Synthesis and Hydrolysis of Poly(norbornene)/Poly(acrylic acid) Graft Copolymers Synthesized via a Combination of Atom-Transfer Radical Polymerization and Ring-Opening Metathesis Polymerization

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Received December 5, 2003
Revised Manuscript Received May 31, 2004

Introduction

Graft copolymers offer the unique possibility of tailoring material properties through selection of the polymer backbone and the side chains. Through changes of these segments, properties such as morphology,[1,2] order−disorder transitions,[3] and phase behavior[4] can be modified. Additionally, through the use of graft or hyperbranched polymers, polymer solution properties such as critical overlap concentration, persistence length, diffusion behavior, and viscosity can be controlled.[3,5−7] Examples in the literature of graft structures having a pronounced effect on material properties are numerous. Staikos et al. showed that grafting of amphiphilic poly(*N*-isopropylacrylamide) to a semirigid carboxymethylcellulose backbone gave thermoresponsive polymers with an increase in viscosity of over four orders of magnitude from 25 to 60 °C.[8] Peppas and co-workers have investigated the complexation phenomena of poly(methacrylic acid-*g*-ethylene oxide) as a pH-dependent trigger for drug release from hydrogels,[9−11] while Okana[12] and Tenhu[13] researched the thermosensitive phase behavior of graft copolymers as a function of graft number and distribution. Additionally, graft copolymers have been investigated as potential surfactants.[14] Despite these elegant reports in the literature, the controlled and modular synthesis of graft copolymers still remains a challenge. Only a limited number of reports are available that describe the use of well-defined polymerization methods toward the synthesis of graft copolymers.[15−17] Fréchet and co-workers reported an elegant synthesis of graft copolymers combining nitroxide-mediated living radical polymerization and atom-transfer radical polymerization (ATRP).[15] Matyjaszewski and Müller both have introduced ATRP initiators onto a polymeric scaffold in a postpolymerization reaction to generate molecular brushes with hydrophilic cores and hydrophobic side chains that adopt rigid-rod conformations in solution.[16,17] Herein, we report a simple synthetic strategy toward the rapid and easy synthesis of graft copolymers by combining two highly controlled polymerization methods: ring-opening metathesis polymerization (ROMP)[18−20] and ATRP.[21−23] Additionally, we report the potential evolution or attenuation of the resulting polymer properties as a function of composition, concentration, temperature, or pH by using polymer degradation via hydrolysis.

To achieve these goals, we have designed a graft copolymer system that utilizes a polymer backbone containing terminal polymer initiation sites along its side chains that are bonded to the polymer backbone via hydrolyzable ester linkages. The graft identity is being used to generate and control polymer properties. ROMP is the polymerization method of choice for the construction of the primary polymer backbone, owing to the functional group tolerance of the catalyst, $Cl_2(PCy_3)_2Ru(=CHPh)$, **1**,[20] while ATRP has been employed as the polymerization method for the synthesis of graft polymers due to the control of the propagation and, more importantly, the site-specific initiation of the polymerization.[21−23] This strategy is an alternative to the earlier reported polymerization of macromonomers via ROMP.[24] The macromonomer strategy uses norbornene-terminated polymers such as poly(styrene) that can be polymerized into graft copolymers by using ROMP of the strained cyclic terminal groups. Interestingly, this strategy can also be used for the formation of random graft copolymers.[24] While very successful, the macromonomer strategy is not modular because for each new graft composition, new macroinitiators have to be synthesized. Our strategy, in contrast, starts with the ROMP of the norbornenes followed by the controlled radical polymerization of the grafts. This strategy allows for the use of a large number of monomers for the graft composition. The only prerequisite for the monomers used is that they must be able to be polymerized via ATRP.

The combination of ROMP and ATRP has been used before to generate novel liquid crystalline morphologies[25] and block copolymers,[26−29] thereby giving precedence for our ROMP/ATRP strategy. However, no literature reports are available of the combination of ATRP/ROMP, two highly functional group tolerant polymerization methods, for the design and synthesis of graft copolymers, thereby allowing for full control over the graft copolymers syntheses and ultimately materials properties.

