4960 *Macromolecules* **2006,** *39,* 4960−4965

Synthesis of Star Polymers by a Combination of ATRP and the “Click” Coupling Method

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Received April 27, 2006; Revised Manuscript Received May 13, 2006

ABSTRACT: Three-arm and four-arm star polystyrene (PS) polymers were synthesized by a combination of atom transfer radical polymerization (ATRP) and click coupling chemistry. The click reaction between an azido-terminated PS (PS−N_3) and an alkyne-containing multifunctional compound proved to be fast and efficient. All coupling reactions were finished within 3 h, proven by the disappearance of signals from the azido groups in NMR spectra and the high yields of the coupled products by GPC analysis. For the model coupling reaction between a PS−N_3 polymer and a dialkyne-containing compound, the final yield of the coupled PS−PS polymer was ca. 95%. When a PS−N_3 polymer was reacted with a trialkyne-containing or tetraalkyne-containing compound, the yields of 3-arm star and 4-arm star polymers were around 90% and 83%, respectively. The influence of several parameters on the efficiency of the click coupling reaction was studied, including the molecular weight of the PS−N_3 polymer, the presence of an added reducing agent, Cu(0), and the stoichiometry between the azido and alkynyl groups. The results indicated that the yield of the coupled product was higher when a lower molecular weight PS−N_3 was employed in conjunction with a small amount of reducing agent, and the molar ratio of azido and alkynyl groups was close to 1.

Introduction

Star polymers containing multiple arms connecting at a central core have the simplest structure of numerous possible branched topologies.[1] Interest in star polymers arises from their compact structure and globular shape, which predetermines their low viscosity when compared to linear analogues and makes them suitable materials for several applications. Synthesis of star polymers, which began in the 1950s with living anionic polymerization, has recently received increased attention due to the development of controlled/living radical polymerization (CRP).[2,3] Typically, star polymers are synthesized via CRP by one of two strategies: core-first[4−10] and arm-first.[11−19] The arm-first strategy can be further subcategorized according to the procedure employed for star formation. One method is chain extension of a linear arm precursor with a multivinyl cross-linking agent, and the other is coupling linear polymer chains with a multifunctional linking agent or “grafting-onto” a multifunctional core. Although both methods were successfully used for star synthesis in anionic polymerization, to date only the former procedure, using a multivinyl cross-linking agent, has been applied in CRP for synthesis of star polymers containing multiple arms and/or functionalities. The main problem encountered when using the latter coupling method for star synthesis is a nonselective and slow reaction between the polymer chain end and the multifunctional coupling agent. In anionic polymerization, this problem is solved by using an excess of linear chains and purification of the final star polymers by repeated fractionation to remove the unreacted linear chains. However, this problem becomes more complicated in radical polymerization because radicals generated at the chain ends participate in an inevitable side reaction, radical−radical termination, which is avoided in an anionic polymerization since the chain ends are anions. Hence, in CRP techniques, using an excess of linear chains in the reaction produces a significant amount of termination products rather than star polymers. To avoid termination reactions between two linear chain-end radicals, it has become necessary to modify the chain-end functionality of living polymers, synthesized by CRP techniques, prior to forming the stars.

Atom transfer radical polymerization (ATRP)[20−22] is a particularly attractive CRP process for synthesis of chain-end-functionalized polymers.[23] The polymers produced by ATRP preserve terminal halogen atom(s) that can be successfully converted into various desired functional chain-end groups through appropriate transformations, especially nucleophilic substitutions. The modified chain-end group, such as a hydroxyl group or an amino group, cannot react with itself but can react with an appropriate functional group on the multifunctional coupling agent, such as a carboxylic acid group by esterification, to form a star polymer. However, a commonly encountered drawback, when using such a method, is a low yield of star products due to the slow and inefficient reactions between the modified polymer chain ends and multifunctional linking agents. In other words, highly efficient site-specific organic reactions are required in order for star synthesis to be highly successful.

