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Dendronized polymers with ureido-pyrimidinone groups: an efficient strategy to tailor intermolecular interactions, rheology and fracture

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ABSTRACT

A library of poly(methyl methacrylate)-based dendronized polymers with generation numbers $g = 1 - 3$ was prepared, which contain different degrees of dendritic substitution (0 – 50%) with strongly hydrogen bonding 2-ureido-4[1*H*]pyrimidinone (UPy) moieties at their respective $g = 1$ levels. Our rheological and thermal studies demonstrate that the strong intermolecular UPy interactions are suppressed for $g = 2$ and essentially eliminated for $g = 3$. Focusing on samples with short backbone degrees of polymerization ($P_n \approx 40$), the linear viscoelastic response alters from liquid-like in the absence of UPy to gel-like with ever increasing moduli as the UPy content increases. Nonlinear rheological measurements indicate a transition from ductile to brittle behavior and, in parallel, a transition from shear strain thinning to shear strain hardening. This unique behavior makes UPy-DPs promising candidates for the design of new functional materials.

I. INTRODUCTION

Associating polymers are a class of responsive soft materials with versatile properties that can be tailored molecularly via molar mass, molecular structure and bonding interactions (strength, position and distribution of bonding groups).¹⁻³ The versatility of their properties, which can vary from solid-like (for example, gels) to liquid-like, gives them a central role in several technological advances, including self-healing⁴ and reinforced materials⁵⁻⁷, sensors^{8,9}, cosmetics¹⁰, and drug delivery.^{11,12}

Despite the large body of literature on the dynamics of transient networks from associating polymers, tailoring the molecular features of polymers in order to achieve optimal properties, e.g. combine mechanical toughness, ductility, good swelling behavior and self-healing, remains a formidable challenge. To this end, several efforts focused on various ways to alter properties, such as networks with different kinds of interactions or solvent-mediated gelation.¹³⁻¹⁵ Another possibility is to use polymeric systems with complex molecular structures and different kinds of bonds combined with selective functionalization; this offers several opportunities for tailoring intermolecular interactions. To this end, dendronized polymers (DPs) are interesting candidates.^{16,17}

One of the most interesting characteristics of dendronized polymers is the high degree of tunability of their molecular structure. Such polymers can be considered as molecular cylinders the aspect ratio of which can be varied to obtain slender wormlike molecules or compact bulky objects.¹⁸ Subsequently, a variety of mechanical behaviors is attainable by acting on the degree of polymerization of the backbone, P_n , and the generation number of the dendrons, g .^{19,20} An additional degree of freedom in determining the rheology of dendronized polymers is the possibility to insert functional groups in the inner and/or outer parts of the molecules. By way of

example, it was shown that solvatochromic probes covalently attached to the innermost generation can be shielded effectively from the exterior environment from the fourth generation on.²¹ Most of the dendronized polymers synthesized to date possess *tert*-butoxycarbonyl groups (Boc) as topologically peripheral end groups that can form hydrogen bonds,¹⁶ which is directly reflected in their mechanical properties.^{19,20} However, hydrogen bonds formed by Boc groups are relatively weak and give rise to a stiff network only when the degrees of polymerization of the underlying polymers are large enough to provide enhanced correlation between neighboring molecules due to a large number of binding events. As a consequence, the value of the low frequency plateau of the elastic modulus increases.²⁰

Recent developments in synthetic chemistry allowed for the functionalization of complex molecules with strong hydrogen bonding units in order to form supramolecular aggregates.²² Among the variety of hydrogen bonding groups, 2-ureido-4[1*H*]pyrimidinone (UPy) is one of the strongest units used. This group can form an array of four hydrogen bonds with an exceptionally strong dimerization constant in chloroform ($K_{\text{dim}} > 10^6 \text{ M}^{-1}$) and is synthetically readily accessible.²³ Functionalization with UPy has already been proven to be a good strategy to form novel supramolecular polymers^{24–26} and strong transient supramolecular networks^{27–30} starting from rather simple unentangled molecules. Incorporation of UPy groups in structurally complex systems such as dendronized polymers is an unexplored field yet offering the attractive possibility to explore the impact of UPy on the dynamics of dendronized polymers. This concerns two rather different cases: the one, in which the UPy groups are positioned at the ends of the branches and the one, in which they reside in the interior of these thick macromolecules. This latter case is particularly intriguing in that it provides insight into how much steric load

around a UPy group is required in order to shut down its capability to engage in intermolecular hydrogen bonding events.

In this work, we propose an efficient methodology to tailor rheology and fracture by means of controlled intermolecular interactions in DPs. To this end, we have synthesized DPs featuring short backbone degrees of polymerization $P_n \approx 40$, generations $g = 1 - 3$ and a degree of dendritic substitution with UPy moieties ranging from 0 – 50% based on the number of functional groups at the $g = 1$ level. These DPs differ in the openness of their dendritic structure as well as in the average distance between UPy moieties along the backbone. For the first-generation DPs, the UPy moieties are located at the molecular outer “surface”, whereas the UPy moieties become increasingly immersed inside the dendritic structure with increasing g . The thermomechanical properties of these novel systems were investigated as a function of UPy substitution and generation number by differential scanning calorimetry, shear rheology and uniaxial extension. Thickening in shear and ductile-to-brittle transition in extension when the UPy content increases were found. These intriguing features are not typically observed in polymer melts, including DPs, and underline the crucial role of the strong UPy bonds. A specific annealing protocol was followed in order to achieve consistency between measurements on different samples.

II. EXPERIMENTAL SECTION

II.1 Dendronized Polymer Synthesis. The synthetic approach towards DPs of generation numbers $g = 1 - 3$ bearing various fractions of UPy at the $g = 1$ level is outlined in Scheme 1. Reaction of the known macromonomer **1c**¹⁶ with trifluoroacetic acid (TFA) afforded a statistical

mixture of mono- and doubly-deprotected species along with unreacted starting material, from which the desired product was easily isolated by column chromatography owing to the vastly different polarities of the compounds involved. Thus, **2a** was obtained on a multi-gram scale (50 – 60% yield from **1c**). Subsequently, macromonomer **2b** was quantitatively obtained from **2a** in a coupling reaction with CDI-activated 6-methylisocytosine (**3**), which has been demonstrated in the literature to proceed smoothly with primary amines.³¹ The two synthesized monomers, i.e. **1c** bearing two Boc-protected amines and **2b** comprising one Boc and UPy motif each in the side chains, were subjected to radical polymerization as specified in Table 1 to give PG1- P_n -UPy(f). Here, the terms P_n and (f) denote the approximate backbone degree of polymerization and the theoretical molar fraction of UPy (based on the number of end groups in PG1) in the copolymers, respectively. The polymerization conditions were carefully chosen in order to obtain short-chained samples lacking the ability for entanglements (Entries 1 – 6; $M_n \approx 21$ kDa, $P_n \approx 40$ as determined by GPC in DMF). Higher generation numbers ($g = 2,3$; Entries 7 – 14) were synthesized in a g by g fashion, i.e. by applying the commercially available $g = 1$ dendronization reagent **1d** in a two-step deprotection-coupling protocol.¹⁶ The conversion of these postpolymerization dendronization reactions, i.e. the degree of DP structure perfection, was determined by labeling of possibly unreacted peripheral amines with 1-fluoro-2,4-dinitrobenzene (Sanger's reagent) and quantification of the resulting absorbance at 357 nm via UV-Vis spectrophotometry.^{32,33} As the characteristic absorbance band of UPy is centered around 282 nm,³⁴ no interference between UPy and Sanger-labeled sites was assumed. Thus, the calculated degrees of structure perfection exceeded 99% for all g . All details on synthesis and characterization are located in sections S1 and S2 of the Supporting Information. The

rheological investigations were carried out on selected samples, which allowed to extract a comprehensive picture.