The functional monomer design contains three parts: a polymerizable unit for ROMP, a side chain for ATRP initiation, and a linker between the side chain and the polymerizable unit. Functionalized norbornene is the monomer of choice for ROMP since it has been shown to be living under a wide variety of conditions.[19,20] We decided to use esters as hydrolyzable linkages in our polymer system. They are known to hydrolyze over the entire pH range in aqueous solutions, and the mechanisms and kinetics of hydrolysis are well understood.[30] α-Bromoesters are efficient initiators for ATRP and provide both a hydrolyzable linkage and a well-defined and efficient initiation site for polymerization.[31−33] Therefore, our system is composed of a poly(norbornene)-based copolymer backbone with triethylene glycol monomethyl ether side chains interspersed with triethylene glycol esters containing 2-bromopropionate end groups that function as initiation sites for the ATRP. *tert*-Butyl acrylate was used as monomer for the ATRP of the side chains. The *tert*-butyl groups can be removed easily from the polymer to yield poly(acrylic acid) side chains that (i) have a number of important applications, for ex-

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10.1021/ma0358475 CCC: $27.50
Published on Web 07/22/2004

ample, in biomaterials, (ii) can be modified chemically in a straightforward fashion using a variety of reaction pathways, thereby giving us an easy handle for graft copolymer functionalization, and (iii) have interesting polymeric properties including inducing high viscosity. Viscosity can be reduced potentially through the hydrolysis of the ester groups as a function of pH, temperature, and polymer composition.

Experimental Section

Materials and Methods. All reagents were obtained from Aldrich Chemical Co. or Acros and used as received unless noted below. Catalyst **1** was obtained from Strem Chemical and purified by dissolving in oxygen-free benzene followed by filtration and removal of the solvent under inert atmosphere. CH_2Cl_2 and THF were dried by passage through successive columns of Cu^0 and alumina. Triethylene glycol and triethylene glycol monomethyl ether were dried by stirring with sodium metal under argon followed by distillation under reduced pressure. 4,4′-Dinonylbipyridyl was synthesized by the method of Matyjaszewski.[20] NMR spectra were obtained on Bruker AMX 400 MHz or DMX 500 MHz instruments. All spectra were referenced to residual protio signals of the solvent. IR spectra were recorded using a Nicolet 520 FT-IR. Gel permeation chromatography analyses of the ROMP polymers and *tert*-butyl acrylate graft copolymers were performed using a Waters 1420 pump, a Waters 410 refractive index detector, two American Polymer Standard AM GEL/Linear 10 mixed bed columns, CH_2Cl_2 as mobile phase at a flow rate of 1 mL/min, and poly(styrene)s as standards for calibration. GPC analyses for PAA graft copolymers were performed using a Waters 1510 pump, a Waters 410 refractive index detector, and a Waters Ultrahydrogel 2000, 1000, and 500 columns with 0.25 M $NaNO_3$ as the mobile phase at 0.8 mL/min. Poly(acrylic acid) standards were used for aqueous GPC. Compound **2** was prepared as describe in the literature.[34]

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, 2-[2-(2-Methoxyethoxy)ethoxy]ethyl Ester, 3. A solution of triethylene glycol monomethyl ether (4.95 g, 30.2 mmol) and triethylamine (3.51 g, 34.7 mmol) in THF (150 mL) was cooled to 0 °C, and **2** (5.43 g, 34.7 mmol) in THF (25 mL) was added dropwise over 30 min. The reaction mixture was warmed to ambient temperature and stirred for 7 h. The mixture was diluted with diethyl ether (150 mL) and washed with 5% NaOH (aq, 200 mL), 5% HCl (aq, 200 mL)), sat. $NaHCO_3$ (aq, 200 mL), brine (200 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was distilled in vacuo to give bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, 2-[2-(2-methoxyethoxy)ethoxy]ethyl ester as a clear, colorless liquid. Yield: 6.27 g (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.15 (m, 1H), 6.10 (m, 2H), 5.90 (m, 1H), 4.14−4.24 (m, 2H), 3.72−3.65 (m, 8H), 3.60 (t, J = 8 Hz, 2H), 3.27 (s, 3H), 3.19 (br, 1H), 3.02 (br, 1H), 2.94 (m, 1H), 2.88 (br, 1H), 2.22 (m, 1H), 1.93−1.84 (m, 1H), 1.49−1.23 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.72, 174.21, 137.69, 137.29, 135.36, 132.04, 71.67, 70.37, 70.31, 68.96, 63.23, 63.05, 58.79, 49.37, 46.40, 46.08, 45.50, 42.98, 42.81, 42.32, 41.43, 30.16, 29.07. IR (neat): 3060.6, 2946.9, 2879.6, 1731.9, 1451.3, 1334.6, 1108.9, 714.5 cm^{-1}. Elem Anal.: Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.31; H, 8.49.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, Octyl Ester, 4. Compound **2** (3.89 g, 24.9 mmol) in THF (50 mL) was cooled to 0 °C under Ar. A solution of triethylamine (10 mL) and 1-octanol (3.57 g, 27.4 mmol) in THF (20 mL) was slowly added to the reaction flask, and the reaction mixture was warmed to ambient temperature. The reaction mixture was stirred for 4 h and the precipitate removed by filtration. The filtrate was diluted with CH_2Cl_2 (100 mL) and washed with 5% HCl(aq) (100 mL), sat. $NaHCO_3$(aq) (100 mL), water (100 mL), and brine (50 mL) and dried over Na_2SO_4. The solvent was removed and the residue distilled under reduced pressure (72−75 °C, 1.2 Torr) to give bicyclo[2.2.1]hept-5-ene-2-carboxylic acid octyl ester as a clear colorless liquid (72%, 4.49 g, 3:1 *endo*/*exo*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (dd, 1H, J = 3.0, 5.5 Hz, *endo*), 6.05 (m, 2H, *exo*), 5.85 (dd, 1H, J = 2.7, 5.5 Hz, *endo*), 3.9−4.05 (m, 2H), 3.13 (br, 1H, *endo*), 2.96 (br, 1H, *exo*), 2.83−2.89 (m, 2H), 2.12−2.19 (m, 1H, *exo*), 1.78−1.86 (m, 1H), 1.45−1.59 (m, 2H), 1.22−1.39 (m, 16H), 0.82 (t, 3H, J = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.03, 174.53, 137.84, 137.48, 135.62, 132.22, 64.38, 64.13, 49.46, 46.49, 46.20, 45.67, 45.57, 43.21, 43.06, 42.40, 41.50, 31.65, 30.15, 29.06, 29.02, 28.57, 25.83, 22.50, 13.92. IR (neat): 3066.7, 2940.4, 2856.1, 1740.4, 1473.7, 1340.4, 1186.0, 715.8 cm^{-1}. Elem Anal.: Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.67; H, 10.34.

