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An Efficient Route to Macromonomers via ATRP and Click Chemistry

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ABSTRACT: The combination of atom transfer radical polymerization (ATRP) and click chemistry was employed to prepare well-defined ω-(meth)acryloyl macromonomers in an efficient manner. Poly(*n*-butyl acrylate) (PBA), polystyrene (PS), and PS-*b*-PBA were prepared by ATRP and subsequently derivatized to contain azido end groups. The reaction of the azido-terminated polymers with alkyne-containing acrylate and methacrylate monomers resulted in near-quantitative chain end functionalization. Macromonomers of various molecular weights [PBA: $M_n = 2.2-6.4 \times 10^3$ g/mol (DP$_n$ = 16−49); PS: $M_n = 3.2-5.9 \times 10^3$ g/mol (DP$_n$ = 29−55)] and architectures were prepared by this method. The end group transformations required to incorporate the polymerizable functionality were accomplished either as a stepwise series of discrete reactions or as an in situ process, wherein azidation was immediately followed by azide−alkyne coupling in situ. In both cases, the degree of end group functionalization generally exceeded 90%. To demonstrate polymerizability, examples of ω-methacryloyloxy−PBA and ω-acryloyloxy−PS macromonomers were homopolymerized by conventional radical polymerization in toluene. The macromonomers and polymacromonomers were characterized by a combination of gel permeation chromatography using refractive index, light scattering, and viscosity detection, as well as ^{1}H NMR spectroscopy and ^{1}H−^{1}H NMR correlation spectroscopy (COSY). This versatile method of incorporating polymerizable end groups from commercially available reagents should be applicable to a variety of (co)polymers accessible by ATRP.

Introduction

Macromonomers are macromolecules of relatively low molecular weight that are capable of further polymerization.[1−8] During polymerization, macromonomers serve as building blocks to facilitate the synthesis of a variety of branched polymer topologies;[9] homopolymerization is used to prepare star or densely grafted, brush-shaped polymers,[10,11] while copolymerization with low-molecular-weight comonomers results in loosely grafted and statistically distributed graft copolymers.[12−14] For each of these architectures, the identity of the branches is directly dependent on characteristics of the macromonomer such that adequate control of composition, molecular weight, and molecular topology of the macromonomer chain impart a well-defined nature to the resulting branched (co)polymers.

To prepare well-defined branched products, it is important to synthesize macromonomers in a manner that affords the desired level of precision. For instance, molecular weight control of the macromonomer is critical for preparing side chains with specific and uniform dimensions and also because the chain length can have a significant effect on the resulting homopolymerizability.[15−17] Similarly, a high degree of end group functionality is vital because nonpolymerizable impurities are often difficult to remove from polymacromonomer products. The necessity of preparing well-defined structures has led to employment of controlled/living polymerization techniques for macromonomers syntheses.[1−3]

Polymerizable functionalities are generally introduced to polymer chain termini by one of three methods: termination, initiation, or transformation.[2] Termination involves end-capping of a living polymer with a molecule that contains the polymerizable moiety. Initiation typically entails initiating living polymer chains with a molecule that contains a polymerizable functionality that is retained during the polymerization. Chain transformation is a postpolymerization modification procedure in which the polymer end groups are subsequently derivatized to obtain the required functionality.

Most examples of macromonomers have been prepared by living anionic polymerization techniques, as this method affords the requisite high degree of end group functionalization, accurate control of molecular weight, and ease of transforming the resulting end groups by nucleophilic substitution.[1−3] It is possible to prepare polymers with increased functionality under less stringent reaction conditions by controlled/living radical polymerization (CRP).[18−26] CRP techniques facilitate the preparation of a broad variety of polymeric materials with predetermined molecular weights, narrow molecular weight distributions, and high degrees of chain end functionalization. Atom transfer radical polymerization (ATRP) has emerged as one of the most widely used CRP methods due to facile experimental setup and the availability of inexpensive initiators and catalysts.[19−22] Because of the versatility and efficiency of end group functionalization afforded by ATRP, it is highly suitable for the preparation of macromonomers with chains composed of a variety of monomer units.

Macromonomer synthesis by ATRP has generally involved preparation of polymers with polymerizable end groups that are inactive under ATRP conditions.[27−35] However, to prepare macromonomers that can subsequently be polymerized by CRP, a postpolymerization modification route is necessary to prevent end group consumption that leads to branching. For example, Mueller et al. prepared macromonomers with methacrylate end groups by using hydroxyl-functionalized ATRP initiators that facilitated esterification with methacryloyl chloride after polymerization.[36,37] Muehlebach et al.[16] and Couvreur et al.[38] prepared polymers with (meth)acrylate termini by nucleophilic substitution of the halogen end groups with (meth)acrylic acid. While these approaches were indeed efficient, extension to (co)-

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polymers containing hydroxy- or carboxy-functional monomer units may result in side reactions during chain end functionalization. Because of the ability of ATRP to polymerize functional monomers, it would be advantageous to extend the concept of macromonomer preparation by postpolymerization modification to also include enhanced functional group tolerance.

