Model Transient Networks from Strongly Hydrogen-Bonded Polymers

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ABSTRACT: Random copolymers consisting of n-butyl acrylate backbones with quadruple hydrogen-bonding side chains based on 2-ureido-4[1H]-pyrimidinone (UPy) have been synthesized via controlled radical polymerization and postpolymerization functionalization. Through this synthetic strategy high UPy monomer content (15 mol %) can be reached while maintaining low polydispersity and excellent control over molecular weight, providing model reversible networks with well-defined molecular architecture. Despite low Tgs and a lack of entanglements or crystallinity, these materials behave as thermoplastic elastomers through the strong but reversible association of UPy groups. Bulk properties such as the plateau modulus, tensile modulus, and relaxation time scale are primarily determined by the average distance between UPy’s along the chain. Starting from a difunctional initiator, triblock copolymers can also be synthesized containing a homopolymer midblock and random copolymer end blocks, effectively concentrating the hydrogen-bonding groups near the chain ends. By controlling both the average composition and distribution of UPy’s along the polymer chain, macroscopic material properties such as stiffness and resistance to creep can be independently tuned.

Introduction

Thermoplastic elastomers (TPEs) encompass a broad class of materials that can be processed, for example, by molding or extrusion, at elevated temperatures yet are elastomeric at ambient temperature. Typically such behavior arises through a phase-separated microstructure in which “hard” domains are bridged by “soft” rubbery chains; when a stress is applied to the material, the hard domains serve to pin the polymer chains and prevent macroscopic deformation, while the rubbery chains provide elasticity through the connectivity of the network. Transient networks, in which the junctions can be reversibly broken and re-formed, are interesting from both fundamental and applied standpoints; many reversibly associating polymers have been synthesized for use as rheological property modifiers or physical gels, and numerous theories have been presented1−6 to describe their equilibrium and dynamic properties.

The reversible junctions in transient networks typically contain areas of hydrophobic associations,7−10 hydrogen bonding,11−17 metal−ligand interactions,18,19 or ionic associations.20,21 In many cases such junctions are poorly defined aggregates with unknown association strength and kinetics, but in a few transient network materials bulk properties have been directly correlated to defined polymer microstructure or well-characterized reversible interactions leading to important insights into the properties of these systems. In an early series of papers, Stadler and Freitas22−24 studied the rheological behavior of polybutadiene lightly modified with double-hydrogen-bonding phenylureazole groups, finding that even with light substitution along the backbone the storage modulus plateau was broadened and shifted to lower frequencies (although the overall network properties were primarily dictated by the highly entangled polymer backbone and the crystallization of the phenyl urazole side chains). More recently, reversible networks based on metal−ligand coordina-tion have been synthesized and the macroscopic material properties directly related to the coordination dynamics;25−28 in this case it was found that formation of a strong network required not just a high association constant but also slow dynamics of the reversible bond. Additionally, supramolecular gels based on hydrogen bonding in ionic liquids have been demonstrated and their rheological properties related to the strength and number of hydrogen bonds as well as stoichiometry of donor and acceptor units.29,30

To broaden the scope and applicability of supramolecular polymer chemistry, many new strongly hydrogen-bonding moieties have been synthesized31−37 and incorporated into network-forming materials.12−15,38−41 The strength and specificity of multiple-hydrogen-bonded (MHB) groups vary widely, from weakly complementary pyridine−phenol pairs32 to extremely strong, self-complementary 6-H-bonded dimers.31 The 2-ureido-4[1H]-pyrimidinone (UPy) group first reported by Sijbesma et al.31 was developed as a synthetically accessible, exceptionally strong (Kdim = 6 × 107 M−1 in CDCl3) quadruple-hydrogen-bonded dimer in order to create highly thermally responsive polymeric materials. By attaching UPy’s to both ends of short, low-Tg oligomers, materials were produced which, at low temperature, bonded end to end to give high molecular weight polymer chains. On heating, the bonds between the oligomers dissociate and the material flows like a liquid. A number of other telechelic, UPy-based materials have been demonstrated to show similar behavior;43−46 although useful, they generally rely on crystallization of the UPy dimers into long stacks to achieve mechanical stability, similar to the crystallization typically seen in segmented polyurethane thermoplastic elastomers. Later work showed that the nature of the linker joining the UPy group to the polymer chain dramatically affects the macroscopic properties. When an additional urea or urethane is present near the UPy group, lateral hydrogen bonding between dimers is enhanced,

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which results in the crystallization of the dimers into long stacks.\textsuperscript{39} Alternately, bulky substituents near UPy’s prevent such crystallization while linear alkyl chains enhance it.\textsuperscript{40} In both cases, the presence of crystalline stacks (rather than simple pairwise UPy–UPy association) was shown to be crucial for network formation and good mechanical properties.

