase-separated state.

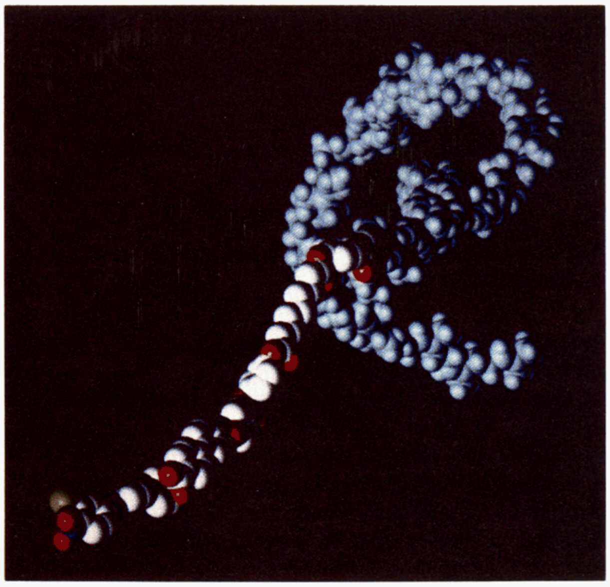


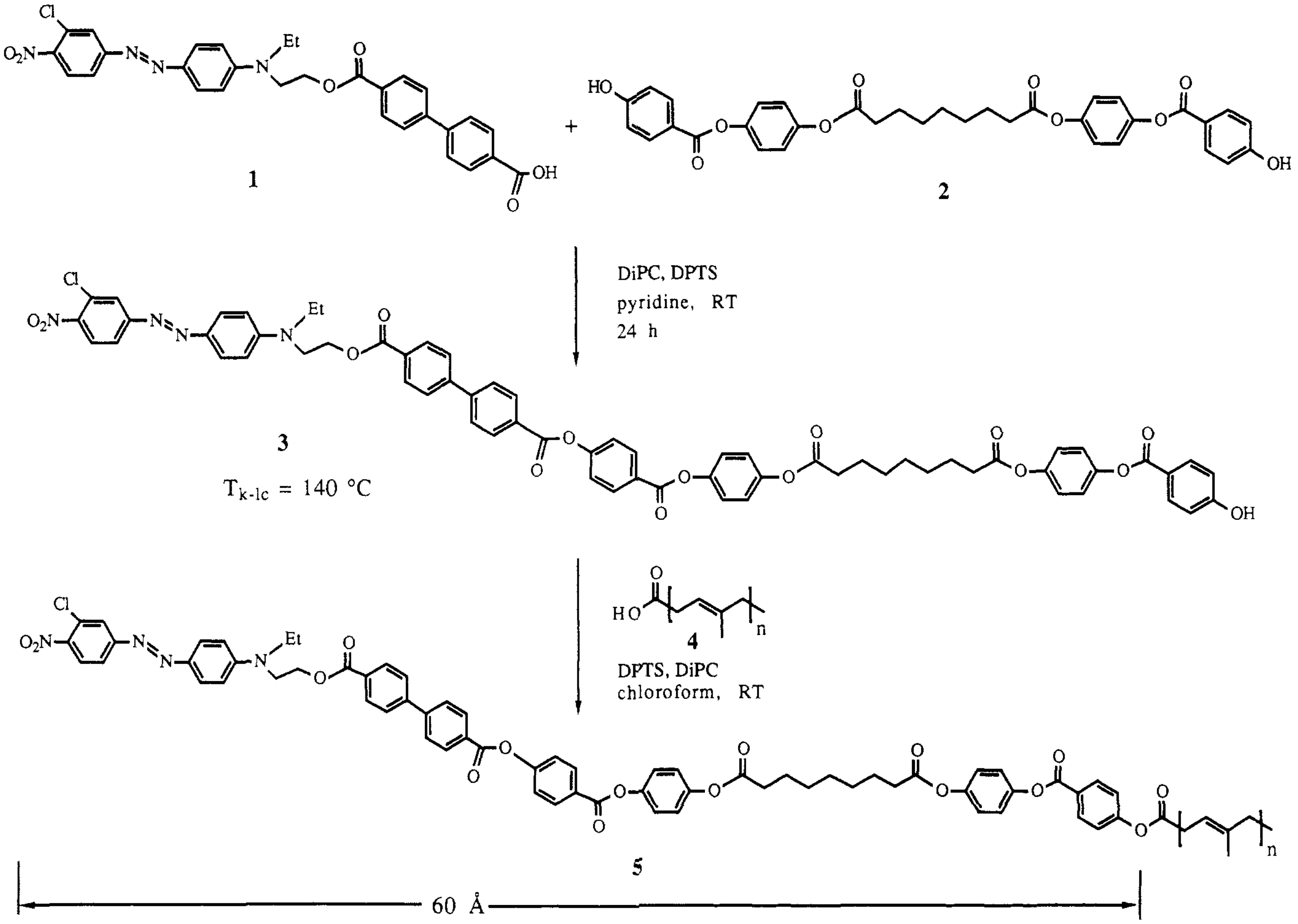
Figure 1. Molecular graphics representation of the energy-minimized conformation of an isolated molecule of rodcoil **5** showing both rod and coil segments covalently linked to share the same molecular backbone.