Efficient and specific reactions are desirable for postpolymerization modification to be highly successful and widely applicable. Recently, Sharpless et al. have coined the term *click chemistry* to describe a set of highly efficient and specific organic reactions that can be conducted in a range of environments under relatively nonstringent reaction conditions.[39] As an example, the modified Huisgen 1,3-dipolar cycloaddition of organic azides[40] with terminal alkynes in the presence of a $\mathrm{Cu^I}$ catalyst results in near-quantitative preparation of 1,4-disubstituted 1,2,3-triazole products under moderate reaction conditions.[41,42] This procedure can be conducted in aqueous or organic media with little or no side reactions. Several groups have reported the application of azide−alkyne coupling reactions in the functionalization of polymeric materials.[43−57] The particular combination of ATRP and postpolymerization modification by click chemistry is a promising strategy to synthesize various functionalized polymers.[50−59]

Herein, we demonstrate the applicability of azide−alkyne coupling for preparing well-defined macromonomers in an efficient manner from commercially available reagents. Poly(*n*-butyl acrylate) (PBA), polystyrene (PS), and PS-*b*-PBA were prepared by ATRP and subsequently derivatized to contain azido end groups. Reaction of the azido-terminated polymers with alkyne-containing acrylate and methacrylate monomers resulted in near-quantitative chain end functionalization to yield macromonomers with various molecular weights and architectures. Typically, a stepwise procedure was used in which the azido-terminated polymer was isolated and purified before reaction with the alkyne species. However, an in situ end group transformation process was also conducted. In this case, the bromine-terminated polymers isolated after ATRP were transformed to azido end groups and subsequently reacted in situ with alkyne-functionalized (meth)acrylates. This method of incorporating polymerizable end groups is highly versatile due to the orthogonal reactivity inherent to click chemistry and should be applicable to any typical (co)polymer accessible by ATRP.

Experimental Section

Materials. Methyl 2-bromopropionate (MBP, Aldrich 98%), *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), CuBr (Aldrich 98%), propargyl acrylate (PgA, Aldrich 98%), propargyl methacrylate (PgMA, Alfa Aesar 98%), *N*,*N*-dimethylformamide (DMF, Aldrich 99.9%), toluene (Aldrich 99.5%), tetrahydrofuran (THF, Aldrich 99%), 2-propanol (Aldrich 99.9%), and $\mathrm{CDCl_3}$ (Aldrich 99.8 at. % D) were used as received. Styrene (Sty, Aldrich 99%) and *n*-butyl acrylate (BA, Fluka 99%) were passed through basic alumina columns to remove inhibitor immediately prior to polymerization. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Polymer Synthesis. The polymerizations of Sty[54] and BA[60] were conducted with conditions modified from previously reported methods. For all polymerizations, oxygen was removed by three freeze−pump−thaw cycles followed by backfilling with nitrogen. Briefly, PS was prepared by ATRP ([Sty]/[MBP]/[CuBr]/[PMDETA] = 100:1:1:1, 40 vol % toluene, 80 °C). The polymerization was stopped by cooling and exposing the reaction mixture to air. The mixture was diluted with THF and passed through a neutral alumina column to remove the catalyst, and the polymer was isolated by precipitation into methanol. PBA was prepared by ATRP ([BA]/[MBP]/[CuBr]/[PMDETA] = [100]:[1]:[0.5]:[0.5], 10 vol % toluene, 70 °C). The polymerization was stopped by cooling and exposing the reaction mixture to air. The mixture was diluted with THF, passed through a neutral alumina column for catalyst removal, and the polymer was isolated by removing the monomer and solvent under vacuum. For PS and PBA, the monomer conversion or stoichiometry was varied to prepare polymers of various molecular weights. PS-*b*-PBA block copolymer was prepared by ATRP of BA from a PS−Br macroinitiator (M_n = 1000 g/mol, PDI = 1.23) ([BA]/[PS−Br]/[CuBr]/[PMDETA] = 50:1:0.25:0.25, 40 vol % toluene, 70 °C). The resulting block copolymer was isolated in a manner analogous to that described above for the preparation of PS homopolymer. In all cases, the monomer conversion was limited to achieve bromine end group retention.[61]

Synthesis of Azido-Terminated Polymers. The bromo-terminated polymers (PS−Br, PBA−Br, and PS-*b*-PBA−Br) were reacted with $\mathrm{NaN_3}$ (1.1 equiv) at room temperature in DMF (0.05 M−Br) to yield azido-terminated polymers ($\mathrm{PS{-}N_3}$, $\mathrm{PBA{-}N_3}$, and PS-*b*-$\mathrm{PBA{-}N_3}$, respectively).[62−64] The (co)polymers were isolated by precipitation into methanol ($\mathrm{PS{-}N_3}$ and PS-*b*-$\mathrm{PBA{-}N_3}$) or by removal of the solvent under vacuum ($\mathrm{PBA{-}N_3}$).