Examples of UPy-based segmented TPEs have also been presented in which the MHB groups comprise the “hard” segments of longer chains,\textsuperscript{47,48} and several groups have also begun to incorporate UPy groups into higher molecular weight polymers as side chains via random copolymerization of a UPy-functional alkene\textsuperscript{15} or methacrylate monomer.\textsuperscript{14,38,49,50} Although the low solubility of the UPy methacrylate monomer limited its incorporation to 10 mol % or less, a higher degree of control over the bulk properties can be achieved via this route by varying any number of parameters including the concentration of UPy’s in the chain, the total molecular weight, and the type of comonomer. In particular, it has been demonstrated that the melt viscosity and adhesive properties of random copolymers of \textit{n}-butyl acrylate and UPy-methacrylate\textsuperscript{44} together with the creep compliance of adhesive properties of random copolymers of ethylhexyl methacrylate and UPy-methacrylate\textsuperscript{48} can be widely varied by the concentration of UPy’s along the backbone.

Although prior work has addressed the question of how the overall concentration of UPy monomer in random copolymers affects the bulk properties, most of the materials studied were synthesized via conventional radical polymerization leading to poor control over the chain architecture, molecular weight, and polydispersity. In this work we demonstrate a new synthetic strategy involving postpolymerization functionalization which allows well-defined precursor polymers to be prepared via atom transfer radical polymerization (ATRP) of \textit{n}-butyl acrylate and a Boc-protected amine functional monomer. This allows for architectural control and higher incorporation of UPy’s in the final polymers as well as effective control over the chain length and repeat unit distribution. By keeping the primary chain length below the entanglement molecular weight, the effects of the reversible interaction on the dynamics can be isolated from those due to retraction, in contrast with most prior examples of bulk transient networks. As a result, new questions about these materials, such as the relative importance of backbone molecular weight and overall concentration of UPy’s, can be addressed. Additionally, we show that by controlling the distribution of UPy’s along the chain through a triblock-like architecture it is possible to greatly improve the utility of such materials while minimizing the amount of functional monomer required.

**Experimental Section**

**Methods.** All synthetic procedures were performed under an inert atmosphere of dry nitrogen unless stated otherwise. \textit{N,N-Dimethylformamide} (DMF) was dried over 4 \text{Å} molecular sieves. \textit{tert-Butyl} 6-hydroxyhexyl carbamate was prepared as reported by Forbes et al.\textsuperscript{35} \textit{Tris-[2-(dimethylamino)ethyl]amine} (Me\textsubscript{2}TREN) was prepared as reported by Queffelec et al.\textsuperscript{52} 2-(1-Imidazolylcarbonylamino)-6-methyl-4-[1\text{H}-pyrimidinone was prepared as reported by Keizer et al.\textsuperscript{53} Ethane-1,2-diy bis(2-bromo-2-methylpropanoate) was synthesized as reported by Matyjaszewski et al.\textsuperscript{54} \textit{n}-Butyl acrylate was purified by passing over neutral alumina. Acryloyl chloride was distilled prior to use. All other chemicals were obtained from Aldrich and used as received.

Analytical TLC was performed on commercial Merck plates coated with silica gel GF254 (0.24 mm thick).\textsuperscript{1} \textit{H} NMR (500 MHz) and \textsuperscript{13}C NMR (125 MHz) were performed on a Bruker AVANCE 500 spectrometer at room temperature. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). The following splitting patterns are designated as: singlet; d, doublet; t, triplet; q, quartet; b, broad; m, multiplet; and dd, double doublet. Carbon chemical shifts are reported downfield from TMS using the resonance of the deuterated solvent as the internal standard.

Size exclusion chromatography was carried out at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer and six Waters Styragel columns (five HR-5 μm and one HWM-20 μm) using THF as eluent (flow rate: 1 mL/min). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The molecular weights of the polymers were calculated relative to linear polystyrene standards. Fourier transformed infrared spectroscopy was performed using a PerkinElmer Spectrum One spectrometer equipped with a Universal ATR accessory. Spectra are the sum of 16 scans acquired at a resolution of 4 cm\textsuperscript{-1}. Electrospray ionization time-of-flight (ESI-TOF) data were obtained on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer.

