

Atom Transfer Radical Polymerization of *tert*-Butyl Acrylate and Preparation of Block Copolymers

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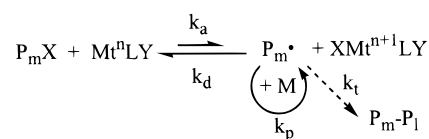
ABSTRACT: Atom transfer radical polymerization (ATRP) of *tert*-butyl acrylate is reported. Controlled polymerizations were performed using a CuBr/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine catalyst system in conjunction with an alkyl bromide as the initiator. Low molecular weight polymers with narrow molecular weight distributions were obtained by the addition of a solvent to create a homogeneous catalytic system. The addition of the solvent was necessary to decrease the polymerization rate and afford low polydispersity materials. This differs from the ATRP of methyl or *n*-butyl acrylate using this catalytic system, which do not require the addition of a solvent to obtain well-defined polymers. Subsequent hydrolysis of the polymer in refluxing dioxane with addition of HCl afforded poly(acrylic acid). Characterization using ¹H NMR and FT-IR confirmed complete hydrolysis of the ester group. Further use of poly(*tert*-butyl acrylate) as a macroinitiator for block copolymerizations followed by hydrolysis of the ester group produced amphiphilic block copolymers. In addition, the preparation of an ABC triblock copolymer of poly(*tert*-butyl acrylate)-*b*-poly(styrene)-*b*-poly(methyl acrylate) by ATRP is reported.

Introduction

The field of radical polymerization has exploded within the past few years with the advent of controlled radical polymerization processes.¹ These methods provide chemists with the ability to synthesize polymers with predictable molecular weights and block copolymers with high blocking efficiency and to prepare novel chain architectures that have been elusive using ionic methods. One such process is atom transfer radical polymerization (ATRP).^{2,3} This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (Mtⁿ) complexed by ligands L and Y) reacts with an alkyl halide (P_m-X) to generate a radical (P_m•) and a higher oxidation state metal complex (XMtⁿ⁺¹LY, *k*_a). This radical then adds monomer to generate the polymer chain (*k*_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (*k*_d), according to Scheme 1. The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains (the sum of active and dormant species) is small (≤10%). Some early termination will lead to the formation of the Cu(II) species, but this is necessary to establish control via the persistent radical effect.⁴ Several metal/ligand systems have been used to catalyze this process, and a variety of monomers have been successfully polymerized.^{5–7}

As of late, simple amine ligands have been used for ATRP because of their relatively inexpensive cost and commercial availability, compared to unsubstituted² and alkyl-substituted bipyridines,^{8,9} alkylpyridine imines,¹⁰ alkylated tris(2-aminoethyl)amine (TREN),¹¹ and picolylamines,¹² which are not commercially available and must be synthesized. While bidentate amines such as *N,N,N',N'*-tetramethylethylenediamine have not given

Scheme 1. Equilibrium/Propagation Expression for ATRP



the desired control over the polymerizations, triamines and tetraamines such as *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) and *N,N,N',N'',N''',N'''*-hexamethyltriethylenetetraamine (HMTETA) are efficient as ligands for the Cu-mediated systems. Specifically, using the CuBr/PMDETA catalyst system allows the polymerization ATRP of methyl acrylate,¹³ *n*-butyl acrylate,¹⁴ and 2-hydroxyethyl acrylate¹⁵ to occur under milder conditions than the CuBr/4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) system in terms of both lower catalyst concentrations and lower temperatures.¹⁶ There have been recent reports by Bednarek et al.^{17,18} that suggest this catalyst system may be involved in a transfer reaction, resulting in elimination of the halogen end group. The conditions utilized in those experiments, however, are different from those presented here, and we hope to illustrate that this catalyst system is a viable one for the preparation of well-defined polymers (vide infra).

In this laboratory, the focus has been on using Cu-based catalytic systems for ATRP. Comparable to many ionic polymerization methods, ATRP is sensitive to the presence of acids. Although the acid may affect the active species as it would in a cationic or anionic process, it can also destroy the metal catalyst by displacing the halogen on the copper complex. If this happens to the Cu(II) species, deactivation cannot occur. Additionally, since many of the ligand systems utilized are nitrogen-based, protonation of the nitrogen may occur, disrupting its coordination to the metal center. The solution to this problem, for both ATRP and anionic methods, has been to polymerize protected monomers, followed by a deprotection step to generate the polyacid.^{19,20} Protected

