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Simultaneous “Click Chemistry” and Atom Transfer Radical Emulsion Polymerization and Prepared Well-Defined Cross-Linked Nanoparticles

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ABSTRACT: Simultaneous “click chemistry” and atom transfer radical emulsion polymerization (ATREP) to prepare well-defined macromolecules and cross-linked nanoparticles are first reported in this work. First, simultaneous “click chemistry” and ATREP of styrene were conducted in the presence of *p*-xylylene diazide, using propargyl 2-bromoisobutyrate (PBiB) as initiator, Tween-20 as emulsifier, copper(I) bromideas catalyst, and pentamethyldiethylenetriamine (PMDETA) as ligand. The simultaneous reactions sharing a same catalyst system gave rise to diblock polystyrene (PS) with controlled molecular weight and narrow molecular weight distribution. The resulting polymers were characterized by gel permeation chromatography (GPC), FT-IR, and ^{1}H NMR spectroscopy. Then, well-defined cross-linked PS nanoparticles with diameter in the range of 50−150 nm were prepared from a simultaneous “click chemistry” and ATREP of a mixed styrene and 4-vinylbenzyl azide using 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne (BMP) as initiator, Tween-20 as emulsifier, copper(I) bromide as catalyst, and PMDETA as ligand. Well-preserved nanostructures of particles in tetrahydrofuran (THF) and dimethylformamide (DMF) solvents reveal the nanoparticles have a cross-linked structure. The size and morphology of nanoparticles were also characterized by photon correlation spectroscopy and transmission electron microscope. The size of nanoparticles is very uniform and can be regulated by changing the ratio of monomer and initiator as well as the amount of emulsifiers. The cross-linked PS nanoparticles were more thermally stabile than PS from ATREP.

1. Introduction

The development of controlled/living free radical polymerizations[1] (CFRP), especially atom transfer radical polymerization (ATRP),[2−6] provides an extremely powerful tool for the synthesis of polymers with predefined molecular weights and narrow molecular weight distributions. Attributable to the advantages in economic and environment of products from emulsion polymerization, atom radical emulsion polymerization (ATREP) (or ATRP under emulsion polymerization condition)[7−11] has been well studied recently. Homopolymers,[12] block copolymers,[13,14] gradient copolymers,[15] cross-linked polymeric particles,[9,16] and core−shell organic/inorganic nanoparticle hybrids[17] have been successfully prepared by ATREP.

“Click chemistry”, a powerful organic synthesis approach popularized by Sharpless et al.,[18,19] has some important features such as fidelity, high efficiency, and operational simplicity. 1,3-Dipolar cycloaddition of azides and alkynes in the presence of copper(I) catalytic species is one of the most pronounced “click chemistry” reactions, which leads to the formation of 1,4-disubstituted 1,2,3-triazole rings. As a mature technique, 1,3-dipolar cycloaddition has been employed to prepare a variety of novel macromolecular architectures,[20−22] such as block,[23] star,[24−27] miktoarm star,[28,29] graft,[30,31] dendrimer,[32,39] dendrimer-like polymers,[34,35] and functional materials.[36,37] Recently, combination of “click chemistry” and ATRP provides a novel approach to the preparation of functional polymers by using functional initiators[38−40] or converting halogen species of ATRP polymers into azido groups.[41−44]

Interestingly, ATRP not only shares a number of attractive features with 1,3-dipolar cycloaddition, such as high tolerance toward a wide range of functional groups and protic solvents,[45] but also shares a same copper catalyst system.[46] The combination of these two reactions in a “one-pot” process has already been reported.[46−49] The influence of solvent, catalyst concentration, temperature, and various azido chemicals on simultaneous copper(I)-catalyzed 1,3-dipolar cycloaddition or “click chemistry” and ATRP was studied by Haddleton’s group.[50] Although simultaneous ATRP and “click chemistry” have been exploited with moderate success, it would be interesting to study the simultaneous “click chemistry” and ATRP under emulsion polymerization conditions (ATREP) for both academic research and industrial applications.

PS nanoparticles have wide applications in photonic crystals,[51,52] drug delivery,[53] and fabrication of periodic structures.[54] Cross-linked PS nanoparticles are especially interesting to scientists due to their improved solvent-resistant property and thermal stabilities. Here we described a simple approach to the preparation of well-defined block copolymers and cross-linked nanoparticles via simultaneous “click chemistry” and ATREP. At first, “click chemistry” and ATREP of styrene were conducted in the presence of *p*-xylylene diazide, using propargyl 2-bromoisobutyrate (PBiB) as initiator, Tween-20 as emulsifier, copper(I) bromide as catalyst, and pentamethyldiethylenetriamine

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(PMDETA) as ligand. The simultaneous reactions under a same catalyst system gave rise to diblock polystyrene (PS) with controlled molecular weight and narrow molecular weight distribution. Second, well-defined cross-linked PS nanoparticles with diameter in the range of 50−150 nm were obtained from a simultaneous "click chemistry" and ATREP of a mixed styrene and 4-vinylbenzyl azide using 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne (BMP) as initiator, Tween-20 as emulsifier, copper(I) bromide as catalyst, and PMDETA as ligand.