Stepwise End Group Modification via Azide−Alkyne Coupling. The azido-terminated polymers were reacted with PgA or PgMA according to the following general procedure derived from Lutz et al.[52] A solution of polymer (0.1 $\mathrm{M{-}N_3}$ in DMF), PMDETA (0.5 equiv), and PgA or PgMA (1.3 equiv) was purged with nitrogen to remove oxygen and transferred via cannula to a vial containing CuBr (0.5 equiv) under a nitrogen environment. The reaction was allowed to proceed at room temperature for 24 h. After this time, the reaction mixture was exposed to air, and the solution was passed through a column of neutral alumina. The resulting (meth)acryloyloxy-endcapped polymer [ω-(meth)acryloyloxy-polymer] was isolated by reprecipitation into methanol three times (PS and PS-*b*-PBA) or by removal of the solvent under vacuum (PBA).

In Situ End Group Modification. After ATRP and subsequent isolation, bromo-terminated polymer was placed in a nitrogen-purged vial and dissolved in deoxygenated DMF (0.1 M −Br). $\mathrm{NaN_3}$ (1.1 equiv) was added and allowed to react for 24 h at room temperature, after which PgA or PgMA (1.3 equiv) and CuBr (0.5 equiv) were added. The resulting solution was allowed to stir at room temperature for 24 h before the reaction mixture was exposed to air, and the mixture was passed through a column of neutral alumina. The resulting ω-(meth)acryloyloxy-polymer was isolated by precipitation into methanol three times (PS and PS-*b*-PBA) or by removal of the solvent under vacuum (PBA).

Macromonomer Polymerization of ω-Methacryloyloxy−PBA. A solution of AIBN (11.2 mg, 0.0683 mmol) in toluene (1.85 mL) was purged with nitrogen for 10 min and transferred to a sealed and nitrogen-filled vial containing ω-methacryloyloxy−PBA macromonomer (1.66 g, 0.741 mmol, M_n = 2240 g/mol, M_w/M_n = 1.08). When the macromonomer was fully dissolved, the solution was heated to 60 °C, and samples were removed periodically by syringe over a period of 21 h.

Macromonomer Polymerization of ω-Acryloyloxy−PS. A solution of AIBN (1.9 mg, 0.0116 mmol) in toluene (0.37 mL) was purged with nitrogen for 10 min and transferred to a sealed and nitrogen-filled vial containing ω-acryloyloxy−PS macromonomer (0.37 g, 0.116 mmol, M_n = 3200 g/mol, M_w/M_n = 1.10). When the macromonomer was fully dissolved, the solution was heated to 60 °C, and samples were removed periodically by syringe over a period of 3 h.

Analysis. Gel permeation chromatography (GPC) was conducted in DMF at 50 °C with a flow rate of 1.0 mL/min (Viscotek GPC pump; ViscoGel I series G3000 and G4000 mixed-bed columns, molecular weight range $0-60 \times 10^3$ and $0-400 \times 10^3$ g/mol, respectively). Detection consisted of a Viscotek refractive index detector operating at $\lambda = 660$ nm, a Viscotek UV−vis detector operating at $\lambda = 254$ nm, and a Viscotek model 270 series platform, consisting of a laser light scattering detector (operating at 3 mW, $\lambda = 670$ nm with detection angles of 7° and 90°) and a four-capillary viscometer. Macromonomer and polymacromonomer

Scheme 1. Postpolymerization End Group Transformations of Polystyrene (PS) and Poly(*n*-Butyl Acrylate) (PBA) during (Meth)Acrylate Macromonomer Preparation