Table 1. ROMP Polymer Compositions

polymer	monomer 1 (mg)	monomer 2 (mg)	t_{100} (h)[a]
7 (5)	**3** (294)	**6** (22)	9.2
7 (10)	**3** (278)	**6** (44)	9.6
7 (20)	**3** (248)	**6** (88)	10.5
8 (15)	**4** (231)	**6** (66)	7.5

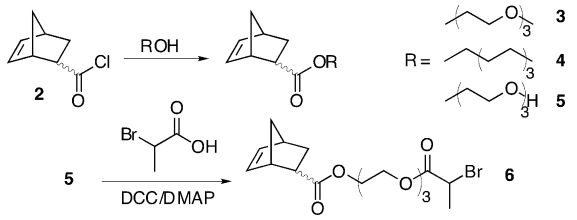
[a] t_{100} = time to 100% conversion as measured by NMR spectroscopy in CD_2Cl_2.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, 2-[2-(2-Hydroxyethoxy)ethoxy]ethyl Ester, 5. Compound **2** (3.63 g, 23.2 mmol) was treated with triethylene glycol (3.66 g, 24.4 mmol) as described above for compound **3** to give bicyclo[2.2.1]-hepta-5-ene-2-carboxlylic acid, 2-[2-(2-hydroxyethoxy)ethoxy]-ethyl ester as a clear colorless liquid (5.21 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (m, 1H), 6.10 (m, 2 H), 5.90 (m, 1H)-, 4.14−4.24 (m, 2H), 3.72−3.65 (m, 8H), 3.60 (t, J = 8 Hz, 2H), 3.19 (br, 1H), 3.02 (br, 1H), 2.94 (m, 1H), 2.88 (br, 1 H), 2.22 (m, 1 H), 1.93−1.84 (m, 1H), 1.49−1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.13, 174.61, 137.94, 137.64, 135.59, 132.22, 72.40, 70.41, 70.23, 69.09, 63.23, 63.05, 61.58, 49.46, 46.53, 46.16, 45.58, 43.07, 42.88, 41.50, 30.22, 29.11. IR (neat): 3460 (br, −OH), 3060, 2940, 2870, 1730, 1630 (shoulder), 1450, 1190, 1110, 712 cm^{-1}. Elem Anal.: Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.28; H, 8.29.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, 2-[2-(2-Hydroxyethoxy)ethoxy]ethyl-2-bromopropionate, 6. A solution of **5** (3.00 g, 11.1 mmol), 4-*N*,*N*-(dimethylamino)pyridine (1.40 g, 11.5 mmol), and 2-bromopropionic acid (1.90 g, 12.4 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C under Ar. Dicyclohexylcarbodiimide (2.33 g, 11.3 mmol) was added; the mixture was warmed to ambient temperatures and stirred for 12 h. The white precipitate was removed by filtration and the filtrate concentrated under reduced pressure. The residue was purified by column chromatography (1:3 ethyl acetate:hexanes, silica gel) to give bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, 2-[2-(2-hydroxyethoxy)ethoxy]ethyl-2-bromopropionate as a clear colorless liquid. Yield: 3.10 g (69%, 4:1 *endo*/*exo*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (dd, 1H, J = 3.0, 5.6 Hz, *endo*), 6.10 (dd, 1H, J = 2.9, 5.6 Hz, *exo*), 6.07 (dd, 1H, J = 2.9, 5.4 Hz, *exo*), 5.89 (dd, 1H, J = 2.8, 5.6 Hz, *endo*), 4.39 (d, 1H, J = 6.9 Hz), 4.35 (d, 1H, J = 6.9 Hz), 4.29 (t, 2H, J = 4.7 Hz, *endo*), 4.22 (t, 1H, J = 4.7 Hz, *exo*), 4.07−4.17 (m, 2H), 3.61−3.72 (m, 8H), 3.19 (br, 1H, *endo*), 3.02 (br, 1H, *exo*), 2.92−2.96 (m, 1H), 2.87 (br, 1H, *endo*), 2.22 (dd, 1H, J = 4.4, 10.0 Hz, *exo*), 1.84−1.91 (m, 1H), 1.80 (d, 3H, J = 6.9), 1.67 (br, 1H, *exo*), 1.23−1.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.21, 174.68, 170.22, 138.06, 137.73, 135.68, 132.31, 70.66, 70.49, 69.26, 68.77, 64.96, 63.41, 63.22, 49.57, 46.64, 46.26, 45.70, 43.18, 43.01, 42.50, 41.60, 39.85, 30.33, 29.22, 21.58. IR(neat): 3066.7, 2982.5, 2870.2, 1747.4, 1677.2, 1459.6, 1333.3, 722.8 cm^{-1}. Elem Anal.: Calcd for $C_{17}H_{25}BrO_6$: C, 50.38; H, 6.22. Found: C, 50.45; H, 6.18.

