Macromolecules **2005,** *38,* 6015−6023

Influence of Random Branching on Multiple Hydrogen Bonding in Poly(alkyl methacrylate)s

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Received March 31, 2005; Revised Manuscript Received May 19, 2005

ABSTRACT: A series of linear and randomly branched poly(alkyl methacrylate)s with pendant 2-ureido-4[1*H*]-pyrimidone (UPy) groups, which form quadruple hydrogen bonds, were synthesized, and the role of molecular topology on intermolecular hydrogen bonding was investigated. In solution rheological studies of poly(methyl methacrylate-*co*-UPy methacrylate) (PMMA-*co*-UPyMA) copolymers, a branched copolymer in the nonassociated state displayed a larger entanglement concentration (C_e) than a linear copolymer of equal molar mass. However, C_e of the branched copolymer approached the C_e of the linear analogue as the degree of hydrogen bond associations increased in solution, which suggested the reduced chain dimensions of the branched structure were overcome upon intermolecular association of the UPy groups. A series of linear and branched poly(2-ethylhexyl methacrylate-*co*-UPy methacrylate) (PEHMA-*co*-UPyMA) copolymers with 0−10 mol % UPy were utilized for melt rheological studies. A decrease in zero shear viscosity (η_0) and relaxation time suggested that branching reduced entanglement couplings for the unfunctionalized PEHMA homopolymer, and the η_0 and relaxation time of the branched and linear polymers approached each another as the UPy content was increased from 0 to 10 mol %. Furthermore, as the UPy content was increased in the copolymer, the plateau modulus (G_N^0) systematically increased, and the plateau region systematically broadened independent of the chain architecture. Thus, reversible hydrogen-bonding associations between UPy groups dominated the rheological behavior of linear and branched chains in both solution and the melt phase.

Introduction

The introduction of branching dramatically influences the melt, solution, and solid-state properties of polymers.[1−4] Unlike short chain branches (SCB), long chain branches (LCB) significantly alter polymer flow properties since the branch length is sufficiently long to form entanglement couplings.[5] In general, LCB are utilized to control rheological and processing properties, while SCB influence thermal behavior and mechanical properties. The dependence of viscosity on shear rate is drastically different for LCB polymers compared to linear analogues. For example, branched polymers generally have significantly higher viscosities at low shear rates and significantly lower viscosities at high shear rates due to shear thinning compared to a linear polymer of equal molar mass.[6] Several branching parameters influence solution and melt rheological behavior including branch length, degree of branching, and chain architecture (random, star-branched, comb, H-branched, etc.). A recent review from our laboratories has summarized the effect of branching on melt, solution, and solid-state polyester properties.[7]

The zero shear rate viscosity (η_0) dependence on weight-average molar mass (M_w) is well-known for linear, flexible polymer chains.[8] Below a critical entanglement molar mass (M_c), the chains are unentangled in the melt, and η_0 scales proportionally to M_w. Above M_c, where entanglement couplings dominate the flow properties, η_0 follows a 3.4 power law dependence with M_w. Researchers have shown that a significant departure from the η_0−M_w relationship exists for branched chains due to a reduced hydrodynamic volume at low molar mass and increased entanglement couplings at higher molar mass.[9] In particular, star polymers exhibit an exponential increase in η_0 with arm molecular weight (M_a),[10,11] and Lusignan et al. demonstrated that randomly branched polyesters exhibit a 6.0 power law dependence when the branch molar mass (M_b) exceeds M_c.[5] Because of the exceptionally strong increase in η_0 with M_w, processing very high molar mass linear and branched polymers is often difficult. Thus, significant interest has focused on combining covalent and noncovalent interactions for the synthesis of polymers that display excellent mechanical properties at ambient temperatures and thermoreversibility at processing temperatures.

Meijer and co-workers initially demonstrated supramolecular structure via multiple hydrogen bonding,[12−15] and many researchers have subsequently utilized these multiple hydrogen-bonding sites for the formation of associating polymers.[16−21] Research efforts from our laboratories demonstrated that poly(alkyl acrylates) with pendant 2-ureido-4[1*H*]-pyrimidone (UPy) groups, which form quadruple hydrogen bonds, strongly aggregate in moderately nonpolar solvents, such as toluene and chloroform ($CHCl_3$), and dissociate in relatively more polar solvents such as tetrahydrofuran (THF).[22] More recently, the influence of UPy groups on the solution rheological behavior and electrospinning performance was displayed for a series of linear poly(alkyl methacrylate) copolymers.[23] However, less attention has focused on the melt phase behavior of polymers that are functionalized with multiple hydrogen-bonding groups. Stadler et al. observed an increase in η_0 and shear thinning onset at lower frequencies with increasing urazole content in melt rheological experiments with urazole-functionalized polybutadienes.[24] Moreover, the plateau modulus broadened and slightly increased with the number of hydrogen-bonding groups per chain,

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10.1021/ma050667b CCC: $30.25

which indicated the formation of thermoreversible cross-links. In related work, Stadler et al. showed polybutadienes that were modified with urazole groups that contain carboxylic acids (4-urazoylbenzoic acid) formed crystalline, supramolecular domains in the polymer melt due to the self-assembly of these functional groups.[25] Many other researchers have probed the intermolecular associations of ion-containing polymers in melt and solution rheological studies.[26−29]

Intermolecular associations between pendant hydrogen-bonding groups in a polymer main chain form a reversible physical network structure, and these contact points are often considered reversible branch points. While the formation of these reversible branches is known to be a function of temperature, solvent polarity, and mechanical energy, limited attention has focused on the interplay between multiple hydrogen bond associations and covalent branching in polymers. For instance, intermolecular interactions between UPy groups may be hindered due to covalent branching, although the proximity of the UPy group to the covalent branch point is an important consideration. In fact, intramolecular UPy associations may be preferred to intermolecular associations in branched polymers as branched chains have a smaller hydrodynamic volume relative to linear chains of equivalent molar mass. Pruthtikul et al. studied associations between hydroxyl and ester carbonyl groups in hyperbranched and linear polymers.[30] They observed functional groups were screened, and consequently the degree of associations decreased in the branched architectures due to their compact, globular structures.