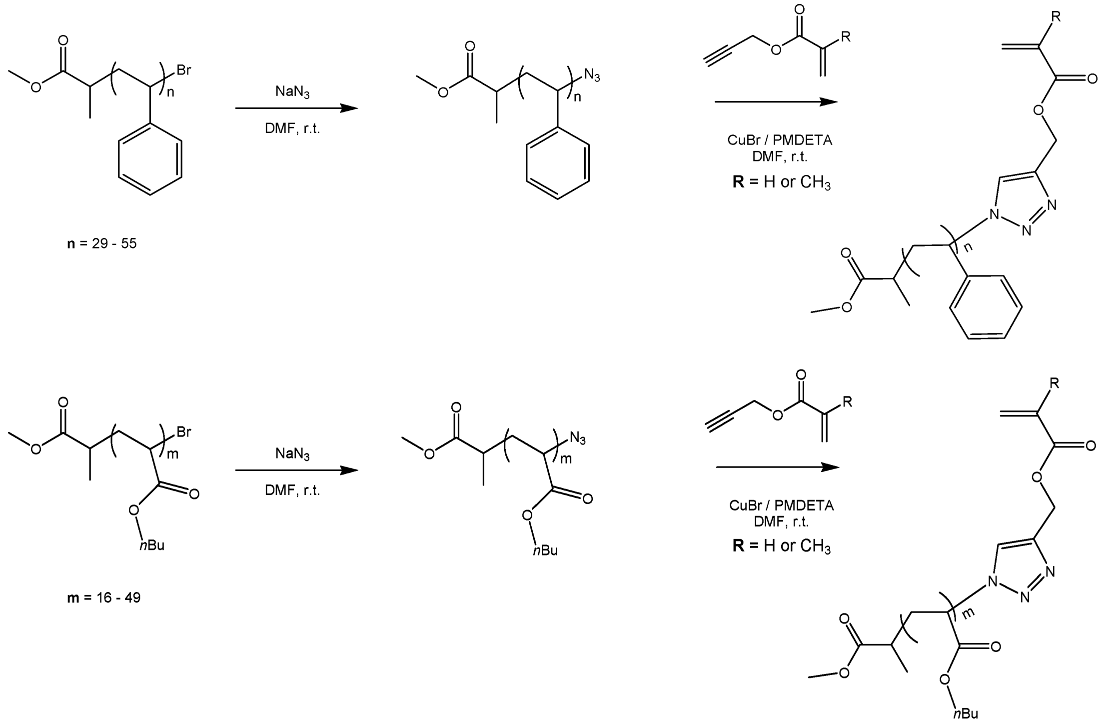


Table 1. ω-(Meth)acryloyloxy Macromonomers Prepared by ATRP and Postpolymerization Modification by Azide−Alkyne Coupling

			GPC[c]			NMR[d]		
polymer	ω end group	functionalization method	M_n (g/mol)	DP_n	M_w/M_n	M_n (g/mol)	DP_n	f[e] (%)
PS	acryloyl	*a*	3200	29	1.10	3210	29	>95
PS	acryloyl	*b*	3230	29	1.08	3290	30	91
PS	acryloyl	*a*	4090	38	1.09	4670	43	>95
PS	methacryloyl	*a*	5880	55	1.04	5990	56	>95
PS	methacryloyl	*a*	3450	32	1.10	3770	35	>95
PBA	acryloyl	*b*	2440	18	1.13	1700	12	93
PBA	acryloyl	*b*	6260	48	1.14	5980	45	>95
PBA	methacryloyl	*a*	2240	16	1.08	1870	13	>95
PBA	methacryloyl	*b*	6400	49	1.08	6450	49	93
PS-*b*-PBA	acryloyl	*a*	5 350	8 (PS) 34 (PBA)	1.34	5 090	8 (PS) 32 (PBA)	81

[a] Azidation and in situ click reaction (polymer−Br → polymer−N_3 → ω-(meth)acryloyloxy−polymer) [b] Conventional stepwise modification procedure (polymer−Br → polymer−N_3 → purification/isolation → ω-(meth)acryloyloxy−polymer) [c] Determined by gel permeation chromatography with conventional calibration based on polystyrene standards. [d] Determined by comparing ^{1}H NMR peak areas of polymer backbone protons with protons on either the α or ω chain terminus. [e] Degree of macromonomer end group functionalization as determined by comparing ^{1}H NMR peak areas of macromonomer vinyl protons with protons from the initiator residues on the α chain terminus.

molecular weights were determined using conventional calibration based on polystyrene standards and triple detection methods, respectively. ^{1}H NMR spectroscopy and two-dimensional ^{1}H−^{1}H correlation spectroscopy (COSY) were conducted in $CDCl_3$ with a Bruker Avance 400 spectrometer operating at 400 MHz.

Results and Discussion

Synthesis of Bromine-Terminated Polymers. ATRP was employed to synthesize a variety of polymeric precursors that were subsequently modified to incorporate (meth)acrylate end groups (Scheme 1). Because of the control afforded by ATRP, polymers with a range of molecular weights and low polydispersities were accessible [PBA: $M_n = 2.2-6.4 \times 10^3$ g/mol ($DP_n = 16-49$); PS: $M_n = 3.2-5.9 \times 10^3$ g/mol ($DP_n = 29-55$)] (Table 1). In each polymerization, conversion was limited to less than 60% to ensure end group retention. Model systems were synthesized from BA or Sty by ATRP with CuBr/PMDETA as the catalyst. In addition to a range of homopolymers with various molecular weights, an example of a PS-*b*-PBA was also prepared. High degrees of end group functionalization for the Br-terminated polymers were confirmed by agreement between molecular weights obtained by GPC and ^{1}H NMR spectroscopy.

End Group Functionalization. Nucleophilic substitution of the resulting Br end groups was achieved by reaction with NaN_3 in DMF at room temperature (Scheme 1).[62−64] Quantitative conversion to azido chain ends was confirmed by ^{1}H NMR spectroscopy. For the PS homopolymers, conversion of PS−Br to PS−N_3 was confirmed by observing the shift of the ω-terminal methine from $\delta = 4.5$ ppm to $\delta = 3.9$ ppm (Figure 1; H_a and H_b). For the case of PBA, overlap of the ω-terminal methine proton with the methylene protons of PBA (−COO−C***H***$_2$CH$_2$CH$_2$CH$_3$) at $\delta = 3.8-4.2$ ppm prevented confirmation of end group transformation by conventional ^{1}H NMR spectroscopy. However, COSY provided clear evidence that

