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ABC Triblock Copolymers Prepared Using Atom Transfer Radical Polymerization Techniques

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ABSTRACT: Triblock copolymers (or, alternatively, terpolymers) of the type ABC, where A, B, and C represent distinct blocks based on different monomers, have been prepared using atom transfer radical polymerization (ATRP) techniques. Various macroinitiators, including mono- and difunctional poly(*tert*-butyl acrylate), difunctional poly(styrene), and trifunctional p(St), were prepared and used for block copolymerizations with different monomers, including methyl acrylate, methyl methacrylate, and vinylpyridine. The block copolymers were characterized by gel permeation chromatography to determine chain end functionality and by ^{1}H NMR to measure the final composition of the block copolymers. Additionally, guidelines are presented for preparing block copolymers using ATRP techniques. Topics addressed include approaches to retaining the chain end functionality, achieving a high blocking efficiency, as well as strategies to maintain control over the ATRP reaction.

Introduction

ABC triblock copolymers comprised mostly of diene-, styrene-, methacrylate-, or pyridine-based monomers have been studied extensively.[1−5] These well-defined structures have elicited fascination not only for theoreticians modeling phase behavior[6−10] but also in the physical realm for studying morphological transitions.[5,11,12] The phase behavior of these systems is governed by the Flory interaction parameter between two domains, χ, and is strongly influenced by the weight fraction of the various blocks present in the copolymer.[3,7,10] The morphological possibilities for these copolymers can range from a basic lamellar structure[2] to highly complex core−shell gyroid morphology[12] and even to a unique knitting pattern.[5] Blending these types of block copolymers with other copolymers enables additional manipulation of the morphological patterns.[13] Until now, however, the monomers comprising the ABC triblock copolymers have been limited to those that can be polymerized either anionically[1] or by group transfer polymerization.[14] Recently, examples of inorganic/organic hybrid ABC triblock copolymers synthesized by combining living anionic ring-opening polymerization with atom transfer radical polymerization (ATRP) have been presented,[15] in addition to ABC triblock copolymers synthesized wholly by ATRP[16] or through reversible addition fragmentation chain transfer (RAFT).[17] Here we strive to demonstrate that ABC triblock copolymers of various chain architectures and monomer combinations can be successfully prepared using ATRP[18−23] methods.

The key to the controlled synthesis of block copolymers in ATRP is to maintain high chain end functionality, i.e., limit termination and side reactions, and to balance the reactivity of the end group with that of the monomer, i.e., avoid slow initiation. While the latter consideration is not as problematic as it is in anionic[24] or carbocationic polymerizations[25] and can be overcome through a careful choice of the block order, radical termination cannot be completely avoided due to the nature of the polymerization process. It can be limited, however, through the careful choice of the polymerization conditions and through adjustment of the equilibrium between the active and dormant species, often by adding a “persistent radical” in the form of a higher oxidation state metal.[16] This report focuses on the preparation of copolymers using these approaches to obtain well-defined multiblock copolymers. Several different catalyst systems, based predominantly on linear amine ligands, as well as different synthetic methodologies (i.e., the halogen exchange technique[26]) were utilized to successfully prepare these copolymers.

Experimental Section

1. Materials. Styrene (St, Acros, 99%) was dried over CaH_2 and then distilled under reduced pressure (65 °C/35 mmHg). *tert*-Butyl acrylate (tBA, Aldrich, 98%) was extracted three times with 5% aqueous NaOH and then washed with distilled water. After drying over $CaCl_2$ and filtering off the drying agent, the monomer was distilled under vacuum (60 °C/60 mmHg). Methyl acrylate (MA, Acros, 99%) and methyl methacrylate (MMA, Acros, 99%) were also dried over CaH_2 and then distilled at ambient pressure. CuBr (Acros, 98%) and CuCl (Acros, 99%) were purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. Methyl 2-bromopropionate (MBrP, Acros, 99%) was distilled at ambient pressure. Anisole (Aldrich, 99%), dimethyl 2,6-dibromoheptanedioate (DMDBHD, Aldrich, 97%), *N*,*N*,*N*′,*N*″,*N*″-pentamethydiethylenetriamine (PMDETA, Acros, 99+%), *N*,*N*,*N*′,*N*″,*N*‴′,*N*‴′-hexamethyltriethylenetetraamine (HMTETA, Aldrich, 97%), and the DOWEX MSC-1 macroporous ion-exchange resin (Aldrich, 20−50 mesh) were all used as received. 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane (TBiBPE) was prepared according to a previously published procedure.[27] Tris[(2-dimethylamino)ethyl]amine (Me_6TREN) was prepared according to a literature procedure.[28] Deoxygenation consisted of bubbling N_2 through the solution for approximately 15 min before introducing it into the flask.

2. Characterization. Monomer conversion was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column. Injector and detector temperatures were kept constant at 250 °C with a heating rate of 40 °C/min (conditions for St: isothermal at 80 °C for 4 min; for tBA: 40

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°C for 2 min followed by an increase to 80 °C and held for 3 min; for MA: 40 °C for 2 min followed by an increase to 180 °C and held for 2 min; for MMA: 40 °C for 2 min followed by an increase to 80 °C and held for 3 min). Polymer molecular weights were estimated using either a GPC system equipped with a Waters WISP 712 autosampler, Polymer Standards Service columns (guard, 10^2 Å, 10^3 Å, and 10^5 Å), and a Waters 410 RI detector against linear polystyrene standards or poly(methyl methacrylate) standards in THF (1 mL/min) at 35 °C or a system equipped with a Waters U6K manual injector, Polymer Standards Service columns (guard, 10^2 Å, 10^3 Å, and 10^4 Å), and a Waters 410 RI detector against linear poly(methyl methacrylate) standards in DMF with 50 mM LiBr added (1 mL/min) at 60 °C. Toluene was used as an internal standard for both systems. ^{1}H NMR characterization was performed in $CDCl_3$ (using TMS as an internal standard) on a Bruker 300 MHz instrument. All reported resonances are in ppm.

