Ureidotriazine-Based Supramolecular Copolymers

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Received October 9, 2002
Revised Manuscript Received January 6, 2003

Supramolecular polymers,[1] in which noncovalent interactions, such as hydrogen bonds[2] or metal coordination,[3] keep the repeating units together, offer exciting prospects for materials with novel properties because the interactions are reversible. Functionalization of covalent polymers with hydrogen-bonding groups has also proven to be a fertile concept in polymer science.[4] Recently, we have introduced supramolecular polymers based on the self-complementary quadruple hydrogen bonding units ureidopyrimidinone[5] (UPy) and ureidotriazine[6] (UTr). Because of the moderate (2×10^4 M^{-1}, UTr)[7] to high (6×10^7 M^{-1}, UPy)[8] association constants between the units, reversible polymers with a high degree of polymerization were obtained. UTr -based supramolecular polymers **1** with trialkoxyphenyl substituents were shown to form highly ordered, helical columnar structures in alkane solvents due to a combination of hydrogen-bonding and solvophobic interactions.[6]

Like their covalent counterparts,[9] supramolecular copolymers will have the possibility to phase separate, giving a wealth of microphase-separated morphologies, provided the value of χN, the product of the Flory−Huggins parameter χ and the total degree of polymerization N, is sufficiently high, and the interactions between the segments are strong.[10] The combination of reversibility and phase separation gives new opportunities for functional materials.[11−13] When the noncovalent links between monomer units in a supramolecular copolymer are self-complementary, the block size is not fixed, and depending on the conditions the structure may vary from random copolymer through a microphase-separated block copolymer to a macrophase-separated blend. In the present paper we report on ureidotriazine-based supramolecular copolymers consisting of rigid-rod-like and coil-like segments.

The rigid-rod-like segments are formed by monomers **1**, while the random coils are formed by poly(ethylene/butylene)s that are functionalized with either one or two ureidotriazine units (molecules **2** or **3**, respectively) (Chart 1). The concept is schematically represented in Figure 1.

Compounds **2** and **3** were prepared from hydroxy-terminated poly(ethylene butylene)s (M_w 3900 and 3500 g/mol, respectively) by cyanoethylation with acrylonitrile, reduction to the amine-terminated polymer, conversion to the isocyanate with phosgene, and finally reaction with trialkoxyphenyldiaminotriazine to give the UTr-terminated polymers. For compound **2**, an average molecular weight (M_n) of 4372 g mol^{-1} and a polydispersity of 1.13 were found with MALDI−TOF (matrix-assisted laser desorption ionization−time-of-flight) MS. The ^{1}H NMR spectra of **2** and **3** in CDCl$_3$ show the characteristic NH signals of dimerized UTr units at 10.2, 9.85, and 9.25 ppm, showing that UTr association is not prevented by the polymer chains. Functionalization with UTr has a strong effect on the materials properties of the telechelic poly(ethylene/butylene), which is transformed from a viscous liquid to a soft and elastic solid upon functionalization.

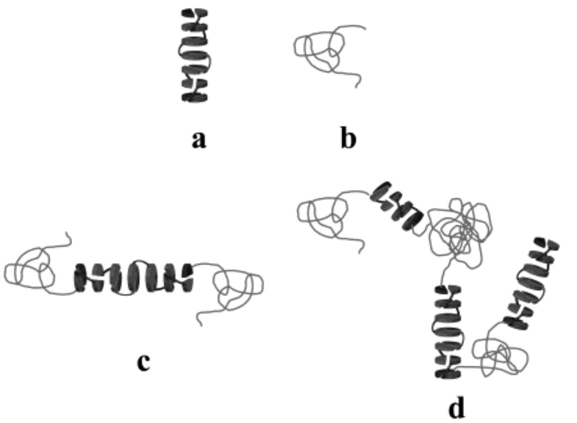

Figure 1. Schematic representation of the organization of **1** in helical columns (a), random coils of poly(ethylene/butylene) (b), block copolymer of **1** and **2** (c), and block copolymer of **1** and **3** (d).

The aggregation of compounds **2** and **3** in dodecane-d_{26} was studied in detail using small-angle neutron scattering (SANS) on 0.5 and 2 wt % solutions (Figure 2).

The scattered intensities were found to be fitted well using a homogeneous cylinder model. Interactions between the aggregates were neglected, and only the form factor of cylindrical structures was used to fit the scattering cross section dΣ/dΩ(Q) (see Supporting Information).