Scheme 1. Synthesis of UPy-functionalized dendronized (co)polymers. (i) LAH, THF, $-10\text{ }^{\circ}\text{C}$; (ii) MAC, Et_3N , CH_2Cl_2 , $0\text{ }^{\circ}\text{C}$; (iii) TFA, CH_2Cl_2 ; (iv) **3**, Et_3N , DMF; (v) AIBN, (CDB,) DMF, $65\text{ }^{\circ}\text{C}$; (vi) TFA, $0\text{ }^{\circ}\text{C}$; (vii) Et_3N , DMAP, DMF.

Table 1. Conditions and results for the RAFT polymerization of **1c** and **2b** to give PG1-UPy. PG2-UPy and PG3-UPy were obtained via divergent growth.

polymerization ^a							GPC analysis ^c		
entry	sample	method	feed (1c : 2b)	$f_{2b,th}$ (mol %)	$f_{2b,exp}^b$ (mol %)	yield (%)	M_n (kDa)	PDI	P_n
1	PG1-40-UPy0	RAFT	1:0	0.0	0.0	83	21.4	1.1	41
2	PG1-40-UPy5	RAFT	9:1	5.0	5.5	88	19.3	1.2	37
3	PG1-40-UPy10	RAFT	4:1	10.0	10.1	82	23.2	1.2	43
4	PG1-40-UPy25	RAFT	1:1	25.0	25.1	80	22.8	1.2	41
5	PG1-40-UPy33	RAFT	1:2	33.3	33.4	92	20.5	1.1	37
6	PG1-40-UPy50	RAFT	0:1	50.0	50.0	87	20.9	1.2	38
dendronization ^d							GPC analysis ^c		
entry	sample	Coverage ^e (%)		yield (%)		M_n (kDa)	PDI	P_n	
7	PG2-40-UPy0	99.8		72		50	1.1	41	
8	PG2-40-UPy5	99.8		70		44	1.1	36	
9	PG2-40-UPy25	99.7		69		44	1.2	40	
10	PG2-40-UPy50	99.1		70		35	1.2	38	
11	PG3-40-UPy0	99.8		81		105	1.1	40	
12	PG3-40-UPy5	99.9		77		94	1.1	37	
13	PG3-40-UPy25	99.2		85		86	1.2	41	
14	PG3-40-UPy50 ^f	99.1		78		61	1.2	37	

^aCarried out at a concentration of 1.0 g mL⁻¹ in DMF at 65 °C using azobisisobutyronitrile (AIBN) as the initiator and cumyl dithiobenzoate (CDB) as the chain transfer agent in RAFT. ^bDetermined by ¹H NMR spectroscopy. ^cGPC in DMF at 45 °C calibrated with poly(methyl methacrylate) standards. ^dCarried out at a concentration of 1.0 g·mL⁻¹ in DMF at room temperature. ^eDetermined by UV-labeling with 1-fluoro-2,4-dinitrobenzene (Sanger's reagent). Additional information on the UV-labeling procedure can be found in section S4 of the Supporting Information. ^fThis sample exhibited substantial foaming at high temperatures and was not investigated further.

II.2 Gel Permeation Chromatography. Gel permeation chromatography (GPC) using DMF containing LiBr ($c = 1 \text{ g L}^{-1}$) as the eluent was performed on a VISCOTEK GPCmax VE-2001 instrument (Malvern, UK) equipped with D5000 columns ($300 \times 8.0 \text{ mm}$), refractive index (RI), viscometry (differential pressure) and light scattering (LS; 15° and 90° angles) detectors.

Column oven and detector temperatures were regulated to 45 °C. All samples were filtered through 0.45 µm PTFE syringe filters (Macherey-Nagel, Germany) prior to injection and the flow rate was 1 mL min⁻¹. Poly(methyl methacrylate) standards with peak molecular weights (M_p) of 0.10, 0.212, 0.66, 0.981 and 2.73 MDa (Polymer Laboratories Ltd., UK) were used for calibration. The number average molar masses (M_n), weight average molar masses (M_w) and polydispersity values (PDI) of the synthesized polymers were determined by light scattering using the commercially available OmniSEC software (Malvern, UK). Typical results are shown in section S5 of the Supporting Information.

II.3 Thermal Analysis. Differential scanning calorimetry (DSC) measurements were conducted on a DSC Q1000 (TA Instruments, USA) over a temperature range from -90 °C to 250 °C in an atmosphere of nitrogen. Approximately 4 – 25 mg of dried sample was weighed into an aluminum DSC pan and covered with a punched cap. The samples were subjected to ≥ 2 heating/cooling cycles with a linear heating/cooling rate of 10 °C min⁻¹. The glass transition temperatures (T_g) were determined from the second heating runs and analyzed using the commercially available Universal Analysis software (TA Instruments, USA). Results are presented in section S6 of the Supporting Information.

II.4 Rheology.

II.4.1 Annealing of the samples. The samples tested in nonlinear shear and uniaxial extension, i.e. PG1-40 with a UPy content ranging from 0 to 25%, were pre-annealed in a vacuum oven at 100 °C for 8 days in order to avoid ageing effects. The pre-annealing temperature is well-above the glass transition of such samples (see section III.2). However, our TGA measurements

confirm that $T = 100\text{ }^{\circ}\text{C}$ is in the safe range for preventing degradation during long-time annealing (for exemplary TGA traces cf. section S7 of the Supporting Information).

After pre-annealing, the samples were cooled-down and stored in vacuum at room temperature. In order to carry out rheological measurements, the pre-annealed samples are shaped to discoid specimens with a radius of 3 – 4 mm and a thickness of 0.8 – 2 mm. In general, compression molding in vacuum is used to obtain the discs. However, the samples obtained with compression molding at high temperature were difficult to extract from the mold because of their brittleness at room temperature. For this reason, the annealed powders were cold-pressed to discoid capsules using vacuum molding at room temperature. The capsules were loaded into the rheometer and allowed to melt and homogenize at $T_g + 50\text{ }^{\circ}\text{C}$ for 20 minutes. Thereafter, the temperature was lowered to $T_g + 30\text{ }^{\circ}\text{C}$ and rheological measurements were started. Whenever possible, the leftovers coming from filament breaking in nonlinear extension or fracture in nonlinear shear were recycled and cold-pressed to new specimens. Possible degradation was excluded in simple shear before each nonlinear measurement by performing frequency sweeps in the linear regime and checking for overlap with previous data. For uniaxial extension, possible degradation was ruled out by verifying the reproducibility of the transient measurements and the consistency with data at different stretching rates.