Ring-Opening Metathesis Polymerizations. A 0.2 M solution of the desired monomers (**3** and **6** or **4** and **6**) in CD_2Cl_2 was purged with argon. An exact amount of **1** to give the desired 50:1 monomer-to-initiator ratio was then added to the solution, and the reaction mixture was stirred until the polymerization was complete, as determined by NMR spectroscopy. The polymerization was quenched by the addition of ethyl vinyl ether, and the solvent was removed under reduced pressure to give the desired copolymers. Purification was accomplished by repeated precipitations. Table 1 sum-

Scheme 1. Synthesis of Norbornene Monomers



marizes the compositions of the polymers used in this study. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.52−514 (br, vinyl, 2H), 4.41 (q, 1H, α-bromoester H, J = 6.9 Hz), 4.32 (t, 2H, J = 4.7 Hz), 4.26−3.98 (br, 2H, ester H), 3.76−3.60 (br, 8H, ether side chain H), 3.54 (t, 2H, J = 4.9 Hz), 3.37 (s, 3H), 3.24−3.05 (br), 3.03−2.67 (br), 2.65−2.33 (br), 2.14−1.50 (br), 1.84 (d, 3H, J = 6.9 Hz), 1.47−1.05 (br).

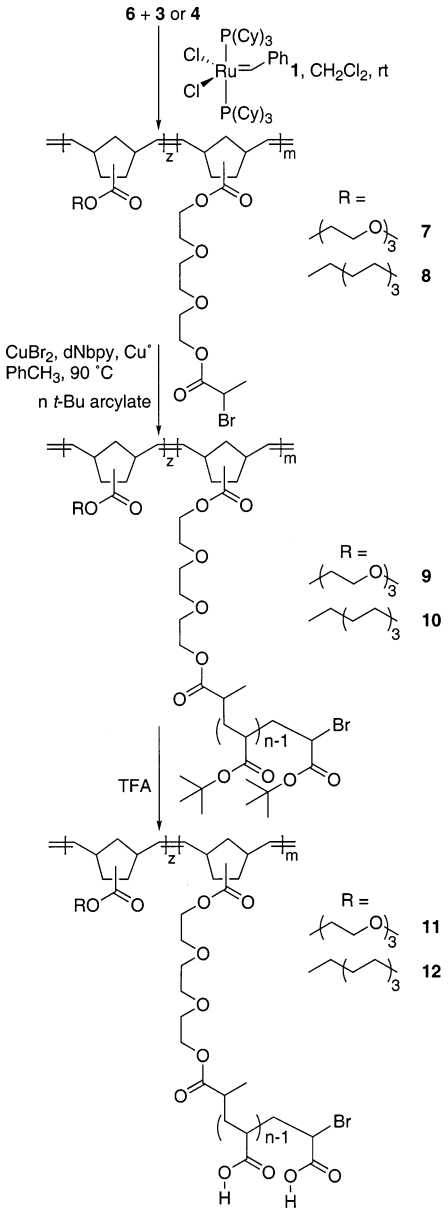
Atom-Transfer Radical Polymerization. ATRP of *tert*-butyl acrylate from polymers **7** and **8** was performed using Cu(dNbpy)Br as the mediator in degassed toluene solutions at 90 °C (dNbpy = 4,4′-dinonylbipyridyl).[35] The mediator was generated in situ by the comproportionation of $CuBr_2$ and Cu^0 in the presence of dNbpy.[35] Cu(I)/dNbpy/[I] ratios were set at 1:1:5 for all polymerizations and monomer-to-initiator ratios at 1300:1; the polymerizations were carried out to 50−60% conversions, as measured by NMR spectroscopy comparison of the acrylate signals to the toluene solvent signal. Polymerizations were quenched by opening the reaction vessel to air while cooling with liquid nitrogen. The polymer solutions were filtered through a bed of silica gel to remove the catalyst and copper metals and vacuum-dried at 60 °C. Removal of the *tert*-butyl protecting groups was achieved by treatment of the polymers with a 1:1 mixture of dry trifluoroacetic acid and dry CH_2Cl_2 at ambient temperature for 3 h under an inert atmosphere. The solvent was removed under reduced pressure and dried under vacuum for 24 h at ambient temperature. *tert*-Butyl-protected polymers: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.85 (br, poly(norbornene) vinyl), 4.89 (br, ester H, poly(norbornene)), 4.32 (br, poly(norbornene) ether side-chain H), 3.86 (s, poly(norbornene) side chain −OMe), 2.31−2.19 (br, polymer backbone CH), 1.82−1.70 (br, polymer backbone CH), 1.62−1.49 (br, polymer backbone CH_2), 1.46−1.37 (br, *tert*-butyl CH_3). Deprotected polymers: ^{1}H NMR (DMSO-d_6, 300 MHz): δ 4.21 (br, poly(norbornene) ester), 3.97 (br, poly(norbornene) PEG side chains), 2.20 (br, 1H, pAA), 1.8−1.2 ppm (br, 2H, pAA), 1.37 (s, 9H, residual *tert*-butyl groups).