In the present work, the interplay between covalent branching and noncovalent reversible branching is probed using solution and melt rheology. First, the influence of branching on solution rheology and the entanglement concentration (C_e) was determined for poly(methyl methacrylate) PMMA. Branched PMMA copolymers with pendant UPy groups (PMMA-*co*-UPyMA) were synthesized to determine the influence of branching and hydrogen bonding on the solution rheological behavior. Solution rheological studies were performed on PMMA-*co*-UPyMA copolymers, and melt rheological studies were performed on a lower glass transition temperature (T_g) poly(2-ethylhexyl methacrylate-*co*-UPy methacrylate) (PEHMA-*co*-UPyMA) series. PEHMA-*co*-UPyMA copolymers were utilized for the melt studies since unlike PMMA-*co*-UPyMA, these copolymers possess a T_g lower than the UPy hydrogen-bonding dissociation temperature (typically in the range of 80−100 °C).[22]

Experimental Section

Materials. All reagents were used without further purification. Methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (EHMA) were purchased from Sigma Aldrich and passed through a neutral alumina column to remove radical inhibitors. Ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobis(isobutyronitrile) (AIBN) were purchased from Aldrich and used as received. The UPy methacrylate monomer was synthesized in our laboratories, and a detailed synthetic methodology was published earlier.[22] All other solvents and reagents were purchased from commercial sources and were used without further purification.

Instrumentation. Molar masses were determined at 40 °C in tetrahydrofuran (HPLC grade) at 1 mL min^{-1} using polystyrene standards on a Waters 717 Autosampler SEC system equipped with three in-line PLgel 5 μm MIXED-C columns, a Waters 410 RI detector, a Viscotek 270 dual detector, and an in-line Wyatt Technology Corp. miniDAWN multiple angle laser light scattering (MALLS) detector. ^{1}H NMR spectroscopy was performed on a Varian Unity 400 spectrometer at 400 MHz in $CDCl_3$ or THF-d_8.

Solution rheology was performed with a VOR Bohlin strain-controlled solution rheometer at 25 ± 0.2 °C using a concentric cylinder geometry in steady shear mode. Melt rheology was performed on a TA Instruments AR 1000 stress-controlled rheometer. A 25 mm parallel plate geometry was used for all samples, and strain amplitudes were limited to the linear viscoelastic regime over a frequency range of 0.1−100 Hz. The temperature was varied from 20 to 120 °C for PEHMA-*co*-UPy containing less than 5 mol % UPy. Samples with higher degrees of UPy modification were investigated between 50 and 150 °C due to an increase in T_g with percent functionalization. Time−temperature superposition (TTS) was performed on the linear and branched PEHMA-*co*-UPyMA copolymers with a reference temperature of 65 °C. While TTS was obeyed for the linear and randomly branched unfunctionalized PEHMA, the UPy-containing copolymers did not obey TTS. The superposition breakdown is due to different temperature dependencies of the chain segment relaxations and hydrogen-bonding association dynamics. This phenomenon is discussed further in the Results and Discussion section.

Synthesis of Linear and Branched PMMA Homopolymer and PMMA-*co*-UPyMA Copolymers. For the synthesis of linear (0 wt % EGDMA) and randomly branched PMMA, MMA (25 g, 250 mmol) and EGDMA ranging in concentration from 0 to 1.0 wt % compared to MMA were added to a 250 mL round-bottomed flask equipped with a magnetic stir bar. The monomers were diluted with ethyl acetate (100 g, 80 wt %), and the initiator AIBN (0.1−1.2 wt % compared to MMA) was added to the flask. The round-bottomed flask was equipped with a water condenser, sparged with N_2 for 10 min, and placed in a 70 °C oil bath. The polymerization was allowed to proceed for 24 h under continuous N_2 flow. The polymer was precipitated into methanol and dried under vacuum at 90 °C for 24 h.

For the synthesis of PMMA-*co*-UPyMA, MMA (7 g, 70 mmol) and UPy methacrylate (1.03 g, 3.7 mmol) monomers were added to a 250 mL round-bottomed flask with a magnetic stir bar and diluted with THF (92.3 g, 92 wt %). For the synthesis of randomly branched copolymers EGDMA (0.80 mg, 0.40 mmol) was also added to the round-bottomed flask. Finally, the initiator AIBN (40 mg, 0.5 wt %) was added to the reaction vessel. The round-bottomed flask was equipped with a water condenser, sparged with N_2 for 10 min, and placed in a 70 °C oil bath. The polymerization was allowed to proceed for 24 h under continuous N_2 flow. The polymer was precipitated into 2000 mL of a 9:1 methanol:water solution and dried under vacuum at 90 °C for 24 h. Quantitative incorporation of the UPy methacrylate was confirmed using ^{1}H NMR spectroscopy.