II.4.2 Simple shear. Linear measurements were performed on a Physica MCR702 (Anton Paar, Germany), equipped with a hybrid temperature control (CTD180) and on an ARES rheometer (TA, USA) equipped with a convection oven. Linear measurements were carried out with 8 mm and 4 mm parallel plate geometries. The samples were cold pressed to discoid specimens (see section II.4.1) of the proper diameter and allowed to melt in the rheometer.

Nonlinear shear measurements were performed with a homemade cone-partitioned plate geometry to prevent artefacts from edge fracture instability.³⁵ The temperature for nonlinear shear was chosen as $T_g + 45$ °C for most of the samples.

II.4.3 Uniaxial extension. Extensional measurements were performed on a filament stretching rheometer (Vader 1000 from Rheo Filament ApS). The specimens were formed to cylinders of 6 mm diameter with cold-pressing. Nonlinear extensional measurements on the samples investigated were performed at $T_g + 29$ °C. The aspect ratio $\Lambda_0 = h/R_0$ of the samples ranged from 0.73 to 0.97, with h being the height of the sample and R_0 being the radius.

III. RESULTS AND DISCUSSION

III.1 DP composition and UPy-dimerization. The monomer composition ratios in the PG1-UPy polymers were determined by ¹H NMR spectroscopy in CDCl₃. The spectra reveal the existence of extensive four-fold hydrogen bonding via the 4[1*H*]-pyrimidinone dimer due to the presence of characteristic peaks at 13.0, 11.9 and 10.3 ppm corresponding to the UPy-NH signals.³⁶ Because of the unfavorable broadening of these signals, we called on the ratio of integrals associated with the allylic proton in the pyrimidinone ring (5.8 ppm) of **2b** and the proton resonances originating from the peripheral *tert*-butyl groups (1.4 ppm) in **1c** and **2b** for the determination of the copolymer compositions. In all cases, the observed polymer composition was found to be within a very narrow range compared to the feed molar ratio, suggesting a statistical distribution of both monomers in the PG1-UPy copolymers due to arguably identical reactivity ratios and no significant promotion of chain transfer by the UPy motif (cf. Table 1 and section S3 of the Supporting Information).

In the case of PG1, the UPy groups are located at the topological periphery of the grafted dendrons. Hence, they can participate in both inter- and intramolecular associations. For higher polymer generations, the UPy groups remain at the $g = 1$ level, i.e. they are immersed in the dendritic structure and surrounded by the large $g = 2$ or $g = 3$ dendrons. The NMR spectra of these higher generation DPs indicate that UPy-dimerization takes place in all samples with the exception of PG3-40-UPy5. However, the above discussed dimer signals cannot normally be used to differentiate between inter- or intramolecular UPy-associations as the chemical shifts would be identical. Thus, the question of whether steric load in the neighborhood of UPy groups can block-off intermolecular dimerization cannot be addressed spectroscopically by NMR. In the case of PG3-40-UPy5, however, the typical signals of the UPy dimer are absent suggesting the presence of non-dimerized, single UPy moieties (cf. section S3 of the Supporting Information). Such a case has so far never been observed in UPy chemistry due to its extraordinarily high dimerization constant. While this surprising observation does not help the issue with intra- versus intermolecular dimerization in the other cases, it suggests that the dimers in the other PG3-40-UPy samples with higher UPy content are intramolecular serving as a means of molecular reinforcement within the interior of the macromolecules. To confirm this conclusion by independent studies and to investigate the situation for the PG2-40-UPy series, rheological measurements seemed ideally suited as they directly sense even subtle intermolecular interactions.

III.2 Differential Scanning Calorimetry. The thermal transition of the synthesized DPs reflects the reduced segmental mobility originating from the enhanced steric hindrance around the polymeric backbone and the approach to the actual glass, respectively, as well as the effect of

hydrogen bonding. Hence, we assign the “glass temperature” (T_g) to the detected single transition in DSC (cf. Figure S4(a) of section S6 of the Supporting Information). The presence of only one T_g for the copolymers suggests that the copolymerization of the two macromonomers **1c** and **2b** proceeded in a random fashion, as already indicated by the results from ^1H NMR spectroscopy (*vide supra*). Figure 1(a) illustrates the compiled T_g values of the PG1-40-UPy copolymers as a function of UPy content and a numerical summary can be found in section S6 of the Supporting Information. The presence of dendrons of first generation around the PMMA backbone induces a plasticizing effect which promotes a decrease of T_g with respect to the bare polymer backbone. On the other hand, such an effect is opposed by supramolecular groups which restrict local motion of the dendrons. As shown previously in the literature for other randomly UPy-functionalized copolymers, the T_g values of the PG1-40-UPy samples increase in a linear fashion with the number of hydrogen bonding side groups (from $\sim 38^\circ\text{C}$ in PG1-40-UPy0 to $\sim 127^\circ\text{C}$ in PG1-40-UPy50).^{27–29} At virtually identical backbone chain lengths ($P_n \approx 40$), the enthalpy steps involved in the glass transition of these copolymers decrease with increasing UPy content, consistently, as inferred from the relative DSC heat flow traces normalized by the sample weight (cf. Figure S4(a) of the Supporting Information). Moreover, the concomitant broadening of the transition becomes particularly apparent from the respective differentiated DSC traces (cf. Figure S4(b)). The observed results can be rationalized by the formation of a supramolecular network involving the strongly hydrogen bonding UPy groups, which act as temporary cross-links. By increasing the number of UPy groups in the copolymers, the network’s mesh size is reduced and, hence, chain dynamics are slowed down and the available free volume is decreased.

By comparison, the interpretation of the results obtained for the higher-generation DPs in this study appears more complex, as the segmental mobility of these DPs becomes additionally

related to the generation number. Increasing the dendron generation increases both the number of dangling end groups and the number density of the branching points, i.e. the compactness of the structure. However, end groups and branching sites affect the glass transition in opposite directions: On the one hand, increased branching affords denser packing and reduces the local segmental mobility, which ultimately leads to an increase of T_g . On the other hand, a larger number of peripheral end groups enhances local fluctuation and effects a decrease of T_g .^{37–39} Figure 1b illustrates the compiled T_g values of the DPs containing 5, 25 and 50% UPy as a function of generation, along with the data on the respective DPs without UPy-groups (a numerical summary of the T_g values obtained for DPs with $g = 2,3$ is provided in section S6 of the Supporting Information). In the case of PG1-40-UPy0, PG1-40-UPy5 and PG1-40-UPy25, the T_g values saturate with increasing polymer generation, which is in line with existing reports indicating that the glass temperature increases with g before approaching a final value after approximately the fourth generation.^{19,20,39,40} The observed saturation of T_g is owed to the bulky pendant side groups of these DPs and reflects their enhanced backbone rigidity with increasing dendron generation. In this regard, it can also be considered analogous to the respective saturation with molar mass in linear polymers and dendrimers.^{41,42} With the exemption of the series containing 50% UPy, the difference in T_g values between the first- and third-generation DPs of each series narrows down with increasing UPy content. Based on the virtually identical T_g values of PG3-40-UPy5 and PG3-40-UPy0, it can be reasoned that the UPy moieties in PG3-40-UPy5 are completely immersed in the interior of the DP. Consequently, the possibility for specific intermolecular hydrogen bonding interactions by the UPy moieties is effectively inhibited due to steric shielding by the surrounding dendrons. Moreover, the arguably highly statistical incorporation of the UPy-bearing monomer **2b** into the polymer combined with the