2. Experimental Section

2.1. Materials. The monomers styrene (St, 97%) and 4-vinylbenzyl chloride (VBC, 90%) were purchased from Acros Organic Co. of Geel, Belgium. St was used after removal of inhibitors in a ready-to-use disposable inhibitors-removal column. Propargyl alcohol (99%), 2-bromoisobutyryl bromide (98%), and pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich Chemical Co. and used as received. Sodium azide (99%), CuBr (99%), Tween-20, triethylamine (96%), dimethylformamide (DMF), tetrahydrofuran (THF), and other materials were purchased from Shanghai Chemical Reagent Plant. ATRP initiator, propargyl 2-bromoisobutyrate, was synthesized as described in the literature.[55]

2.2. Chemical Synthesis. *2.2.1. Synthesis of Vinylbenzyl Azide* (*VBA*). Sodium azide (5.85 g, 90.0 mmol), 4-vinylbenzyl chloride (10.0 g, 70.2 mmol), and DMF (100 mL) were added into a 250 mL flask. After stirring at room temperature for 4 h, the reaction mixture was poured into water and extracted with diethyl ether three times. The organic phase was washed with brine, dried over $MgSO_4$, and then concentrated. The crude product was further purified by passing a silica gel column using mixed diethyl ether/hexanes (1:19) as eluent. Yield = 84%. ^{1}H NMR ($CDCl_3$): 4.59 (2H, CH_2), 5.30 (1H, $=CH_2$), 5.81 (1H, $=CH_2$), 6.73 (1H, $CH=$), 7.27 (2H, ArH), 7.47 (2H, ArH). FTIR (cm^{-1}): $\nu_{(N=N=N)}$ = 2098 cm^{-1}.

2.2.2. Synthesis of p-Xylylene Diazide (*XDA*). Sodium azide (6.50 g, 0.10 mol), *p*-xylylene dibromide (6.60 g, 0.03 mol), 20 mL of DMF (20 mL), and benzene (20 mL) were added into a 100 mL round-bottom flask. The reaction was kept stirring at 75 °C for 6 h. Afterward, the reaction mixture was poured into a beaker with deionized water (200 mL). The organic layer was extracted with benzene (20 mL) three times and dried with anhydrous Na_2SO_4. Pure *p*-xylylene diazide was obtained as an oily liquid. Yield = 94%. ^{1}H NMR ($CDCl_3$): 7.27 (4H, ArH), 4.23 (4H, CH_2). FTIR (cm^{-1}): $\nu_{(N=N=N)}$ = 2096 cm^{-1}. *Caution: XDA and sodium azide are highly toxic and present a severe explosion when shocked or heated.*

2.2.3. Synthesis of Diethyldipropargyl Malonate. Diethyl malonate (20.00 g, 0.13 mol), sodium ethoxide (6.30 g, 0.28 mol), and dry ethanol (150 mL) were added into a 250 mL flask. After 30 min, propargyl bromide (32.6 g, 0.28 mol) was slowly added to the flask at 60 °C. Then the mixture was refluxed overnight. After removal of the alcohol, the residue was diluted with water and extracted with ethyl ether. The organic layer was dried with anhydrous Mg_2SO_4. After removal of the ether by rotary evaporation and purification by distillation under reduced pressure, a colorless solid was obtained. Yield = 94%. ^{1}H NMR ($CDCl_3$): 4.25 (4H, CH_2), 2.98 (4H, CH_2), 2.03 (2H, $\equiv$CH), 1.26 (6H, CH_3). FTIR (cm^{-1}): $\nu_{(\equiv CH)}$ = 3311 cm^{-1}.

2.2.4. Synthesis of 4,4′-Bis(*hydroxymethyl*)*-1,6-heptadiyne.* Diethyldipropargyl malonate (20.08 g, 0.08 mol) in THF (100 mL) was slowly added to a stirred suspension of $LiAlH_4$ (8.03 g, 0.20 mol) in THF (300 mL). After stirring for 4 h at room temperature, water was carefully added until no H_2 was produced. After removal of the THF by rotary evaporation, the residue was extracted with diethyl ether three times and then dried over Na_2SO_4. After removal of the solvent by distillation, the solid residue was recrystallized from toluene to give rise to a white crystalline solid. Yield = 70%. ^{1}H NMR ($CDCl_3$): 3.68 (4H, CH_2), 2.54 (2H, OH), 2.34 (4H, CH_2), 2.02 (2H, CH). FTIR (cm^{-1}): $\nu_{(C\equiv CH)}$ = 3305 cm^{-1}.

2.2.5. Synthesis of 4,4-Bis((*2′-bromo-2′-methylpropionyloxy*)*-methyl*)*-1,6-heptadiyne* (*BMP*). 4,4′-Bis(hydroxymethyl)-1,6-heptadiyne (3.25 g, 21.4 mmol), Et_3N (6.70 mL, 45.3 mmol), and dry Et_2O (45 mL) were introduced into a 250 mL three-neck round-bottom flask equipped with a condenser, a dropping funnel, and a nitrogen inlet/outlet. After cooling to 0 °C, 2-bromoisobutyryl bromide (10.4 g, 45.0 mmol) in dry Et_2O (5 mL) was added slowly, with continuous stirring for 1 h. Then, the reaction temperature was raised to room temperature. The reaction was kept stirring for another 24 h. The $(C_2H_5)_3N\cdot HBr$ was removed by filtration. The solution was then dried over $MgSO_4$ for 10 h. After removal of the solvent by rotary evaporation and purification by passing a silica gel column using mixed diethyl ether/hexanes (1:4) as eluent, a colorless liquid was obtained. Yield = 73%. ^{1}H NMR ($CDCl_3$): 3.30 (4H, CH_2), 2.38 (4H, CH_2), 1.97 (2H, $\equiv$CH), 1.95 (12H, CH_3). FTIR (cm^{-1}): $\nu_{(\equiv CH)}$ = 3300 cm^{-1}. MS: m/z = 427.14 [M + 1].