Results and Discussion

The monomers were synthesized from 5-norbornene-2-carbonyl chloride (**2**) through the condensation of either triethylene glycol monomethyl ether or triethylene glycol to yield **3** and **5**, respectively (Scheme 1). Initiators for ATRP were made by the coupling of 2-bromopropionic acid to **5** to yield monomer **6**. These monomers contain ethylene glycol-based side chains to enhance solubility in polar solvents. To study the effects of hydrophobicity on polymer hydrolysis, monomer **4** was synthesized by condensation of 1-octanol with **2**.

Ring-opening metathesis polymerization of monomers **3** or **4** with monomer **6** was performed using **1** (Scheme 2).[20] The rates of polymerization for monomers **3**, **4**, and **6** were measured by following characteristic upfield shifts of the olefin signals of the norbornene as a function of time at room temperature using NMR spectroscopy. The rates of **3** and **6** are the same within experimental error, with complete conversion of a 50:1 monomer-to-catalyst ratio of either monomer in 12 h at ambient temperatures. This kinetic data in conjunction with the strong resemblance of the polymerizable units—in both cases a norbornene with an ester linkage and a long spacer unit—suggests that the polymerization

Scheme 2. Syntheses of Random Graft Copolymers.



behaviors of **3** and **6** are identical and that a random copolymerization of these monomers most likely produces statistical copolymers. However, the rate of polymerization of **4** was approximately twice that of **6**, with complete polymerization in less than 8 h. Therefore, copolymers of **4** and **6** may not have a complete random distribution of repeating units, but partially a blocky-type structure. Copolymers **7** were synthesized with 5, 10, and 20 mol % of **6** with monomer **3**, and copolymer **8** was synthesized by combining 15 mol % of **6** with monomer **4**.[36] The compositions of the copolymers were determined by ^{1}H NMR spectroscopy through the comparison of the norbornene vinylene signals (6.1−5.8 ppm) to the α-bromo ester methine signal at 4.4 ppm. ATRP of *tert*-butyl acrylate was performed using Matyjaszewski's method and were carried out to 50−60% conversion to avoid any potential cross-linking that may occur by bimolecular termination (Table 2).[35]