In the past few years, “click reactions”, as termed by Sharpless et al.,[24] have gained a great deal of attention due to their high specificity, quantitative yields, and near-perfect fidelity in the presence of most functional groups. The most popular click chemistry reaction is the copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyne leading to 1,2,3-triazole.[25−27] Recent publications on this click reaction indicate that it is a versatile method for synthesis of functional polymers,[28−35] bioconjugated polymers,[36] and polymers with complex topologies.[37−45] Therefore, it is promising to apply this click coupling reaction to the synthesis of star polymers.

Herein, we report the first synthesis of star polymers by a coupling procedure using a combination of ATRP and click chemistry. Polystyrene (PS) linear chains with high azido chain-end functionality coupled with multifunctional alkyne-containing coupling agents under a mild condition to produce linear and star polymers with different arm numbers.

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10.1021/ma060926c CCC: $33.50

Experimental Section

Synthesis of Dialkyne-Containing Coupling Agent (1). A clean, dry round-bottom flask containing 70 mL of methylene chloride (dried overnight with $MgSO_4$) was cooled to 0 °C in ice−water bath. The solvent was purged with N_2 for 30 min before *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (1.95 g, 10.2 mmol), bis(2-hydroxyethyl) disulfide (0.655 g, 4.25 mmol), and pentynoic acid (1.0 g, 10.2 mmol) were added sequentially. Under magnetic stirring, 0.125 g of 4-(*N*,*N*-dimethylamino)pyridine in 2 mL of dried CH_2Cl_2 was added into this mixture within 5 min. The reaction mixture was allowed to stir for 40 h at room temperature before washed successfully with 300 mL of 1 M HCl solution, 300 mL of 1 M NaOH solution, and 200 mL of 1 M NaCl solution. The organic layer was dried with anhydrous $MgSO_4$ overnight before the solvent was removed in vacuo, yielding a transparent viscous liquid. The yield of coupling agent **1** was 1.05 g (79%), and its structure was verified by ^{1}H NMR spectroscopy (δ, $CDCl_3$ as solvent): 4.40 ppm (t, J = 6.7 Hz, 4H, $\mathbf{C}\boldsymbol{H}_2O$), 2.95 ppm (t, J = 6.6 Hz, 4H, $\mathbf{C}\boldsymbol{H}_2S$), 2.50−2.65 ppm (m, 8H, $C\boldsymbol{H}_2C\boldsymbol{H}_2C(=O)$), and 2.00 ppm (t, J = 2.5 Hz, 2H, $\mathbf{C}\boldsymbol{H}{\equiv}C$).

Synthesis of Trialkyne-Containing Coupling Agent (2). The synthesis and postpurification procedures for coupling agent **2** were similar to those of **1**, except that 1,1,1-tris(4-hydroxyphenyl)ethane (0.87 g, 2.83 mmol) was used to react with pentynoic acid (1.0 g, 10.2 mmol). The yield of **2** was 1.31 g (85%), and its structure was verified by ^{1}H NMR spectroscopy (δ, $CDCl_3$ as solvent): 2.20 ppm (s, 3H, $C\boldsymbol{H}_3C(Ar)$), 7.00−7.10 ppm (q, J = 9.0 Hz, 12H, ***Ar***), 2.83 (t, J = 7.3 Hz, 6H, $\mathbf{CH}_2C\boldsymbol{H}_2C(=O)$), 2.65 ppm (t, J = 7.3 Hz, 6H, $\mathbf{C}C\boldsymbol{H}_2CH_2$), and 2.00 ppm (t, J = 2.7 Hz, 3H, $\mathbf{C}\boldsymbol{H}{\equiv}C$).