2.3. Simultaneous "Click Chemistry" and Atom Transfer Radical Emulsion Polymerization (ATREP). *2.3.1. Preparation of Diblock Copolymer of Styrene via Simultaneous "Click Chemistry" and ATREP.* A typical polymerization was carried out as follows: St (2.87 g, 27.6 mmol), PBiB (62.8 mg, 0.3 mmol), XDA (25.9 mg, 0.14 mmol), H_2O (40 mL), and Tween-20 (2.00 g) were introduced into a 100 mL round bottom flask. After an emulsion formed, the flask was degassed with argon for 20 min. Then, CuBr (39.70 mg, 0.28 mmol) and PMDETA (47.80 mg, 0.28 mmol) were added. The flask was put into an oil bath at 90 °C under stirring for 1 h. Then, the polymer was obtained by addition of methanol to break the emulsion, and centrifugation. The obtained polymers were diluted with THF and passed through a neutral alumina to remove the copper catalysts and emulsifiers. Then, the polymer solution was precipitated into an excess of methanol. About 2.4 g of bromo-double-terminated polystyrene was obtained after drying in a vacuum oven for 24 h ($M_n = 1.08\times10^4$, PDI = 1.28, yield = 83%).

2.3.2. Preparation of Cross-Linked PS Nanoparticles via Simultaneous "Click Chemistry" and ATREP. For a typical preparation of cross-linked PS nanoparticles via simultaneous "click chemistry" and ATRP: St (1.60 g, 15.4 mmol), BMP (69.30 mg, 0.15 mmol), VBA (49.00 mg, 0.31 mmol), and Tween-20 (2.00 g) were dispersed in H_2O (40 mL) medium with magnetic stir in a 100 mL round bottom flask. After the formation of emulsion, the flask was degassed with argon for 20 min. Then CuBr (44.40 mg, 0.31 mmol) and PMDETA (53.40 mg, 0.31 mmol) were added into the system, and the reaction was kept stirring under a nitrogen atmosphere at 90 °C for 1 h. Then, the emulsion was dialyzed against deionized water in cellulose acetate tubing in order to remove copper catalyst system and emulsifiers. Methanol was added to break the emulsion. About 1.42 g of cross-linked nanoparticles was obtained by centrifuge (yield = 89%).

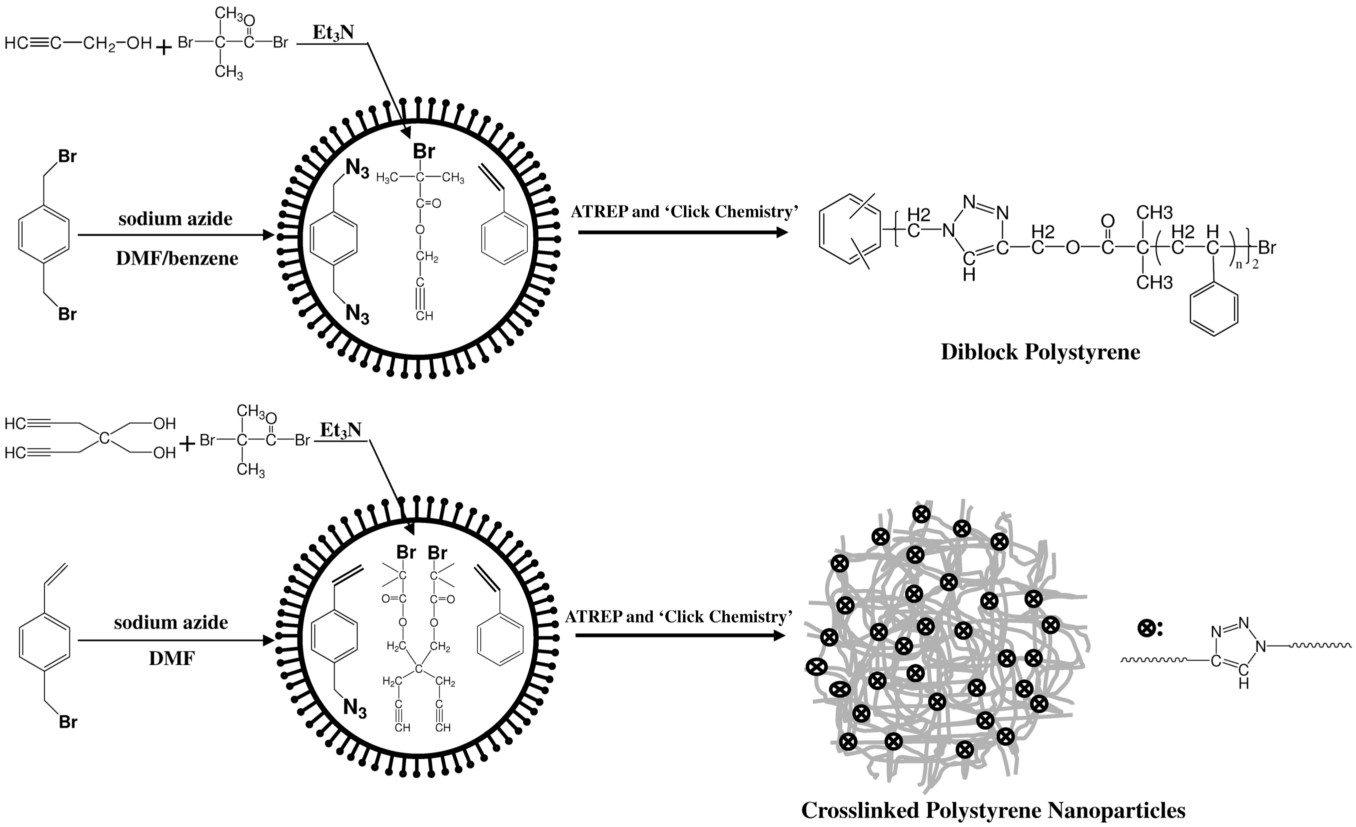
2.4. Characterization. The chemical structures of the VBA, PBiB, XDA, and PS block were characterized by ^{1}H NMR spectroscopy on a Bruker ARX 300 MHz spectrometer, using $CDCl_3$ as the solvent in 1000 scans and a relaxation time of 2 s. Gel permeation chromatography (GPC) was performed on an HP 1100 high-pressure liquid chromatograph (HPLC), equipped with an HP 1047A refractive index detector and a Plgel MIXED-C 300-7.5 mm column (packed with 5 μm particles). The column allows the separation of polymers over a wide molecular weight range of 200−3 000 000. THF was used as the eluent at a low flow rate of 1 mL/min at 35 °C. Polystyrene standards were used as the references. Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet Instrument Co. MAGNA-IR 750 spectrometer. The sample was dispersed in a KBr disk. Mass spectrometry analysis was carried out on a Perkin-Elmer Sciex spectrometer. The thermal stability of the