3. Polymerization Procedures. A. For a Typical Monofunctional tBA Polymerization. CuBr (0.391 g, 2.73×10^{-3} mol) and $CuBr_2$ (30 mg, 1.4×10^{-4} mol) were added to a dry round-bottom flask (rbf) equipped with a stir bar. After sealing it with a rubber septum, the flask was degassed and back-filled with nitrogen three times and then left under nitrogen. Acetone (10 mL) and tBA (40.0 mL, 2.7×10^{-1} mol) were added, both of which were deoxygenated and added via syringes that had been purged with nitrogen. The complexing agent, PMDETA (0.60 mL, 2.9×10^{-3} mol), was added, and the solution was stirred until the Cu complex had formed. The solution changed from cloudy and colorless to clear and light green. After complex formation, MBrP (0.61 mL, 5.5×10^{-3} mol) was added to the flask, an initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. After 390 min, a sample was dissolved in toluene, and GC analysis showed a monomer conversion of 96%. GPC analysis showed the polymer had a number-average molecular weight (M_n) = 7300 and a polydispersity index (PDI = M_w/M_n) = 1.11.

B. For a Typical Difunctional tBA Polymerization. CuBr (25 mg, 1.7×10^{-4} mol) and DMDBHD (239 mg, 6.8×10^{-4} mol) were added to a 25 mL rbf. The flask, containing a stir bar, was degassed and back-filled with nitrogen three times before introducing deoxygenated tBA (10.0 mL, 6.8×10^{-2} mol), acetone (3 mL), and anisole (200 μL, as an internal standard) via purged syringes. PMDETA (36 μL, 1.7×10^{-4} mol) was added and the copper complex formed. The solution was homogeneous. An initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. After 370 min, a sample was removed and dissolved in toluene. GC analysis indicated the monomer conversion was 53%, and GPC analysis gave a M_n = 6300 and a PDI = 1.16.

C. For a Typical Difunctional St Polymerization. CuBr (372 mg, 2.6×10^{-3} mol) and DMDBHD (4.51 g, 1.3×10^{-2} mol) were added to a 100 mL rbf equipped with a stir bar. The flask was degassed and back-filled with nitrogen three times before introducing deoxygenated St (30.0 mL, 2.6×10^{-1} mol) and anisole (0.75 mL, as an internal standard) via purged syringes. PMDETA (0.54 mL, 2.6×10^{-3} mol) was added and the copper complex formed. The solution was green and heterogeneous. An initial sample was removed, and the flask was placed in an oil bath thermostated at 100 °C. Dark precipitate formed after a short heating time. After 100 min, a sample was removed and dissolved in THF, and the conversion was measured by GC (59%). GPC analysis gave a M_n = 1100 and a PDI = 1.17.

D. For a Typical Three-Arm Star Polymerization of St. CuBr (187 mg, 1.3×10^{-3} mol) and TBiBPE (4.93 g, 6.5×10^{-3} mol) were added to a 25 mL rbf containing a stir bar. The flask was degassed and back-filled with nitrogen three times before introducing deoxygenated St (15.0 mL, 1.3×10^{-1} mol) and anisole (5.0 mL, to dissolve the initiator) via purged syringes. The solution was heated at 100 °C for about 5 min to dissolve the initiator. After cooling, the PMDETA (0.26 mL, 1.3×10^{-3} mol) was added and the copper complex formed. The solution was brown/green and heterogeneous. An initial sample was removed, and the flask was placed in an oil bath thermostated at 100 °C. Dark precipitate formed almost immediately upon heating. After 360 min, a sample dissolved in THF had a monomer conversion of 57% and a M_n = 1560 with a PDI = 1.14, as determined by GPC.

4. Purification Procedures. A. P(tBA) Macroinitiator Purification. The above reaction mixture for the preparation of the difunctional polymer was dissolved in an additional 50 mL of acetone and washed with the DOWEX MSC macroporous ion-exchange resin for about 2 h. After filtering the solution through a column of alumina to remove the resin and any additional copper salts, the acetone was removed by evaporation, and the polymer was dissolved in a minimum amount of diethyl ether (approximately 75 mL). The polymer was precipitated into a 10-fold excess of a 50:50 v:v mixture of methanol and cold water with constant stirring and then isolated by vacuum filtration. The polymer was redissolved in diethyl ether, the precipitation procedure was repeated two more times, and the polymer was dried under vacuum overnight. ^{1}H NMR: $\delta = 1.5$ (s, *tert*-butyl methyl resonance), 1.85 and 2.35 (broad singlets for the backbone protons), 3.75 (s, methoxy resonances from the initiator fragment), $\delta = 4.1$ (m, ω-protons next to the terminal halogen).

B. P(St) Macroinitiator Purification. The above reaction for the preparation of the trifunctional polymer was dissolved in an additional 75 mL of acetone (p(St) is soluble at this molecular weight) and washed with the DOWEX MSC macroporous ion-exchange resin for about 2 h. After filtering the solution through a column of alumina to remove the resin and any additional copper salts, the acetone was removed by evaporation, and the polymer was dissolved in a minimum amount of diethyl ether (approximately 100 mL). The polymer was precipitated into a 10-fold excess of methanol with constant stirring and then isolated by vacuum filtration. The polymer was redissolved in diethyl ether, the precipitation procedure was repeated two more times, and the polymer was dried under vacuum for 24 h. ^{1}H NMR: $\delta = 1.0-3.0$ (broad m, backbone and initiator protons), 4.4−4.6 (broad m, ω-proton adjacent to the halogen), 6.7−7.35 (m, aromatic protons from the initiator and p(St)).