Synthesis of Tetraalkyne-Containing Coupling Agent (3). The synthesis and postpurification procedures for coupling agent **3** were similar to those of **1**, except that pentaerythritol (0.29 g, 2.13 mmol) was used to react with pentynoic acid (1.0 g, 10.2 mmol). The yield of **3** was 0.85 g (73%), and its structure was verified by ^{1}H NMR spectroscopy (δ, $CDCl_3$ as solvent): 4.23 ppm (s, 8H, $CC\boldsymbol{H}_2O$), 2.50−2.65 ppm (m, 16H, $CC\boldsymbol{H}_2C\boldsymbol{H}_2C(=O)$), and 2.00 ppm (t, J = 2.5 Hz, 4H, $\mathbf{C}\boldsymbol{H}{\equiv}C$).

Synthesis of PS−N$_3$. ω-Bromo-terminated PS chain (PS−Br) was prepared by ATRP using CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst and ethyl 2-bromoisobutyrate (EBiB) as initiator. The reaction was stopped at low styrene conversion (<30%) via exposure to air and dilution with THF. The solution was filtered through a column filled with neutral alumina to remove the copper complex before the polymer was precipitated in cold hexane. After purification, the resulting polymer was dissolved in *N*,*N*-dimethylformamide (DMF), NaN_3 (2 times excess to the mole of bromo group) was added, and the resulting solution was allowed to stir at 25 °C overnight. After precipitation into methanol/water mixture (1/1 by volume), ω-azido-terminated PS (PS−N$_3$) was obtained.

Synthesis of Linear and Star Polymers by Click Coupling Reactions. The click coupling reactions between PS−N$_3$ with difference molecular weights and multifunctional coupling agents were conducted in a 10 mL Schlenk flask with DMF as solvent and CuBr/PMDETA as catalyst. Samples were withdrawn periodically for GPC analysis of the reaction products. To monitor the reaction by ^{1}H NMR spectroscopy, nitrogen-purged DMF-d_7 was used as solvent, and the reaction was performed in a NMR tube, sealed with a rubber septum. After 10 h, the polymer solution was exposed to air, diluted with THF, and passed through neutral alumina to remove the copper catalyst. The solvent was removed by rotary evaporation, and the final product was dried under vacuum for 2 days.

Cleavage of Polymers by Reducing Agent. In a typical procedure, 0.1 g of the PS polymer was mixed with 5 mL of 0.08 M tri-*n*-butylphosphine (Bu_3P) in THF. The solution was stirred magnetically at room temperature. Samples were periodically withdrawn for GPC analysis of the product of the reductive cleavage.

Characterization. Styrene conversions were determined using a Shimadzu GC-14A gas chromatograph, equipped with a capillary column (DB-Wax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific), and anisole was used as an internal standard. The apparent molecular weights were determined by GPC equipped with a HPLC pump at flow rate of 1 mL/min THF (Waters, 515) and four columns (guard, 10^5 Å, 10^3 Å, and 100 Å; Polymer Standards Services) in series. Toluene was used as GPC internal standard. A calibration curve based on linear PS standards was used in conjunction with a differential refractive index (RI) detector (Waters, 2410). NMR spectra of the polymer solutions in $CDCl_3$ or DMF-d_7 were collected on Bruker Avance 300 MHz spectrometer at 27 °C.