Differential scanning calorimetry data were acquired on a TA Instruments Q20000 modulated DSC at a heating rate of 5 °C. Data presented are from the second heating after a single cycle from -75 to 100 °C. Rheological measurements were performed on an ARES rheometer from TA Instruments. Most samples were measured using a 25 mm cone and plate geometry (cone angle 0.1 rad), but for high-modulus materials it was necessary to use 8 mm parallel plates with a gap of 0.7 mm. Strain sweeps were performed at each temperature to ensure that measurements were made in the linear viscoelastic regime.

**Synthesis.** 6-(\textit{tert-Butyloxycarbonylamino})hexyl Acrylate (\textit{t-Boc-AHA}). \textit{tert-Butyl} 6-hydroxyhexyl carbamate (20 g, 92 mmol) and triethylamine (20 mL, 138 mmol) in dry methylene chloride (100 mL) were stirred at 0°C. Acryloyl chloride (8.2 mL, 101 mmol) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirred overnight. Water was added (100 mL) to dissolve salts and hydrolyze any remaining acryloyl chloride, and the mixture stirred for 30 min. The organic layer was separated and washed with 1 N HCl (1 × 50 mL), NaHCO\textsubscript{3} (saturated, 1 × 50 mL), and brine (1 × 50 mL) and dried over sodium sulfate. The crude mixture was separated by flash column chromatography eluting with 1% methanol in methylene chloride to give a clear viscous oil (22.2 g, 89%). \textit{H} NMR (CDCl\textsubscript{3}): δ = 6.30 (dd, 1H), 6.04 (dd, 1H), 5.75 (dd, 1H), 4.65 (br, 1H), 4.07 (t, 2H), 3.03 (br, 2H), 1.60 (m, 2H), 1.42 (m, 2H), 1.36 (s, 9H), 1.34–1.25 ppm (m, 4H). \textit{13}C NMR (CDCl\textsubscript{3}): 166.2, 156.0, 130.4, 128.5, 78.8, 64.4, 40.4, 29.9, 28.4, 26.4, 25.6 ppm. FTR-IR (ATR): \textnu\textsubscript{max} = 3364.9, 2932.9, 2860.9, 1710.0, 1692.7, 1636.5, 1619.4, 1516.3 cm\textsuperscript{-1}, ESI-MS (m/z): calcd: 294.17 (M + Na\textsuperscript{+}); found: 294.17 (M + Na\textsuperscript{+}), 310.14 (M + K\textsuperscript{+}).

\(\text{Poly(\textit{n-butyl acrylate}-r-Boc-aminohexyl acrylate)}\), \textit{n}-Butyl acrylate (3.24 g, 25.3 mmol), 6-(\textit{tert-butoxycarbonylamino})hexyl acrylate (0.726 g, 2.70 mmol), methyl 2-bromopropionate (31 mg, 1.9 mmol), and Me\textsubscript{2}TREN (60 mg, 1.9 mmol) were sparged in a round-bottom flask with nitrogen for 10 min. CuBr (27 mg, 1.9 mmol) was added under flowing nitrogen. The flask was sealed and placed in a 70 °C oil bath for 45 min, then the polymerization was quenched by opening the flask to air and diluting with methylene chloride. The reaction mixture was washed with water (3 × 50 mL), 0.1 M EDTA (3 × 50 mL), and brine (1 × 50 mL), then dried over sodium sulfate, and evaporated. Residual monomer was removed by heating the polymer under high vacuum at 50 °C overnight to give P(nBA-r-r-Boc-AHA), \(M_r\), 24 600 g/mol, PDI 1.21 (THF GPC). \textit{H} NMR (CDCl\textsubscript{3}): 4.68, 4.02, 3.10, 2.32, 1.90, 1.60, 1.43, 1.37, 0.93 ppm. \textit{13}C NMR (CDCl\textsubscript{3}): 174.5, 155.97, 79.0, 64.5, 41.4, 40.5, 36.3, 35.4, 30.6, 30.0, 28.4, 26.4, 25.6, 19.1, 13.7 ppm. FTR-IR (ATR): \textnu\textsubscript{max} = 3391.3, 2932.9, 2933.8, 8589.4, 1723.6, 1636.5, 1516.4 cm\textsuperscript{-1}.