Table 1. Characterization of Polystyrene (PS) from Simultaneous “Click Chemistry” and Atom Transfer Radical Emulsion Polymerization

					repeat units			conversion of click chemistry (%)
sample	[St]:[PBiB]:[XDA][a]	time (min)	M_n[b] (g/mol)	polydispersity[c] (PDI)	GPC[d]	theoretical[e]	theoretical[f]	theoretical[g]
PS_a1	100:1:0.5	30	4.2×10^3	1.53	40	25	50	60
PS_a2	100:1:0.5	40	6.1×10^3	1.42	59	33	66	79
PS_a3	100:1:0.5	50	8.2×10^3	1.35	78	40	80	95
PS_a4	100:1:0.5	60	10.8×10^3	1.28	104	53	106	96
PS_a5	100:1:0.5	90	12.7×10^3	1.25	122	62	124	97
PS_a6	100:1:0.5	120	15.3×10^3	1.21	147	74	148	99
PS_b1	200:1:0.5	30	3.9×10^3	1.55	38	24	48	58
PS_b2	200:1:0.5	40	6.4×10^3	1.46	62	35	70	77
PS_b3	200:1:0.5	50	8.8×10^3	1.34	85	46	92	85
PS_b4	200:1:0.5	60	11.6×10^3	1.26	112	60	120	87
PS_b5	200:1:0.5	90	14.5×10^3	1.24	139	73	146	88
PS_b6	200:1:0.5	120	18.7×10^3	1.23	180	94	188	91

[a] Polymerization conditions: [PBiB]:[CuBr]:[PMDETA] = 1:1:1, 2 g of the surfactant of Tween 20, 40 mL of water, and reaction temperature is 90 °C. St = styrene; PBiB = propargyl 2-bromoisobutyrate; PMDETA = pentamethyldiethylenetriamine; XDA = *p*-xylylene diazide. [b] Determined from gel permeation chromatography (GPC) using polystyrene standards as references. [c] PDI = number molecular weight (M_n)/weight-average weight (M_w). [d] Calculated from GPC results with an equation: $[M_n]/104$. [e] Theoretical value calculated from conversion data and supposed no “click chemistry” happened. [f] Theoretical value calculated from conversion data and supposed all “click chemistry” completed. [g] Theoretical value calculated from the GPC result and theoretical repeat units with an equation: ([GPC^d] − [theoretical^e])/[theoretical^e].

Scheme 1. Synthesis of Diblock Polystyrene (PS) and Cross-Linked PS Nanoparticles by Simultaneous “Click Chemistry” and Atom Transfer Radical Emulsion Polymerization (ATREP) (DMF = Dimethylformamide)



PS polymer and nanoparticles was studied on a thermogravimetric analyzer (TGA, PerkinElmer TGA-7), with a heating rate of 10 °C/min under a nitrogen atmosphere. The size and size distribution of cross-linked PS particles were determined by photocorrelation spectroscopy (PCS) using a Zetasizer 3000 HSA. The morphology and size of the CPS particles were studied by TEM (TEM-100SX, Tokyo, Japan).

3. Results and Discussion

3.1. Synthesis Diblock Polymer of Styrene via Simultaneous “Click Chemistry” and Atom Transfer Radical Emulsion Polymerization (ATREP). First, diblock polymers of styrene were prepared via a simultaneous “click chemistry” and atom transfer radical emulsion polymerization (ATREP). Scheme 1 shows the simultaneous “click chemistry” and ATREP of styrene in the presence of *p*-xylylene diazide using propargyl 2-bromoisobutyrate as initiator and CuBr/PMDETA as catalyst system. In such a reaction system, the ATREP of styrene and “click chemistry” between the PBiB as well as propargyl-terminated PS macroinitiators and the XDA proceed simultaneously. Table 1 summarizes the gel permeation chromatography (GPC) results of the PS from simultaneous “click chemistry” and ATREP at different ratio of monomer/initiator as a function of reaction time