All graft copolymers were characterized by ^{1}H NMR spectroscopy (500 MHz). The intensity of the norbornene vinylene proton signals at 6.1−5.8 ppm remained constant compared to the ester signals for the TEG side chains at 4.2−4.0 ppm, showing that the polymer

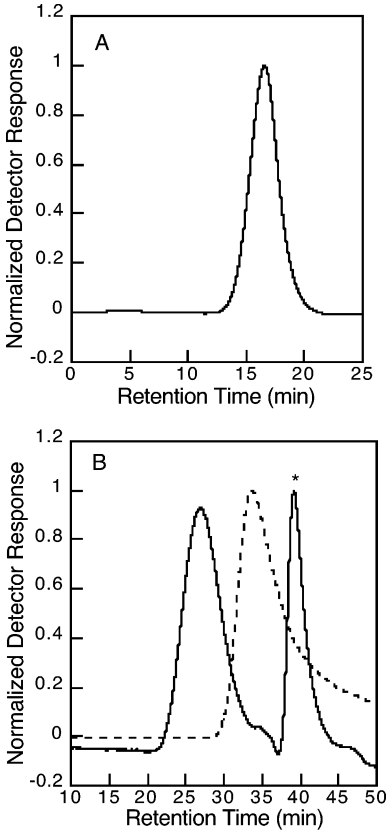


Figure 1. Gel permeation chromatography traces of graft copolymer **11(5)**: (A) GPC trace of *tert*-butylated graft copolymer using methylene chloride as mobile phase; (B) GPC traces using an aqueous solution of 0.25 M $NaNO_3$ as mobile phase of the deprotected polymer (solid line) and deprotected polymer after hydrolysis at 80 °C and pH 9.2 for 24 h (dashed line). Asterisk (*) indicates signal due to salts in the mobile phase.

backbone does not participate in the ATRP reaction. Size exclusion chromatography of the graft copolymers show a single monomodal signal at the end of the polymerization, suggesting that the grafting reaction proceeds with no homopolymer formation (Figure 1A). The removal of the *tert*-butyl groups was achieved by treatment of the polymers with a 1:1 mixture of CH_2Cl_2 and trifluoroacetic acid until the de-*tert*-butylated polymers precipitated. Isolation and purification of the polymers gave the desired graft copolymers containing poly(acrylic acid) side chains.[37] The amount of acrylic acid in the polymer was measured by titration with standardized NaOH. The calculated moles of acid were compared to an equivalent mass of acrylic acid to give the amount of de-*tert*-butylation. Table 3 summarizes the graft copolymer characterizations.

To be able to tailor the physical properties of our graft copolymers, hydrolyzable linkages were engineered into the copolymers to remove the side chains in a controllable manner for potential use in numerous applications where viscosity control is needed or where side-chain removal is desired. It is important to note that all side chains contain two ester groups that can be hydrolyzed. We suggest that the majority of the ester hydrolysis will take place at the ester omega to the norbornene and not alpha. The ester alpha to the norbornene is closer to the polymer backbone and therefore in a more hydrophobic environment than the one in the omega position, thereby being less accessible to water. However, we cannot rule out any ester hydrolysis from the alpha ester. The hydrolyses of the deprotected graft copolymers **11** and **12** were performed at pH 5.3, 7.4, and 9.2 and at 37 ± 0.2 and 80 ± 0.2 °C. Buffer solutions of 0.1 M ionic strength were used and a polymer concentration of 0.50 g/dL was employed. Both Ubbelohde and Ostwald viscometers were employed to follow the loss of viscosity, and individual solvent times at each temperature and pH value were determined. A control sample of linear poly(acrylic acid) was used to determine whether the loss of viscosity is due to cleavage of the side chains or degradation of the poly(acrylic acid) side chains. Reduced viscosities (η_{red}) were determined as a function of time to monitor the loss of viscosity.