\(\text{Poly(\textit{n-butyl acrylate}-r-aminohexyl acrylate)}\) (TFA Salt), P(nBA-r-r-Boc-AHA) (3.00 g) was dissolved in 25 mL of
methylenecarbonate. TFA (25 mL) was added, and the mixture was stirred overnight. Solvent and excess TFA were removed by a rotavap, and residual TFA was removed by coevaporation with methanol followed by heating to 50 °C under high vacuum overnight to give P(nBA-r-UPyA). \( ^1 \)H NMR (CDCl\(_3\)): 7.77, 4.02, 3.04, 2.32, 1.90, 1.60, 1.37, 0.93 ppm. \( ^{13} \)C NMR (CDCl\(_3\)): 174.7, 1677.5, 1524.6 cm\(^{-1}\). FTR-IR (ATR) with methanol followed by heating to 50 °C overnight; the mixture was heated to 100 °C C176.

\textbf{Results and Discussion}

\textbf{Synthesis of Side-Chain UPy-Functionalized Polymers.}

Initial attempts at the synthesis of random copolymers from UPy-functional monomers met with limited success. A UPy-based acrylic monomer was synthesized, and random copolymers with n-butyl acrylate could be prepared at low UPy incorporation (<5 mol %), although the PDIs were typically 1.3–1.5. With higher relative concentrations of UPy, however, the limited solubility of the monomer required the use of significant amounts of solvent in the polymerization. Even when fully soluble in the mixture, the polymerization did not proceed to any discernible degree, presumably due to a weak but significant interaction between the UPy monomer and copper catalyst under the ATRP conditions.

It was fundamentally important to increase the overall loading of UPy in the random copolymers, and to accomplish this, a postpolymerization functionalization strategy was developed as shown in Scheme 1. Rather than polymerizing the UPy-acrylate directly, Boc-protected 6-aminohexyl acrylate (r-Boc-AHA) was copolymerized with n-butyl acrylate. The two monomers are miscible liquids, and even at a feed ratio as high as 3:1 nBA:r-Boc-AHA the polymer composition closely matched the feed. Deprotection of the Boc groups with TFA proceeded smoothly; because of the possibility of transamination between free amines and backbone esters, the TFA salts of the polymers were isolated rather than the neutralized analogues. Neutralization with triethylamine followed by immediate in situ reaction with CDI-activated methylisocytosine afforded the desired P(nBA-r-UPyA), which could be purified by precipitation into methanol. Triblock architectures were achieved through the use of a difunctional ATRP initiator which was used to first polymerize the midblock of nBA; random copolymer end blocks were then grown from Br-PnBA-Br difunctional macrorinitiators.

Although deprotection of the Boc groups proceeded quantitatively as measured by \( ^1 \)H NMR, functionalization yields were typically ~75–85%, measured by comparing integrations of the alkylidene proton from the UPy side groups with the methylene adjacent to the backbone esters (see Supporting Information).

The characteristics of the synthesized polymers are given in Tables 1 and 2; the polymers are named according to the convention \( a-m-c-f, \) where \( a \) is either R for random copolymer or T for triblock, \( m \) is the number-average molecular weight in kg/mol, \( c \) is the overall mol % UPy monomer, and in the case of triblocks \( f \) is the volume fraction of the end blocks.

\textbf{Effects of Chain Functionality.}

\( n \)-Butyl acrylate was chosen as the primary monomer in the random copolymers due to its low \( T_g \), but it was expected that copolymerization with the UPy acrylate monomer might increase the overall \( T_g \) of the polymer, either due to the presence of hydrogen bonds and slowing of the chain dynamics or simply due to the steric effects on the backbone. As shown in Figure 1, a linear increase in \( T_g \) with increasing incorporation of UPy was observed, consistent with prior reports of UPy-functional random copolymers.\(^{49-55}\) note, however, that even at high UPy loadings, the polymer \( T_g \) is still below room temperature and at least 40 °C below the lowest temperature for rheological measurements.
The relation between mole percent UPy monomer and polymer $T_g$, $M_n$, for each polymer was $\sim 24$ kg/mol.

Figure 1. Relation between mole percent UPy monomer and polymer $T_g$, $M_n$, for each polymer was $\sim 24$ kg/mol.