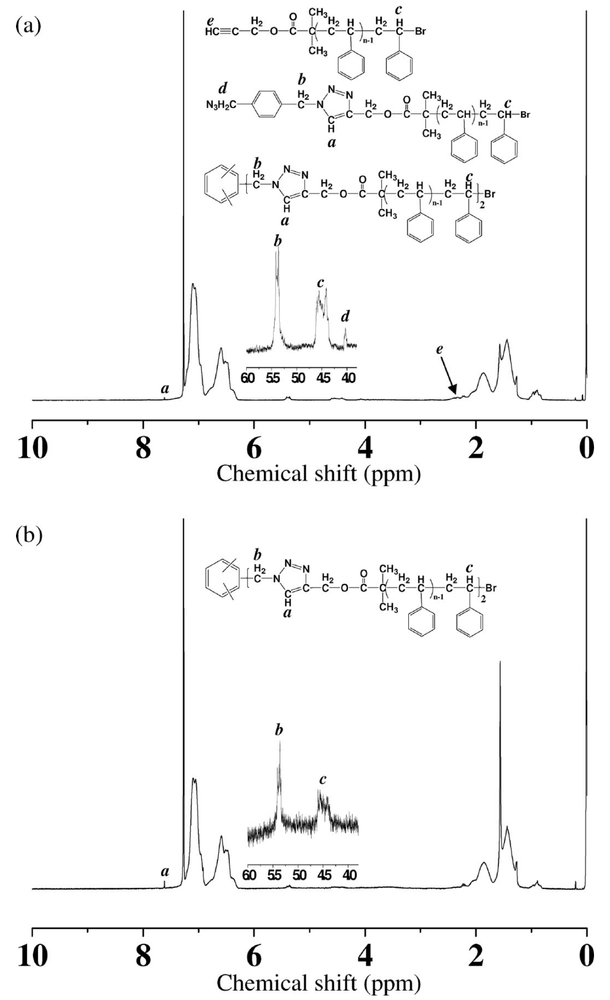


Figure 1. 300 MHz ^{1}H NMR spectra of the polystyrene (PS) from simultaneous "click chemistry" and atom transfer radical emulsion polymerization with different reaction time of (a) 30 min (PSa1 in Table 1, M_n = 4.2 × 10^3 g/mol, PDI = 1.53) and (b) 50 min (PSa3 in Table 1, M_n = 8.2 × 10^3 g/mol, PDI = 1.35).

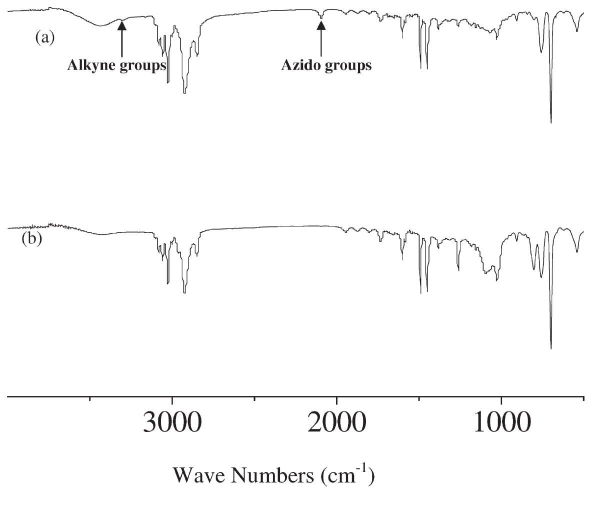


Figure 2. FTIR spectra of the polystyrene (PS) from simultaneous "click chemistry" and atom transfer radical emulsion polymerization (ATREP) with different reaction time of (a) 30 min (PSa1 in Table 1, M_n = 4.2 × 10^3 g/mol, PDI = 1.53) and (b) 50 min (PSa3 in Table 1, M_n = 8.2 × 10^3 g/mol, PDI = 1.35).

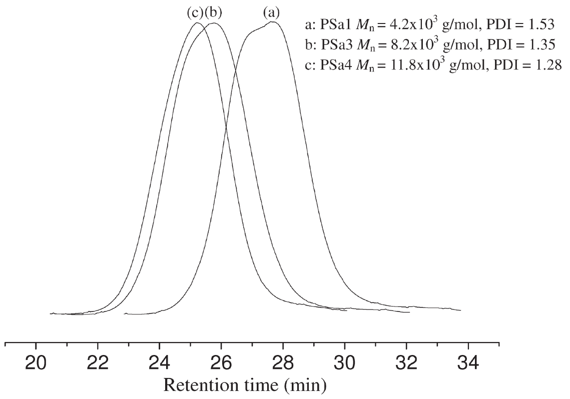


Figure 3. Gel permeation chromatography (GPC) trace of polystyrene (PS) from simultaneous "click chemistry" and atom transfer radical emulsion polymerization (ATREP) with different reaction time of (a) 30 min (PS_a1 in Table 1, M_n = 4.2 × 10^3 g/mol, PDI = 1.53), (b) 50 min (PS_a3 in Table 1, M_n = 8.2 × 10^3 g/mol, PDI = 1.35), and (c) 60 min (PS_a4 in Table 1, M_n = 10.8 × 10^3 g/mol, PDI = 1.28).

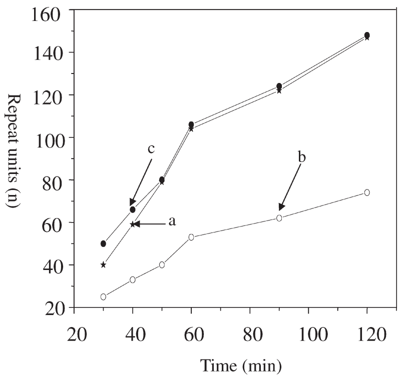


Figure 4. Time-dependent number of repeat units of polystyrene (PS) (a) calculated from GPC results, (b) calculated from conversion data and supposed no "click chemistry" happened (single PS), and (c) calculated from conversion data and supposed all "click chemistry" completed (diblock PS). PS was synthesized with a molar ratio of [St]:[PBiB]:[XDA]:[CuBr]:[PMDETA] = 100:1:0.5:1:1 in 40 mL of water and 2 g of the surfactant of Tween 20 at 90 °C. St = styrene; PBiB = propargyl 2-bromoisobutyrate; PMDETA = pentamethyldiethylenetriamine; XDA = *p*-xylylene diazide.

with a fixed PBiB/XDA ratio (2:1). Data in Table 1 indicate, as the reaction time increases from 30 to 120 min, M_n of PS increases from 4.2 × 10^3 to 15.3 × 10^3 g/mol, while the polydispersity index (PDI) decreases from 1.53 to 1.21, respectively.