large excess of unfunctionalized monomer **1c** (**1c:2b** = 9:1) renders intramolecular UPy-UPy-dimerization unlikely, as substantiated by the results obtained from ^1H NMR spectroscopy. In contrast, dendronization of PG1-40-UPy50 results in a greatly reduced T_g value of PG2-40-UPy50, despite the 50% lower grafting density compared to UPy-unfunctionalized DPs. Evidently, already one dendron generation suffices to significantly reduce the amount of intermolecular UPy-UPy dimerization, with the decrease in the T_g upon dendronization of PG2-40-UPy50 to PG3-40-UPy50 being marked albeit much smaller. Due to the close proximity of UPy moieties in these DPs, a shift from inter- to intramolecular UPy dimerization takes place, as already evidenced by the recorded ^1H NMR spectra of the samples containing 25% UPy (cf. section S3 of the Supporting Information). It is important to note that one distinct advantage of our present polymers is that the degree of polymerization in each homologous series remains virtually constant, which allows for systematic investigation of properties as a function of generation. The results indicate that the thermal properties of the present DPs are predominantly

governed by the number and location of UPy groups in the polymers. Hence, the T_g values of DPs can be tuned via both generation growth and the degree of UPy-functionalization.

III.3 Linear Viscoelasticity.

III.3.1 Ageing protocol and reproducibility of the measurements. In previous work, we have reported that dendronized polymers undergo ageing due to the tendency of dendrons to mutually interpenetrate in order to minimize intermolecular density gradients.²⁰ Because of steric hindrance and cooperative rearrangement of the dendrons, the ageing process is rather slow with

Figure 1. (a) Linear relation between T_g and the UPy content in PG1-UPy; $P_n \approx 40$. (b) T_g as a function of g for PGg featuring 0, 5, 25 and 50% UPy monomer; $P_n \approx 40$. The results were obtained by DSC measured from -50 to 150 °C, 10 °C min^{-1} in N_2 and the lines are drawn to guide the eye.

the required time depending on the initial state of the particular sample. In our previous report on dendronized polymers²⁰ we followed a specific protocol for the equilibration of the samples, namely, we loaded the specimen in the rheometer and monitored the temporal evolution of the dynamic moduli at a fixed temperature until they reached a plateau. Then, we started linear

rheological measurements. In the present work, we used a different annealing strategy in order to facilitate nonlinear rheological measurements. As described in section II.4.1, the samples were annealed in vacuum for a long time (8 days) at high temperature (100 °C) in accordance with their chemical stability. The differences between the two protocols are described in detail in section S8 of the Supporting Information. After the annealing protocol used here, the samples were found to reach a stable state that did not change upon further annealing and the rheological measurements performed before and after recycling of the samples were reproducible, as shown in Figure 2.

Figure 2. (a) Frequency sweep tests performed on different specimens of the sample PG1-40-UPy5 before nonlinear shear ($T = 96$ °C). Specimen 1 was made from polymer after annealing in vacuum. Specimens 2 and 3 were obtained from polymer recycled from previous nonlinear measurements both in shear and extension. (b) Frequency sweep tests performed on different specimens of the sample PG1-40-UPy10 before nonlinear shear ($T = 97$ °C). Specimen 1 was made from polymer after annealing in vacuum. Specimens 2 and 3 were obtained from polymer recycled from previous nonlinear measurements.

III.3.2 Effect of coverage of the outer molecular surface with UPy groups. As described above, Boc groups can be replaced by UPy groups. Figure 3 reports the linear mastercurves of the samples PG1-40-UPy comprising different degrees of substitution of the outer branches, from 0 to 25%. The mastercurves are reported at the same distance from the glass temperature ($T_{\text{ref}} = T_g + 45\text{ }^{\circ}\text{C}$). Time-temperature superposition (TTS) based on a two-dimensional minimization approach was used in order to build the viscoelastic master curves (see section S9 of the Supporting Information). We note that TTS works only apparently as strong hydrogen bonding induces thermoreological complexity, as demonstrated by the Van Gorp-Palmen plots for the different PG1-40-UPy samples (figure S9 of the supporting information). However, the temperature dependence of the apparent shift factor at the same distance from T_g is identical for the different samples (figure S10 of the supporting information). For each sample, the frequency sweep test performed at $T_{\text{ref}} = T_g + 45\text{ }^{\circ}\text{C}$ was used as reference. As expected, increasing the concentration of UPy leads to an enhancement of the viscoelastic properties.²⁸ The sample PG1-40-UPy0 features a liquid-like behavior with $G'' > G'$ over the whole frequency range. At high frequencies, the moduli are parallel with a slope of 0.65 indicating Rouse-Zimm dynamics. At lower frequencies, a neat transition from Rouse-Zimm to terminal behavior is observed.

In the high frequency range, the sample PG1-40-UPy5 has similar behavior as PG1-40-UPy0. However, the transition from high frequency behavior to the terminal regime is characterized by the tendency of the elastic modulus to form a plateau. The plateau of G' becomes evident as the UPy content is increased to 10%. For this sample, G' is larger than G'' in the intermediate frequency range. As the UPy degree of substitution is raised to 25%, the elastic plateau increases by one decade compared to PG1-40-UPy10. Moreover, the sample PG1-40-UPy25 does not approach terminal flow behavior at low frequencies. We note that, given the unentangled

character of the DPs examined here, elasticity (i.e., plateau of G') is essentially provided by supramolecular associations. Concerning the terminal relaxation time τ , we can estimate it as a product of the zero shear viscosity $\eta_0 = \lim_{\omega \rightarrow 0} G''(\omega)/\omega$ by the steady state recoverable compliance $J_e = \lim_{\omega \rightarrow 0} G'(\omega)/G''(\omega)^2$, therefore $\tau = \lim_{\omega \rightarrow 0} G'(\omega)/[\omega G''(\omega)]$. Figure 3(b) shows the product $\eta_0 J_e$ as a function of ω for the four samples investigated. Despite the fact that a plateau is not approached at low frequencies for all samples, an increase of terminal relaxation time upon increase of UPy content is unambiguous.⁴³

Figure 3. Linear viscoelastic mastercurves of the samples PG1-40 with different degree of UPy coverage (from 0 to 25%) reported at the same distance from the glass temperature ($T_{ref} = T_g + 45^\circ\text{C}$).

The increase of the elastic plateau modulus G upon increase of UPy concentration is not surprising. The elastic modulus is given by $G = \nu kT$, where ν is the number density of cross-links. In the specific case, cross-links are provided exclusively by supramolecular interactions. An increase of molecular UPy content induces a proportional increase of the number density ν , and consequently of the elastic plateau modulus G . Slowing down of relaxation dynamics upon

increase of sticky groups per molecule is readily understood based on relatively simple models for simple linear chains, such as the sticky Rouse model.⁴⁴ The latter predicts a terminal relaxation time given by $\tau = \tau_b N_s^2$, with τ_b being the lifetime of a bond and N_s being the number of stickers per chain.⁴⁵ The larger the stickers content, the larger the amount of stickers per chain and, consequently, the larger the terminal time. Considering the high persistence length of DPs, the different HB groups, and the fact that the amount of intermolecular associations with respect to intramolecular ones is affected by Upy concentration, a detailed description of the LVE results based on the sticky-Rouse would be too simplistic. On the other hand, detailed models capable to describe dynamics of complex systems with supramolecular interactions, such as DPs, are yet to be developed. Therefore, we restrict here the discussion to a phenomenological level and a naïve estimation of an average bonding lifetime for Upy-DPs based on sticky Rouse model, which yields a value of the order of 0.1 s at $T = T_g + 45$ °C and $\tau_b \sim 13$ s at $T = T_g + 29$ °C

III.3.3 Shielding the interactions by immersing the UPy groups in the inner part of the molecule.