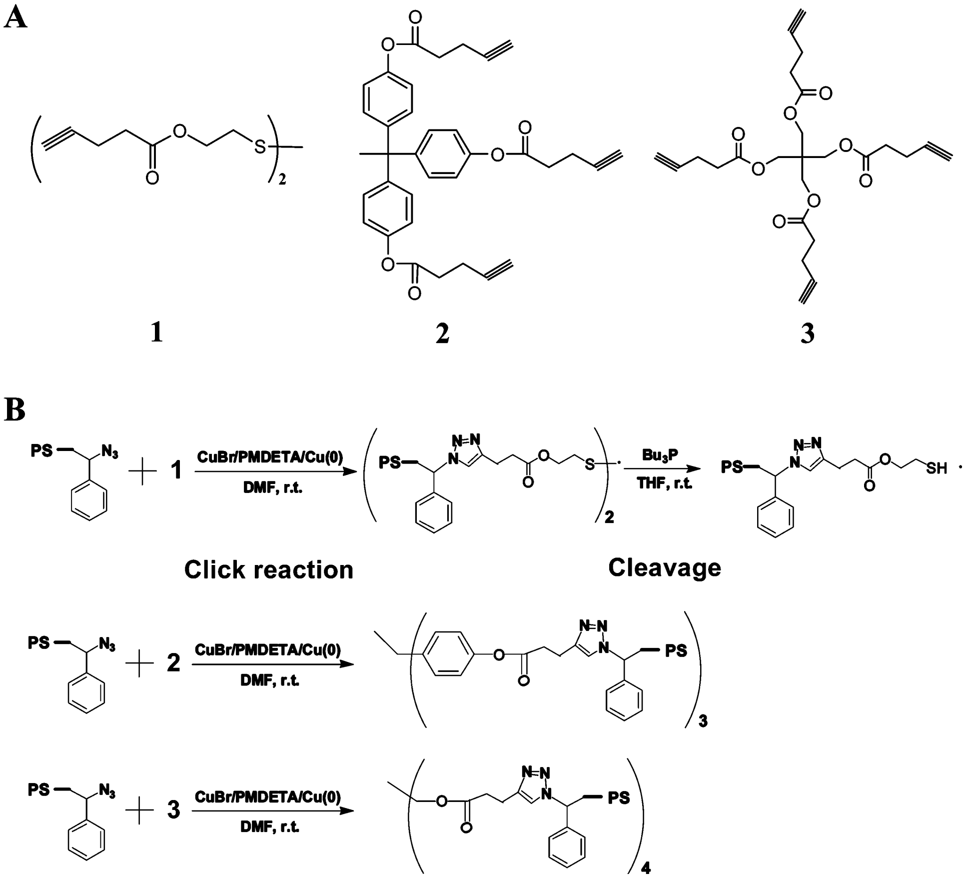
Results and Discussion

PS−Br linear chains were synthesized by ATRP using EBiB as initiator and CuBr/PMDETA as catalyst. The reaction was stopped at low styrene conversion to ensure a high degree of bromine chain-end functionality.[46] After purification, the terminal bromine groups were transformed into azido groups by a nucleophilic substitution reaction with sodium azide.[47] Multifunctional linking agents **1**−**3** were synthesized by reacting pentynoic acid with bis(2-hydroxyethyl) disulfide, 1,1,1-tris(4-hydroxyphenyl)ethane, and pentaerythritol, respectively. The structures of these coupling agents are shown in Scheme 1A. PS−N$_3$ chains were then reacted with the alkyne-containing compounds in DMF with CuBr/PMDETA as catalyst to produce the linear and star PS polymers with different arm numbers, as illustrated in Scheme 1B.

Model Coupling Reactions. The efficiency of the click reaction between the azido chain-end group and alkynyl group on the linking agent was evaluated by performing the model coupling reactions between PS−N$_3$ with different molecular weights and dialkyne-containing compound **1**. The GPC curves in Figure 1A indicate that the coupling reaction between PS−N$_3$ (M_n = 1400 g/mol) and **1** was fast, and essentially all PS−N$_3$ chains were consumed within 3 h, as supported by the disappearance of the elution peak at low molecular weight in the GPC curve of 3 h reaction product (Table 1, entry D1). As discussed above, the click reaction was performed in DMF using CuBr/PMDETA as catalyst, which is the same catalyst for normal ATRP of styrene. It is worth noting that PS−N$_3$ chains can also act as an ATRP initiator under proper conditions because the azido group could act as a pseudo-halogen atom.[48] Therefore, cleavage of the PS product was conducted in order to confirm that the polymer produced in the coupling reaction was the product of a click reaction between PS−N$_3$ and **1**, instead of a product formed by PS radical−radical coupling. Coupling agent **1** contained a disulfide bond, which is labile and reversible cleave in the presence of various reducing agents.[49−51] Cleavage of the PS product in THF was performed using Bu_3P as the reducing agent. The result indicates that cleavage was efficient. Within 1 h all PS chains were cleaved, and the GPC curve of the product overlapped that of the original PS−N$_3$ chains, proving that all of the coupled PS−PS polymers were produced by the click reaction between PS−N$_3$ and alkynyl group on **1**.