The chemical structure of PS polymer was studied by ^{1}H NMR analysis. Parts a and b of Figure 1 show the ^{1}H NMR spectra of PS_a1 (M_n = 4.2 × 10^3 g/mol, PDI = 1.53) and PS_a3 (M_n = 8.2 × 10^3 g/mol, PDI = 1.35) in Table 1, respectively. The chemical shifts in the range of 1.6−2.4 and 6.3−7.4 ppm are attributable to aliphatic $-CH-CH_2-$ and aromatic protons of PS, respectively. In Figure 1a, the presence of the chemical shifts at about 2.4 ppm (peak *e*) attributable to $-C{\equiv}CH$ protons, at about 4.1 ppm (peak *d*) attributable to $-CH_2-N_3$ protons, at about 4.4 ppm (peak *c*) attributable to $-CH_2Br$ protons, at about 5.4 ppm (peak *b*) attributable to $-CH_2-$triazole protons, and at about 7.5 ppm (peak *a*) attributable the protons of triazole rings indicates that the resulting polymers are the mixture of diblock PS, PS ended with azido group, and PS ended with propargyl group. In Figure 1b, the disappearance of the peaks at 2.35 and 4.1 ppm as well as the increase in the peak strength at 7.5 ppm suggests that "click chemistry" was completed. The completion of "click chemistry" allows the

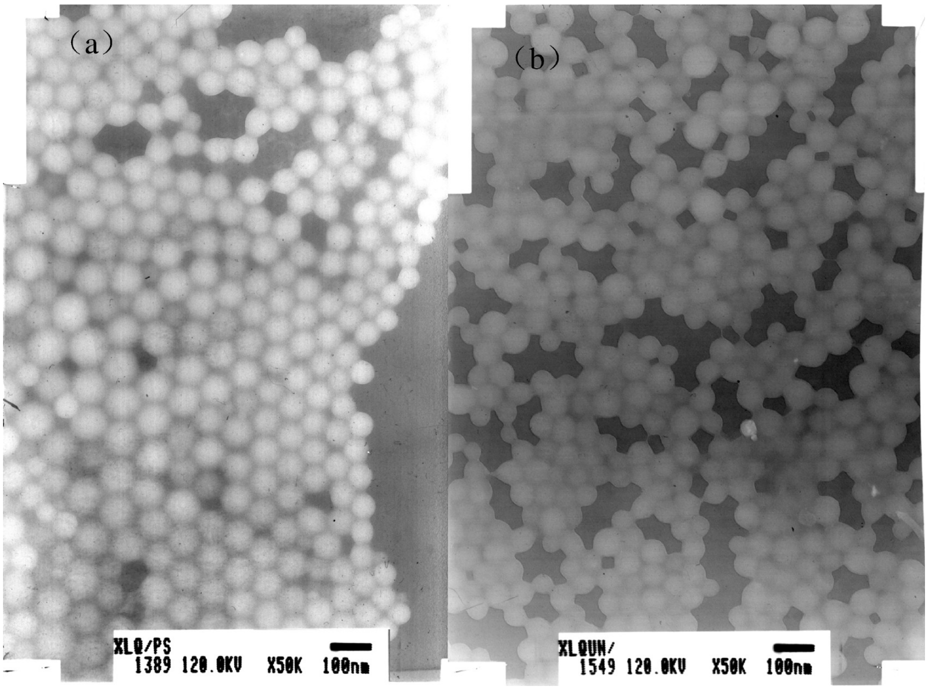


Figure 5. Transmission electron microscopy (TEM) image of (a) the polystyrene (PS) nanoparticles prepared from simultaneous "click chemistry" and atom transfer radical emulsion polymerization with molar ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 100:2:1:2:2 in 40 mL of water and 2 g of Tween 20 at 90 °C for 2 h (PS_n1 in Table 2) and (b) the nanparticles after immersion in tetrahydrofuran for 24 h. VBA = vinylbenzyl azide; BMP = 4, 4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne; PMDETA = pentamethyldiethylenetriamine.

complete formation of diblock PS in the reaction system. The chemical structure of PS polymers from simultaneous "click chemistry" and ATREP was also characterized by FTIR spectroscopy. Parts a and b of Figure 2 show the FTIR spectra of PS_a1 ($M_n = 4.2\times10^3$ g/mol, PDI = 1.53) and PS_a3 ($M_n = 8.2 \times 10^3$ g/mol, PDI = 1.35) in Table 1, respectively. In Figure 2a, the small peaks at about ~3300 cm^{-1} attributable to alkyne groups and at about 2100 cm^{-1} attributable to azido groups indicate, at a reaction time of 30 min, "click chemistry" was not whole completed, and the polymers are a mixture of diblock PS, PS polymer ended with azido group, and PS ended with propargyl group. The disappearance of peaks at about ~3300 cm^{-1} and at about 2100 cm^{-1} in Figure 2b suggests, at a reaction time of 50 min, "click chemistry" was completed and all the polymers became diblock PS polymers. The FTIR results are consistent with those of NMR.

Curves a, b, and c in Figure 3 are the GPC traces of the PS polymers from simultaneous "click chemistry" and ATREP at a reaction time of 30 min (PS_a1 in Table 1), 50 min (PS_a3 in Table 1), and 60 min (PS_a4 in Table 1), respectively. PS_a1 has a M_n of about 4.2×10^3 g/mol and PDI of about 1.53. As the reaction time increase to 50 and 60 min, the M_n increase to 8.2×10^3 and 10.8×10^3 g/mol, while the PDI decrease to 1.35 and 1.28. This phenomenon can be accounted for by the facts: at the reaction time of 30 min, the "click chemistry" was partially happened; thus, the prepared polymers are the mixture of diblock PS and PS polymers, which lead to a high PDI; as the reaction time increase to 50 and 60 min, "click chemistry" reaction continues, leading to more and more generation of PS diblock polymer. Thus, the polymers become more uniform and the PDIs decrease correspondingly. Figure 4 shows the time-dependent number of repeat units of PS calculated from GPC results and theoretical values calculated from polymer conversion, which supposed either no "click chemistry" happens (all single PS) or "click chemistry" completed (all diblock PS). At a reaction time of 30 min, the repeat units of PS from GPC results is 40, which is larger than that (25) of single PS but smaller than that (50) of diblock PS. That means the polymers are the mixture of diblock PS and single PS. With the increase in the reaction time, the number of repeat unit of PS from GPC results approaches the theoretical value of diblock PS, which is consistent with the completion of "click chemistry".