UPy moieties can be immersed in the inner part of the molecule by growing classic generations on top of the first one. As intermolecular bonding mainly occurs between the outermost branches of different molecules, growing classic generations on top of the branches functionalized with UPy should screen strong intermolecular UPy-interactions. Figure 4 shows the mastercurves of UPy-functionalized samples with weakly interacting second- (Figure 4a) and third-generation (Figure 4b) classic dendrons. Since measurements were limited to linear viscoelasticity, the samples were annealed according to the previously used protocol.²⁰ In both cases, increasing the UPy content in the inner part of the molecule from 0 to 25% does not contribute significantly to the plateau modulus. This becomes particularly apparent for $g = 3$ where the screening of UPy groups is much more effective. Note that the terminal regime of PG3-50 is broader than PG1-50

and PG2-50. Also, PG3-50 (with more chain ends and therefore sticky Boc groups) exhibits an elastic plateau which is absent for PG1-50 and PG2-50. The broadness is attributed to a combination of stiffness, polydispersity, exchange of associations (hydrogen-bonding and Boc, and pi-pi stacking, but not intermolecular Upy-associations). Hence, it is evident that it is possible to incorporate a UPy group inside such a macromolecule (DP is third generation) without affecting its linear viscoelastic properties. We speculate that such an embedded group could have specific function, for example with applications in controlled drug release.

Figure 4. (a) linear viscoelastic mastercurves of the samples PG2-40 with UPy ($T_{ref} = T_g + 45$ °C); (b) linear viscoelastic mastercurves of the samples PG3-40 with UPy ($T_{ref} = T_g + 30$ °C).

III.4 Nonlinear Rheology.

III.4.1 Uniaxial extension. PG1-40-UPy samples were subjected to uniaxial extension at the same distance from the glass temperature ($T = T_g + 29$ °C). The results of transient uniaxial extensional measurements are shown in Figure 5. Measurements on the unfunctionalized sample PG1-40-UPy0 were performed at a slightly larger distance from T_g compared to the functionalized ones ($T - T_g = 34$ °C instead of 29 °C). In the range of strain rates explored, PG1-

40-UPy0 exhibits weak strain hardening, which can be barely discerned due to experimental noise. Strain hardening becomes evident for PG1-40-UPy5. The departure of the transient extensional viscosity of such sample from the LVE envelope is indeed unambiguous. Moreover, the stress growth coefficient reaches steady state for the three lowest rates. Both PG1-40-UPy0 and PG1-40-UPy5 exhibit ductile behavior in uniaxial extension, i.e. deformation does not imply failure. Therefore, the samples could be stretched up to the maximum achievable Hencky strains and form thin filaments. Note that the characteristic terminal relaxation time of PG1-40-UPy5 is $\tau_D = 75 \pm 10$ s at the temperature set for extensional tests, i.e. $T = T_g + 29 = 80$ °C (evaluated according to the same procedure as in Figure 3(b), see also section S10 of the Supporting Information). From the inverse of τ_D we obtain a characteristic frequency, $\omega_c = 0.013 \pm 0.001$ rad/s. Based on this value, we note that ductile behavior is observed even when the strain rate exceeded the inverse of the characteristic time of the material. Some of the thin filaments originating from extension of such samples are displayed in Figure 6 (1-4). Concerning samples with larger UPy fraction, it was not possible to detect strain hardening because brittle fracture occurred as soon as extensional viscosity departed from the LVE envelope. This behavior is generally observed when the experimental time-scale is smaller than the association lifetime of supramolecular bonds.⁴⁶ the terminal time of PG1-40-UPy10 at 81 °C is about 800 s (cf. section S10 of the Supporting Information). Since DPs of first generation possess two branches per repeating unit, the total number of branches per molecule at $P_n = 40$, is $N_b = 80$. Considering 10% of UPy fraction, we obtain a number of stickers per chain $N_s = N_b \times 0.1 = 8$. As above-mentioned, an approximative estimation of the bond lifetime based on the sticky Rouse model yields $\tau_b \sim 13$ s. If we consider the inverse of the strain rate as characteristic experimental time-scale, at the two highest strain rates the estimated bonding lifetime would be larger than the

experimental timescale for PG1-40-UPy10. Such condition determines strain hardening due to stretch of the side-branches before dissociation of the terminal groups. However, strain hardening occurs even at the lowest rates. We speculate that this is due to the cooperativity of supramolecular associations and topological constraints in hindering the complete decorrelation of the side-dendrons before stretching of branches occurs (Velcro picture) even at the lowest rates. The transition from ductile to brittle behavior upon increase of the UPy molecular content can be explained tentatively from a microscopic perspective by considering the evolution of the particular structure of UPy-functionalized dendronized polymers in uniaxial extensional flow. The configuration of such polymers in the molten state is akin to short bulky objects with finite extensibility preferably oriented parallel to each other along the flow direction, with the dendrons of one DP locked at the edge to the dendrons of neighboring DPs via strong hydrogen bonds exerted by the UPy groups. Upon application of uniaxial extensional deformation, molecules tend to orient in the direction of flow and possibly become stretched. The orientation/stretching process cause local motion and stretching of the dendrons locked by hydrogen bonding via UPy groups. The finite extensibility of the molecular subunits between sticky groups is responsible for substantial resistance to extensional flow and strain hardening of the UPy functionalized samples. Typical images of catastrophic failure with samples PG1-40-UPy10 and PG1-40-UPy25 are shown in Figure 6 (5-8). We note that brittle behavior was observed at strain rates larger than the inverse of the terminal relaxation time. Similar behavior was observed for PG1-40-UPy25.

Figure 5. Extensional transient viscosity of UPy-DPs. (a) PG1-40-UPy0 at $T = 72\text{ }^{\circ}\text{C}$; (b) PG1-40-UPy5 at $T = 80\text{ }^{\circ}\text{C}$; (c) PG1-40-UPy10 at $T = 81\text{ }^{\circ}\text{C}$. Extensional measurements on the sample PG1-40-UPy25 are shown in Figure S12, section S11 of the Supporting Information. Extensional rates are indicated in the corresponding panels with the symbol E .

If the fraction of Upy groups is below 5%, the modulus of the DPs is relatively low and they can deform elastically, giving rise to ductile response. With such a low fraction, bond breaking is not

accompanied by easy recombination (which becomes less probable), hence this may lead to local dissipation of the elastic energy. If the bonding density is increased beyond 10%, the Velcro picture is relevant with bond breaking and reformation taking place in a cooperative fashion. At a certain stretch rate, the global breaking of bonds leads to material failure (brittle fracture) without possibility for immediate reformation. Typical examples are shown in Figure 6 (5-8).