Table 1. P(nBA-r-UPyA) Random Copolymers

<table>
<thead>
<tr>
<th>sample</th>
<th>$M_n$ (precursor polymer)</th>
<th>DP</th>
<th>mol % UPy</th>
<th>$M_n$ P(nBA-r-UPyA)</th>
<th>$n$ UPy's/chain</th>
<th>$M_{UPy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-21-5.5</td>
<td>21,000</td>
<td>155</td>
<td>5.5</td>
<td>21,400</td>
<td>8.5</td>
<td>2520</td>
</tr>
<tr>
<td>R-25-7.2</td>
<td>24,600</td>
<td>178</td>
<td>7.2</td>
<td>25,500</td>
<td>13</td>
<td>1970</td>
</tr>
<tr>
<td>R-24-9.6</td>
<td>23,500</td>
<td>166</td>
<td>9.6</td>
<td>24,300</td>
<td>16</td>
<td>1530</td>
</tr>
<tr>
<td>R-21-13.3</td>
<td>21,100</td>
<td>144</td>
<td>13.3</td>
<td>22,100</td>
<td>19.1</td>
<td>1160</td>
</tr>
<tr>
<td>R-18-4.5</td>
<td>9,600</td>
<td>71</td>
<td>4.5</td>
<td>9,800</td>
<td>3.2</td>
<td>3040</td>
</tr>
<tr>
<td>R-18-4.1</td>
<td>32,500</td>
<td>242</td>
<td>4.1</td>
<td>33,000</td>
<td>10</td>
<td>3170</td>
</tr>
</tbody>
</table>

$^a$THF GPC, PS equivalent. $^b$H NMR. $^c$Calculated.

Table 2. P(nBA-r-UPyA)-b-PnBA-b-P(nBA-r-UPyA) Triblock Copolymers

<table>
<thead>
<tr>
<th>sample</th>
<th>$M_n$ (midblock PnBA)</th>
<th>$M_n$ (total)</th>
<th>mol % UPy (midblock)</th>
<th>mol % UPy (net)</th>
<th>$n$ UPy's/block</th>
<th>$n$ UPy's/chain</th>
<th>$f_{Ablock}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-27-3.5-55</td>
<td>12,100</td>
<td>26,600</td>
<td>6.5</td>
<td>3.5</td>
<td>7.1</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>T-28-3.6-45</td>
<td>15,500</td>
<td>28,300</td>
<td>8.0</td>
<td>3.6</td>
<td>7.7</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>T-28-3.3-39</td>
<td>17,400</td>
<td>28,300</td>
<td>8.6</td>
<td>3.3</td>
<td>7.1</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>

$^a$THF GPC, PS equivalent. $^b$H NMR.

Figure 2 shows the overall effects on rheological properties of the increase in mole fraction of UPy acrylate in random copolymers at constant molecular weight (irreversible changes in the rheological data began to occur at temperatures greater than 120 °C so higher temperature data are not included in the master curves). It is immediately clear how significantly the polymer properties change with the addition of even a few mole percent of strongly hydrogen-bonding monomer. For reference, the master curve generated for a high molecular weight PnBA homopolymer ($\sim 170$ kg/mol, well above $M_c$ of 20 kg/mol) is also shown; compared to all the UPy-functional polymers considered here it is the only one that is entangled, and the longest relaxation time is greater than 50 s at 120 °C. It should also be noted that in the construction of the master curves no vertical shift of the data was needed, demonstrating that the plateau modulus $G_N$ is not a strong function of temperature and that because of the very large value of $K_{lim}$ there are very few free UPy’s even at the highest temperatures measured.

Since the molecular weights of these polymers are all near the entanglement molecular weight of PnBA, the existence of a plateau modulus is entirely due to the presence of a transient network structure. Figure 3 shows the relationship between the plateau modulus $G_N$ and mole fraction of UPy in polymers with comparable molecular weights $\sim 24$ kg/mol. A number of similar materials have been studied previously, including polymers containing UPy groups either at the chain ends or randomly spaced along the backbone. For these materials, thermoplastic elastomer-type behavior was attributed to the presence of stacked aggregates of UPy dimers (similar to the “hard” phase in polyurethane TPEs) which were observed through DSC and AFM. No melting transition has been observed by DSC in the P(nBA-r-UPyA) materials considered here, and wide-angle X-ray scattering experiments (WAXS, see Supporting Information) confirmed a lack of crystalline domains.