3.2. Preparation of the Cross-Linked Polystyrene Nanoparticles via Simultaneous "Click Chemistry" and ATREP. Well-defined cross-linked PS nanoparticles were prepared via simultaneous "click chemistry" and ATREP of a mixture styrene and 4-vinylbenzyl azide (VBA), using 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne (BMP) as initiator, Tween-20 as emulsifier, copper bromide(I) as catalyst, and pentamethyldiethylenetriamine (PMDETA) as ligand. In this work, the molar ratio of VBA and BMP is fixed at 2:1 for all the polymerizations. Figure 5a shows transmission electron microscopy (TEM) image of the nanoparticles prepared from simultaneous "click chemistry" and ATREP with molar ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 100:2:1:2:2 in 40 mL of water and 2 g of Tween 20 at 90 °C for 2 h (PSn1 in Table 2). The nanoparticles are very uniform with an average of diameters of about 80 nm. The size and size distribution of nanoparticles were also characterized by photocorrelation spectroscopy (PCS). Figure 6a shows the size and size distribution of PSn1 particle in Table 2 dispersed in water from PCS study. The value of nanoparticles from PCS is comparable to that from TEM. The cross-linked structure or the solvent-resistant properties of PS nanoparticle were studied by immersion of nanoparticles into THF and DMF solvent. Figure 5b shows the TEM image of the nanoparticles of PSn1 in Table 2 after immersion in THF for 24 h. The well-preserved nanostructure of the particles suggests that PS nanoparticles have cross-linked structure. The inset picture of the Figure 6b shows the PSn1 nanoparticles (in Table 2) dispersed in THF. The cloudy of the solution

Table 2. Diameters and Thermal Properties of Cross-Linked Polystyrene (PS) Nanoparticles

sample	TEM (nm)[f]	PCS		decomposition temperature[i] (°C)
		D_n[g] (nm)	D_w[h] (nm)	
PS_n1[a]	80.3 ± 10	75.4	72.1	376.9
PS_n2[b]	105.2 ± 12	99.6	94.3	370.6
PS_n3[c]	141.7 ± 15	138.7	130.5	364.5
PS_n4[d]	73.2 ± 8	69.3	64.4	371.1
PS_n5[e]	50.9 ± 9	45.5	40.9	372.2

[a] Molar feed ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 100:2:1:2:2, emulsifier is 5% of 40 mL of deionzed water. St = styrene; VBA = vinylbenzyl azide; PMDETA = pentamethyldiethylenetriamine; BMP = 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne. [b] Molar feed ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 200:2:1:2:2, emulsifier is 5% to 40 mL of deionzed water. [c] Molar feed ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 300:2:1:2:2, emulsifier is 5% to 40 mL of deionzed water. [d] Molar feed ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 200:2:1:2:2, emulsifier is 6% to 40 mL of deionzed water. [e] Molar feed ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 200:2:1:2:2, emulsifier is 7% to 40 mL of deionzed water. [f] Average particle size of 100 nanoparticles, determined from transmission electron microscopy images. [g] D_n = number-average diameter. [h] D_w = weight-average diameter. [i] Determined from thermogravimetric analysis results.

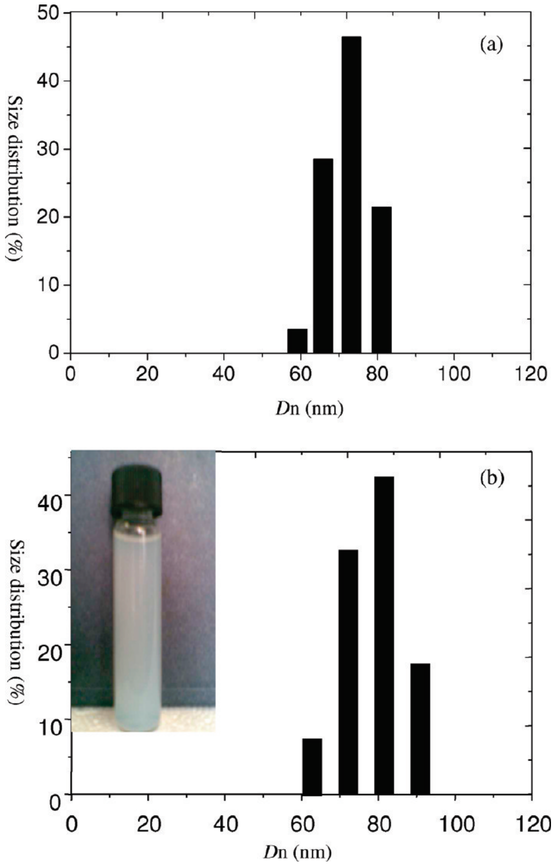


Figure 6. Size and size distribution of (a) the cross-linked polystyrene (PS) nanoparticles dispersed in water prepared from simultaneous "click chemistry" and atom transfer radical emulsion polymerization (ATREP) with molar ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 100:2:1:2:2 in 40 mL of water and 2 g of Tween 20 at 90 °C for 2 h (PS_n1 in Table 2) and (b) these nanoparticles dispersed in tetrahydrofuran. The inset of (b) is the photograph of cross-linked PS nanoparticles dispersed in tetrahydrofuran solvent. VBA = vinylbenzyl azide; BMP = 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne; PMDETA = pentamethyldiethylenetriamine; D_n = number-average diameter.

suggests that the nanoparticles have a cross-linked structure and are stable in THF. Glasser coupling of acetylene could occur in the presence of CuBr and ligand.[56] In order to confirm that the cross-linking of nanopartilces is not from a side reaction of acetylene coupling, a control experiment was carried out under the same conditions as the preparation of cross-linked nanopaticles by "click chemistry" and ATREP, except adding VBA. No cross-linking nanoparticle formation suggests that the cross-linking is from the "click chemistry" instead from the acetylene coupling side reaction. Figure 6b also shows the size and size distribution of PSn1 nanoparticles (in Table 2) dispersed in THF from PCS study. It is interesting to find that the size and size distribution of the nanoparticles dispersed in THF are larger than those dispersed in water. The higher value of the nanoparticles size from PCS attributes to swelling of the nanoparticle in THF, which is a good solvent for PS polymer. The swelling of nanoparticles also enlarges the size difference. There is about 5% weight loss in PS nanoparticles after THF washing. The weight loss could be accounted for the extraction of uncoupled PS from the cross-linked particles.