The ^{1}H NMR spectra of the PS−Br, PS−N$_3$, and the product of click reaction are shown in Figure 2. It is clearly seen that the azido functionality in the PS−N$_3$ precursor polymers was initially high (peak H$_c$, δ = 4.0 ppm**)**, and after a 3 h coupling reaction with **1**, all azido groups were consumed and converted into 1,2,3-triazole groups. This is supported by the disappearance of the proton peak at 4.0 ppm and the appearance of a new proton peak at ca. 5.1 ppm (peak H$_d$). Integration of the peak at 5.1 ppm indicates that after 3 h 97% of the azido groups reacted with the alkynyl groups and formed 1,2,3-triazole groups, which is in good agreement with the peak splitting result

Scheme 1. (A) Structures of Dialkyne-Containing (1), Trialkyne-Containing (2), and Tetraalkyne-Containing (3) Coupling Agents and (B) Schematic Illustration of Synthesis of Linear, 3-Arm, and 4-Arm Star PS Polymers by Click Reactions



of the GPC curve of the PS−PS coupling product using Gaussian function (Figure 1B). After 3 h, the area fraction of the coupled PS−PS polymer in the GPC curve was around 95%. The rest of the PS chains, with ca. 5% area fraction, are expected to be a mixture of PS without azido functionality and PS chains containing a mono-triazole group at the one chain end.

Cu(0) was purposely added to reaction D1 (Table 1) because the CuBr amount was so small that the influence of air oxidation of Cu(I) could be significant. The added Cu(0) should reduce an oxidized Cu(II) species back to Cu(I) and therefore compensate for inadvertent oxidation of Cu(I) during the coupling reactions. The presence of the reducing agent Cu(0) in D1 had a positive influence on click coupling efficiency when compared to a similar reaction without Cu(0) (entry D2, Table 1). The reaction in run D1 was faster than D2, and the final yield of coupled PS−PS polymer in D1 was 4% higher than in D2. A similar trend was found when reaction D3 was compared to D4, both of which used a longer PS−N_3 chain (M_n = 6800 g/mol) to react with **1**. These results support our hypothesis that the Cu(I) concentrations in reactions D1 and D3 were higher than those in D2 and D4.

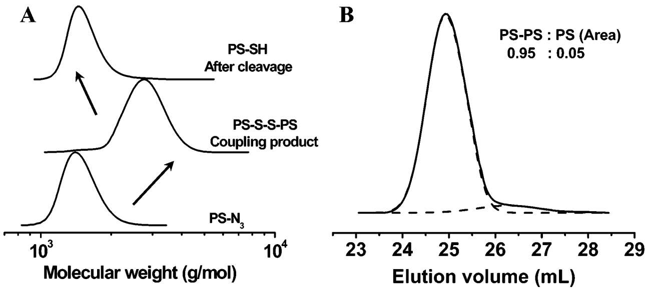


Figure 1. (A) GPC curves of PS−N_3 (M_n = 1400 g/mol, M_w/M_n 1.03), its coupling product with **1**, and the cleavage product. (B) Peak splitting of the GPC curve of the coupling product using Gaussian function. Experimental conditions (Table 1, entry D1): [PS−N_3]/[**1**]/[CuBr]/[PMDETA] = 1/0.5/0.5/0.5 = 0.02 M, Cu(0)/CuBr = 1/1 by weight, rt in DMF; linear PS standards for calibration.