Figure 6. Ductile to brittle transition of UPy-DPs: 1. PG1-40-UPy0 ($E=0.01$); 2. PG1-40-UPy0 ($E=0.03$); 3. PG1-40-UPy5 ($E=0.01$); 4. PG1-40-UPy5 ($E=0.03$); 5. PG1-40-UPy10 ($E=0.1$); 6. PG1-40-UPy10 ($E=0.3$); 7. PG1-40-UPy25 ($E=0.01$); 8. PG1-40-UPy25 ($E=0.03$).

III.4.2 Simple shear. Nonlinear shear experiments on the unfunctionalized sample PG1-40-UPy0 revealed a shear thinning behavior with reduced deformability.²⁰ Incorporation of strongly hydrogen bonding units to DPs causes a remarkable transition from shear thinning to transient shear hardening behavior (Figure 7). At UPy concentration of 5%, as the shear rate is increased beyond 1 s^{-1} , the transient viscosity increases beyond the LVE prediction (Figure 7(a)). The strain hardening is more apparent as the shear rate increases. A similar behavior is observed with 10% of UPy. When the molecular UPy content is increased to 25%, the samples fracture around

the peak viscosity region at the onset of strain hardening (Figure 7(d)). This behavior is unique to these UPy-functionalized DPs. It has not been reported in molten polymers or classic DPs.^{20,47}

Figure 7. Nonlinear startup shear measurements on UPy-DPs. (a) PG1-40-UPy0 at $T = 88\text{ }^{\circ}\text{C}$; (b) PG1-40-UPy5 at $T = 96\text{ }^{\circ}\text{C}$; (c) PG1-40-UPy10 at $T = 97\text{ }^{\circ}\text{C}$; (d) PG1-40-UPy25 at $T = 120\text{ }^{\circ}\text{C}$. Shear rate values are indicated in the corresponding panels with the symbol D .

Strain hardening in shear has been already observed for aqueous solutions of associative polymers and attributed to chain stretching of segments trapped by supramolecular bonds.^{48–50}

In analogy to the extensional behavior, strain hardening in shear is attributed to stretching of the dendrons before bond-breakage occurs. In particular, the transition from ductile to brittle behavior in extension can be related to the capacity of UPy-DPs to undergo shear thinning in simple shear. Figure 8 reports the applicability of Cox-Merz rule to UPy-DPs. The applicability of such rule to the unfunctionalized sample is confirmed. However, the introduction of small amounts of UPy to the molecules implies the failing of Cox-Merz. In particular, the steady state viscosity of the sample PG1-50-UPy5 tends to shear thinning at larger values of shear rate compared to the linear prediction, however when shear thinning occurs, the power-law decay of viscosity has a larger exponent than the LVE prediction (faster decay of viscosity upon shear rate). Both ductile samples have the ability to shear thin in nonlinear shear. The strain hardening in shear has the same origin as in extension, i.e. stretching of the dendrons before hydrogen bonds are broken. In this view, larger dendrons of generation 2 and 3 are expected to show a However, when the UPy content is less than 5%, the molecules can easily disengage from each other and diffuse (a distance equivalent to their center of mass). Hence, they display shear thinning in shear and ductility in extension.

Figure 8. Applicability of the Cox-Merz rule for UPy-DPs. Temperatures and shear rates are the same as Figure 7.

On the other hand, the samples PG1-40-UPy10 and PG1-40-UPy25 do not really have the possibility to shear thin, as it can be observed in Figure 8. Indeed, sample PG1-40-UPy10 exhibits failure of Cox-Merz rule as for PG1-UPy5. Moreover, catastrophic failure occurs before shear thinning is observed. Strong shear fracture hinders the possibility to detect steady state viscosity in the shear thinning regime. A similar behavior is observed also for PG1-40-UPy25.

Figure 9 depicts the strain hardening factor of PG1-40-UPy5 and PG1-40-UPy10, i.e. the transient nonlinear shear viscosity normalized by the viscosity evolution in linear regime. A larger capacity of strain hardening of PG1-40-UPy10 compared to PG1-40-UPy5 is apparent. Such capacity is attributed to the larger amount of stretch of the dendrons before the molecules become uncorrelated owing to the disruption of the hydrogen bonds. In this respect, we conjecture that the amount of hardening is dictated by the finite extensibility of the segments

between two inter-molecular Upy-bonds. Indeed strain hardening in shear is a characteristic feature of FENE models.⁵¹⁻⁵³ Based on this picture, Upy-DPs of second and third generation are expected to show a less pronounced shear strain hardening as the number of segments between branches, and consequently the extensibility parameter, are larger compared to Upy-DPs of first generation. Investigation along this direction is subject of future work. Figure 10 shows that the transient viscosity overshoot at high shear rates scales with the strain, the value ($\gamma_{max} = 3.1 \pm 0.2$) of which is larger compared to that of unfunctionalized samples (PG1-40-Upy0, $\gamma_{max} = 2.3 \pm 0.2$). This means that the dendrons locked by UPy are effectively stretched compared to the unfunctionalized samples.

Figure 9. Strain hardening factor as a function of time for the samples PG1-40-Upy5 (blue symbols) at $T=96^\circ\text{C}$ and PG1-40-Upy10 (red symbols) at $T=97^\circ\text{C}$.

Figure 10. Transient shear viscosity of the sample PG1-40-UPy5 plotted as a function of strain.

IV. CONCLUDING REMARKS

We have investigated the linear and nonlinear rheological properties of a series of short-chained dendronized polymers with $P_n \approx 40$ and generation numbers $g = 1 - 3$, in which 0 to 50% of the branches at the $g = 1$ level carry strongly hydrogen bonding UPy groups. Different annealing protocols have revealed an unusual dependency of the characteristic times on the thermal history of the samples. This is attributed to the correlation between the thermal history and the degree of interdigitation of the samples. Linear measurements indicate enhanced viscoelastic properties upon increasing the UPy content of the macromolecules, which are not typically observed in molten polymers, including the classic DPs. Nonlinear uniaxial extensional experiments show a transition from ductile to brittle at the same distance from the glass temperature. This is attributed to the reduced availability of free ends for dissipating elastic energy as the UPy

concentration increases. Further, the presence of UPy groups in PG1 causes the onset of strain hardening in nonlinear shear. Such a remarkable behavior is attributed to strong intermolecular forces arising from the interaction of the locked dendrons under shear (akin to a Velcro picture). Regarding the PG2 and PG3 samples with UPy groups in the interior (at the $g = 1$ level), we find that already one dendron generation beyond $g = 1$ suffices to effectively block-off intermolecular UPy interactions, as proven by the virtually identical mechanical response of both DPs. This is in stark contrast to shielding experiments with structurally closely related DPs which carry solvatochromic probes at the $g=1$ level instead of UPy. While solvent is still able to swell the corresponding DPs up to the fourth generation, the similarly sized UPy groups evidently cannot mutually interpenetrate beyond the second generation. The very fact that UPy groups are part of a macromolecule and not as independent as solvent molecules seems to have a bearing on this unexpected finding. The absence of intermolecular dimerization was used to create a situation in which the UPy groups could not dimerize at all, a case which because of the high binding constant had never been observed. In PG3-40-UPy5, the UPy groups are so spaced out along the main chain that they cannot find each other anymore resulting in the absence of the so typical UPy dimer signals in NMR spectroscopy. The high degree of tunability of both linear and nonlinear properties and the unique nonlinear behavior in shear and extension makes these novel polymers with only around 40 repeating units promising candidates for the design of new functional materials.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