Synthesis of Linear and Branched PEHMA-*co*-UpyMA. EHMA (9 g, 45 mmol) and UPy methacrylate (1.34 g, 4.8 mmol) monomers were added to a 250 mL round-bottomed flask with a magnetic stir bar and diluted with THF (119 g, 92 wt %). The quantity of UPy methacrylate was subsequently varied to target different levels of functionalization of the copolymer. For the synthesis of randomly branched copolymers EGDMA (107 mg, 0.54 mmol) was also added to the round-bottomed flask. Finally, the initiator AIBN (10.3 mg, 0.1 wt %) was added to the reaction vessel. The round-bottomed flask was equipped with a water condenser, sparged with N_2 for 10 min, and placed in a 70 °C oil bath. The polymerization was allowed to proceed for 24 h under continuous N_2 flow. The polymer was precipitated into 2000 mL of methanol and dried under vacuum at 80 °C for 24 h. Quantitative incorporation of the UPy methacrylate was confirmed using ^{1}H NMR spectroscopy.

Results and Discussion

Synthesis and Characterization of Linear and Branched Poly(alkyl methacrylates) with Pendant UPy Groups.

Conventional free-radical polymerization methodologies were utilized to synthesize linear and

Table 1. Molar Mass and Contraction Factor Values for PMMA Homopolymers

EGDMA concn (wt %)	AIBN concn (wt %)	M_w (g/mol)[a]	M_w/M_n[a]	g'[a]
0	0.1	230 000	1.81	1.0
0.5	0.8	182 000	5.60	0.84
0.8	1.0	213 000	4.37	0.69
1.0	1.2	180 000	3.59	0.42

[a] SEC conditions: THF, MALLS, viscosity detector, 40 °C.

branched analogues of the following compositions: PMMA, PMMA-*co*-UPyMA random copolymers, and PEHMA-*co*-UPyMA random copolymers. Since the T_g of a PMMA homopolymer is higher than the hydrogen bond dissociation temperature of the UPy group, the PEHMA copolymers were synthesized for the melt rheological studies. Both copolymers were considered random on the basis of the linear T_g increase of the functionalized poly(alkyl methacrylates) with an increase in UPy molar concentation.[22] In addition, other researchers have also observed a linear increase in T_g with an increase in the mol % hydrogen-bonding groups.[31] Table 1 shows the reaction conditions, molar mass, and contraction factors (g') of the PMMA homopolymers synthesized at 70 °C using a conventional azo initiator. The ratio of EGDMA and AIBN was varied to maintain approximately equal M_w (180−232 kg/mol) with varying levels of branching as measured by g'. The well-established value of g' is defined in eq 1

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \tag{1}$$

where $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of branched and linear chains of equal molar mass. Since the hydrodynamic volume of a branched chain is smaller than a linear chain of equal molar mass, g' decreases as the degree of branching increases.[32] A method for determining the contraction factors was reported previously.[33] As shown in Table 1, the g' values range from 1.0 for linear PMMA, synthesized with 0 wt % EGDMA, to 0.42 for highly branched PMMA, synthesized with 1.0 wt % EGDMA.

Scheme 1 illustrates the free radical polymerization of a branched poly(alkyl methacrylate) with pendant UPy groups. The cartoon depicts reversible branch points formed via noncovalent association of pendant UPy groups. It should be noted that UPy associations in Scheme 1 are depicted in both an intermolecular and intramolecular fashion. Scheme 2 shows the quadruple hydrogen bond interaction between pendant UPy groups for linear PMMA-*co*-UPyMA copolymer. In the limit of complete UPy association, the copolymer forms a reversible network structure. Table 2 summarizes the molar mass, chemical composition, and branching data for the linear and branched UPy copolymers. There are a range of M_w values from 110 to 161 kg/mol and 152 to 183 kg/mol for the PEHMA-*co*-UPyMA and PMMA-*co*-UPyMA copolymers, respectively. Incorporation of the hydrogen-bonding comonomer in the polymer was limited to 10 mol % due to limited solubility of the UPy methacrylate comonomer into the polymerization solvent. The polymerization solution was turbid at monomer concentrations greater than 10 mol % presumably due to limited solubility of the UPy methacrylate monomer in THF.

Effect of Random Branching and Intermolecular Interactions on Solution Rheology Properties and the Entanglement Concentration. The randomly branched PMMA was dissolved in dimethylformamide (DMF) at concentrations ranging from 2 to 15 wt %. Steady shear rate sweeps were performed between 90 and 1000 s^{-1}, and all solutions displayed Newtonian behavior over this shear rate range. The specific viscosity (η_{sp}) in eq 2

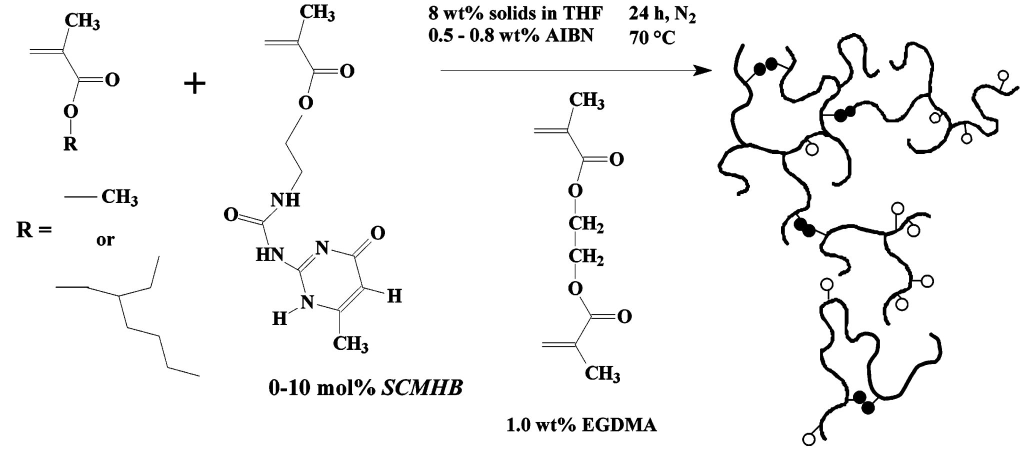
$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} \tag{2}$$