Research in the area of rod–coil structures would be greatly facilitated by access to systems of well-defined molar mass. Most experimental work to date on rod–coil structures has been performed on diblock or triblock systems in which polymers such as polybutadiene or polystyrene are coupled to polypeptide blocks. In these systems the polypeptide blocks assume a rodlike α–helical conformation, and microphase-separated layered structures have been reported.[8–10] However, polypeptides are difficult to synthesize with narrow molecular weight distributions and are also prone to folding. The system we are currently studying allows us to synthesize monodisperse rod and coil segments.

The coil block of the rodcoil polymer reported here is a polyisoprene segment prepared by anionic polymerization in moisture and oxygen-free benzene. Polymerization was initiated by adding *n*-butyllithium, 1.6 M in hexane as received from Aldrich, to the reaction vessel via a gas-tight syringe. After 30 min of reaction, the vessel was cooled to 0 °C and dry and deoxygenated THF was added as a 1:3 mixture of THF/benzene. After 2 min ultradry CO_2 gas was bubbled into the reaction mixture to terminate the living anions, causing the yellow solution to turn colorless. The solution was then poured into 400 mL of a 0.1 N HCl/methanol solution, resulting in carboxylated polyisoprene end groups. The polymer precipitate was recovered and dried overnight under vacuum at 60 °C. Separation of carboxylated and uncarboxylated polyisoprene was achieved by flash chromatography using 100% methylene chloride. The uncarboxylated and carboxylated polyisoprene had R_f values of 1.0 and 0.0, respectively.

The rod portion of the rodcoil copolymer consists of two main fragments, **1** and **2**, shown in Scheme I. The terminal fragment **1** contains an azo dye, 4-[ethyl-(2-hydroxyethyl)amino]-3′-chloro-4′-nitroazobenzene (Disperse Red 13), coupled to the rigid monomer 4,4′-biphenyldicarboxylic acid. In a 500-mL single-neck round-bottomed flask fitted with a Claisen adapter, rubber septum, and nitrogen adapter was placed 0.5 g (1.43 mmol) of the dye, 1.74 g (7.15 mmol) of 4,4′-biphenyldicarboxylic acid, 0.084 g (0.29 mmol) of 4-(*N*,*N*′-dimethylamino)-pyridinium 4-toluenesulfonate (DPTS),[11] 0.4 mL (2.5

Scheme I



mmol) of diisopropylcarbodiimide (DiPC), and 20 mL of pyridine. The solution was stirred for 24 h at room temperature under a nitrogen atmosphere and then poured into 500 mL of methanol. The precipitate was collected, washed with methanol, and then dried under vacuum at 80 °C for 24 h. Further purification of the crude product by flash chromatography was achieved using a 9:1 mixture of chloroform/methanol. The product had a R_f value of 0.4, and the yield was 40%.