All synthetic procedures and NMR spectra; GPC and DSC traces; Complementary rheological data (PDF)

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Notes

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REFERENCES AND NOTES

- (1) Bosman, A. W.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymers at Work. *Mater. Today* **2004**, 7 (4), 34–39.
- (2) Seiffert, S.; Sprakel, J. Physical Chemistry of Supramolecular Polymer Networks. *Chem. Soc. Rev.* **2012**, 41 (2), 909–930.
- (3) Yang, L.; Tan, X.; Wang, Z.; Zhang, X. Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions. *Chem. Rev.* **2015**, 115 (15), 7196–7239.
- (4) Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. Self-Healing and Thermoreversible Rubber from Supramolecular Assembly. *Nature* **2008**, 451 (7181), 977–980.
- (5) Croisier, E.; Liang, S.; Schweizer, T.; Balog, S.; Mionić, M.; Snellings, R.; Cugnoni, J.; Michaud, V.; Frauenrath, H. A Toolbox of Oligopeptide-Modified Polymers for Tailored Elastomers. *Nat. Commun.* **2014**, 5.
- (6) Luo, M.-C.; Zeng, J.; Fu, X.; Huang, G.; Wu, J. Toughening Diene Elastomers by Strong Hydrogen Bond Interactions. *Polymer (Guildf)*. **2016**, 106, 21–28.
- (7) Baeza, G. P.; Sharma, A.; Louhichi, A.; Imperiali, L.; Appel, W. P. J.; Fitié, C. F. C.; Lettinga, M. P.; Van Ruymbeke, E.; Vlassopoulos, D. Multiscale Organization of Thermoplastic Elastomers with Varying Content of Hard Segments. *Polymer (Guildf)*. **2016**, 107, 89–101.

- (8) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; Sandanayake, K. R. A. S. Molecular Fluorescent Signalling with “Fluor-Spacer-Receptor” Systems: Approaches to Sensing and Switching Devices via Supramolecular Photophysics. *Chem. Soc. Rev.* **1992**, *21* (3), 187–195 DOI: 10.1039/CS9922100187.
- (9) Sangeetha, N. M.; Maitra, U. Supramolecular Gels: Functions and Uses. *Chem. Soc. Rev.* **2005**, *34* (10), 821–836.
- (10) Boekhoven, J.; Stupp, S. I. 25th Anniversary Article: Supramolecular Materials for Regenerative Medicine. *Adv. Mater.* **2014**, *26* (11), 1642–1659.
- (11) Li, J.; Loh, X. J. Cyclodextrin-Based Supramolecular Architectures: Syntheses, Structures, and Applications for Drug and Gene Delivery. *Adv. Drug Deliv. Rev.* **2008**, *60* (9), 1000–1017.
- (12) Webber, M. J.; Appel, E. A.; Vinciguerra, B.; Cortinas, A. B.; Thapa, L. S.; Jhunjhunwala, S.; Isaacs, L.; Langer, R.; Anderson, D. G. Supramolecular PEGylation of Biopharmaceuticals. *Proc. Natl. Acad. Sci.* **2016**, *113* (50), 14189–14194.
- (13) Steed, J. W. Supramolecular Gel Chemistry: Developments over the Last Decade. *Chem. Commun.* **2011**, *47* (5), 1379–1383.
- (14) Appel, E. A.; del Barrio, J.; Loh, X. J.; Scherman, O. A. Supramolecular Polymeric Hydrogels. *Chem. Soc. Rev.* **2012**, *41* (18), 6195–6214.

- (15) Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. Self-Healing Supramolecular Gels Formed by Crown Ether Based Host–Guest Interactions. *Angew. Chemie Int. Ed.* **2012**, *51* (28), 7011–7015.
- (16) Guo, Y.; van Beek, J. D.; Zhang, B.; Colussi, M.; Walde, P.; Zhang, A.; Kröger, M.; Halperin, A.; Dieter Schlüter, A. Tuning Polymer Thickness: Synthesis and Scaling Theory of Homologous Series of Dendronized Polymers. *J. Am. Chem. Soc.* **2009**, *131* (33), 11841–11854.
- (17) Schlüter, A. D.; Rabe, J. P. Dendronized Polymers: Synthesis, Characterization, Assembly at Interfaces, and Manipulation. *Angew. Chemie Int. Ed.* **2000**, *39* (5), 864–883.
- (18) Schlüter, A. D.; Halperin, A.; Kröger, M.; Vlassopoulos, D.; Wegner, G.; Zhang, B. Dendronized Polymers: Molecular Objects between Conventional Linear Polymers and Colloidal Particles. *ACS Macro Lett.* **2014**, 991–998.
- (19) Pasquino, R.; Zhang, B.; Sigel, R.; Yu, H.; Ottiger, M.; Bertran, O.; Aleman, C.; Schlüter, A. D.; Vlassopoulos, D. Linear Viscoelastic Response of Dendronized Polymers. *Macromolecules* **2012**, *45* (21), 8813–8823.
- (20) Costanzo, S.; Scherz, L. F.; Floudas, G.; Kröger, M.; Schweizer, T.; Schlüter, A. D.; Vlassopoulos, D. Rheology and Packing of Dendronized Polymers. *Macromolecules* **2016**, *49* (18), 7054–7068.

- (21) Gstrein, C.; Zhang, B.; Abdel-Rahman, M. A.; Bertran, O.; Aleman, C.; Wegner, G.; Schluter, A. D. Solvatochromism of Dye-Labeled Dendronized Polymers of Generation Numbers 1-4: Comparison to Dendrimers. *Chem. Sci.* **2016**, 7 (7), 4644–4652.
- (22) Stals, P. J. M.; Li, Y.; Burdyńska, J.; Nicolaÿ, R.; Nese, A.; Palmans, A. R. A.; Meijer, E. W.; Matyjaszewski, K.; Sheiko, S. S. How Far Can We Push Polymer Architectures? *J. Am. Chem. Soc.* **2013**, 135 (31), 11421–11424.
- (23) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science* (80-.). **1997**, 278 (5343), 1601–1604.
- (24) Kautz, H.; van Beek, D. J. M.; Sijbesma, R. P.; Meijer, E. W. Cooperative End-to-End and Lateral Hydrogen-Bonding Motifs in Supramolecular Thermoplastic Elastomers. *Macromolecules* **2006**, 39 (13), 4265–4267.
- (25) Söntjens, S. H. M.; Renken, R. A. E.; van Gemert, G. M. L.; Engels, T. A. P.; Bosman, A. W.; Janssen, H. M.; Govaert, L. E.; Baaijens, F. P. T. Thermoplastic Elastomers Based on Strong and Well-Defined Hydrogen-Bonding Interactions. *Macromolecules* **2008**, 41 (15), 5703–5708.
- (26) Zha, R. H.; de Waal, B. F. M.; Lutz, M.; Teunissen, A. J. P.; Meijer, E. W. End Groups of Functionalized Siloxane Oligomers Direct Block-Copolymeric or Liquid-Crystalline Self-Assembly Behavior. *J. Am. Chem. Soc.* **2016**, 138 (17), 5693–5698.