5. Block Copolymerizations. A. For a Typical AB Diblock. Bromo-terminated p(tBA) (M_n = 7300, 3.0 g, 4.4×10^{-4} mol), CuBr (63 mg, 4.4×10^{-4} mol), and DMB (0.126 g, as an internal standard) were added to a 10 mL rbf containing a stir bar. The flask was sealed with a rubber septum and then degassed and back-filled with nitrogen three times. Deoxygenated St was added (5.0 mL, 4.4×10^{-2} mol) via a purged syringe, and the polymer was dissolved. PMDETA (92 μL, 4.4×10^{-4} mol) was added, and the solution was stirred. The complex formation was visually confirmed through a change in the solution from cloudy and colorless to clear and light green. An initial sample was removed, and the flask was heated to 100 °C in a thermostated oil bath. After 140 min, GC analysis of a sample dissolved in THF showed the monomer conversion was 94%. The polymer had a M_n = 18 200 and a PDI = 1.11. The polymer was dissolved in THF (approximately 50 mL) and then filtered through a column of alumina to remove the copper catalyst. It was precipitated into a 10-fold excess of methanol and then isolated by vacuum filtration. Two additional precipitation cycles were performed followed by 12 h of drying under vacuum. ^{1}H NMR: $\delta = 1.5$ (s, *tert*-butyl methyl resonance), 2.3 and 1.9 (broad resonance, backbone protons), 6.5−7.1 (broad m, aromatic protons in p(St)). The composition (37% p(tBA), 63% p(St)) was calculated on the basis of the ratio of the area for the aromatic protons of p(St) to the total area for the block copolymer.

B. For a Typical ABC Triblock. CuBr (4.1 mg, 2.8×10^{-5} mol), bromo-terminated p(tBA)-*b*-p(St) (M_n = 18 200, 0.51 g, 2.8×10^{-5} mol), and DMB (66 mg, as an internal standard) were added to a 5 mL rbf equipped with a stir bar. The flask was sealed with a rubber septum and then degassed and back-filled with nitrogen three times. MA (1.0 mL, 1.1×10^{-2} mol), which had been degassed, was added via a purged syringe. After the polymer had dissolved, PMDETA (5.8 μL, 2.78×10^{-5} mol) was added. The copper complex formed, and the solution became homogeneous. An initial sample was removed, and the

Table 1. Detailed Experimental Conditions and Results from Block Copolymerizations Performed Using ATRP Methods

entry	macroinitiator	monomer ([M]/[I])	[Cu]/[I] (Cu(I))	[L]/[I] (L)	solvent (vol %)	temp (°C)	time (min)	conv (%)	M_n	PDI
1	p(tBA)[a]	St (100)	1 (CuBr)	1 (PMDETA)	bulk	100	140	94	18 200	1.11
2	p(tBA)-p(St)	MA (400)	1 (CuBr)	1 (PMDETA)	bulk	70	210	23	24 800	1.10
3	p(St)$_2$[b]	tBA (70)	1 (CuBr)	1 (PMDETA)	25% acetone	60	195	68	11 200	1.16
4	p(St)-[p(tBA)]$_2$	MA (200)	0.5 (CuBr)	0.5 (PMDETA)	50% anisole	70	450	72	27 300	1.14
5	p(St)$_2$[b]	tBA (70)	0.5 (CuBr)	0.5 (PMDETA)	25% acetone	60	600	80	13 600	1.23
6	p(St)-[p(tBA)]$_2$	MMA (400)	2 (CuCl)	2.1[c] (HMTETA)	50% acetone	60	510	69	48 500[d]	1.21
7	p(tBA)$_2$[e]	MMA (400)	2 (CuCl)	2 (HMTETA)	50% acetone	60	380	70	50 800[d]	1.19
8	p(tBA)-[p(MMA)]$_2$	4VP (400)	0.5 (CuCl)	0.5 (Me$_6$TREN)	50% 1-propanol	60	300	16[f]	81 700[g]	1.43
9	p(St)$_3$[h]	tBA (150)	0.25 (CuBr)	0.25 (PMDETA)	bulk	60	240	77	18 000	1.33
10	[p(St)-p(tBA)]$_3$	MA (200)	0.5 (CuBr)	0.5 (PMDETA)	50% anisole	70	280	30	28 700	1.22
11	[p(St)-p(tBA)]$_3$	MMA (400)	1 (CuCl)	1 (HMTETA)	50% acetone	60	230	48	31 900[d]	1.55
12	[p(St)-p(tBA)]$_3$	MMA (400)	3 (CuCl)	3 (HMTETA)	75% acetone	60	440	56	63 800[d]	1.25

[a] tBA:MBrP:CuBr:CuBr$_2$:PMDETA − 50:1:0.5:0.525:0.025, 25% acetone, $T = 60$ °C, conv = 96%, time = 390 min, $M_n = 7300$, PDI = 1.11. [b] St:DMDBHD:CuBr:PMDETA − 20:1:0.2:0.2, bulk, $T = 100$ °C, conv = 59%, time = 100 min, $M_n = 1100$, PDI = 1.17. [c] 0.1 equiv of CuCl$_2$ (rel to initiator) was also added to this polymerization. [d] Determined vs linear p(MMA) standards. [e] tBA:DMDBHD:CuBr:PMDETA − 100:1:0.25:0.25, 25% acetone, $T = 60$ °C, conv = 53%, time = 370 min, $M_n = 6300$, PDI = 1.16. [f] Determined via ^{1}H NMR. [g] Determined in DMF using linear p(MMA) standards. [h] St:TBriB:CuBr:PMDETA − 20:1:0.2:0.2, 25% anisole, $T = 100$ °C, conv = 57%, time = 360 min, $M_n = 1600$, PDI = 1.14.

flask was heated at 70 °C in a thermostated oil bath. A sample removed after 210 min and dissolved in 3 mL of toluene had a monomer conversion of 23% with GPC analysis indicating a $M_n = 24\,800$ with a PDI = 1.10. The polymer was diluted with acetone and washed with the DOWEX MSC macroporous ion-exchange resin for about 1 h. It was then filtered to remove the resin, and the solvent was removed by evaporation. After dissolving the polymer in 10 mL of diethyl ether, it was precipitated into a 10-fold excess of methanol. The precipitation cycle was repeated two more times, and then the polymer was dried under vacuum for 12 h. ^{1}H NMR: $\delta = 1.5$ (s, *tert*-butyl methyl resonance), 2.3 and 1.9 (broad, backbone protons), 3.7 (s, methoxy protons on p(MA)), 6.5 and 7.1 (aromatic protons from the p(St)). The composition (30% p(tBA), 53% p(St), 18% p(MA)) was calculated on the basis of the ratio of the area for the aromatic protons of p(St) and the methoxy protons of the p(MA) to the total area for the block copolymer.