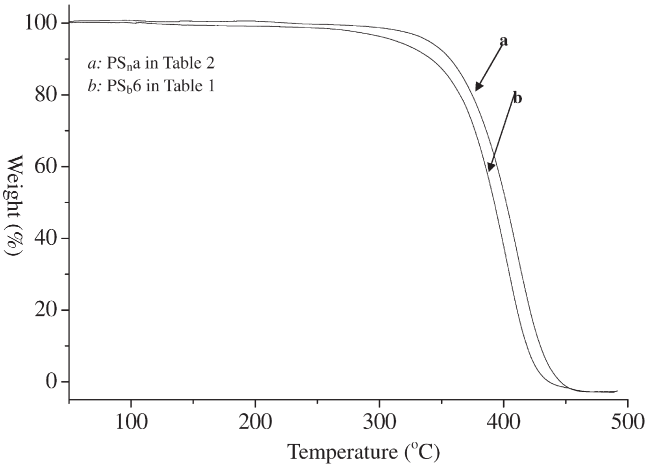


Figure 7. Thermogravimetric analysis of (a) the polystyrene (PS) nanoparticles prepared from simultaneous "click chemistry" and atom transfer radical emulsion polymerization (ATREP) with molar ratio of [St]:[VBA]:[BMP]:[CuBr]:[PMDETA] = 100:2:1:2:2 in 40 mL of water and 2 g of Tween 20 at 90 °C for 2 h (PS_n1 in Table 2) and (b) linear PS prepared from ATREP (PS_b6 in Table 1, M_n = 18.9 × 10^3 g/mol, 1.23). VBA = vinylbenzyl azide; BMP = 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne; PMDETA=pentamethyldiethylenetriamine.

The size of the cross-linked nanoparticles can be regulated by changing the monomer/initiator ratio as well as the amount of Tween 20. Table 2 summarizes the results of PS nanoparticles prepared via simultaneous "click chemistry" and ATREP at various polymerization conditions. As the monomer/initiator ratios increase from 100 to 300, the sizes of PS nanoparticles increase from 80 to 140 nm, respectively. The increase in the concentration of St monomer leads to size augmentation of the micelle droplet at fixed amount of surfactants. Thus, larger nanoparticles were obtained. The size of the resulting nanoparticles can also be tuned by changing the amount of Tween 20. Table 2 also shows, as the concentration of Tween increase from 5% to 7%, the size of the particles reduced from 105 to 50 nm, respectively. The number of particles nucleated per unit volume of water (N_p) is proportional to the surfactant concentration. The higher the concentration of the emulsifier, the more the number of nucleation seeds in reaction system. Thus, the increase in the concentration of emulsifier leads to the decrease in the size of nanoparticles.

The prepared cross-linked nanoparticles exhibit an improved thermal stability. Figure 7 shows the thermogravimetric analysis (TGA) of cross-linked nanoparticles (PS_n1 in Table 2) (curve a) and the linear PS prepared from ATREP (PS_b6 in Table 1, $M_n = 18.7 \times 10^3$ g/mol, PDI = 1.23) (curve b). In nitrogen, the weight loss of PS polymer commences at 280 °C. For PS_n1 nanoparticles, the weight loss commences at 320 °C. All the cross-linked PS nanoparticles prepared from simultaneous "click chemistry" and ATREP exhibit a higher thermal stability than that of linear PS polymer from the ATREP (Table 1). The thermal decomposition of linear PS is initiated at the "weak links" by depropagation, leading to the formation of St and short chain oligomers. The volatilization of these small molecules results in the weight loss. For the cross-linked PS nanoparticles, the presence of cross-linked points in nanoparticle hinders the formation of volatilized small molecules. Thus, the cross-linked nanoparticles exhibit an improved thermal stability.

4. Conclusions

We developed a simple approach to prepare well-defined macromolecules and cross-linked nanoparticles via simultaneous "click chemistry" and ATREP. "Click chemistry" and ATREP of styrene were conducted in the presence of *p*-xylylene diazide, using propargyl 2-bromoisobutyrate (PBiB) as initiator, gave rise to the well-defined diblock copolymer of PS. The polydispersity index (PDI) of polymers decreases with the process of "click chemistry". At a reaction time of about 1 h, the "click chemistry" was almost completed, which allows the preparation of well-defined macromolecules with PDI of about 1.2. Well-defined cross-linked PS nanoparticles with diameter in the range of 50−150 nm were prepared from a simultaneous "click chemistry" and ATREP of a mixture styrene and 4-vinylbenzyl azide using 4,4-bis((2′-bromo-2′-methylpropionyloxy)methyl)-1,6-heptadiyne (BMP) as initiator. The size of the nanoparticles can be regulated by changing the monomer/initiator ratio or the amount of the emulsifiers. The cross-linked nanoparticles are uniform and exhibit excellent solvent-resistant properties to THF and DMF. The cross-linked nanoparticles also have an improved thermal stability. In nitrogen, the weight loss of nanoparticles commences at about 320 °C, which is much higher than that (280 °C) of linear PS polymers from ATREP.

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