where η_s is the solvent viscosity and η_0 is the zero shear viscosity, was utilized to determine the dependence of the branched PMMA solution viscosity on concentration. Colby et al. has measured the entanglement concentration (C_e), which is defined as the transition between the semidilute unentangled and semidilute entangled regime, from the dependence of η_{sp} on concentration.[34] The following scaling arguments are obeyed for neutral chains that do not associate in solution: $\eta_{sp} \sim C^{1.25}$ in the semidilute unentangled regime, and $\eta_{sp} \sim C^{4.8}$ or $C^{3.75}$ depending on the solvent quality.[35] The value of C_e is the concentration in the semidilute regime where chain overlap and interpenetration topologically constrain motion in the form of entanglements.

Figure 1 illustrates the concentration dependence of solution viscosity for four PMMA homopolymers of approximately equivalent M_w and varying levels of branching (g' ranges from 1.0 to 0.42). The slope in the unentangled regime was approximately 1.4 for all homopolymers, and the slope in the entangled regime was approximately 4.0, which indicated DMF was slightly better than a Θ solvent for PMMA. For clarity, the C_e of linear PMMA (6.5 wt %) is denoted in Figure 1 as the break between the two scaling relationships. As g' decreased from 1.0 (linear chain) to 0.42, C_e systematically increased from 6.5 to 14 wt %, which suggested the branched chains do not entangle in solution as readily as the linear chains. The inset of Figure 1 shows the variation of C_e with the contraction factor, g'. Other researchers have also shown that branching dramatically influences the transition from unentangled to entangled behavior in solution.[36−38] At constant molar mass, the dimensions of a polymer coil decrease with increased branching, and thus highly branched topologies have fewer entanglement couplings with surrounding chains.

Recently, our laboratories have reported the influence of quadruple hydrogen bond associations on solution rheology and C_e for linear poly(alkyl methacrylate) copolymers with pendant UPy groups.[23] In a fashion similar to our earlier studies, the solvent dielectric constant (D) strongly influenced the level of hydrogen bond associations in linear and branched copolymers. The copolymers were dissolved in a mixture of DMF (D = 37 at 25 °C) and $CHCl_3$ (D = 4.8 at 25 °C) that ranged from 100% DMF to 20/80 DMF/$CHCl_3$ w/w. It is well-known that DMF inhibits hydrogen bonding, and thus, C_e for the linear PMMA-*co*-UPyMA systematically decreased with the $CHCl_3$ composition of the cosolvent due to a larger number of intermolecular associations in solution. Moreover, the dependence of η_{sp} on concentration in the semidilute entangled regime increased with the degree of associations, in agreement with

Scheme 1. Free Radical Polymerization of Poly(alkyl methacrylate) with Pendant UPy Groups



Scheme 2. Quadruple Hydrogen Bond Interaction between UPy Groups for Linear PMMA-*co*-UPyMA

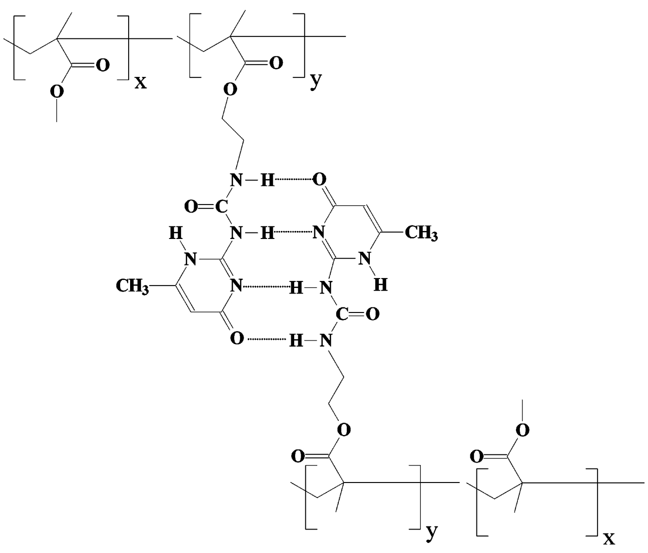


Table 2. UPyMA Content and Molar Mass Data for Linear and Branched Poly(alkyl methacrylates)

poly(alkyl methacrylate)	UPy content (mol %)	EGDMA concn (wt %)	M_w (g/mol)[a]	M_w/M_n[a]	g'[a]
PMMA-*co*-UPyMA	5	0	183 000	1.92	1.0
	5	1.0	152 000	2.45	0.85
PEHMA-*co*-UPyMA	0	0	146 000	2.84	1.0
	0	1.0	161 000	2.31	0.68
	5	0	128 000	1.78	0.96
	5	1.0	132 000	1.92	0.74
	10	0	110 000	1.89	1.0
	10	1.0	137 000	3.18	0.70

[a] SEC conditions: THF, MALLS, viscosity detector, 40 °C.

predictions by Rubinstein and Semenov.[39] A randomly branched PMMA-*co*-UPyMA was also synthesized to compare the solution rheology behavior with the aforementioned linear copolymer since the interplay between UPy associations and branching has not presently been described in the literature. The dissociation of multiple hydrogen-bonding sites into a highly branched architecture is expected to have significant ramifications on both solution and melt processing.

