

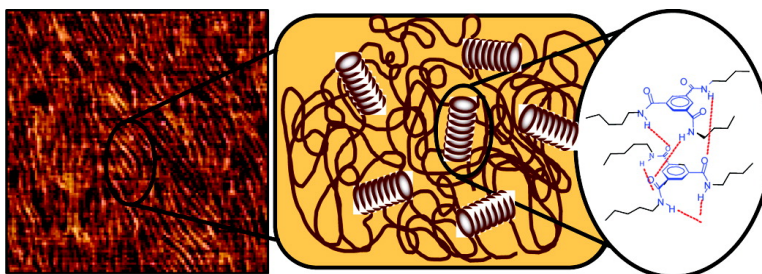
Communication

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Supramolecular Materials from Benzene-1,3,5-tricarboxamide-Based Nanorods

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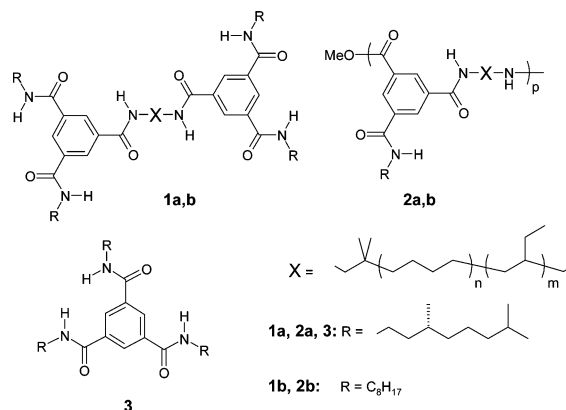
Motifs exhibiting directional and reversible interactions have been the foundation for the development of supramolecular polymers, i.e., polymers exhibiting macroscopic material properties as a result of noncovalent interactions between the monomers or macromers.^{1–3} Not only is the strength of the noncovalent interactions important to obtain polymer properties but also is the propensity of the motif to phase segregate, as convincingly shown by Stadler and Rowan.^{4,5} This phase segregation results in strong multiple cross-linking points with order in two or three dimensions within the soft polymer matrix, leading to materials with thermoplastic elastomeric properties. Bouteiller recently proposed a class of materials that would physically cross-link by the self-association of functional groups forming long supramolecular chains in one dimension (1D).⁶ Such well-defined nanorods embedded in an amorphous polymer matrix would be an interesting addition to the field of supramolecular polymer chemistry since they would combine high strength and spatial control with reversibility. Our group recently showed the presence of 1D columnar structures in telechelic poly(ethylene butylene) (PEB) and poly(ϵ -caprolactone) functionalized with both lateral and end-to-end hydrogen-bonding functionalities by the introduction of both the ureidopyrimidone (Upy) and urea group.^{7,8}

We here propose the benzene-1,3,5-tricarboxamide (BTA) motif for supramolecular materials based on phase segregated nanorods in a polymer matrix.⁹ The BTA motif forms a 1D polymer in solution and in the solid state as a result of the three-fold α -helix-type arrangement of the intermolecular hydrogen bonds.^{10,11} CD spectroscopy revealed that the introduction of chiral side chains results in columnar structures with a preferred helicity in a highly cooperative fashion.¹¹ Since the lateral interactions in BTAs suffice to form a columnar structure, we anticipated that end-capping or copolymerizing low-molecular weight (MW) telechelic polymers with BTAs may result in supramolecular materials. With the BTA motif inducing physical cross-linking via the formation of nanorods, elastomeric properties can be expected in these supramolecular materials.

Amine telechelic poly(ethylene butylene) (PEB) ($M_n = 3.5$ kDa, polydispersity = 1.08) was converted into dumbbell-shaped molecules **1a,b** and into copolymers **2a,b** (Scheme 1) via a straightforward synthetic approach (see SI for details). The copolymers **2a,b** demonstrated molecular masses in the range of 27–33 kDa, corresponding to degrees of polymerization of around 5, and polydispersities of around 1.7. As a reference, the chiral disk-shaped BTA **3** encompassing three (*R*)-3,7-dimethyloctyl side chains was included (Scheme 1). We selected chiral derivatives in this study to evaluate the presence of helicity in the columnar structure in solution and in the solid state by using CD spectroscopy. The latter offers an additional tool to investigate the dynamics of the system.