C. For a Typical ABA Triblock. The procedure was the same as that for the preparation of the AB diblock copolymer (Experimental Section 5A). Details about the experimental conditions for specific reactions can be found in Table 1. The procedure differs slightly when using MMA, due to the high end group reactivity.

CuCl (13 mg, 1.3×10^{-4} mol) was added to a 5 mL rbf equipped with a stir bar, which was sealed with a rubber septum, and then degassed and back-filled with N$_2$ three times. Deoxygenated acetone was added (2.6 mL) followed by HMTETA (35 μL, 1.3×10^{-4} mol). The complex solution was homogeneous and light green. Difunctional bromo-terminated p(tBA) (0.392 g, 6.3×10^{-5} mol, $M_n = 6300$) was added to a separate 15 mL rbf, which was placed under nitrogen via three degassing/back-filling cycles. Deoxygenated MMA (2.6 mL, 2.5 $\times 10^{-2}$ mol) and anisole (100 μL, as an internal standard) were added, and the polymer was dissolved. The catalyst solution was cannula-transferred into the macroinitiator solution, an initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. A sample was removed at 380 min, dissolved in toluene, and analyzed by GC. The monomer conversion was 70% with GPC analysis indicating a M_n = 50 800 and a PDI = 1.19 (vs linear p(MMA) standards in THF). The purification procedure was as described above for the other block copolymers; however, the precipitation solvent was hexanes rather than methanol or water/methanol. The polymer was dried under vacuum for 12 h. ^{1}H NMR: $\delta = 0.9$, 1.0, 1.9 (s, 3 MMA methyl group resonances due to stereochemical differences), 1.5 (s, *tert*-butyl methyl resonance), 3.6 (s, methoxy protons on p(MMA). The composition (14% p(tBA), 86% p(MMA)) was calculated on the basis of the ratio of the area for the methoxy protons of p(MMA) to the total area for the block copolymer.

D. For a Typical ABCBA Pentablock. The procedure for the chain extension with MA was as described above for the monofunctional ABC triblock copolymer using the CuBr/PMDETA catalyst, with the amounts of reagents adjusted on the basis of the moles of macroinitiator used (Experimental Section 5B; details in Table 1). The procedure for the chain extension with MMA was as described above for the ABA block copolymer where an equimolar amount of catalyst (CuCl/HMTETA) was used relative to the concentration of end groups (Experimental Section 5C). Again, the amounts of reagents were adjusted on the basis of the moles of macroinitiator used. The procedure for the chain extension with 4VP was slightly different.

CuCl (21 mg, 2.1×10^{-4} mol) was added to a dry 10 mL rbf, which was sealed with a rubber septum and degassed and back-filled with N$_2$ three times. Deoxygenated 1-propanol (5 mL) was added via syringe followed by Me$_6$TREN (57 μL, 2.1×10^{-4} mol). The solution was deep green in color. The resulting concentration of CuCl/Me$_6$TREN was 4.2×10^{-2} M. The chloro-terminated p(MMA)-p(tBA)-p(MMA) macroinitiator (0.51 g, 1.7×10^{-5} mol, $M_n = 30\,330$) was put in a separate 10 mL rbf. The flask was sealed with a rubber septum and degassed and back-filled with N$_2$ three times. Deoxygenated 1-propanol (0.53 mL) and 4VP (0.73 mL, 6.8×10^{-3} mol) were added to the flask. The mixture was heated at 60 °C for approximately 30 min to dissolve the polymer. A portion of the catalyst solution was added (200 μL) to make the final concentration of catalyst 4.2×10^{-3} M. The solution turned yellow and was viscous. The reaction flask was placed in an oil bath thermostated at 60 °C. After 5 h, stirring was no longer possible, and the flask was removed from the heat. The monomer conversion was 16%, as determined by ^{1}H NMR, and the $M_n = 81\,700$ with a PDI = 1.43 (determined in DMF against linear p(MMA) standards). The reaction mixture was dissolved in THF (about 30 mL) and then filtered through a column of alumina. The volume of the solution was reduced to approximately 10 mL, and the solution was precipitated into a 10-fold excess of hexanes. The polymer was isolated and redissolved in THF (15 mL), the precipitation cycle was repeated two more times, and the mixture was dried under vacuum for 12 h. ^{1}H NMR: $\delta = 0.9$, 1.0, 1.8 (s, 3 MMA methyl group resonances due to stereochemical differences), 1.5 (s, *tert*-butyl methyl resonance), 1.9, 2.2 (broad resonances for backbone protons), 3.6 (s, methoxy protons on p(MMA), 6.2, 8.3 (broad doublets for the aromatic protons of p(4VP)). The composition (10% p(tBA), 67% p(MMA), 23% p(4VP)) was calculated on the basis of the ratio of the area for the methoxy protons of p(MMA) and the aromatic protons of p(4VP) to the total area for the block copolymer.

E. For a Typical Three-Arm Star with AB Diblock Arms. The procedure for these chain extensions was the same as for the monofunctional AB block copolymers (Experimental Section 5A) with the amount of reagents adjusted according to the concentration of macroinitiator used (details in Table 1).