The fitted cross-sectional radius was found to be in the range 23−25 Å for **2** and **3**, compared to 15 Å for columnar aggregates of **1**.[6] The fitted length of the aggregates (previously established to be approximately 70 nm for a 0.2 wt % solution of **1**)[6] was fairly concentration independent at 10 nm for **2**, while in aggregates of bifunctional compound **3**, the fitted length was strongly concentration dependent and increased from 20 ± 1 to 205 ± 64 nm when the concentration was increased from 0.5 to 2 wt %.

Copolymer formation of bifunctional **1** with monofunctional **2** was studied with rheology in dodecane, a solvent in which **1** forms highly viscous solutions which show pronounced shear thinning caused by the presence of extended columnar aggregates. Measurements on 10^{-3} M solutions of **1** containing increasing amounts of monofunctional **2** show that the presence of the latter molecule strongly reduces solution viscosity (Figure 3a), indicating that **2** interacts with **1** to form copolymers. Presumably, **2** acts as a chain stopper which reduces the size of aggregates of **1**.

Further evidence for the formation of supramolecular triblock copolymer structures from **1** and **2** in dodecane

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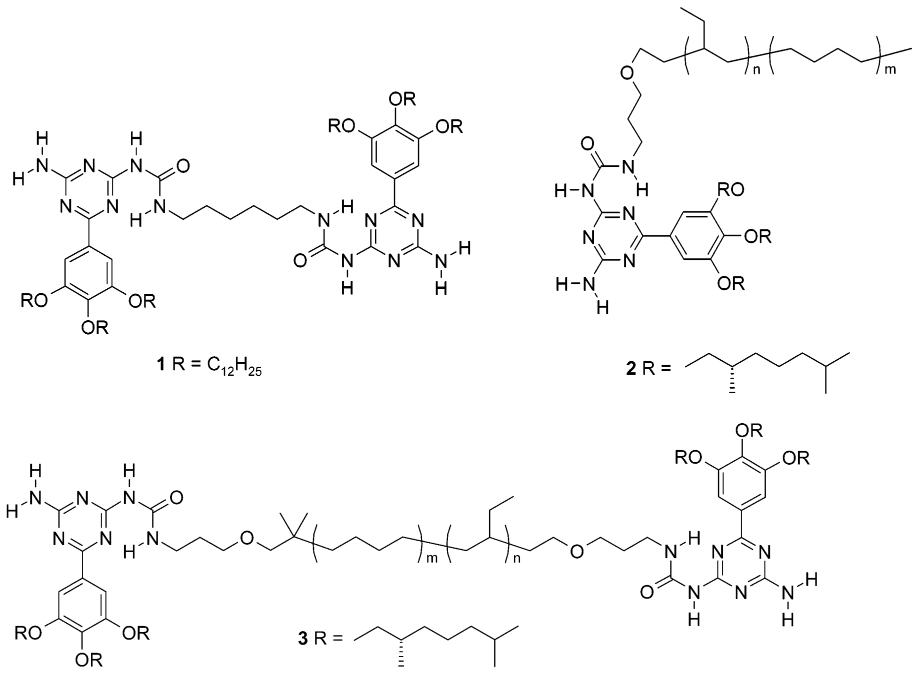
10.1021/ma025723c CCC: $25.00