The chiral derivatives **1a**, **2a**, and **3** were studied in solution with UV and CD spectroscopy to verify the columnar helical structure found for **3** in solution for dumbbell-shaped BTAs or even

Scheme 1



polymeric BTAs. Chiral **1a** was dissolved in dodecane ($c = 8 \times 10^{-6}$ M), and its UV and CD spectra were compared to those of chiral **3** measured in heptane ($c = 2.1 \times 10^{-5}$ M) (Figure 1). In the UV spectrum of dumbbell-shaped **1a** in dodecane (see SI), the λ_{\max} at 208 nm (typical for molecularly dissolved BTA species)^{11b} was absent, indicating that the BTA units were aggregated. Moreover, the CD spectrum of **1a** was similar in shape and amplitude to the CD spectrum of **3** suggesting that the helical columnar order present in the disk-shaped BTAs is retained in the dumbbell-shaped BTAs in solution.

Copolymer **2a** could not be measured in alkane solution as a result of its poor solubility. Since **2a** is an amorphous polymer (see below), we spin-coated films with a thickness of 274 nm from a CHCl_3 solution on quartz plates and measured CD and UV of the films. A clear CD effect was observed for **2a**, similar in shape as observed for **1a** and **3** (Figure 1, inset). The CD effect was independent of the orientation of the quartz slide with respect to

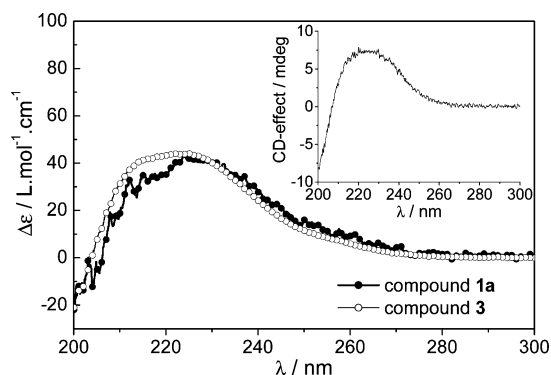


Figure 1. CD spectra of **1a** ($c = 8 \times 10^{-6}$ M in dodecane) and **3** ($c = 6.5 \times 10^{-5}$ M in heptane). The concentration independent molar ellipticity $\Delta\epsilon$ was used on the y-axis. (Inset) CD spectrum of **2a** spin-coated on a quartz slide with a film thickness of 274 nm.

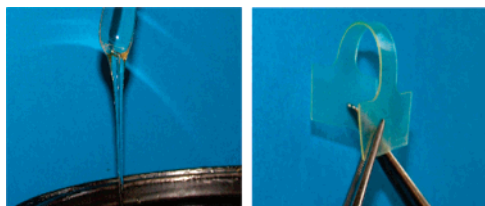


Figure 2. Amine telechelic PEB before (left) and after (right, compound **1b**) functionalization with a BTA moiety.

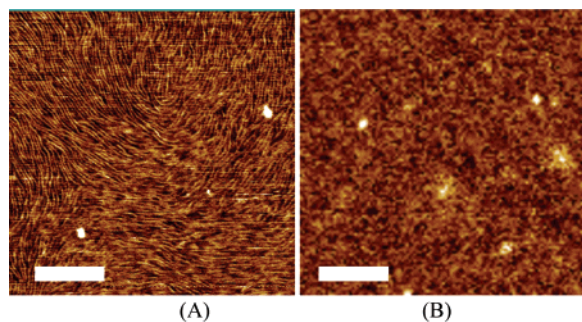


Figure 3. AFM phase image of (A) **1a** and (B) **2b**. The scale bar is 100 nm.

the beam, and no linear dichroism effects were present. This suggests that the columnar helical order present in **3** in solution is retained in **1a** and **2a**.