F. For a Typical Three-Arm Star with ABC Triblock Arms. For a chain extension with MA, the procedure was the same as for that for monofunctional ABC diblock copolymers (Experimental Section 5B). The procedure for chain extension with MMA was the same as that described for the ABA chain extension where separate catalyst and initiator solutions were prepared (Experimental Section 5C). Further information about the experimental details can be found in Table 1.

Results and Discussion

The copolymers that are discussed below were fully characterized using GPC analysis, which provided information about the polydispersity and the blocking efficiency, and by ^{1}H NMR spectroscopy, which was used to determine the composition of the resulting polymers. The experimental molecular weight values determined from GPC analysis, using either linear p(St) or p(MMA) standards, although reported to make a comparison between the different copolymers, are not expected to be similar to the theoretical molecular weight values as determined from the following equation: $M_n = M_{n,macro} + ((\Delta[M]/[I]_0)(MW_{monomer}))$.[29,30] This is due to the potential differences between the behavior of a block copolymer in solution (whether linear or branched) vs that of the linear homopolymer standards. The compositions determined by ^{1}H NMR more accurately reflect the expected results than do molecular weights obtained by the GPC analysis. Additionally, the monomer conversions reported in the Experimental Section were targeted to obtain either a certain molecular weight, as in the case of the low molecular weight p(St) stars, or the conversion obtained at the time the reaction was stopped, as for the chain extension with 4VP. Further details regarding the kinetics of particular monomer systems have been published elsewhere.[16,19,26,30,31] Furthermore, following the literature convention, all the materials are referred to as copolymers; alternatively, however, the ABC triblock copolymers could also be called triblock terpolymers (or pentablock terpolymers for the ABCBA type) to distinguish them from ABA triblock copolymers that are only composed of two monomers.

I. ABC Triblock Copolymers. A bromine-terminated monofunctional poly(*tert*-butyl acrylate) (p(tBA), M_n = 7300, PDI = 1.11) macroinitiator was used for a block copolymerization with styrene (St), resulting in a block copolymer with M_n = 18 200 and a PDI = 1.11 (Table 1, entry 1). This AB diblock copolymer was subsequently used as a macroinitiator for copolymerization with methyl acrylate (MA) (Table 1, entry 2). The polymerization was catalyzed by the CuBr/PMDETA system under high dilution and reached 23% monomer conversion after 3.5 h. The resulting copolymer had a M_n = 24 800 and a PDI = 1.10. The composition determined from ^{1}H NMR was 30% p(tBA), 53% p(St), and 18% p(MA). The GPC traces, shown elsewhere,[16] indicated that the chain-end functionality was high, and there was very little tailing to lower molecular weight, demonstrating that termination was negligible in the chain extensions.

II. ABCBA Pentablock Copolymers. Difunctional p(St) (M_n = 1100, PDI = 1.17) was prepared using the CuBr/PMDETA catalyst system. This copolymer was chain extended with tBA, again using the CuBr/PMDETA catalyst system, to produce an ABA block copolymer with M_n = 11 200 and a PDI = 1.16. Subsequent chain extension with MA produced an ABCBA triblock copolymer with a M_n = 27 300 and a PDI = 1.14. The composition was 38% p(tBA), 52% p(MA), and 10% p(St), as determined from ^{1}H NMR analysis in $CDCl_3$. The GPC traces show that functionality is maintained throughout the block additions, as there appeared to be complete consumption of the macroinitiator for all additions, and that the molecular weight distribution remains narrow even after the last block has been added (Figure 1). More details about the polymerization conditions can be found in Table 1, entries 3 and 4.

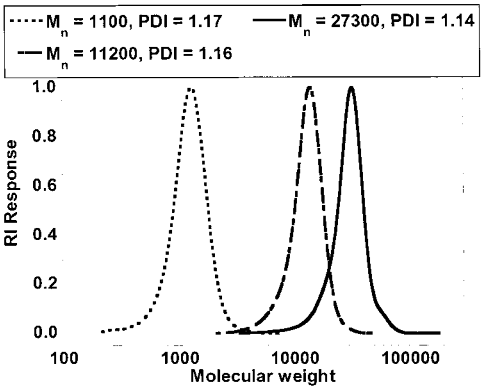


Figure 1. GPC traces of difunctional p(St) (dotted line), p(tBA)-*b*-p(St)-*b*-p(tBA) (dashed line), and p(MA)-*b*-p(tBA)-*b*-p(St)-*b*-p(tBA)-*b*-p(MA) (solid line) in THF (experimental details in Table 1, entries 3 and 4).

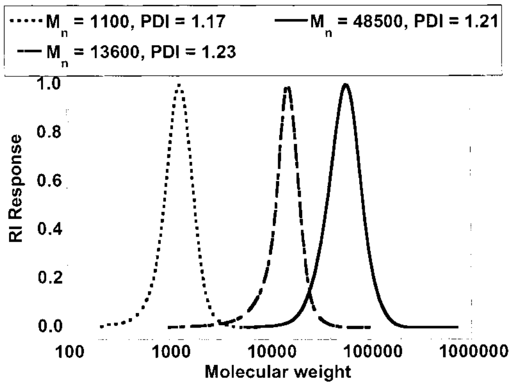


Figure 2. GPC traces of difunctional p(St) (dotted line), p(tBA)-*b*-p(St)-*b*-p(tBA) (dashed line), and p(MMA)-*b*-p(tBA)-*b*-p(St)-*b*-p(tBA)-*b*-p(MMA) (solid line) in THF (experimental details in Table 1, entries 5 and 6).