Chart 1



1 R = $C_{12}H_{25}$

2 R =

3 R =

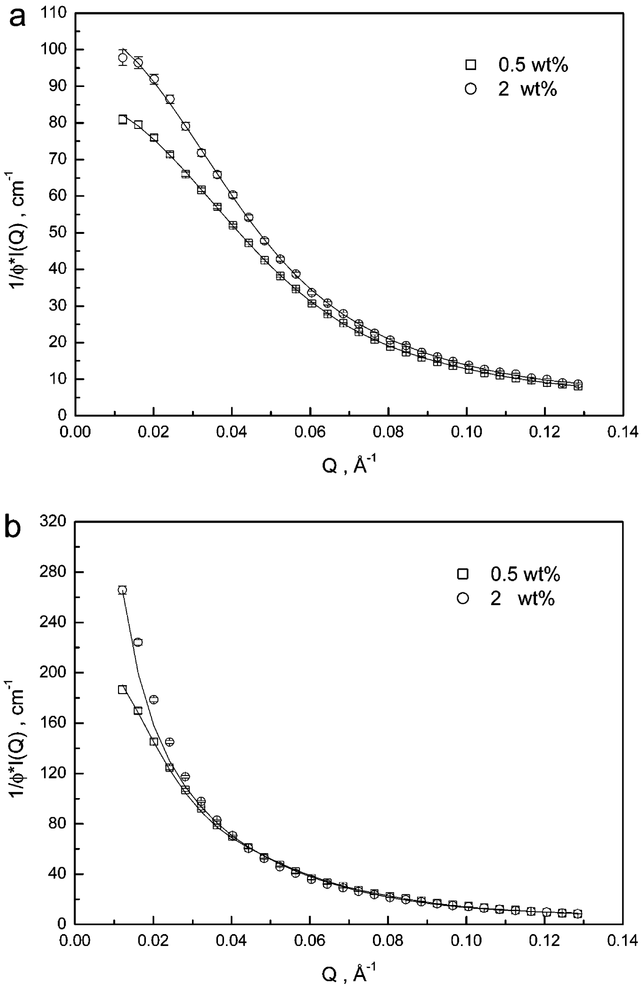


Figure 2. SANS data for solutions of compounds **2** (a) and **3** (b) at 0.5 and 2 wt % in dodecane-d_{26}.

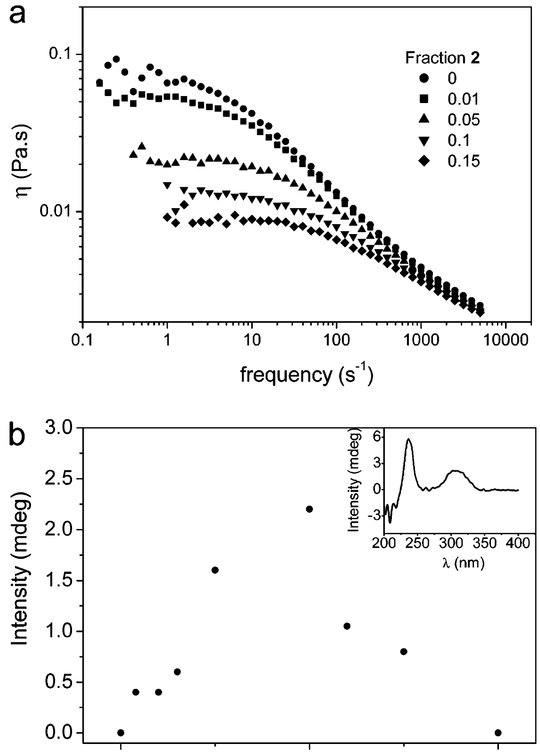


Figure 3. (a) Steady-state shear measurements of mixed solutions of **1** (1×10^{-3} M) and **2** in dodecane at 20 °C. (b) "Sergeant and soldiers" experiment showing the intensity of the CD effect at $\lambda = 306$ nm of dodecane solutions of achiral **1** containing different fractions of chiral **2**. Inset: CD spectrum of an equimolar mixture of **1** and **2**.

solution comes from CD spectroscopy. The CD spectrum of achiral compound **1**, which was shown to form helical columnar aggregates in dodecane solution,[6] does not show a Cotton effect, because right- and left-handed helical aggregates are equally abundant. In dodecane solutions of **2**, with chiral side chains attached to the UTr group, Cotton effects are not observed either, indicating the absence of a preferred helical superstructure. Mixtures of achiral **1** and chiral **2** were studied in a "sergeant and soldiers"[14] kind of experiment, in which the relative ratio of **1** and **2** is varied at constant total