Table 1. Summary of Model Click Reactions between PS−N_3 and Coupling Agent 1[a]

	M_n PS−N_3 (g/mol)[b]	Cu(0)	area fraction in GPC−RI PS−PS	PS
D1	1400	yes	0.95	0.05
D2	1400	no	0.91	0.09
D3	6800	yes	0.89	0.11
D4	6800	no	0.84	0.16
D5[c]	18100	yes	0.80	0.20

[a] Experimental conditions: [PS−N_3]/[**1**]/[CuBr]/[PMDETA] = 1/0.5/0.5/0.5, [PS−N_3] = 0.02 M, Cu(0)/CuBr = 1/1 w/w when Cu(0) was applied, rt in DMF. [b] Measured by GPC in THF with RI detector, calibration with linear PS as standard. [c] [PS−N_3] = 0.005 M, due to the high molecular weight of PS−N_3.

The influence of the molecular weight of the PS−N_3 precursor on the efficiency of the coupling reaction was also studied. Three samples of PS−N_3, with different molecular weights as determined by GPC, were coupled with **1** using an equimolar ratio of azido and alkynyl groups. Table 1 summarizes the results of these click reactions (entries D1, D3, and D5). It was found that increasing the molecular weight of PS−N_3 decreased the final yield of the coupled PS−PS polymer. All click reactions were performed at the same concentration of azido group except D5, in which the solution of PS−N_3 was diluted 4-fold due to the lower solubility of high-molecular-weight PS chains in DMF. Possible reasons for the decrease in click chemistry efficiency with increase of PS−N_3 molecular weight include lower azido

Table 2. Synthesis of 3-Arm and 4-Arm Star Polymers by Click Coupling Reactions[a]

	coupling agents	M_n PS−N_3 (g/mol)[b]	N_3/alkyne (mol)	area fraction in GPC−RI			
				4-arm star	3-arm star	PS−PS	PS
T1	**2**	1400	1/1		0.90	0.08	0.02
T2	**2**	1400	1/1.1		0.69	0.25	0.06
T3	**2**	1400	1/1.3		0.47	0.38	0.15
T4	**2**	6800	1/1		0.83	0.12	0.05
T5	**3**	1400	1/1	0.83	0.12	0.03	0.02

[a] Experimental conditions: [PS−N_3]/[CuBr]/[PMDETA] = 1/0.5/0.5, [PS−N_3] = 0.02 M, Cu(0)/CuBr = 1/1 w/w, rt in DMF. [b] Measured by GPC in THF with RI detector, calibration with linear PS as standard.

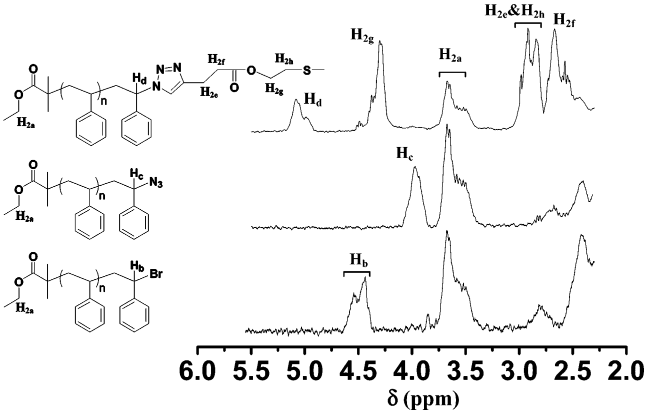


Figure 2. ^{1}H NMR spectra of PS−Br, PS−N_3, and the product of click coupling reaction (Table 1, entry D1); NMR condition: 27 °C, $CDCl_3$ as solvent.

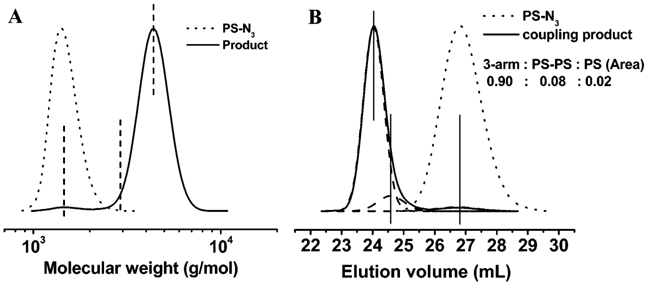


Figure 3. (A) GPC curves of PS−N_3 (M_n = 1400 g/mol, M_w/M_n 1.03) and its coupling product with **2**. (B) Peak splitting of the GPC curve of the coupling product using Gaussian function. Experimental conditions (Table 2, entry T1): [PS−N_3]/[**2**]/[CuBr]/[PMDETA] = 1/0.33/0.5/0.5 = 0.02 M, Cu(0)/CuBr = 1/1 by weight, rt in DMF; linear PS standards for calibration.