Figure 2 depicts the concentration dependence of viscosity for a branched copolymer ($g' = 0.85$). The branched PMMA-*co*-UPyMA displayed similar behavior to the linear counterpart as C_e systematically decreased from 12 wt % in DMF to 5 wt % in 20/80 DMF/CHCl$_3$ due to increased intermolecular associations in the relatively nonpolar solvent. Moreover, the power law exponent in the semidilute entangled regime increased with decreasing solvent polarity, in a fashion similar to the linear copolymer. The power law exponent for the randomly branched PMMA-*co*-UPy increased from 4.8 in DMF to 6.5 in the 20/80 DMF/CHCl$_3$ cosolvent. Figure 3 compares C_e for the linear and branched PMMA-*co*-UPyMA copolymer as a function of solvent polarity. As shown in Table 2, the linear and branched PMMA-*co*-UPyMA copolymers had g' values of 1.0 and 0.85, respectively, while the molar mass and percent functionalization of the two copolymers were approximately equal. When DMF was used as the solvent, the chains were in the nonassociated state, and the branched copolymer displayed a significantly higher C_e compared to the linear copolymer due to its smaller chain dimensions. However, as the CHCl$_3$ composition of the cosolvent was increased, the C_e of the branched chain approached the C_e of the linear chain due to the formation of reversible, multiple hydrogen-bonded cross-links. Consequently, the decrease in entanglement couplings due to the branched architecture was overcome in the limit of complete association between pendant UPy groups when the chain behaves as a reversible network. Moreover, the reduced hydrodynamic volume of the branched chain does not significantly inhibit hydrogen bond associations, since a reversible network formed in the CHCl$_3$-rich solutions for both the linear and branched topologies.

It is apparent that branched polymers with multiple hydrogen-bonding sites afford significant processing advantages compared to functionalized, linear analogues of equal molar mass. In Figure 3 the branched chains in the unassociated state (0 mol % CHCl$_3$) possessed a larger C_e compared to the linear chains, which indicated fewer entanglements couplings between the branched chains. However, in the associated state (80 mol % CHCl$_3$) the linear and branched chains had nearly equivalent values for C_e, suggesting a similar degree of entanglements. Thus, the branched copolymers would be significantly easier to process in the unassociated state compared to the linear copolymers, while still retaining sufficient entanglements in the associated state due to the reversible network structure of the multiple hydrogen bond sites.

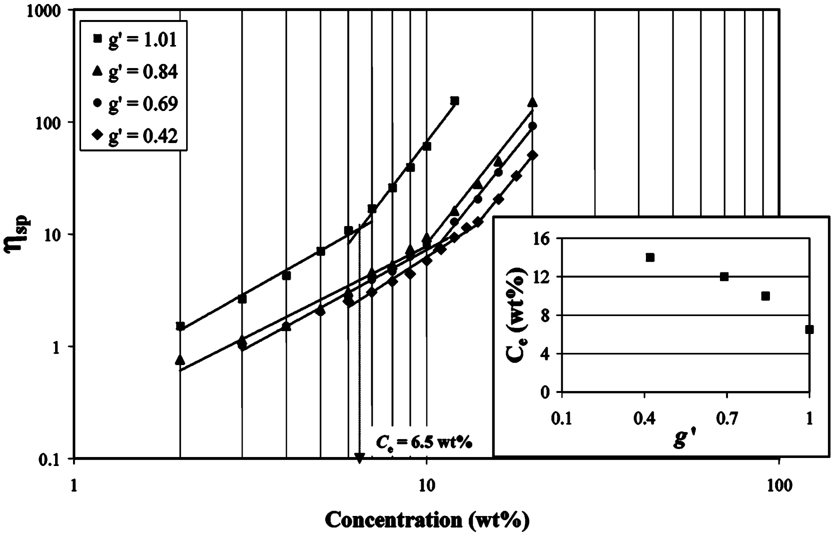


Figure 1. Concentration dependence of η_{sp} for linear and branched PMMA.

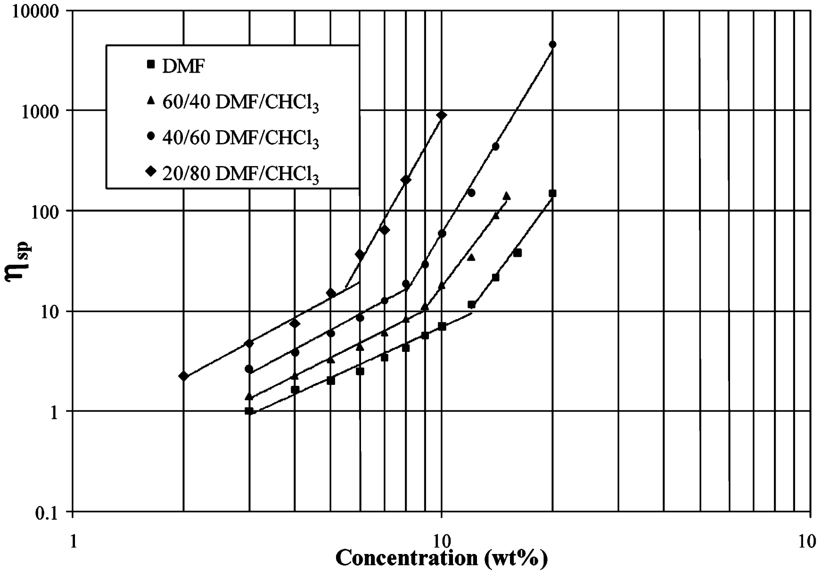


Figure 2. Influence of solvent polarity on the entanglement concentration for branched PMMA-*co*-UPyMA (M_w = 152 000 g/mol, g' = 0.85).