The synthesis of **2** involved a procedure used earlier for a homologous compound in our laboratory[12] (different aliphatic spacer). The rod segment, **3**, was then synthesized by adding 0.074 g (0.13 mmol) of **1**, 0.2 g (0.33 mmol) of **2**, 0.019 g (0.065 mmol) of DPTS, 0.05 mL (0.325 mmol) of DiPC, and 20 mL of pyridine to a single-neck flask fitted with a Claisen adapter, rubber septum, and nitrogen inlet. The solution was stirred at room temperature for 24 h under a nitrogen atmosphere and poured into methanol. The precipitate was then recovered and dried at 60 °C. Further purification of the crude product was achieved by flash chromatography using a 95:5 mixture of methylene chloride/ethyl acetate ($R_f = 0.6$). Preparative liquid chromatography (LC) was required using the same mixture as before for further purification of the product from *N*-acylureas formed during the synthesis. The purified product, **3**, is a red material which was characterized by polarized optical microscopy. Using a Linkham THM 600 hot stage on a Leitz Laborlux 12 POL, a liquid crystalline texture was observed upon melting at 140 °C (Figure 2). The coupling of carboxylated polyisoprene, **4**, to mesogen **3** involved the mild esterification method described by Moore and Stupp[11] using chloroform as the solvent. Further purification of the product was achieved by flash chromatography using a 9:1 mixture of methylene chloride/ethyl acetate. Rodcoil product **5** is a red, rubberlike substance or viscous liquid depending on the molar mass of the polyisoprene segment. Compared to the coil homopolymer, the product displays a more rubbery behavior and exhibits a higher resistance to flow under its own weight.

The molecular weight and polydispersity of the polyisoprene was characterized before and after coupling to the mesogen using a Waters GPC and THF as the eluent. The specific rodcoil copolymer characterized here by transmission electron microscopy (TEM) had a weight-average molecular weight of 7686 (relative to polystyrene) and a rod volume fraction, f_{rod}, of 0.20, calculated using the method in ref 1. We find that polydispersities remain the same before and after coupling to the mesogen and range between 1.03 and 1.13.

We carried out a preliminary characterization of morphology in the rodcoil product by TEM. Samples were prepared by casting films from dilute solution (0.05 wt %) onto carbon-coated glass slides in a solvent atmosphere. The solvent used was cyclohexane, good for the polyisoprene but poor for the mesogen, and the solutions sat unstirred for 24 h before films were cast. The films were held under vacuum for 24 h in order to remove solvent and then floated onto water, picked up on copper grids, and exposed to vapors of OsO_4 from a 4% aqueous solution. Samples were also prepared by annealing at 140 °C under vacuum for 12 h before exposing to OsO_4.

Examination in a Phillips CM-12 at 100 kV revealed microphase-separated structures immediately after casting films. Since OsO_4 selectively stains the polyisoprene, regions containing predominantly coil segments appear

Figure 2. Optical micrograph between cross polarizers revealing a liquid crystalline phase in compound **3** at 164 °C (magnification 320×).

dark relative to domains enriched in rod segments. As shown in Figure 3, the as-cast microstructure of the rodcoil polymer shows strips or ribbons and small aggregates containing rod segments in a matrix of polyisoprene. The strips either assemble in parallel or remain isolated in which case they reveal curvature and occasionally intersect themselves or other strips. They measure approximately 100 Å in thickness and can have lengths of up to 1 μm. Surrounding them are small aggregates of rougly the same thickness that in places appear to form rows and/or register in parallel with the sides of strips. Upon annealing the morphology appears predominantly lamellar with regularly spaced rod and coil domains, which form a fingerprint-like texture (see Figure 4). The average thickness and length of the rod layers decrease after annealing to 70 Å and 0.1 μm, respectively, while the coil layers average 50 Å in thickness. The layers vary in orientation across the sample in ways that are reminiscent of disclinations.