From the magnitude of the plateau modulus $G_N$ it is possible to calculate a network strand density $n$, and molecular weight between reversible network points $M_c$ ($M_n$ is the number-average molecular weight of the parent chains, and
the term in parentheses is the standard (Flory) correction for the effect of loose chain ends which are not network active and thus do not contribute to the plateau modulus).

\[
G_N = \psi_xRT = \frac{5RT}{M_c} \left(1 - \frac{2M_c}{M_n}\right)
\] (1)

In Figure 4, \(M_c\) is compared with the average molecular weight between UPy repeat units, \(M_{UPy}\). Interestingly, as the mole fraction of UPy increases, the two values converge, indicating that a greater fraction of PnBA strands bounded by MHB groups are elastically active in the network. At \(\sim 7\) mol% UPy and above it appears that every UPy side group is active, which indicates that at these high UPy concentrations loops between adjacent UPy’s on the same chain are almost entirely absent.

**Effects of Primary Molecular Weight.** In contrast to the master curves changing significantly with increasing UPy content at constant molecular weight, when the UPy content is held constant and the molecular weight is increased, the master curve shapes look qualitatively similar as shown in Figure 5. In all cases the materials appear to be rheologically simple, displaying a plateau and narrow transition region to liquidlike terminal behavior, with the main differences being the breadth of the curve and the height and extent of the plateau (also note that in these samples \(T_g\) increases only slightly with molecular weight and increasing number of UPy’s per chain, as shown in Figure 7).

Figure 6 shows how \(G_N\) relates to the molecular weight at a constant UPy content of \(\sim 4\)% UPy; at molecular weights higher than 9.6 kg/mol the plateau modulus remains fairly constant. This is understandable considering the average number of UPy groups per chain in the 9.6 kg/mol sample (R-10-4.5) is between 3 and 4, and a connectivity of three is required for the formation of a network. With such a low average functionality there must be some chains which contain one or no UPy groups, neither of which contributes to the network structure. Despite the large difference in \(G_N\) between the lowest and higher molecular weight materials, Figure 7 shows that when corrected for chain ends the fraction of UPy’s which are active in the network (reflected in the difference between \(M_c\) from eq 1 and \(M_{UPy}\), Table 1) is relatively constant with molecular weight. Beyond a critical minimum, then, the primary chain molecular weight appears to minimally affect the bulk properties. Note, however, that all molecular weights in this series are expected to be unentangled. Much higher molecular weight polymers which would have entanglements as well as UPy groups are likely to show slower terminal relaxations.

**Tuning Material Properties by the Distribution of MHB Groups.** It is clear that the overall concentration of MHB groups, or more appropriately the average distance between them, influences the mechanical properties of associating random copolymers to a much greater extent than the length of the polymer chain. In prior studies of transient networks it has also been demonstrated that the distribution of associating groups along the polymer chain is an important parameter to control\(^{57-68}\); a “blocky” random structure leads to correlations between associating segments, slowing the
dynamics and producing stronger effective interchain interactions for a given average composition.

To achieve a similar “blocky” architecture in the current system, a PnBA homopolymer block was first polymerized from a difunctional initiator followed by growth of amino-containing random copolymer end blocks, as shown in Scheme 2, followed by UPy functionalization as described previously (Scheme 1). Because of the demonstrated control in these ATRP reactions, it is straightforward to match the total molecular weight and overall UPy content while varying the homopolymer midblock molecular weight. Accordingly, a series of triblock copolymers were synthesized with overall molecular weights of ∼24 kg/mol and number of UPy’s per chain of ∼7 with increasing the midblock molecular weight and associated increase in the end block UPy concentration; the polymer characterization data are given in Table 2.

It has been demonstrated previously that, in addition to crystallization of hydrogen-bonding units in functional copolymers, microphase separation can play a major role in the bulk properties of such materials. Only a weak scattering peak is observed by small-angle X-ray scattering for each of the triblocks (Figure 8a), and the intensity of the peak increases with increasing concentration of the UPy’s toward the chain ends. Because the scattering peak of T-28-3.3-39 (Figure 8b) shows only a minor change in intensity or position with temperature despite having the highest effective γN due to its greater chemical mismatch between the midblock and end blocks, it can be concluded that no microphase separation is taking place and the peak arises primarily from correlation hole scattering in the disordered melt.