The graft copolymers all showed a rapid decrease in viscosity at 80 °C at pH 9.2 relative to the control (Table 4). A 20−50% loss in 6 h in the η_{red} was observed for copolymers **11(5)**, **11(10)**, and **11(20)**. At pH 7.4, the starting viscosity was significantly lower and the rate of viscosity loss was much slower than that at pH 9.2 and 80 °C. At pH 5.3, the initial η_{red} of copolymers **11(5)**, **11(10)**, and **11(20)** was intermediate between that of pH 7.4 and 9.2. A possible explanation could be the degree of ionization at these pH values. Different degrees of ionization will result in different polymer architectures directly influencing initial viscosities. At intermediate pH values, the pAA side chains are both protonated and deprotonated, and intergraft interactions could prevent the polymer from adopting a fully extended conformation with a resulting drop in initial η_{red}. At 37 °C, the same trends were observed, but with a significant drop in the rate of viscosity loss. These results are in sharp contrast to the rates of viscosity loss of graft copolymers **12(15)**, which gave results similar to the control polymers at pH 9.2 and 80 °C. All viscosity data are summarized in Table 4.

The viscosity results clearly suggest that temperature, pH, the graft density, and the nature of the ROMP backbone and the linker play an important role in the

Table 2. ATRP Grafting Reaction Conditions

polymer	[M][a]g	[I][b]	[$CuBr_2$][c]	[Cu^0]	[dNbpy]	*t*/conv[d]	yield[e]	yield AA[f]
11(5)	21.6 g 168 mmol	0.75 g 130 μmol	2.9 mg 12.9 μmol	21.2 mg	10.6 mg 25.9 μmol	7.25 h (55%)	11.45 g (51%)	6.02 g
11(10)	21.4 g 167 mmol	0.38 g 129 μmol	2.9 mg 12.9 μmol	22.3 mg	10.7 mg 25.7 μmol	6.40 h (57%)	11.79 g (54%)	6.42 g
11(20)	21.8 g 170 mmol	0.20 g 131 μmol	2.9 mg 12.9 μmol	20.9 mg	10.5 mg 26.1 μmol	6.20 h (59%)	12.43 g (56%)	6.87 g
12(15)	22.0 g 172 mmol	0.24 g 130 μmol	2.9 mg 12.9 μmol	19.4 mg	10.8 mg 2.64 μmol	6.30 h (60%)	12.74 g (57%)	7.03 g
pAA[g]	21.6 g 168 mmol	0.24 g 129 μmol	2.9 mg 12.9 μmol	21.4 mg	10.6 mg 25.9 μmol	4.1 h (60%)	12.29 g (57%)	6.90 g

[a] Molar concentration of monomer in toluene. [b] Molar concentration of initiating species in toluene. [c] Initial molar concentration of copper(II) in the reaction flask. [d] Conversion as measured by NMR spectroscopy. [e] Yield of *tert*-butyl-protected polymer. [f] Yield of polymer after treatment with TFA/CH_2Cl_2. [g] Initiated with ethyl 2-bromopropionate.

Table 3. Graft Copolymer Characterization

initial polymer	% init[a]	poly(norbornene)s M_w[b] × 10^3	poly(norbornene)s PDI[b]	poly(*tert*-butyl acrylate) graft copolymers[c] M_w[b] × 10^3	poly(*tert*-butyl acrylate) graft copolymers[c] PDI[b]	poly(acrylic acid) graft copolymers[c] M_w[d] × 10^3	poly(acrylic acid) graft copolymers[c] PDI[d]	% AA
7 (5)	4.9	23	1.29	170	1.67	436	1.79	89 ± 2
7 (10)	9.6	25	1.32	181	1.72	302	2.74	91 ± 2
7 (20)	19.6	24	1.31	162	1.68	602	2.23	89 ± 2
8 (15)	15.1	25	1.24	173	1.77			79 ± 3

[a] Mole % initiator as determined by ^{1}H NMR spectroscopy. [b] M_w and PDI values determined by GPC vs poly(styrene) standards in CH_2Cl_2. [c] M_w as determined by GPC. Graft copolymers do not assume a random coil conformation in solution and the values reported here do not reflect the actual M_w of the polymers. [d] GPC in 0.25 M $NaNO_3$(aq).