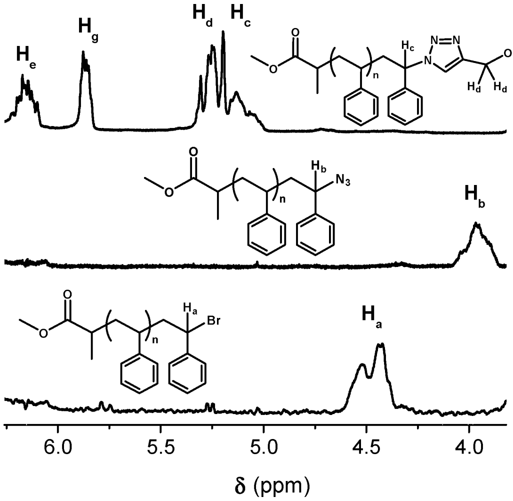


Figure 1. ^{1}H NMR spectra and peak labels for bromine-terminated polystyrene (PS−Br), azido-terminated polystyrene (PS−N$_3$), and the polystyrene macromonomer after reaction with propargyl acrylate (ω-acryloyloxy−PS). H_f peak is obscured by the adjacent aromatic region (not shown).

end group transformation was near-quantitative by demonstrating a shift from $\delta_{\mathrm{PBA(H)-Br}} = 4.2$ ppm to $\delta_{\mathrm{PBA(H)-N_3}} = 3.8$ ppm.

After purification and isolation, the azido-terminated polymers were dissolved in DMF and reacted with a slight excess of PgA or PgMA in the presence of CuBr at room temperature. Although a ligand is not necessary for sufficient solubility of the copper catalyst in DMF,[65] PMDETA was employed to ensure enhanced rates of reaction and increased end group functionalization. After catalyst removal, the resulting polymers were precipitated and/or dried under vacuum to remove unreacted PgA or PgMA. The extent of conversion of the terminal azido groups to (meth)acryloyl moieties was monitored by ^{1}H NMR spectroscopy. The degree of end group functionalization (f) for PS−N$_3$ was easily determined from conventional one-dimensional proton spectra (Figure 1). The appearance of vinyl peaks from the acrylate end group and the shift of the terminal benzylic methine proton from $\delta = 3.8$ ppm for PS−N$_3$ to $\delta = 5.2$ ppm for ω-acryloyloxy−PS are indicative of conversion to the polymerizable end groups. The degree of end group functionalization was quantified by comparing peak areas of the vinyl protons to that of the methyl group from the initiator residue at $\delta = 3.5$ ppm (Table 1). In all cases, $f > 90\%$ was observed, and in most cases, near-quantitative functionalization was achieved.

For the PBA macromonomers, COSY was employed to confirm complete consumption of the azido-terminated polymer after functionalization with PgA or PgMA. Figure 2 shows the COSY spectrum and the corresponding peak assignments for a PBA macromonomer with an acrylate end group ($M_n = 2440$ g/mol, $M_w/M_n = 1.13$). The absence of off-diagonal cross-peaks indicative of correlation of the terminal methine PBA($\boldsymbol{H}$)Br at $\delta = 4.2$ ppm or PBA($\boldsymbol{H}$)−N$_3$ at $\delta = 3.8$ ppm with the adjacent terminal unit backbone methylene protons at $\delta = 2.2$ ppm or $\delta = 1.9$ ppm, respectively, suggests the azido-terminated polymer is completely consumed. Off-diagonal correlation of peaks at $\delta = 4.7$ ppm and $\delta = 3.0$ ppm indicate coupling between the terminal methine PBA($\boldsymbol{H}$)-acrylate and adjacent terminal unit backbone methylene protons. Corroborative evidence of efficient end group functionalization was provided by integration of the vinyl and initiator residue peaks of the one-dimensional spectra in a manner similar to that described for the PS macromonomers (Table 1).