functionality and unbalanced stoichiometry between azido and alkynyl groups. Determining the exact stoichiometry becomes more difficult when the mass fraction of chain-end group on the polymer chain is lower.

All these results confirm that the click reaction between the terminal azido group on the PS−N_3 samples and the alkynyl group on the coupling agent is fast and highly efficient. All of the functional groups were quantitatively converted into 1,2,3-triazole groups. Therefore, the application of click coupling reaction was further extended to the synthesis of polymers with more complex microstructures, such as 3-arm and 4-arm star polymers.

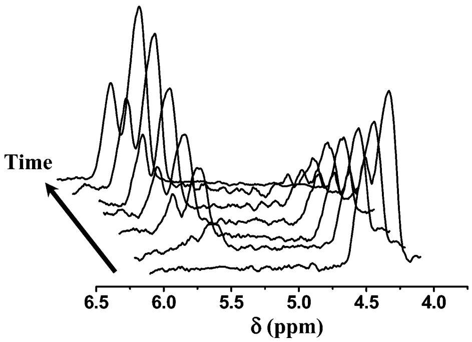


Figure 4. ^{1}H NMR spectra of the reaction products (Table 2, entry T1) at different reaction times (0, 5, 10, 18, 26, 40, and 120 min). NMR conditions: 27 °C, DMF-d_7 as solvent.

Synthesis of Star Polymers by Click Coupling Reactions. First, 3-arm star polymers were produced by the coupling reaction between PS−N_3 polymers and the trialkyne-containing coupling agent **2**. Figure 3A shows the GPC curves of the PS−N_3 chain and its coupling product (Table 2, entry T1). It was found that when the molar ratio of azido group to alkynyl group was 1:1, the coupling reaction between PS−N_3 and **2** was very efficient. After 3 h, a new elution peak appeared at higher molecular weight, which was completely separated from the elution peak of the PS−N_3 precursor. In the GPC curve of the coupling product, the tiny peak with the same elution volume as the initial PS−N_3 sample represents mono-PS chains, and the main peak is a combination of the 3-arm star PS polymer and a coupled PS−PS polymer (dashed vertical lines in Figure 3A). The result of peak splitting of this GPC curve indicates that the area ratio of 3-arm star, PS−PS coupled polymer and mono-PS chain is 0.90:0.08:0.02 (Figure 3B). In other words, 98% of the PS chains reacted with the trialkyne-containing coupling agent.

The coupling reaction between PS−N_3 (M_n = 1400 g/mol) and **2** was also conducted in an NMR tube with DMF-d_7 as solvent in order to monitor the reaction by ^{1}H NMR spectroscopy (Figure 4). Conversion of azido group was determined as a function of time by monitoring the proton from the unreacted (PS−$CH_2C\boldsymbol{H}(C_6H_5)$−$N_3$, δ = 4.4 ppm**)** PS chains and the proton from the reacted (PS−$CH_2C\boldsymbol{H}(C_6H_5)$−triazole, δ = 5.5 ppm) PS chains. With an equimolar amount of PS−N_3 and alkynyl groups, nearly all of the azido groups were reacted and quantitatively converted to 1,2,3-triazole groups within 2 h because the peak at 4.4 ppm was undetectable after 2 h.