Viscoelasticity of Poly(alkyl methacrylates) with Pendant UPy Groups. The interplay between intermolecular associations and branching in melt rheology was also investigated. A series of linear and randomly branched poly(2-ethylhexyl methacrylate-*co*-UPy methacrylate) (PEHMA-*co*-UPyMA) random copolymers were synthesized with UPyMA composition ranging from 0 to 10 mol %. Previous melt rheological experiments with UPy-containing poly(alkyl acrylates) determined that the hydrogen-bonding dissociation temperature was ~80 °C.[22] It should be noted that UPy groups reversibly dissociate in an equilibrium fashion, and thus there is not a discrete temperature at which all UPy sites dissociate. However, it is expected that the equilibrium shifts to the nonassociated state above 80 °C, and thus it was important to utilize a copolymer with a T_g well below 80 °C, such as PEHMA-*co*-UPyMA in the melt studies rather than the higher T_g PMMA-*co*-UPyMA copolymers.

As mentioned previously, rheology data for both linear and randomly branched PEHMA-*co*-UPyMA did not permit time−temperature superposition (TTS) treatments. In particular, the loss modulus (G'') isothermal curves did not overlap in the rubbery plateau region for the hydrogen-bonding copolymers. This was attributed to different temperature dependencies of the chain relaxation and hydrogen-bonding associations in the PEHMA-*co*-UPyMA melt dynamics. In general, it is expected that TTS is valid for temperatures where the UPy groups are dissociated and chain entanglements dominate the viscoelastic response, while TTS should break down at lower temperatures due to a shift in the equilibrium of dissociated UPy groups to the associated state. Muller, Seidel, and Stadler have also observed breakdown of TTS for hydrogen-bonding functionalized chains in melt rheological studies.[40] They reported two transitions in the rubbery plateau. A high-frequency transition in the rubbery regime was attributed to association dynamics between hydrogen-bonding units, while the lower frequency transition marked the onset of the terminal regime. While G'' did not obey superposition for the 5 and 10 mol % UPy copolymers, the storage modulus (G') displayed relatively good superposition over the terminal and rubbery plateau regimes (Figure 4). Table 3 shows the Williams−Landel−Ferry (WLF) parameters, C_1 and C_2, obtained from shifting

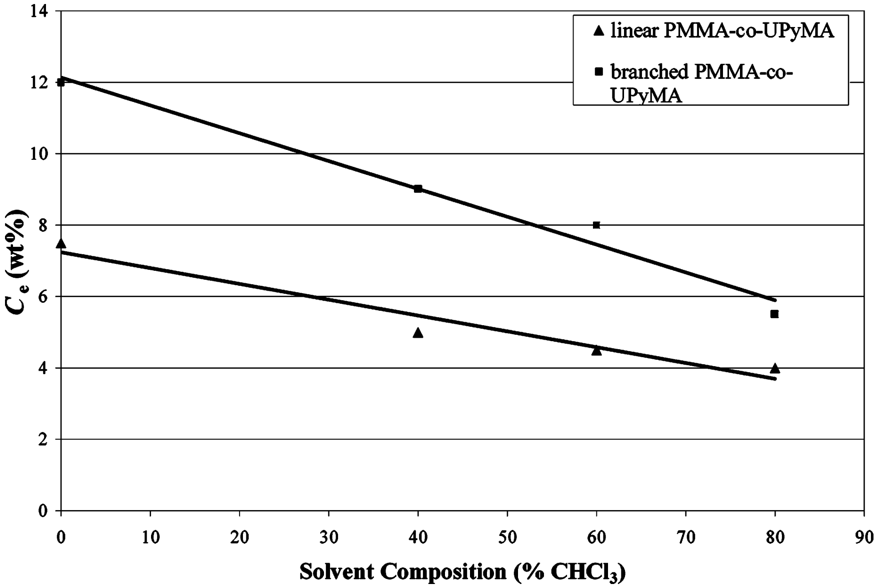


Figure 3. Comparison of the influence of solvent composition on C_e for the linear (M_w = 183 000 g/mol, g' = 1.0) and branched PMMA-*co*-UPyMA copolymer (M_w = 152 000 g/mol, g' = 0.85).

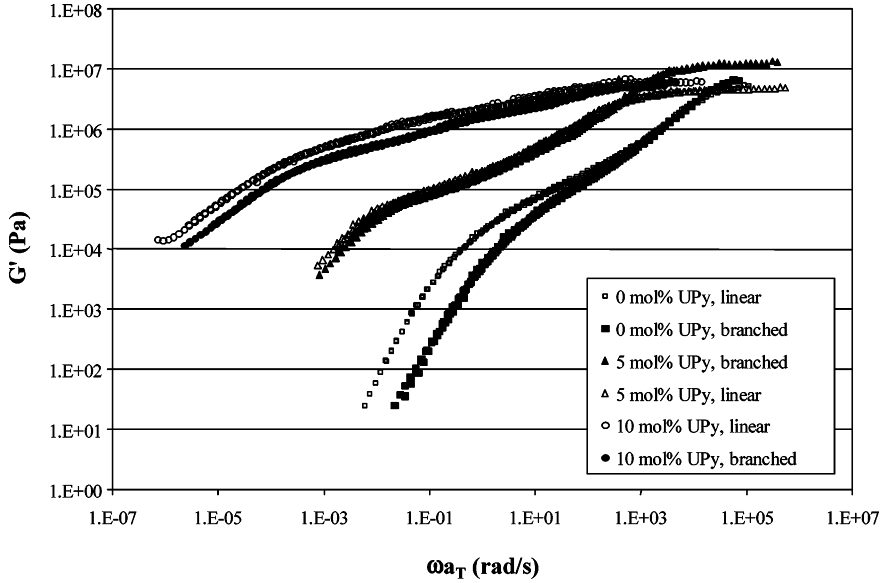


Figure 4. Storage modulus master curves for the PEHMA-*co*-UPyMA series. Molar mass and branching information is shown in Table 2.