Our results clearly show the propensity of the rodcoil system to microphase separate and form periodic structures. We do not know yet the full details of the three-dimensional morphology of the periodic structures or of the orientation of the rodlike segments' director relative to the plane of thin films. We also do not know the conformations that rod and coil segments assume as they pack within the structures. The thickness of the rod domains in the annealed sample approximates that of the extended rodlike, mesogenic, segment. This suggests that rod domains, isolated by layers of coil domains, could be forming nanoscale liquid crystals in the product's micro-

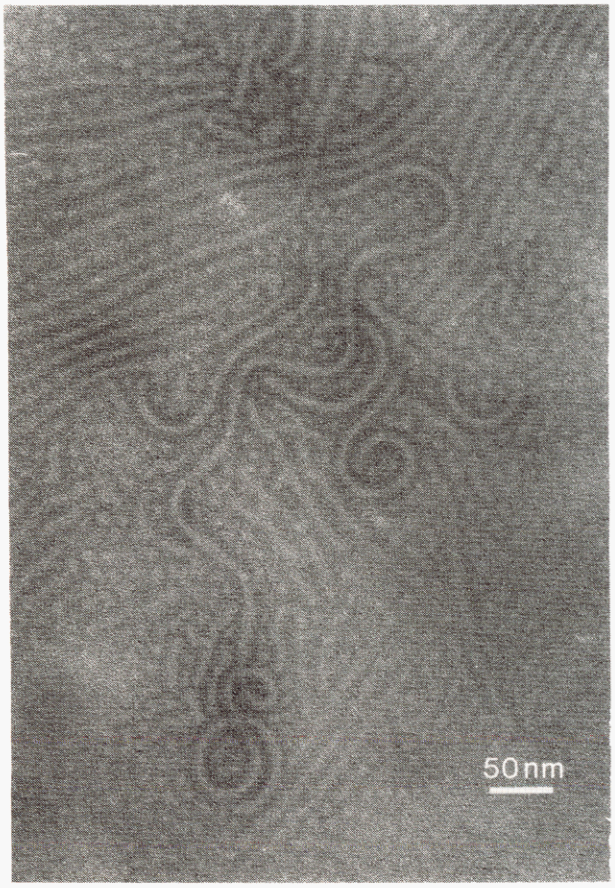


Figure 3. TEM micrograph of rodcoil polymer **5** before annealing the film cast from cyclohexane. Rodlike segments are found within the lighter regions measuring 100 Å, while the darker regions contain coillike segments.

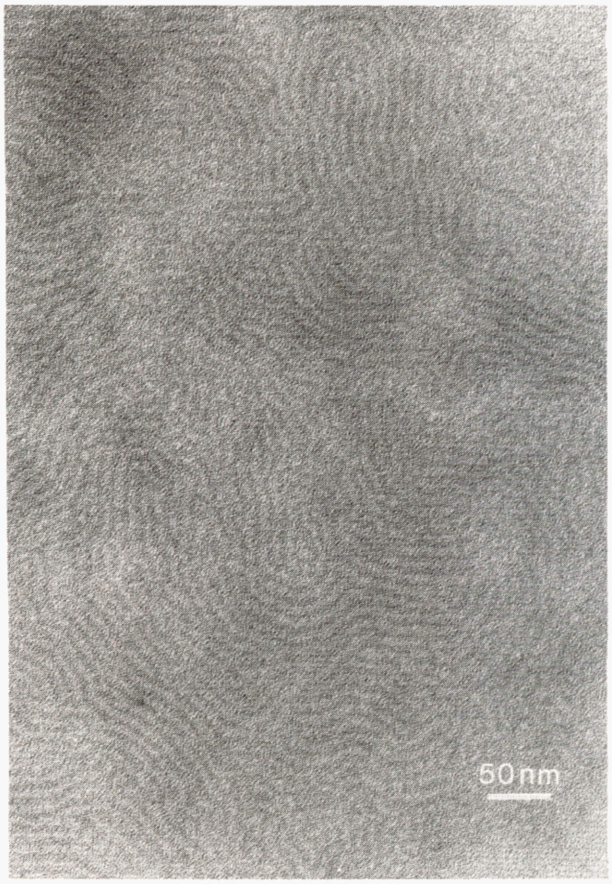


Figure 4. TEM micrograph of rodcoil polymer **5** after annealing at 140 °C for 12 h and staining with OsO_4. The rod-containing domains have an average thickness of 70 Å.

structure. While the exact temperatures of order–disorder transitions are not known, preliminary work indicates that disordering transitions indeed occur in the range 80–220 °C. A more detailed study of the system is underway which includes the synthesis of rodcoils having varying f_{rod} values.

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