From the rheological master curves shown in Figure 9 several observations can be made. By concentrating the UPy’s near the ends of the chain, the plateau modulus \(G_N\) remains essentially constant but the width of the plateau is dramatically increased. This combination of effects leads to a significant decrease in the crossover frequency, and as a consequence these materials show solidlike behavior over much longer time scales than the corresponding random copolymer. Thus, despite the inhomogeneous UPy distribution, the network structure (i.e., the relative numbers of intra- and interchain hydrogen bonds) does not change appreciably, yet the dynamics are dramatically slowed. The key effect of controlling the distribution of UPy’s along the chain is thus to decouple two macroscopic parameters, namely the stiffness (characterized by the plateau modulus) and relaxation time scales (reflected in the breadth of the master curve). By adopting a triblock-type architecture in which the UPy’s are concentrated near the ends of the chain, the relaxations take place over longer and longer times, whereas the plateau modulus is determined by the average chain composition.

**Dynamic Behavior and Reversible Network Theory.** Dissociation of the hydrogen bonding for the polymer side chains is expected to be a thermally activated process showing Arrhenius-type behavior. The adherence to the Arrhenius relation, but one with a much lower activation energy. This point is confirmed in Figure 10, which shows the temperature dependence of the shift factors \(\alpha_T\) used to construct the rheological master curves. Plotting \(\alpha_T\) versus inverse temperature yields a straight line in all cases,
indicating Arrhenius behavior, and the slope of the line can be used to calculate a flow activation energy $E_a$ (shown in Figure 11). It is immediately clear that the UPy-based materials show a much stronger temperature dependence than PnBA homopolymer and that $E_a$ increases slightly with UPy content, each manifestations of the thermoreversibility of hydrogen bonding. Figure 11 also demonstrates that this small increase in flow activation energy with UPy content is correlated with the (local) average distance between UPy’s along the chain—at a given average distance between UPy groups the $E_a$ values for the triblock copolymers and the random copolymers are nearly the same.

Many theoretical treatments of reversibly associating polymer solutions have been proposed, but the most relevant to the current system was developed by Rubinstein and Semenov.1,2,70 Although the majority of their work addresses associating polymers in dilute or semidilute solution, the theory has also been extended to very high concentrations, far from the gel point (in analogy to the polymer melt). In the limit of high binding strength, intramolecular associations (loops) were predicted to become significant, but at high polymer concentrations the majority of associations are intermolecular. More importantly, because of the very low concentration of unassociated stickers, a given pair will break and re-form many times before finally separating, leading to an effective bond lifetime $\tau^*_b$ greater than the bare bond lifetime $\tau_b$. In this work $\tau^*_b$ is measured from the frequency at which the storage modulus has dropped to 90% of its plateau value (see the Supporting Information for a comparison with an alternative measure of $\tau_b$, namely the network strand lifetime measured at the crossover frequency). The theory also predicts a longest relaxation time greater than $\tau^*_b$ arising from the fact that the associating polymers are essentially Rouse-like chains—the stickers can be considered “beads” with a higher monomer friction coefficient and an effective bead jump time of $\tau^*_b$, and the “springs” are the spacers between them.

From Figure 12a it can be seen that the effective bond lifetime $\tau^*_b$ increases significantly with increasing concentration of UPy in the network. The lifetime of small molecule UPy dimers in solution40 was previously found to depend strongly on the polarity of the solvent and ranged from 80 ms (chloroform saturated with water) to 1.7 s (toluene). The PnBA environment considered here is relatively polar, and so the bare lifetime should be low; R-10-4.5, which showed a dropoff of the plateau at the highest frequency, provides an upper limit to the UPy dimer lifetime $\tau^*_b$ in PnBA at 25°C, although NMR exchange experiments would be necessary to determine its
actual value.\textsuperscript{71} In every other material studied here, the effective bond lifetime is significantly higher. From Figure 12b it is also clear that $\tau_b^*$ depends somewhat on the UPy distribution, suggesting that the average (local) distance between stickers along the chain influences the dynamic behavior in these materials. Presumably as the distance between two stickers along the chain is decreased, the relaxation of stress will require their concurrent unbinding. As a result, increasing the local concentration of UPy's leads to a correlation of their dynamics (also reflected in the flow activation energy, Figure 11), and as previously demonstrated,\textsuperscript{27} it is the dynamics of unbinding and binding that dominate the macroscopic response.