The physical properties of dumbbell-shaped BTAs **1** and copolymers **2** were then studied in the solid state. While amine telechelic PEB is a liquid at room temperature, **1a,b** and **2a,b** were obtained as transparent, elastic solids. As an example, the dramatic visual change in properties of PEB and BTA end-capped PEB (compound **1b**) is shown in Figure 2. Differential scanning calorimetry (DSC) of **1a** showed a T_g at -60 °C and a small transition around 195 – 215 °C ($\Delta H = 2.63$ J/g for **1a** and $\Delta H = 2.79$ J/g for **1b**). With polarization optical microscopy (POM), we observed a mobile, birefringent texture typical for a nematic phase starting from 60 °C up to the clearing temperature around 200 °C. Infrared (IR) spectra in the solid state of **1a,b** showed vibrations at positions typical for amides involved in three-fold α -helical-type hydrogen bonding as evidenced by comparison with compound **3** ($\nu(\text{NH}) = 3240$ cm^{-1} , $\nu(\text{C=O}) = 1642$ cm^{-1} and $\nu(\text{C-N}) = 1562$ cm^{-1} for **1a,b** and ($\nu(\text{NH}) = 3226$ cm^{-1} , $\nu(\text{C=O}) = 1637$ cm^{-1} and $\nu(\text{C-N}) = 1563$ cm^{-1} for **3**). Variable-temperature IR (see SI) revealed a gradual shifting of the characteristic vibrations starting from 75 °C and allowed us to attribute the transition around 200 °C to the loss of the intermolecular hydrogen bonds. The NH, C=O, and C-N vibrations in the IR spectra of the copolymers **2a,b** were at similar positions as observed for dumbbell-shaped compounds **1a,b** and typical of intermolecularly hydrogen-bonded amides. DSC traces for the copolymers **2a,b** revealed a T_g at -57 °C and a small transition at around 185 °C ($\Delta H = 1.87$ J/g for **2a** and 2.12 J/g for **2b**). In this case, no liquid crystalline phase was observed with POM.

Atomic force microscopy (AFM) of compound **1a** displayed a fibrillar structure which is indicative for phase segregation between the PEB soft phase and the BTA columnar aggregates (Figure 3A). The diameter of the fibrils was estimated around 6 nm and their length at 500 – 800 nm. This suggests that nanorods indeed are present in the soft polymer matrix. The morphology is reminiscent of the morphologies previously observed for Ury-urea modified PEB, although the dimensions are smaller in the case of **1a**.⁷ AFM

of copolymer **2b** shows a less developed morphology than the one observed for **1a** (Figure 3B). Although phase segregation is clearly present in the morphology of **2b**, a more rodlike structure was observed with a diameter of 6 nm, but with much shorter lengths (20 – 30 nm), indicating that the aspect ratio is significantly lower than the aspect ratio observed for **1a**.

Although dumbbell-shaped BTAs **1a,b** appeared as elastic solids, the material properties were not sufficient to allow tensile testing to be performed. Gratifyingly, the elasticity in copolymers **2a,b** was more pronounced than the elasticity (qualitatively) observed for **1a,b**. Therefore, we performed tensile tests on **2b** (see SI). The stress–strain curve was typical for a thermoplastic elastomer. The E -modulus was 3.4 ± 0.2 MPa, indicative for a soft rubber. The yield stress and the strain at break were 1.42 ± 0.07 MPa and $497 \pm 43\%$, respectively. These values compare well with those of Ury-urea functionalized PEB,⁸ poly(urea EB)¹² analogues, and bis-urea grafted poly(dimethylsiloxane).⁶

In conclusion, we have shown for the first time that telechelic polymers end-capped or copolymerized with BTA's lead to supramolecular materials. The intrinsic phase segregation of BTA nanorods with an amorphous polymer such as PEB results in thermoplastic elastomeric behavior. Our current research is devoted to apply this principle to other classes of polymers and to incorporate functional BTAs into the columnar aggregates.

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Supporting Information Available: Experimental procedures and analysis of **1**–**3**, tensile data, AFM images of **1b**, variable temperature IR, UV, and CD spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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