A different bromine-terminated p(tBA)-p(St)-p(tBA) ABA block copolymer (M_n = 13 600, PDI = 1.23, Table 1, entry 6) was used as a macroinitiator for a block copolymerization with MMA (M_n = 48 500, PDI = 1.21, against p(MMA) standards). CuCl was used as the Cu(I) species to invoke the halogen exchange and enhance the rate of initiation over the rate of propagation. Without the halogen exchange, the efficiency of cross-propagation from an acrylate to a methacrylate is poor.[26] In addition, the HMTETA ligand was used as the complexing agent to avoid the heterogeneity associated with the corresponding PMDETA complex in MMA. An important note is that a 1:1 molar equivalent of the complex was used relative to the concentration of *end groups*, not relative to the concentration of initiator (vide infra). Figure 2 contains the GPC traces of the difunctional macroinitiator, the ABA block copolymer, and the ABCBA triblock copolymer. The entire distribution moves progressively toward higher molecular weights,

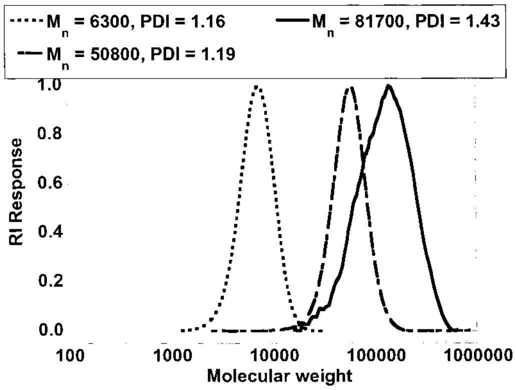


Figure 3. GPC traces of difunctional p(tBA) (dotted line, in THF), p(MMA)-*b*-p(tBA)-*b*-p(MMA) (dashed line, in THF), and p(4VP)-*b*-p(MMA)-*b*-p(tBA)-*b*-p(MMA)-*b*-p(4VP) (solid line, in DMF) (experimental details in Table 1, entries 7 and 8).

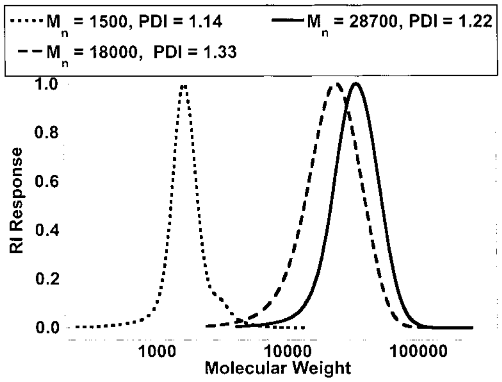


Figure 4. GPC traces of trifunctional CH_3C-[p(St)-Br]$_3$ (dotted line), CH_3C-[p(St)-*b*-p(tBA)-Br]$_3$ (dashed line), and CH_3C-[p(St)-*b*-p(tBA)-*b*-p(MA)-Br]$_3$ (solid line) in THF (experimental details in Table 1, entries 9 and 10).

again indicating the presence of high chain-end functionality and high blocking efficiency. The composition determined by ^{1}H NMR in $CDCl_3$ was 69% p(MMA), 27% p(tBA), and 4% p(St). More detailed experimental conditions can be found in Table 1, entries 5 and 6.

A difunctional p(tBA) macroinitiator ($M_n = 6300$, PDI = 1.16) was chain extended with MMA using the CuCl/HMTETA catalyst system to form an ABA block copolymer with $M_n = 50\ 800$ and a PDI = 1.19 (vs p(MMA) standards). This copolymer was subsequently chain extended with 4-vinylpyridine (4VP) using a CuCl/tris[(2-dimethylamino)ethyl]amine (Me_6TREN) catalyst.[31] The final ABCBA triblock copolymer had a $M_n = 81\ 700$ with a PDI = 1.43 against linear p(MMA) standards in *N*,*N*-dimethylformamide. This polymer sample could not be analyzed using THF as the mobile phase. The GPC traces show some overlap with the macroinitiator, but the majority of the polymer appears to have grown (Figure 3). The composition of the purified polymer as determined by ^{1}H NMR analysis was 10% p(tBA), 23% p(4(VP)), and 67% p(MMA). Experimental details can be found in Table 1, entries 7 and 8.

III. Trifunctional ABC Triblock Copolymers. A trifunctional p(St) macroinitiator (Y(A)$_3$, $M_n = 1500$, PDI = 1.14) was chain extended with tBA to form a trifunctional AB block copolymer (Y(AB)$_3$) with a $M_n = 18\ 000$ and a PDI = 1.33. The arms were extended further with MA to form ABC triblock copolymer arms (Y(ABC)$_3$, $M_n = 28\ 700$, PDI = 1.22). The experimental molecular weights as determined by the GPC deviate from those determined theoretically ($M_{n,theo} = 23\ 200$); however, the composition determined from ^{1}H NMR (66% p(tBA), 30% p(MA), and 4% p(St)) indicates that the molecular weights are overestimated by the GPC. Details on the experimental conditions can be found in Table 1, entries 9 and 10. The GPC traces shown in Figure 4 indicate that the chain end functionality is high, and even though the high molecular weight shoulder in the original macroinitiator indicated some star–star coupling occurred, it did not affect the synthesis of the block copolymers.[29] This is not unexpected because the polymers are multifunctional; coupling of the stars will simply reduce the number of active sites but not prevent the growth of the remaining arms.