Table 3. WLF Parameters That Were Determined by Shifting G' Data for Linear and Randomly Branched PEHMA-*co*-UPy

chain topology	UPy content (mol %)	C_1	C_2 (K)	C_1C_2
linear	0	9.10	135	1230
branched	0	7.62	136	1040
linear	5	11.12	140	1550
branched	5	9.19	115	1060
linear	10	15.46	200	3090
branched	10	12.67	189	2400

the G' data. The product C_1C_2 significantly increased for 10 mol % UPy functionalized copolymers in accordance with increased flow activation energies for associating polymers in the melt.[41]

Figure 4 shows the G' master curve for the linear and branched PEHMA-*co*-UPyMA copolymer at a reference temperature of 65 °C. Isothermal curves were collected at temperatures up to 120 °C, which is significantly above the reported 80 °C hydrogen bond dissociation temperature. A narrow plateau modulus (G_N^0) region was observed for the linear and branched unfunctionalized PEHMA homopolymer, which suggested the presence of entanglements. However, the transition region of the linear homopolymer extended to lower frequencies compared to the branched PEHMA, since some of the branches were not long enough to entangle and the branch segments relaxed via short time scale motions. It is apparent that the functional groups formed reversible cross-links due to the presence of a terminal regime for all levels of UPy content in Figure 4. It should be noted that the terminal regime portion of the master curves were constructed at temperatures greater than 100 °C, indicating the dissociation of some fraction of the UPy groups. Moreover, the value of G_N^0 systematically increased, and the plateau region systematically broadened with the level of multiple hydrogen-bonding groups. The viscoelastic behavior of the UPy-modified copolymers is qualitatively consistent with previous experimental results[24] and theoretical

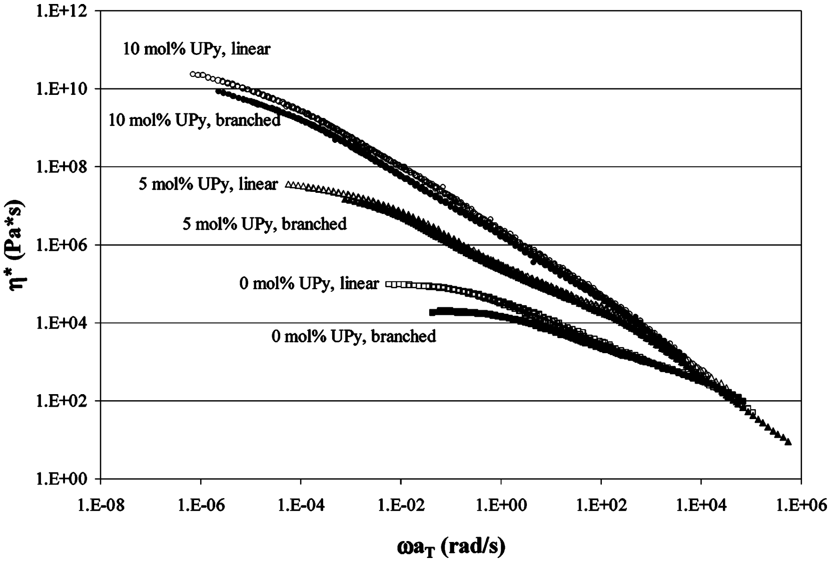


Figure 5. Dynamic viscosity master curves for the PEHMA-*co*-UPyMA series. Molar mass and branching information is shown in Table 2.

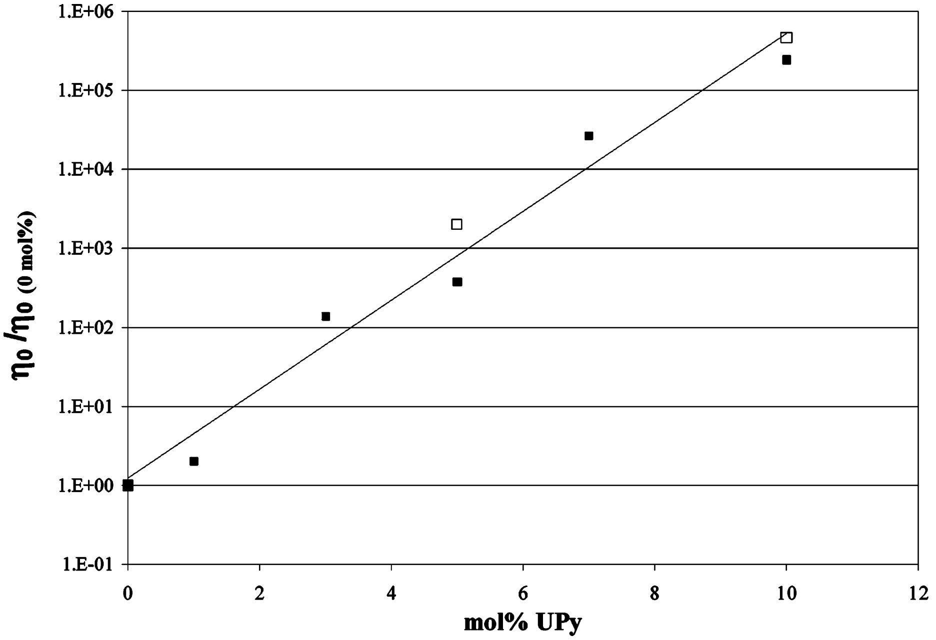


Figure 6. Relative zero shear viscosity enhancement for a UPy-containing poly(alkyl methacrylate). The closed and open symbols represent linear and branched copolymers, respectively.