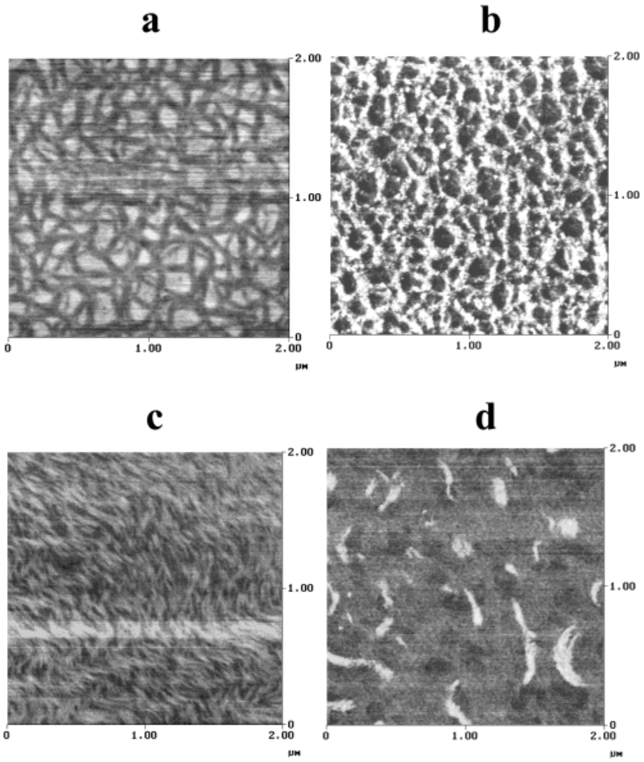


Figure 4. AFM phase images of 1:1 (w/w) blends of **1** with **2** and **3**: (a) spin-coated sample of **1** and **2**; (b) spin-coated sample of **1** and **3**; (c) drop-cast sample of **1** and **3**; (d) sample (c) annealed at 60 °C for 1 h.

concentration of UTr chromophores. Remarkably, a Cotton effect is observed in the mixtures, with a maximum intensity when equal amounts of **1** and **2** are present (Figure 3b). The experiment shows that in dodecane solution molecules of **1** bias the helical sense of columns of **2**, demonstrating the formation of supramolecular block copolymers of **1** and **2**.

In the solid state, copolymers of **1** with **2** or **3**, prepared by evaporation of mixed hexane solutions containing various ratio's of these molecules, were studied using DSC, optical polarization microscopy (OPM), and AFM. DSC thermograms of the pure compound **2** shows a T_g at -64 °C and a melting point at -23 °C, approximately the same values as in the OH-terminated PEB starting material. The T_g of **3** is found at -56 °C, and similar to telechelic PEB functionalized with ureidopyrimidone groups,[15] the melt transition at -23 °C is suppressed.

Supramolecular polymer **1** is a discotic liquid crystalline material with a melting temperature of -25 °C, a mesophase to mesophase transition at 148 °C, and a clearing point of 178 °C.[6] In 1:1 (w/w) blends of **1** with **2** or **3**, the clearing point shifts from 178 to 186 and 188 °C for blends with **2** and **3**, respectively, while the other transitions of pure **1** are not observed in the blends.

Blending behavior of **1** with **2** or **3** was also studied with tapping mode AFM on thin films, prepared by spin-coating and drop-casting of hexane solutions on glass plates. No contrast was observed in films of pure **1**, **2**, and **3**. However, in spin-coated 1:1 (w/w) blends of **1** with either **2** or **3**, fiberlike aggregates were observed (Figure 4).

The morphology of the blends is dependent on sample history. Whereas spin-coated samples of blends of **1** with **3** gave fiberlike structures with an average thickness of 42 nm (Figure 4b), drop-cast samples resulted in smaller aggregates with sizes between 17 and 42 nm (Figure 4c). However, upon annealing the drop-cast sample for 1 h at 60 °C, larger clusters of up to 90 nm are formed (Figure 4d), surrounded by a matrix consisting of soft and hard segments, showing that macrophase separation between hard domains of **1** and softer domains of **3** is occurring. The morphology of the supramolecular block copolymers does not change when the amount of hard blocks is increased.

We conclude that polymers **2** and **3** form supramolecular copolymers with **1** in solution as well as in bulk. In solution, copolymer formation between **1** and **2** is witnessed by significant induction of chirality from chiral compound **2** to achiral **1**. In bulk, phase separation between components results in a fibrillar morphology which coarsens upon annealing. In the present system, incompatibility between components results in phase separation, although at the same time strong interaction between the phases is maintained through hydrogen bonding. In future work in this area we will further explore this unique feature of supramolecular copolymers.

Acknowledgment. We thank the Laboratory Leon Brillouin (France) for supplying beam time and Dr. A. Brulet for help during SANS measurements.

Supporting Information Available: Experimental details of the synthesis of **2** and **3**; MALDI-TOF MS spectrum of **2**; DSC traces of **1**, **2**, **3** and their blends; details of the fitting procedure for the SANS data and a table of the fitted dimensions of the aggregates of **2** and **3** in dodecane-d_{26}. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA025723C