The same bromine-terminated AB diblock trifunctional initiator (Y(AB)$_3$) was used for a chain extension with MMA. In this case, the first attempt was made with a 1:1 molar equivalent of the CuCl/HMTETA catalyst relative to the initiator (i.e., 1:3 relative to [end groups], details in Table 1, entries 9 and 11). This resulted in a mixture of halogen end groups in the propagating chains that did not activate with the same rate. The GPC traces are shown in Figure 5A for the macroinitiator, the Y(AB)$_3$ diblock copolymer, and the Y(ABC)$_3$ triblock copolymer. There is a significant amount of tailing to the lower molecular weight side of the distribution, which at first might suggest poor functionality in the macroinitiator. However, upon using a 1:1 molar equivalent of catalyst relative to the moles of end groups (i.e., 3:1 relative to [initiator]), the distribution narrowed significantly (Figure 5B, details

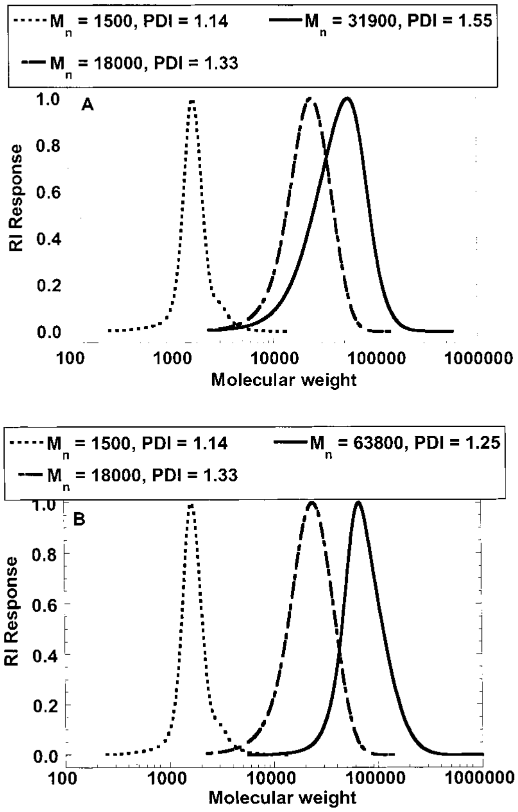
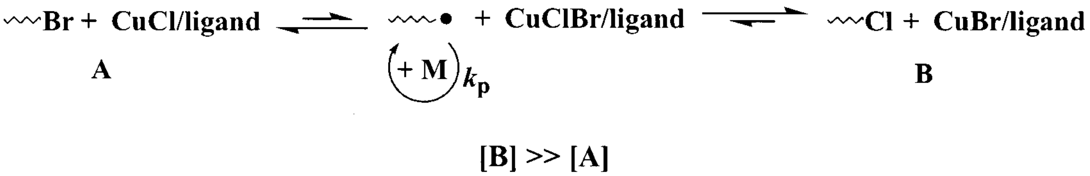


Figure 5. (A) GPC traces of trifunctional CH_3C-[p(St)-Br]$_3$ (dotted line), CH_3C-[p(St)-*b*-p(tBA)-Br]$_3$ (dashed line), and CH_3C-[p(St)-*b*-p(tBA)-*b*-p(MMA)-Br]$_3$ (solid line) in THF using a 1:1 molar equivalent of catalyst relative to *initiator*. (B) GPC traces of trifunctional CH_3C-[p(St)-Br]$_3$ (dotted line), CH_3C-[p(St)-*b*-p(tBA)-Br]$_3$ (dashed line), and CH_3C-[p(St)-*b*-p(tBA)-*b*-p(MMA)-Br]$_3$ (solid line) in THF using a 1:1 molar equivalent of catalyst relative to *end groups* (experimental details in Table 1, entries 9, 11, and 12).

Scheme 1. Illustration of the Mechanism of Halogen Exchange



in Table 1, entries 9 and 12). The composition of the polymer determined by ^{1}H NMR was 66% p(MMA), 33% p(tBA), and 4% p(St). Additionally, as detailed in Table 1, because the concentration of catalyst needed was so high to have efficient blocking, the reaction was run under high dilution to decrease the rate of polymerization.

The outcome of the above reactions indicate that 1 equiv of the catalyst per chain end is necessary for efficient halogen exchange in the linear amine-based system. This differs from the Cu(I)/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) catalyzed polymerization systems in which decreasing the concentration of catalyst to less than equimolar relative to the concentration of end groups did not affect the control over the polymer chains significantly.[26] This is because the equilibrium is more strongly shifted toward **B** (Scheme 1) for the linear amine catalyst system than for the bpy-based system. This means that if a bromine-based (macro)initiator is used in conjunction with a CuCl/amine catalyst, the formed radical will preferentially abstract the Cl from the deactivator, forming Cl-terminated polymer chains and a CuBr/amine catalyst (**A** does not participate significantly (~1%)). In contrast, in the bpy systems, the radical may react with either Br or Cl, resulting in a mixture of halogen chain ends as well as Cu(I) species (both **A** (~10%) and **B** (~90%) participate in the activation/deactivation cycle).

The apparent rate constant of polymerization, k^{app}, is a function of the equilibrium constant for a given system, K_{eq}, as well as the rate constant of propagation for a given monomer, k_{p}. The need for the halogen exchange in ATRP mostly stems from the differences between the dynamics of exchange for a given macroinitiator compared to those of the second monomer, i.e., very different k^{app}. When well-matched, the molecular weights of the polymers will be predictable and the molecular weight distributions narrow. For example, p(St) can be used successfully as a macroinitiator for the ATRP of tBA and vice versa because p(St) activates quickly to form a relatively stable radical (large equilibrium constant); yet, after cross-propagation, deactivation of the tBA radical is fast (smaller equilibrium constant), resulting in total consumption of the macroinitiator before a significant amount of monomer is consumed, even with the large k_{p} for the monomer. The alternate order of addition is also successful because, after the initial cross-propagation step, the styryl-based radical goes through several activation/deactivation cycles before adding monomer,[32] again allowing sufficient time for complete consumption of the p(tBA) macroinitiator. This is detailed in entries 1[16] and 3 in Table 1 and exemplified in Figure 1.