carboxylic acid initiators and initiators with "remote" halogens have also been used for ATRP; however, the free acids always had initiator efficiencies less than 1 (≤ 0.7).²¹ Recently, Armes et al. reported on ATRP of the sodium salts of poly(methacrylic acid) and poly(4-vinylbenzoate) in aqueous media using water-soluble initiators such as poly(ethylene oxide) modified with a bromoisobutyrate end group.^{22,23} While this technique is useful for the preparation of water-soluble block copolymers, it cannot be used to prepare copolymers with hydrophobic blocks. This paper reports on the ATRP of *tert*-butyl acrylate (tBA) using the CuBr/PMDETA catalyst system, as well as deprotection of the polymer to yield poly(acrylic acid). Additionally, poly(*tert*-butyl acrylate) (p(tBA)) macroinitiators were used to prepare block copolymers with various monomers. Hydrolysis of the ester functionality created amphiphilic block copolymers.

Experimental Section

1. Materials. tBA (Aldrich, 98%) was extracted three times with 5% aqueous NaOH and then washed with distilled water. After drying over CaCl₂ and filtering off the drying agent, the monomer was distilled under vacuum (60 °C/60 mmHg). Styrene (Acros, 99%) was dried over CaH₂ and then distilled under reduced pressure (65 °C/35 mmHg). Methyl acrylate (Acros, 99%) was also dried over CaH₂ and then distilled at ambient pressure. (2-Dimethylamino)ethyl methacrylate (Aldrich, 98%) was passed through a column of alumina to remove inhibitor. Methyl 2-bromopropionate (Acros, 99%) was distilled before use. 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. *p*-Dimethoxybenzene (Acros, 99+%), benzene (Acros, 99%), anisole (Aldrich, 99%), dimethyl 2,6-dibromoheptanedioate (DMDBHD, Aldrich, 97%), PMDETA (Acros, 99+%), and HMTETA (Aldrich, 97%) were all used as received.

2. Polymerization Procedure. A. For a Typical Monofunctional tBA Polymerization. CuBr (39.1 mg, 2.73×10^{-4} mol) and CuBr₂ (3.0 mg, 1.4×10^{-5} mol) were added to a dry round-bottom flask (rbf). The flask was sealed with a rubber septum, degassed and back-filled with nitrogen three times, and left under nitrogen. Deoxygenated acetone (1 mL) was added, after which tBA (4.0 mL, 2.7×10^{-2} mol) was added, both via syringes that had been purged with nitrogen. PMDETA (60 μ L, 2.9×10^{-4} mol) was added, and the solution was stirred until the Cu complex had formed. This is easily visualized through a change of the solution from cloudy and colorless to clear and light green. After complex formation, methyl 2-bromopropionate (61 μ L, 5.5×10^{-4} 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 320 min, a sample was dissolved in toluene, and GC analysis showed a monomer conversion of 93%. The polymer had a $M_n = 6000$ and a $M_w/M_n = 1.11$. (Note: for reactions performed at temperatures higher than 60 °C, approximately 2% *p*-dimethoxybenzene or anisole, relative to the volume of monomer, was additionally added. This was to ensure conversion measurements were not affected by loss of solvent or monomer at elevated temperatures.)

B. For a Typical Difunctional tBA Polymerization. CuBr (12 mg, 8.5×10^{-5} mol) and DMDBHD (55 mg, 1.7×10^{-4} mol) were added to a 10 mL rbf. The flask was degassed and back-filled with nitrogen three times before introducing deoxygenated tBA (5.0 mL, 3.4×10^{-2} mol) and anisole (100 μ L, as an internal standard) via purged syringes. PMDETA (18 μ L, 8.5×10^{-5} mol) was added, and the copper complex formed. The solution was heterogeneous. An initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. After 6.5 h, a sample was removed and dissolved in toluene, and GC analysis was performed. Monomer conversion was 79%, with a $M_n = 25\,100$ and a $M_w/M_n = 1.24$.

C. For a Difunctional tBA Polymerization Using Separate Catalyst and Initiator Solutions. CuBr (13 mg, 8.5×10^{-5} mol) was added to a 5 mL rbf, which was degassed and back-filled with nitrogen three times. Deoxygenated tBA (2.5 mL, 1.7×10^{-2} mol) was added along with PMDETA (18 μ L, 8.5×10^{-5} mol). DMDBHD was added to a separate 10 mL flask (67 mg, 1.9×10^{-4} mol), which was degassed and back-filled with nitrogen three times. Deoxygenated tBA (2.5 mL, 1.7×10^{-2} mol) was added along with anisole (100 μ L, as an internal standard). After the copper complex had formed, the catalyst solution was cannula-transferred into the initiator solution, an initial sample was removed, and the flask was placed in a 60 °C oil bath. After 7 h, a sample was removed and dissolved in toluene, and GC analysis was performed. Monomer conversion was 75%, with a $M_n = 17\,300$ and a $M_w/M_n = 1.21$.