- (27) Yamauchi, K.; Lizotte, J. R.; Long, T. E. Thermoreversible Poly(alkyl Acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding. *Macromolecules* **2003**, *36* (4), 1083–1088.
- (28) Feldman, K. E.; Kade, M. J.; Meijer, E. W.; Hawker, C. J.; Kramer, E. J. Model Transient Networks from Strongly Hydrogen-Bonded Polymers. *Macromolecules* **2009**, *42* (22), 9072–9081.
- (29) Lewis, C. L.; Stewart, K.; Anthamatten, M. The Influence of Hydrogen Bonding Side-Groups on Viscoelastic Behavior of Linear and Network Polymers. *Macromolecules* **2014**, *47* (2), 729–740.
- (30) Teunissen, A. J. P.; Nieuwenhuizen, M. M. L.; Rodríguez-Llansola, F.; Palmans, A. R. A.; Meijer, E. W. Mechanically Induced Gelation of a Kinetically Trapped Supramolecular Polymer. *Macromolecules* **2014**, *47* (23), 8429–8436.
- (31) Wong, C.-H.; Chow, H.-F.; Hui, S.-K.; Sze, K.-H. Generation-Independent Dimerization Behavior of Quadruple Hydrogen-Bond-Containing Oligoether Dendrons. *Org. Lett.* **2006**, *8* (9), 1811–1814.
- (32) Zhang, B.; Wepf, R.; Fischer, K.; Schmidt, M.; Besse, S.; Lindner, P.; King, B. T.; Sigel, R.; Schurtenberger, P.; Talmon, Y.; Ding, Y.; Kröger, M.; Halperin, A.; Schlüter, A. D. The Largest Synthetic Structure with Molecular Precision: Towards a Molecular Object. *Angew. Chemie Int. Ed.* **2011**, *50* (3), 737–740.

- (33) Zhang, B.; Yu, H.; Schlüter, A. D.; Halperin, A.; Kröger, M. Synthetic Regimes due to Packing Constraints in Dendritic Molecules Confirmed by Labelling Experiments. *Nat. Commun.* **2013**, *4*, 1–9.
- (34) McKee, J. R.; Huokuna, J.; Martikainen, L.; Karesoja, M.; Nykänen, A.; Kontturi, E.; Tenhu, H.; Ruokolainen, J.; Ikkala, O. Molecular Engineering of Fracture Energy Dissipating Sacrificial Bonds Into Cellulose Nanocrystal Nanocomposites. *Angew. Chemie Int. Ed.* **2014**, *53* (20), 5049–5053.
- (35) Schweizer, T.; Schmidheiny, W. A Cone-Partitioned Plate Rheometer Cell with Three Partitions (CPP3) to Determine Shear Stress and Both Normal Stress Differences for Small Quantities of Polymeric Fluids. *J. Rheol. (N. Y. N. Y.)* **2013**, *57* (3), 841–856.
- (36) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding. *J. Am. Chem. Soc.* **1998**, *120* (27), 6761–6769.
- (37) Stutz, H. The Glass Temperature of Dendritic Polymers. *J. Polym. Sci. Part B Polym. Phys.* **1995**, *33* (3), 333–340.
- (38) Zhu, Q.; Wu, J.; Tu, C.; Shi, Y.; He, L.; Wang, R.; Zhu, X.; Yan, D. Role of Branching Architecture on the Glass Transition of Hyperbranched Polyethers. *J. Phys. Chem. B* **2009**, *113* (17), 5777–5780.
- (39) Luo, X.; Xie, S.; Liu, J.; Hu, H.; Jiang, J.; Huang, W.; Gao, H.; Zhou, D.; Lu, Z.; Yan, D. The Relationship Between the Degree of Branching and Glass Transition Temperature of

- Branched Polyethylene: Experiment and Simulation. *Polym. Chem.* **2014**, 5 (4), 1305–1312 DOI: 10.1039/C3PY00896G.
- (40) Sunder, A.; Bauer, T.; Mülhaupt, R.; Frey, H. Synthesis and Thermal Behavior of Esterified Aliphatic Hyperbranched Polyether Polyols. *Macromolecules* **2000**, 33 (4), 1330–1337.
- (41) Fox, T. G.; Flory, P. J. The Glass Temperature and Related Properties of Polystyrene. Influence of Molecular Weight. *J. Polym. Sci.* **1954**, 14 (75), 315–319.
- (42) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. Physical Properties of Dendritic Macromolecules: A Study of Glass Transition Temperature. *Macromolecules* **1993**, 26 (7), 1514–1519.
- (43) Chen, Q.; Huang, C.; Weiss, R. A.; Colby, R. H. Viscoelasticity of Reversible Gelation for Ionomers. *Macromolecules* **2015**, 48 (4), 1221–1230.
- (44) Chen, Q.; Tudryn, G. J.; Colby, R. H. Ionomer dynamics and the sticky rouse model. *J. Rheol.* **2013**, 57, 1441–1462.
- (45) Chen, Q.; Masser, H.; Shiau, H.-S.; Liang, S.; Runt, J.; Painter, P. C.; Colby, R. H. Linear Viscoelasticity and Fourier Transform Infrared Spectroscopy of Polyether–Ester–Sulfonate Copolymer Ionomers. *Macromolecules* **2014**, 47 (11), 3635–3644.
- (46) Shabbir, A.; Huang, Q.; Chen, Q.; Colby, R. H.; Alvarez, N. J.; Hassager, O. Brittle Fracture in Associative Polymers: The Case of Ionomer Melts. *Soft Matter* **2016**, 12 (36), 7606–7612.

- (47) Graessley, W. W. *Polymeric Liquids and Networks: Dynamics and Rheology*; Garland Sci.: New York, 2008.
- (48) Berret, J.-F.; S, Y.; Winkelman, B.; Calvet, D.; Collet, A.; Viguir, M. Nonlinear Rheology of Telechelic Polymer Networks. *J. Rheol. (N. Y. N. Y.)*. **2001**, 45 (2), 477–492.
- (49) Berret, J.-F.; S, Y. Evidence of Shear-Induced Fluid Fracture in Telechelic Polymer Networks. *Phys. Rev. Lett.* **2001**, 87 (4), 48303.
- (50) Koga, T.; Tanaka, F.; Kaneda, I.; Winnik, F. M. Stress Buildup under Start-Up Shear Flows in Self-Assembled Transient Networks of Telechelic Associating Polymers. *Langmuir* **2009**, 25 (15), 8626–8638.
- (51) Oliveira, P. J. Alternative derivation of differential constitutive equations of the Oldroyd-B type. *J. Non-Newtonian Fluid Mech.* **2009**, 160, 40–46.
- (52) DeAguiar, J. R. An encapsulated dumbbell model for concentrated polymer solutions and melts II. Calculation of material functions and experimental comparisons. *J. Non-Newtonian Fluid Mech.* **1983**, 13, 161–179.
- (53) Herrchen, M.; , H. C. A detailed comparison of various FENE dumbbell models. *J. Non-Newtonian Fluid Mech.* **1997**, 68, 17–42.

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