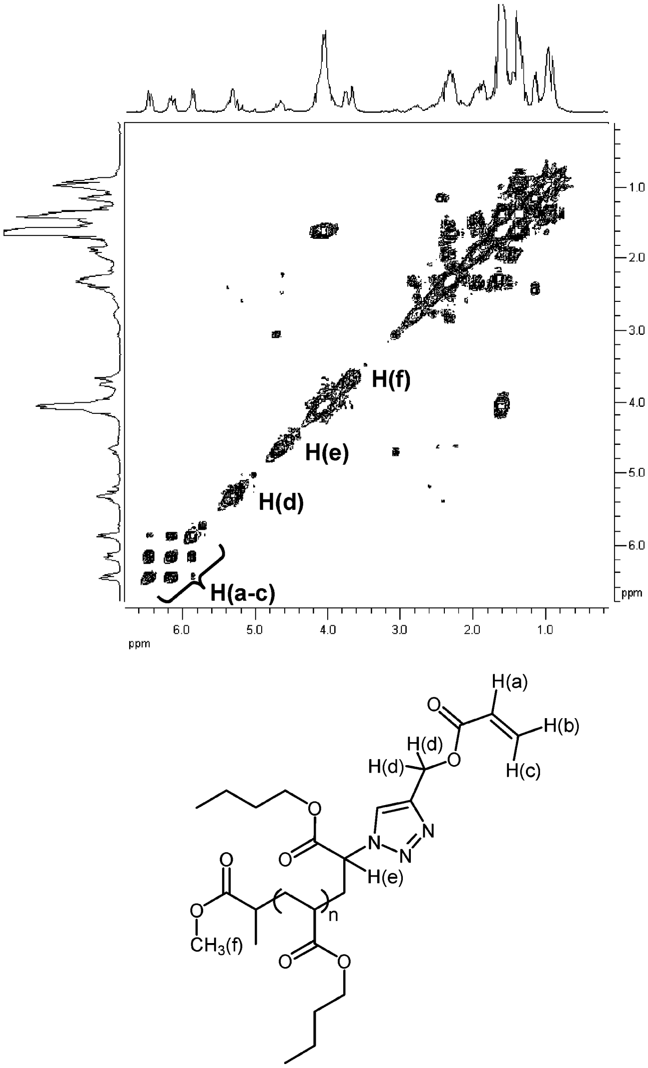
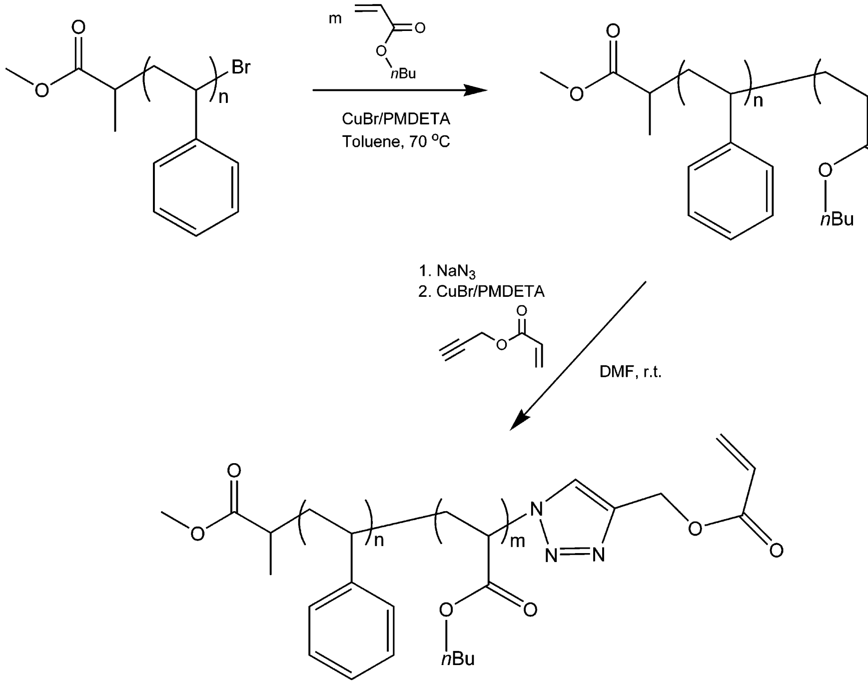


Figure 2. COSY spectrum and peak assignments for ω-acryloyloxy−PBA. No appreciable correlation signals of PBA($\boldsymbol{H}$)Br at $\delta = 4.2$ ppm or PBA($\boldsymbol{H}$)−N$_3$ at $\delta = 3.8$ ppm with the adjacent terminal unit backbone methylene protons at $\delta = 2.2$ ppm or $\delta = 1.9$ ppm, respectively. Off-diagonal correlation of peaks at $\delta = 4.7$ ppm and $\delta = 3.0$ ppm indicate coupling between PBA($\boldsymbol{H}$)-acrylate and the adjacent terminal unit backbone methylene protons. Peaks and correlations from the acrylate end group are visible at $\delta = 4.7-7.8$ ppm. (Correlation of residual solvent peaks removed.)