Within the Rubinstein and Semenov theory, at frequencies lower than that corresponding to $\tau_b^*$ the polymer chains are considered Rouse-like. The Rouse model predictions for the frequency dependence of $G'$ and $G''$ are as follows:\textsuperscript{72}

\begin{equation}
G'(\omega) \approx \frac{k_B T n_s}{n_s^2} \left(\frac{\omega \tau_{\text{max}}}{1 + (\omega \tau_{\text{max}})^2} \right)^2 \frac{1}{1 + (\omega \tau_{\text{max}})^2 + 1} \label{eq:G1}
\end{equation}

\begin{equation}
G''(\omega) \approx \frac{k_B T n_s}{n_s^2} \left(\frac{\omega \tau_{\text{max}}}{1 + (\omega \tau_{\text{max}})^2} \right)^2 \frac{1}{1 + (\omega \tau_{\text{max}})^2 + 1} \label{eq:G2}
\end{equation}

Figure 11. Activation energies $E_a$ calculated from the temperature dependence of $\alpha_T$ (\(\ell^\prime\)): average degree of polymerization between UPy's; in the case of triblocks $\ell$ is calculated based on the local UPy concentration within the random copolymer end blocks.

Figure 12. Effective bond lifetime at 25 °C calculated as described in the text: (a) random copolymers with increasing UPy content $M_n \sim \text{24 kg/mol}$; (b) triblock copolymers with $N_{\text{UPy}} \sim 7$, $M_n \sim \text{24 kg/mol}$, and decreasing PnBA midblock length.

Figure 13. Storage and loss modulus master curves (symbols) and predicted Rouse-like behavior (lines) for three representative samples: (a) R-18-4.1; (b) R-21-13.3; (c) T-28-3.3-39.
Conclusions

A new strategy for the synthesis of random copolymers containing n-butyl acrylate and a strongly hydrogen-bonding side chain based on 2-ureido-4[1H]-pyrimidinone (UPy) has been presented. Parent polymers containing nBA and Boc-protected 6-aminohexyl acrylate were synthesized via ATRP, and postpolymerization functionalization allows much higher levels of incorporation of UPy groups to be achieved when compared to traditional strategies. All the materials currently considered are below the entanglement molecular weight of PnBA, yet all showed high frequency/low temperature rheological behavior indicative of a transient network structure whose plateau modulus depends primarily on the average concentration of UPy's along the chain. Under uniaxial extension, the initial modulus and strain at break also depended strongly on UPy concentration. Comparison of the crossover frequencies showed that with increasing UPy content the effective bond lifetime within the transient network increased, in keeping with prior theoretical predictions. At lower frequencies both the storage and loss modulus were indicative of a transient network structure whose plateau modulus and strain at break also depended strongly on UPy concentration along the chain constant, and increasing the molecular weight had only minor effects on the bulk properties. By altering the macromolecular architecture and distribution of UPy's along the chain, dramatic changes in the dynamic behavior were observed. A series of polymers were synthesized keeping the overall molecular weight and total number of UPy's per chain constant; however, the weight fraction of the PnBA homopolymer midblock was varied which concentrates the UPy near the ends of the chains. The effective bond lifetime in these materials was strongly dependent on the chain architecture, leading to elastomeric behavior over much longer time scales. Understanding these trends will allow for the design of new UPy-based thermoplastic elastomers that fulfill the twin desires of optimal mechanical performance and a high processability.

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Supporting Information Available: 1H NMR, FTIR, and WAXS characterization of random copolymers and a comparison of the two methods for measuring τb. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

Variable temperature solid-state $^{1}$H NMR experiments were performed on related materials (mono-end-functional PnBA) in which the UPy concentration in the melt is much lower and the equilibrium therefore shifted more toward unbound UPy. Even at temperatures as high as 120 °C no evidence of unbound UPy was seen, yet the transition to terminal behavior is often very broad or inaccessible even at high temperatures/low frequencies, particularly at high UPy concentrations.

Several earlier models were also considered for comparison with the data; all failed to capture an essential feature of the rheological master curves, namely the presence of relaxations at times much longer than that corresponding to the $G^\prime/G^\prime$ crossover. This crossover time scale is widely taken to represent $\tau_{\max}$ due to the rapid transition to terminal behavior with decreasing frequency. In these UPy-based materials, however, a transition to terminal behavior with decreasing frequency. In these UPy-based materials, however, a transition to terminal behavior is often very broad or inaccessible even at high temperatures/low frequencies, particularly at high UPy concentration (see e.g. Figure 13).

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