Cooperative End-to-End and Lateral Hydrogen-Bonding Motifs in Supramolecular Thermoplastic Elastomers

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To a large extent, the mechanical properties of polymers are determined by the strength of the physical interactions between chains. Thermoplastic elastomers (TPE's) make sophisticated use of reversible physical interactions.[1] They consist of polymer chains in which strongly interacting segments alternate with weakly interacting segments to give rise to microphase-separated materials with a soft block/hard block morphology. When the hard blocks contain urethane and/or urea groups, strong and specific hydrogen-bonding interactions[2] lead to useful properties, such as a high modulus for a given hard block content.

In recent years, highly directional physical interactions have been applied in a fundamentally different way to form supramolecular polymers.[3] In this novel class of materials, end-functionalization of unimers with functional groups that associate via noncovalent interactions such as multiple hydrogen bonds[4,5] or coordinative bonds[6] results in a strong increase of the virtual molecular weight and in concurrent changes of mechanical and rheological properties.

The use of directional hydrogen bonding within the hard blocks of TPE's has been studied by Stadler and co-workers,[7] who used telechelic hydrogen-bonded polyisobutylenes with relatively weak end-to-end interactions between urazole groups and between benzoic acid groups. Recently, Bouteiller et al.[8] have studied poly(dimethylsiloxane)s with bisurea end groups which aggregate laterally. The authors concluded that aggregation of the end groups into 3-D crystalline domains results in elastomeric behavior, while the formation of hydrogen bonds without crystallization was not sufficient to obtain tensile properties.

Similar conclusions were drawn by Rowan et al.,[9] who noticed that even very weak end-to end interactions can be used to obtain polymers with film-forming properties when the end groups phase segregate.

Here, we study the effect of combining very strong end-to-end association via ureidopyrimidinone (UPy) quadruple hydrogen bonding[10] and directional lateral aggregation via the urea (U) and urethane (T) hydrogen bonding motifs[11] to give supramolecular thermoplastic elastomers with 1-D aggregation of dimerized end groups.

Hydroxy-telechelic poly(ethylene butylene) (PEB, M_n = 3500 g/mol, M_w/M_n = 1.06, degree of functionalization 1.92) was functionalized with lateral hydrogen-bonding functionalities (U-U-PEB-U-U and U-T-PEB-T-U), with end-to-end hydrogen-bonding functionalities (UPy-PEB-UPy), and functionalized with both lateral and end-to-end functionalities (UPy-U-PEB-U-UPy and the previously reported[5] UPy-T-PEB-T-UPy) (Scheme 1).

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Scheme 1. Hydrogen-Bonded Telechelic PEB's
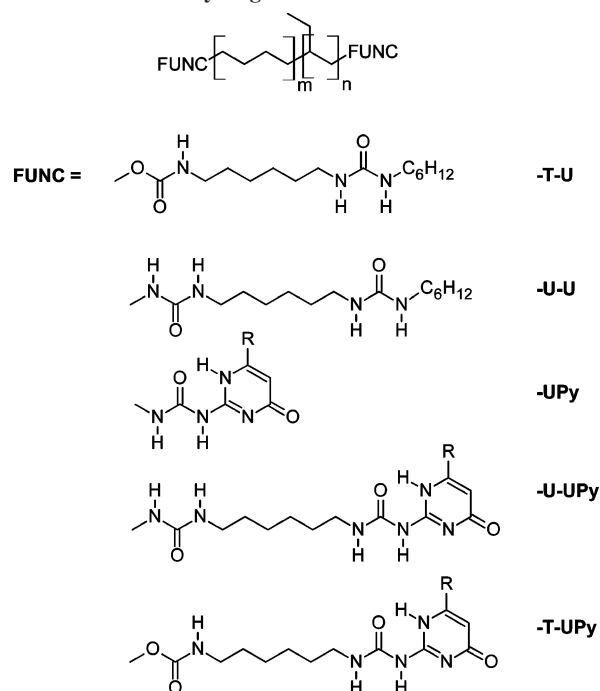
The resulting materials were characterized with DSC, AFM, dynamic mechanical measurements, and tensile testing.