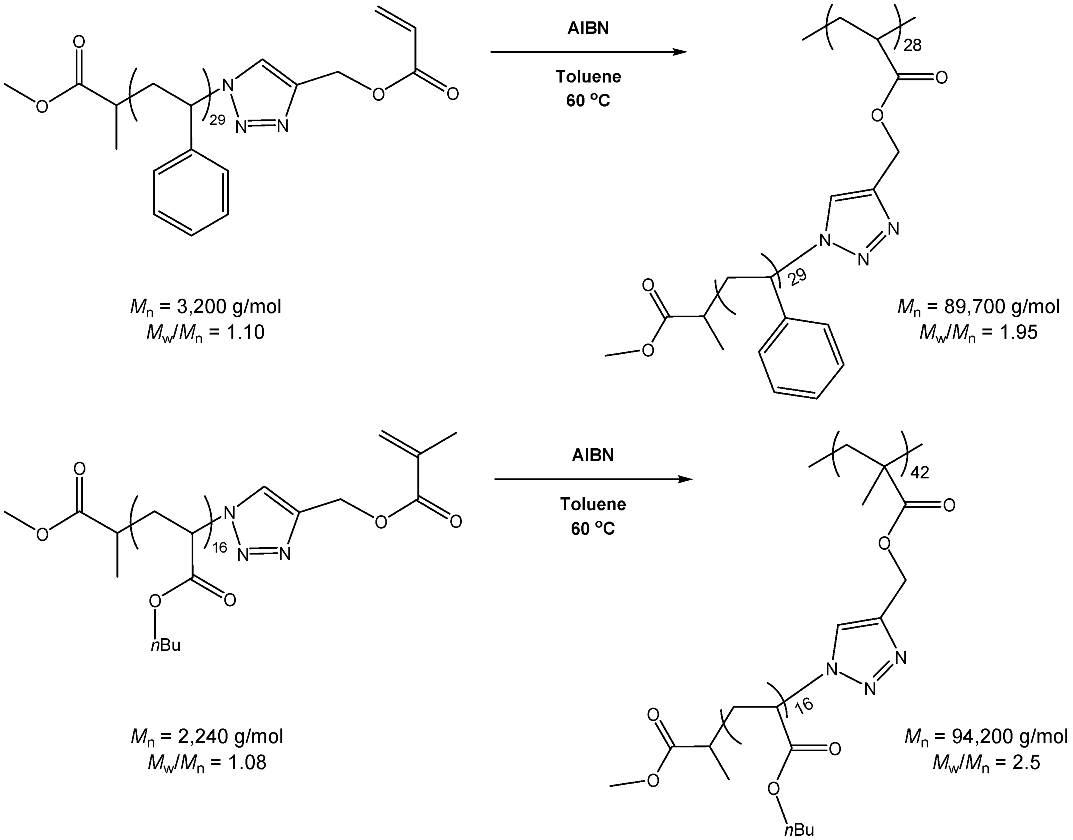
In Situ End Group Functionalization: Azidation and In Situ Coupling Reaction. A second method of postpolymerization modification involved azido substitution of the bromine end groups and direct click reaction with the propargyl (meth)acrylate species without isolation and purification of the azido-terminated intermediate. While this method is an example of an in situ polymer end group functionalization procedure, a distinction should be drawn between this approach and previous reports of one-pot methods that also included in situ polymerization.[53,54] This particular process is experimentally appealing and resulted in high degrees of end group functionalization that were comparable to those observed when the polymer was isolated between modification steps (Table 1).

The concept of macromonomer preparation was further extended by the end group functionalization of a PS-*b*-PBA block copolymer (Scheme 2). Homopolymerization of block macromonomers results in core−shell cylinders or stars, which

Scheme 2. Polymerization of *n*-Butyl Acrylate (BA) from a Polystyrene (PS) Macroinitiator and Subsequent Derivatization by In Situ Azidation/Coupling



Scheme 3. Conventional Radical Homopolymerization of *ω*-Acryloyloxy−PS and *ω*-Methacryloyloxy−PBA Macromonomers



are examples of unimolecular micelles that are structurally stable upon dilution. A PS−Br macroinitiator of M_n = 1000 g/mol and M_w/M_n = 1.23 was used to polymerize BA, resulting in a block copolymer of M_n = 5350 g/mol and M_w/M_n = 1.34. GPC traces of the macroinitiator and the resulting block copolymer confirmed relatively high initiation efficiency during the block copolymerization (Figure 3). After isolation and purification, the block copolymer was derivatized to contain acrylate end groups by the in situ azidation/click process. The resulting block macromonomer had a degree of end group functionalization of 81%, which is slightly lower than values obtained for the homopolymers. This discrepancy most likely results from an increased number of terminated chains combined from the two polymerizations and the comparatively high degree of monomer conversion obtained during the block copolymerization (~70%). Additionally, a small shoulder on the right side of the block

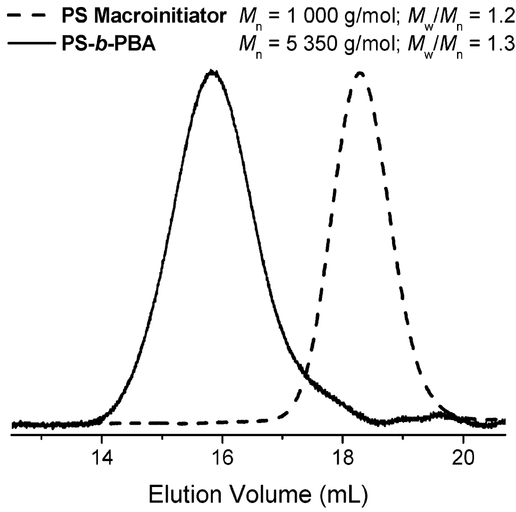


Figure 3. Relative refractive index traces from gel permeation chromatography for a polystyrene (PS) macroinitiator and the resulting polystyrene-*block*-poly(*n*-butyl acrylate) (PS-*b*-PBA) that was subsequently used to prepare a block macromonomer. Block copolymerization conditions: [BA]/[PS−Br]/[CuBr]/[*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine] = 50:1:0.25:0.25, 40 vol % toluene, 70 °C.

copolymer GPC trace is indicative of dead chains arising from homopolymer impurity, and these chains likely contribute to the somewhat low degree of end group functionalization.

Homopolymerization of PS and PBA Macromonomers. To confirm the polymerizability of this set of macromonomers, model systems were chosen for conventional radical homopolymerization initiated with AIBN. *ω*-Acryloyloxy−PS and *ω*-methacryloyloxy−PBA were selected for polymerization in toluene (50 w/v %). Relatively high macromonomer concentrations were chosen to achieve sufficient rates. Because of high molecular weight and low concentration of end groups, the macromonomer polymerization solutions were noticeably viscous prior to addition of the initiator.