When the stoichiometry of azido and alkynyl groups was deliberately unbalanced, such as N_3/alkyne = 1/1.1 or 1/1.3 (entries T2 and T3, Table 2), the ratio of the three species (3-arm star, PS−PS coupled polymer, and mono-PS chain) changed correspondingly. This trend is in agreement with theoretical expectations because the yield of 3-arm star product should strongly decrease as the ratio of azido to alkynyl groups decreases, and correspondingly the yield of PS−PS linked polymer should increase. The molecular weight of the PS−N_3 chains also had an influence on the yield of the 3-arm star polymer. It was found that when the PS−N_3 molecular weight increased from 1400 to 6800 g/mol (entry T4, Table 2), the yield of the star polymer decreased to 83%. As discussed above, this result is possibly caused by the lower chain-end functionality and the less precisely balanced stoichiometry between azido and alkynyl groups.

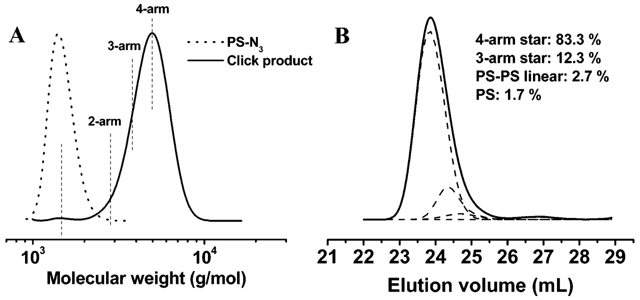


Figure 5. (A) GPC curves of PS$-$N$_3$ (M_n = 1400 g/mol, M_w/M_n 1.03) and its coupling product with **3**. (B) Peak splitting of the GPC curve of the coupling product using Gaussian function. Experimental conditions (Table 2, entry T5): [PS$-$N$_3$]/[**3**]/[CuBr]/[PMDETA] = 1/0.25/0.5/0.5 = 0.02 M, Cu(0)/CuBr = 1/1 by weight, rt in DMF; linear PS standards for calibration.

Four-arm star polymers were also synthesized via click coupling reaction between PS$-$N$_3$ (M_n = 1400 g/mol) and tetraalkyne-containing coupling agent **3**. The GPC results in Figure 5A indicate that after 3 h a new elution peak appeared at higher molecular weight, which was the combination of 4-arm star, 3-arm star, and PS$-$PS linear products (dashed vertical lines). The peak splitting result in Figure 5B suggests that the area ratio of the four species in the final coupling product (4-arm star, 3-arm star, PS$-$PS linear, and mono-PS) was 0.83:0.12:0.03:0.02. On the basis of the calibration curve with linear PS as standard, the apparent molecular weight of the 4-arm star species was ca. 5000 g/mol, which was smaller than the theoretical value (6100 g/mol). This deviation was due to the compact structure of the star polymers, which have a smaller hydrodynamic volume than the linear analogues. All these results clearly indicate that the click reaction is a highly efficient and simple technique for synthesis of star polymers using the coupling method.

Conclusions

The synthesis of star polymers using a “grafting-onto” method was successfully accomplished by preparation of linear and star PS polymers with different arm numbers via a combination of ATRP and click reactions. The click coupling reactions between azido-terminated PS (PS$-$N$_3$) and alkyne-containing multifunctional compounds were fast and highly efficient. All coupling reactions were completed within 3 h. The effect of several parameters, such as the molecular weight of the initial PS$-$N$_3$ samples, the presence of Cu(0) as reducing agent, and the stoichiometry between the azido and alkynyl groups, on the final yield of coupling product was studied. It was found that the fraction of coupling products decreased when the molecular weight of PS$-$N$_3$ chains increased. The yield of coupling product was higher in the presence of Cu(0). The stoichiometry between azido and alkynyl groups also influenced the ratio of species in the final product. The highest yield of the coupling product was obtained when the molar ratio of azido/alkynyl groups was 1. These results broaden the scope of click chemistry reactions in polymer synthesis and will serve as a valuable guideline for the synthesis of star polymers with more complex microstructures.

Acknowledgment. The authors are grateful to the members of the CRP Consortium at Carnegie Mellon University and NSF (Grant DMR 05-49353) for funding.

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MA060926C