The parent hydroxy-telechelic PEB is a liquid at room temperature which shows purely viscous behavior in oscillatory shear experiments. Incorporation at the chain ends of functional groups capable of lateral aggregation via 3 or 4 hydrogen bonds leads to the formation of elastic solids, with melting points that increases from 45 °C for U-T-PEB-T-U to 129 °C for the U-U-PEB-U-U material. The former is a single segment of a segmented, PEB-based poly(urethane−urea) recently reported by Wilkes et al.,[2b] while the latter material can be considered a PEB analogue of the bisurea-functionalized PDMS reported by Bouteiller.[8] In line with the highly directional nature of the hydrogen bonding of UPy moieties, direct functionalization of PEB with the UPy quadruple hydrogen bonding unit in UPy-PEB-UPy gives rise to a noticeable increase in viscosity at 40 °C from 10 to 7×10^3 Pa·s, but it does not lead to the formation of a material with a discernible melting point. The viscosity changes are in line with end-to-end linking of PEB by directional quadruple hydrogen bonds between UPy functional groups, considering that the degree of functionalization of 1.92 of the starting material limits the average number of end-linked unimers to ∼50.

A master curve of oscillatory shear experiments on UPy-PEB-UPy (Figure 1) confirms the directional end-to-end nature of UPy-UPy hydrogen bonding as the storage and loss moduli show terminal relaxation behavior with slopes of 0.96 and 2.05, demonstrating the absence of long-lived lateral interactions. Nevertheless, the formation of supramolecular polymer chains by linear association of unimers results in an entanglement network with characteristic lifetime of 1 s at 40 °C, evident from a viscoelastic transition at higher frequencies.

A dramatic enhancement of mechanical properties was observed when end-to-end and lateral interactions were combined in UPy-U-PEB-U-UPy. In contrast to UPy-PEB-UPy, this material is an elastic solid, with a melting point of 129 °C. The
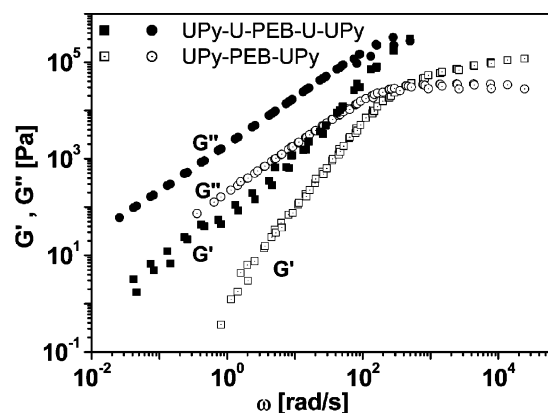
Figure 1. Rheological master curves of UPy-PEB-UPy (□) and of UPy-U-PEB-U-UPy (■). Reference temperatures are 110 and 125 °C, respectively.
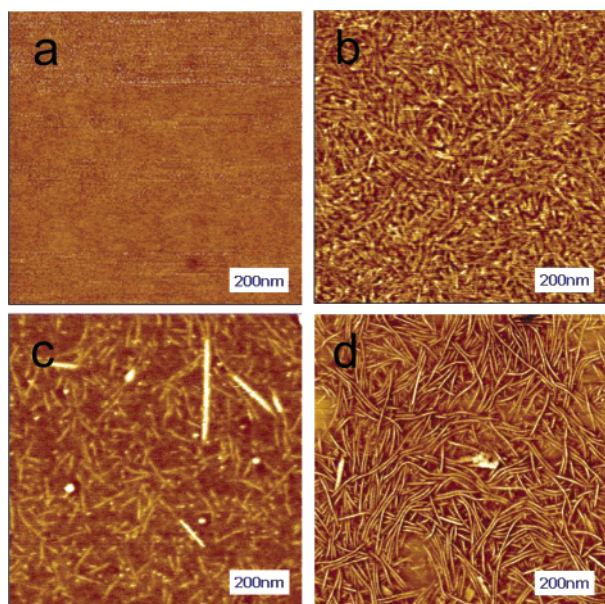

Figure 2. Tapping mode AFM images of thin films of (a) UPy-PEB-UPy, (b) U-U-PEB-U-U, (c) UPy-T-PEB-T-UPy, and (d) UPy-U-PEB-U-UPy.

Figure 3. Tensile testing of solid materials. The true stress σ_{true} (calculated assuming zero volume change) is plotted against the dimensionless extension parameter λ.

presence of a melting point indicates that, in addition to the supramolecular polymerization observed for PEB(UPy)$_2$, the dimerized end groups in UPy-U-PEB-U-UPy aggregate via the lateral hydrogen bonding of urea, confirmed by the IR spectrum of the material, which shows a band of hydrogen-bonded urea carbonyl groups at 1626 cm^{-1}, while a band of free urea groups is absent. Rheology (Figure 1), on the other hand, shows that in the melt long-lived cross-links are absent.

The room temperature morphology of these materials was investigated with tapping mode AFM on thin films drop cast on mica.[12] Indeed, strong differences in morphology were observed between films of UPy-PEB-UPy and UPy-U-PEB-U-UPy. While films of UPy-PEB-UPy lack any distinct features in height or phase mode (Figure 2a), films of UPy-U-PEB-U-UPy feature very distinct, micrometer long fibers[2b,13] with estimated widths <7 nm (Figure 2b). The presence in the AFM image of many crossings of fibers which join nor branch confirms their 1-dimensional character.