AIBN-initiated homopolymerization of *ω*-acryloyloxy−PS ($M_n = 3200$ g/mol, $M_w/M_n = 1.10$) in toluene (50 w/v %) at 60 °C was successful, though somewhat complicated by the high T_g of PS and the rapid increase in viscosity during polymerization. The elevated concentration used to enhance the polymerization rate resulted in vitrification after 3 h (20% macromonomer conversion), and a polymacromonomer of $M_n = 89\,700$ g/mol ($DP_n = 28$) and $M_w/M_n = 1.95$ was obtained.

The polymerization of the *ω*-methacryloyloxy−PBA macromonomer was more robust due in part to the lower T_g of PBA and reduced viscosity of the polymerization solution. *ω*-Methacryloyloxy−PBA ($M_n = 2240$ g/mol, $M_w/M_n = 1.08$) was polymerized in toluene (50 w/v %) at 60 °C with AIBN as the initiator (Scheme 3). Conversion was determined by comparing the evolution of GPC peak areas of macromonomer and polymacromonomer (Figure 4). Polymacromonomer of $M_n = 94\,200$ ($DP_n = 42$) and $M_w/M_n = 2.5$ was obtained after 21 h at a macromonomer conversion of 83%.

While the polymerizability of the classes of acrylate and methacrylate macromonomers prepared herein is successfully demonstrated, optimization of the polymerization conditions was not attempted; detailed investigation regarding the homo- and copolymerization of these macromonomers at various concentrations and temperatures is underway and will be the topic of a future report.

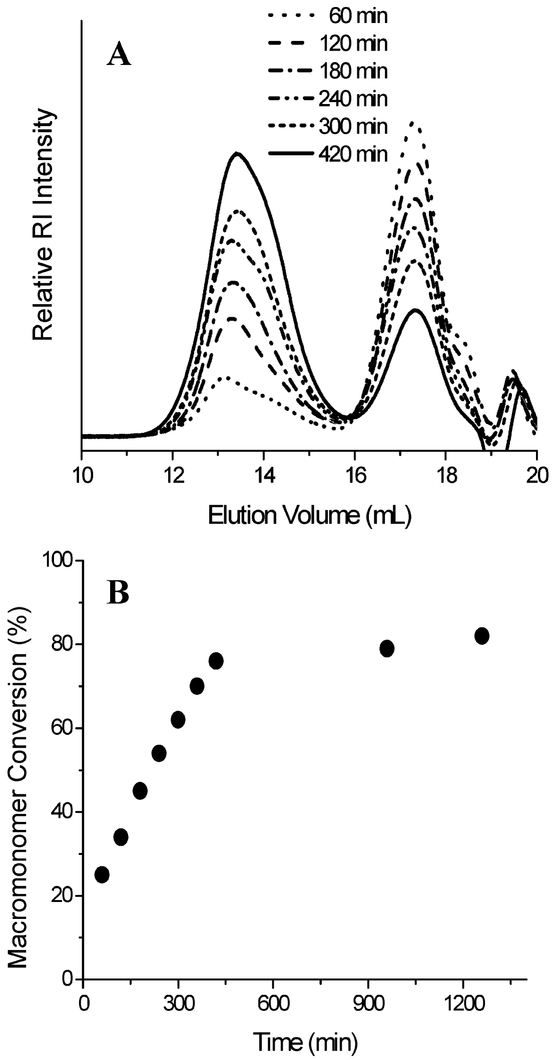


Figure 4. Gel permeation chromatograms (A) and macromonomer conversion (B) as a function of reaction time for the homopolymerization of a *ω*-methacryloyloxy−PBA macromonomer of $M_n = 2240$ g/mol, $M_w/M_n = 1.08$, $f > 95\%$.

Conclusions

PS, PBA, and PS-*b*-PBA (co)polymers with controlled molecular weights and narrow molecular weight distributions were prepared by ATRP. The resulting bromine end groups were displaced by reaction with sodium azide, and the resulting azido-terminated polymers were coupled with propargyl (meth)-acrylate. The end group transformations required to incorporate the terminal polymerizable functionality were highly efficient and could be accomplished either as a stepwise series of discrete reactions or as an in situ process, with azidation being immediately followed by azide−alkyne coupling. In both cases, the degree of end group functionality generally exceeded 90%. To demonstrate polymerizability, examples of PS and PBA macromonomers were successfully homopolymerized by conventional radical polymerization.

The particular combination of ATRP and click chemistry is a promising strategy to synthesize macromonomers due to both the high degree of end group functionalization and the efficient postpolymerization modification afforded by Cu^I-catalyzed azide−alkyne coupling. Other methods of preparing macromonomers by modification of polymers prepared by ATRP could have limited applicability due to potential side reactions with functional groups contained along the polymer backbone. However, the specificity and fidelity inherent to click chemistry may facilitate employment of this method to prepare macromonomers from essentially any monomer polymerizable by ATRP.

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