Table 4. Hydrolysis Data for Graft-pAA Polymers

polymer	*T* (°C)	pH	η_{red}[a] (dL/g)	η_{red} at 6 h (dL/g)[b]	η_{red} at 24 h (dL/g)[b]
11(5)	80	9.2	28.7	20.7 (28%)	–
11(10)	80	9.2	4.10	2.88 (30%)	–
11(20)	80	9.2	11.2	8.84 (21%)	5.16 (54%)
11(5)	80	7.4	0.812	0.775 (4.6%)	0.720 (12%)
11(10)	80	7.4	0.337	0.263 (22%)	0.205 (39%)
11(20)	80	7.4	0.652	0.490 (25%)	0.376 (43%)
11(5)	80	5.3	2.81	2.31 (18%)	2.02 (28%)
11(10)	80	5.3	0.847	0.733 (14%)	0.619 (27%)
11(20)	80	5.3	2.85	1.96 (31%)	1.38 (52%)
11(5)	37	9.2	20.7	20.7 (0%)[c]	20.2 (2.4%)
11(10)	37	9.2	3.04	2.84 (7.0%)	2.67 (12%)
11(20)	37	9.2	11.6	11.2 (4.0%)	11.0 (5.1%)
11(5)	37	7.4	0.864	0.840 (2.8%)	0.817 (5.4%)
11(10)	37	7.4	0.329	0.312 (5.1%)	0.307 (6.6%)
11(20)	37	7.4	0.606	0.597 (1.5%)	0.570 (5.9%)
11(5)	37	5.3	3.43	3.41 (0.58%)	3.33 (2.9%)
11(10)	37	5.3	1.08	1.01 (6.5%)	0.961 (11%)
11(20)	37	5.3	3.49	3.47 (0.57%)	3.43 (1.7%)
12(15)	80	9.2	8.78	8.05 (7.7%)	7.03 (20%)
12(15)	23	9.2	6.89	6.73 (2.2%)	6.48 (5.9%)
pAA	80	9.2	4.07	3.90 (4.1%)	3.83 (5.8%)
pAA	37	9.2	7.21	7.16 (0.63%)	7.14 (0.91%)

[a] Initial η_{red} measured at temperature in aqueous buffer at noted pH values. [b] Values in parentheses are the loss in viscosity expressed in percent of the original measured viscosity. [c] Within error and significant digits, no loss in viscosity was noted.

tuning of the viscosity and ultimately the polymer properties. Several possible reasons for the loss of the viscosity of the aqueous polymer solutions over time are imaginable, including the removal of the side chains through hydrolysis, changes in the overall polymer structure, and the formation or breaking of noncovalent interactions. To further elucidate the possible mechanism of viscosity loss, gel permeation chromatography (GPC) experiments were carried out before and after treatment of the graft copolymers with the aqueous conditions outlined above. Example chromatograms for polymer **11(5)** treated at pH 9.2 and 80 °C are presented in Figure 1. After 24 h of hydrolysis, the GPC traces show a new low molecular weight signal with no observable initial graft copolymer remaining, suggesting fast and efficient hydrolysis of the graft copolymers to lower molecular weights polymers, most likely linear poly(acrylic acid)s and poly(norbornene)s.[38] Another indication that hydrolysis may play the dominant role in the reduction of the viscosity is the experimental data for polymer **12**. The hydrophobic nature of the ROMP backbone combined with the alkyl linkers may limit the availability of water for nucleophilic addition onto the ester groups, impeding hydrolysis of these groups. Nevertheless, we cannot conclusively say that the loss in viscosity is only due to polymer hydrolysis. While hydrolysis may be the main mechanism of polymer degradation, the exact reasons for the decrease in viscosity may be manifold, including the loss of molecular weight through hydrolysis as well as changes in the lower molecular weight polymer structures from random coil structures for the hydrophilic graft copolymers to collapsed polymer particles of the poly(norbornene) scaffolds after hydrolysis. However, the GPC data in conjunction with the lack of viscosity loss of the control polymers, poly(acrylic acid) and **12**, suggest that polymer hydrolysis plays an important role in the reduced viscosities measured for all graft copolymers based on **11**.

Conclusion. In summary, we have developed a novel strategy toward the formation of graft copolymers via a combination of ROMP and ATRP. Combination of these two highly controlled polymerization methods allows for a modular approach toward the synthesis of graft copolymers since the backbone length, the graft density, and the graft length can be varied in a highly controlled manner. It is important to note that this methodology is not limited to *tert*-butyl acrylates but can potentially be adapted to any monomer that can be polymerized by ATRP. The graft copolymer architecture can be used to control the attenuation of viscosity of aqueous solution, through control of polymer composition, temperature, and pH. The application of this system may reach to areas where controlled viscosity generation and/or loss plays an important role. Furthermore, the controlled hydrolyses of polymer side chains off a polymer backbone are essential in biomaterials such as drug delivery systems.

Acknowledgment. The authors thank Halliburton Energy Services for financial support of this work. The assistance of Dr. Arron Karcher for the GPC analysis of the poly(acrylic acid) graft copolymers is gratefully acknowledged.

References and Notes

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MA0358475