The striking effect of lateral urea hydrogen bonding on the elastomeric properties of the UPy telechelic supramolecular polymer prompted us to reinvestigate UPy-T-PEB-T-UPy, with the possibility of urethane lateral hydrogen-bonding interactions. This elastomeric material was previously shown to display a
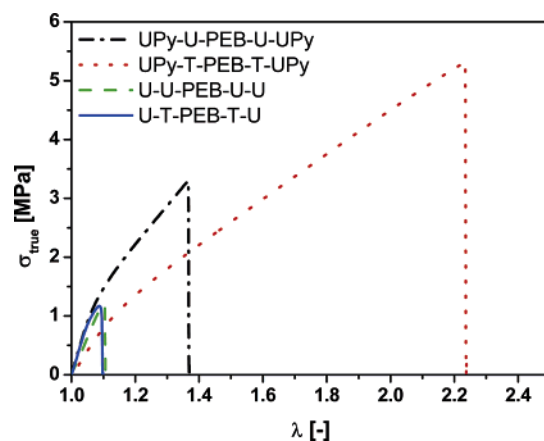
temperature-dependent low-frequency plateau in the storage modulus, indicating the presence of a low density of long-lived entanglements in the melt.[5] Reinvestigation of this material with DSC showed that solution cast material has a melting point of 69 °C, and AFM confirmed the presence of fibrillar aggregates at room temperature (Figure 2c), although they are shorter and less densely packed than in UPy-U-PEB-U-UPy, indicating that aggregation is not complete. Indeed, FTIR showed bands of free urethane carbonyl groups at 1733 cm^{-1}. Tensile testing nicely demonstrates the effect of cooperative end-to-end and lateral interactions on mechanical properties. The materials with only laterally interacting end groups (U-T-PEB-T-U and U-U-PEB-U-U) are relatively brittle, with a strain at break of 10%. The absence of chains that run through multiple hard blocks results in mechanical failure when chains are pulled out of the hard blocks. In the UPy-U-PEB-U-UPy material, the molecular weight between hard blocks is the same as for U-T-PEB-T-U and U-U-PEB-U-U, resulting in a similar Young modulus (17 MPa), but the strain at break is increased nearly 4-fold because the quadruple hydrogen bonds in the central UPy-UPy part of the hard blocks increase the force required for chain pull-out.

The UPy-T-PEB-T-UPy material represents an intermediate in between UPy-U-PEB-U-UPy and UPy-PEB-UPy. Here, only part of the end groups is present in hard blocks. Therefore, the hard block content is lower and the average molecular weight between hard blocks is higher. This results in a lower Young modulus of 8.0 MPa. Remarkably, in molded tensile bars, a modulus of 5 MPa was measured. This is in line with the absence of a melting peak in the second heating run in DSC, which indicates that the fibrillar morphology is less developed in samples obtained from the melt.

UPy-T-PEB-T-UPy shows a higher rate of stress relaxation than UPy-U-PEB-U-UPy (see Supporting Information). This may be ascribed to the presence of UPy dimers in UPy-T-PEB-T-UPy which are not laterally aggregated in fibers. Therefore, these dimers may dynamically break and recombine under stress, resulting in plastic deformation. As a consequence, failure in this material occurs at a significantly higher strain than in UPy-U-PEB-U-UPy. Because concentration of stresses is reduced by plasticity, strain at break is also higher for UPy-T-PEB-T-UPy, in which the end groups are only partially aggregated into fibers. Although the values of strain at break of the supramolecular materials are significantly lower, tensile strength approaches that of their covalent, segmented analogues.[2b]

In conclusion, we have demonstrated that the presence of laterally aggregating urea groups in UPy-based supramolecular

polymer UPy-U-PEB-U-UPy gives rise to 1-D aggregation of end groups in long fibers. Despite low molecular weight of the covalent PEB chains in this material (3500 g/mol), noticeable elastic properties are observed below the melting point due to a combination of supramolecular polymerization and nanophase segregation. Compared to low molecular weight polymers which lack the strong end-to-end hydrogen bonding of the UPy groups, the mechanical properties of UPy-U-PEB-U-UPy are enhanced because chain pullout from fibrils is more difficult from the fibers which combine end-on and lateral interactions.[14]

Supporting Information Available: Experimental details for the preparations of the polymers; DSC traces, AFM methods, and stress relaxation experiment of UPy-T-PEB-T-UPy and UPy-U-PEB-U-UPy. This material is available free of charge via the Internet at http://pubs.acs.org.

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