This is contrary to what occurs when either p(St) or p(tBA) is used as the macroinitiator for a methacrylate polymerization. The methacrylate ATRP reactions have the largest equilibrium constants, resulting in a mismatch with either styrene- or acrylate-based macroinitiators. Once cross-propagation occurs and methacrylate chain ends are formed, which is rapid because the monomer is very reactive, activation is fast, resulting in a large concentration of active species and a fast polymerization. This causes what appears to be slow cross-propagation because the macroinitiator will not be fully consumed before the amount of monomer consumption is significant, regardless of the smaller k_{p} for the monomer. The final polymers will have higher polydispersities than is desirable. The only way to overcome this discrepancy is to alter the equilibrium, and this is accomplished by using the bromine-terminated macroinitiators with CuCl-based catalysts, as discussed above. After cross-propagation, the rate of activation of the methacrylate-terminated polymer chain will be lower and, therefore, the equilibrium constant will be smaller, allowing for a better match between less reactive macroinitiators and the methacrylate monomers. However, because the styryl-based radical may deactivate and “switch” before the addition of any monomer, there may still be slow cross-propagation in this system, simply because both equilibrium constants have been lowered, rather than just one. The propionate-based radical, on the other hand, is sufficiently active to add to a methacrylate monomer without deactivating first. Therefore, the ratio of the rate of cross-propagation (k_{12}) to the rate of the first deactivation step (k_{d1}) will also affect the blocking efficiency. For these reasons, p(tBA) was used as the macroinitiator for chain extensions with MMA, and the halogen exchange was employed. Further details about the acrylate/methacrylate system with and without the halogen exchange have been reported elsewhere.[30]

Figures 3 and 4 demonstrate the effectiveness of the blocking using macroinitiators with p(tBA) chain ends for the polymerization of MMA, and entries 6 and 7 in the table outline the experimental details. A small amount of $CuCl_2$ was added to the ABCBA block copolymerization (entry 7) in an effort to accelerate deactivation, reduce the concentration of active species, and reduce the proportion of termination that might occur. As the rate of this reaction was slow in the presence of the added $CuCl_2$ (69% monomer conversion after 8.5 h), no $CuCl_2$ was added to the polymerization in entry 8, the chain extension of difunctional p(tBA) with MMA. The resulting block copolymer was used as a macroinitiator for an ATRP reaction with 4VP and utilized the CuCl/Me_6TREN catalyst system, which is effective in polymerizing this monomer (entry 8).[31] This strongly binding ligand prevents coordination of the monomer to the copper center; however, the catalyst complex must be prepared prior to the introduction of the monomer in order for the polymerization to be successful (see Experimental Section 5D).

In the final effort to demonstrate that ATRP can be utilized effectively to prepare ABC triblock copolymers composed of various chain architectures, a trifunctional p(St) macroinitiator was chain extended with tBA, followed by either MA or MMA. The MA reaction was performed with a low concentration of catalyst and under high dilution to limit star–star coupling (entry 10). The same precautions were taken for the chain extension with MMA; however, since the concentration of the CuCl/HMTETA catalyst needed to be equimolar to the concentration of end groups in order to have efficient blocking, the volume fraction of solvent was increased to compensate for the increased catalyst concentration (entry 12).

Conclusions

This work illustrates that ATRP can be used successfully to prepare ABC triblock copolymers with various chain architectures and incorporating various monomers into the polymer backbone. Polymers were prepared that were monofunctional, difunctional, and trifunctional with styrene, *tert*-butyl acrylate, methyl acrylate, methyl methacrylate, and 4-vinylpyridine as monomers. The chain end functionality at each step was assessed using GPC analysis, and the composition of the purified copolymers was determined using ^{1}H NMR spectroscopy. These polymers had controlled molecular weights and narrow molecular weight distributions. The optimized synthetic conditions were presented, and some key points about the strategies used to develop these methods are listed below.

1. The chain end functionality of the macroinitiators must be maintained to have high blocking efficiency. This may require the addition of deactivator (Cu(II)) or the use of a solvent to reduce the concentration of radicals and the contribution of termination (Table 1, entries 3 (solvent) and 6 (Cu(II))).

2. The macroinitiator must be chosen so that the chain end is reactive enough with the monomer to have efficient cross-propagation. Macroinitiators that are based on monomers that have large equilibrium constants can be used to initiate the ATRPs of monomers with lower equilibrium constants (i.e., poly(methacrylates) for acrylates or styrenes); proceeding in the opposite direction may result in inefficient cross-propagation due to incomplete consumption of the macroinitiator before a significant amount of monomer has been consumed (Table 1, entries 7 and 8).

3. Halogen exchange should be employed when polyacrylate macroinitiators are used to polymerize methacrylate monomers. This enhances the rate of cross-propagation over the rate of propagation of the second block and enhances the efficiency of block copolymer formation. The exchange reaction strongly favors a complete halogen exchange when linear polyamines are used as the ligands, requiring an equimolar ratio of catalyst to end groups to have high blocking efficiency (Table 1, entries 11 and 12). Preparing the catalyst solution separately from the macroinitiator solution is essential so that exchange does not occur before cross-propagation. Unfortunately, exchange prior to cross-propagation may occur with p(St) macroinitiators, resulting in a low efficiency of cross-propagation.

4. 4-Vinylpyridine can be incorporated into the block copolymers using the CuCl/Me$_6$TREN catalyst system. This monomer generally requires a chlorine-based initiator, which again may affect the possible block order in the copolymer (Table 1, entry 8).

5. Adjusting the choice of the ligand, adding a solvent, or varying the temperature to achieve a homogeneous catalytic state is recommended. If the concentration of activator in solution is too low, there potentially will not be enough deactivator formed to control the polymerization, and it will resemble a conventional radical process. If the activator is soluble initially but the deactivator precipitates as the polymerization progresses, the equilibrium will shift toward the active side and the concentration of active species increases, increasing both the rates of the polymerization and termination. This can result in poor chain end functionality, which will affect the blocking efficiency significantly.

Following the above suggestions to develop block copolymerization strategies using ATRP should lead to the successful preparation of the desired materials. ATRP is a powerful and versatile tool mainly because the system can be tuned to fit particular monomers or catalyst systems and offers the control needed to synthesize well-defined materials for specific applications.

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