predictions for other associated polymer compositions.[42] The terminal region was shifted to lower frequencies as the hydrogen bond associations disrupted the reptation process of the chains, and the formation of physical cross-links through UPy associations was consistent with an increase in G_N^0 with hydrogen-bonding functionality. However, two distinct plateau regions were not observed for the UPy series. Leibler, Rubinstein, and Colby predicted at time scales longer than the Rouse relaxation time (τ_e) and shorter than the time scale at which hydrogen-bonding groups dissociate (τ) result in a plateau modulus, which is a function of both cross-links and chain entanglements. Then, when the hydrogen-bonding groups dissociate at time scales longer than τ, the plateau modulus would decrease to the value of a linear chain without hydrogen bond associations.[42] As mentioned previously, two distinct plateau moduli were experimentally measured for polymers functionalized with phenylurazole groups, which form bidendate hydrogen bonds in a complementary fashion.[40] Unlike the phenylurazole groups, UPy groups form a quadruple hydrogen bond association, which result in much larger association constant ($K_a > 10^6$ M^{-1} in nonpolar environments).[43] Thus, the UPy association lifetime is relatively longer than the bidendate phenylurazole lifetime, and the transition for physical cross-links may extend into the terminal region, making it difficult to separate relaxations of chain entanglements and hydrogen bond dissociation. This interpretation is similar to the proposed melt dynamics of ionomers, where overlap of terminal relaxations and electrostatic relaxations has been reported.[44] Indeed, it is evident in Figure 4 that the terminal regime broadened with increasing UPy composition, and the limiting value of $G' \sim \omega^2$ witnessed for the unfunctionalized PEHMA was not observed. The terminal regime is very sensitive to the breadth of the molar mass distribution, particularly at higher molar mass since different size chains relax at different times.[8]

Thus, some fraction of the UPy groups remained in the associated state and effectively broadened the molar mass distribution, thereby resulting in the broad terminal response. Again, this is consistent with overlap between the relaxations attributed to chain dynamics and dissociation of UPy groups.

Figure 4 also shows that the plateau region and terminal region for the UPy copolymers were similar for both linear and branched topologies. Unlike the unfunctionalized PEHMA, where the terminal regime of the linear polymer extended to lower frequency than the branched polymer, both the linear and randomly branched UPy containing copolymers have nearly identical values of G_N^0 and terminal transitions. This suggests that the reversible network structure based on multiple hydrogen bond associations control the melt dynamics independent of the polymer architecture.

The dynamic viscosity master curve is plotted as a function of the reduced frequency in Figure 5. The linear PEHMA homopolymer had a larger value of η_0 and displayed shear thinning behavior at lower frequencies compared to the branched chain. This was attributed to fewer chain entanglements between the randomly branched PEHMA due to its reduced chain dimensions compared to the linear homopolymer of equal molar mass. The value of η_0 significantly increased with hydrogen-bonding content due to strong intermolecular interactions in the melt. Moreover, the onset of shear thinning shifted to lower frequencies with an increase in the degree of functionalization. The enhancement in shear thinning of the UPy copolymer was attributed to the significantly longer relaxation times due to the formation of a reversible network structure. However, the random branching in the PEHMA-*co*-UPy copolymers did not hinder the associations between UPy groups. There was a slight decrease in the zero shear viscosity for the branched chain compared to the linear chain of equal functionalization level and M_w due to the reduced chain dimensions of the branched polymer.

Figure 6 shows the zero shear viscosity enhancement of the UPy-containing copolymers compared to the PEHMA homopolymer (η_0/η_0 at 0 mol %) as a function of hydrogen-bonding content. The additional η_0 values in Figure 6 are from previous melt rheology investigations of linear UPy-containing copolymers performed in our laboratories.[45] An exponential relationship exists between viscosity enhancement and mol % functionalization in agreement with results by de Lucca Freitas and Stadler.[24] The branched copolymers displayed a relative viscosity enhancement approximately equal to the linear UPy-containing copolymers, and there was no influence of chain topology on the formation of intermolecular UPy associations. Thus, in accordance with solution rheology behavior, hydrogen bonding between the UPy groups dominates the melt rheological response for both the linear and branched copolymers.

Conclusions

The interplay between polymer chain architecture and intermolecular hydrogen bonding was determined for a series of poly(alkyl methacrylates) with pendant UPy groups. The rheological behavior of linear and branched functionalized copolymers displayed there was no significant effect of branching on intermolecular hydrogen bonding in a nonpolar solution environment and the melt phase. A branched PMMA-*co*-UPyMA copolymer in the nonassociated state displayed a larger C_e compared to a linear copolymer of equal molar mass. However, C_e of the branched copolymer approached that of the linear chain as the degree of hydrogen bond associations increased in solution. Thus, the decrease in entanglement couplings due to the reduced chain dimensions of the branched structure was lessened upon intermolecular associations between UPy groups.

Melt rheological studies showed that branching reduced the entanglement couplings for a PEHMA homopolymer as measured by a decrease in both η_0 and relaxation time. However, as the degree of UPy functionalization was increased, the η_0 and the relaxation time of the branched and linear polymers approached each other. Moreover, as the content of pendant UPy groups was increased, the plateau region systematically broadened and G_N^0 systematically increased, which was independent of the polymer topology. The relative zero shear viscosity enhancement of the branched copolymers was also approximately equal to the linear copolymers, which suggested no influence of chain architecture on the formation of intermolecular UPy associations. Consequently, hydrogen bonding between the UPy groups dominated the melt rheological response for both linear and branched chains.

Acknowledgment. This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under Contract/Grant DAAD19-02-1-0275 Macromolecular Architecture for Performance Multidisciplinary University Research Initiative (MAP MURI).

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MA050667B