D. For a Difunctional tBA Polymerization Using Separate Catalyst and Initiator Solutions with Vigorous Deoxygenation of the Initiator Solution. The amounts of reagents used and procedure were as in section C, but before the catalyst solution was transferred into the initiator solution, nitrogen was bubbled through the initiator solution for 20 min. After 6.5 h, the monomer conversion was 71% with a $M_n = 15\,960$ and a $M_w/M_n = 1.21$.

3. P(tBA) Macroinitiator Purification. A 50 mL scale reaction using the above monofunctional p(tBA) procedure (initial concentration ratios tBA:MBRP:CuBr:PMDETA:CuBr₂ = 50:1:0.5:0.525:0.025, 25% acetone, 60 °C; conversion = 96% after 6.5 h, $M_n = 7300$, $M_w/M_n = 1.11$) was purified by dissolving the reaction mixture in approximately 300 mL of additional acetone, washing with DOWEX MSC macroporous ion-exchange resin for about 1 h, and filtering the solution through a column of alumina. Both the resin²⁴ and the alumina serve to remove the copper catalyst from the polymer. The acetone was removed by evaporation, and the polymer was then dissolved in a minimum amount of diethyl ether (~150 mL), after which it was precipitated into a 10-fold excess of a 50:50 v:v water:MeOH solution. After decanting off the solvent, the polymer was redissolved in diethyl ether, and the precipitation procedure was repeated two more times. The final polymer was dissolved in diethyl ether and transferred to a tared container, and the solvent was removed under vacuum. Three resonances were present in the ¹H NMR spectrum (300 MHz, CDCl₃): a sharp one for the *tert*-butyl group ($\delta = 1.5$ ppm) and two broad ones for the backbone protons ($\delta = 1.85$ ppm and $\delta = 2.35$ ppm).

4. Block Copolymerizations. Block copolymerizations were performed in the same manner as a typical polymerization; however, the order of addition was modified.

A. AB Diblocks. 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, which was sealed with a rubber septum, then degassed, and back-filled with nitrogen three times. Deoxygenated styrene was added (5.0 mL, 4.4×10^{-2} mol) via a purged syringe. The polymer was dissolved. PMDETA was introduced (92 μ L, 4.4×10^{-4} mol), and the solution was stirred until the Cu complex had formed. Again, this was visually confirmed through a change in the solution from cloudy and colorless to clear and light green. After complex formation, an initial sample was removed, and the flask was placed in an oil bath thermostated at 100 °C. After 140 min, a sample was dissolved in THF and GC analysis showed the monomer conversion was 94%. The polymer had a $M_n = 18\,150$ and a $M_w/M_n = 1.11$. The polymer was dissolved in about 50 mL of THF, and then the solution was filtered through alumina to remove the copper catalyst. The polymer was precipitated into a 10-fold excess of MeOH and then isolated by vacuum filtration. Two additional precipitation cycles were performed. After drying under vacuum for 12 h, ¹H NMR analysis was performed in CDCl₃. Two broad resonances were visible for the aromatic protons of the p(St) at $\delta = 6.5$ ppm and $\delta = 7.1$ ppm. Broad backbone proton resonances were at $\delta = 2.3$ and 1.9 ppm, along with a sharp singlet corresponding to the *tert*-butyl group at $\delta = 1.5$ ppm. 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.

Methyl acrylate polymerizations were carried out under similar conditions, but at 70 °C. (2-Dimethylamino)ethyl methacrylate was polymerized in 50% anisole solution at 90 °C using CuCl/HMTETA at a 1:1 ratio with the initiator.

B. Asymmetric ABA Triblock. Bromo-terminated p(tBA)-*b*-p(St) ($M_n = 18\,520$, 0.51 g, 2.7×10^{-5} mol), CuBr (3.8 mg, 2.7×10^{-5} mol), CuBr₂ (1.0 mg, 1.4×10^{-6} mol), and DMB (37 mg, as an internal standard) were added to a 5 mL rbf, which was sealed with a rubber septum, then degassed, and back-filled with nitrogen three times. Deoxygenated tBA (0.40 mL, 2.7×10^{-3} mol) and anisole (0.4 mL) were added via purged syringes. The polymer was dissolved. PMDETA was introduced (5.9 μ L, 2.8×10^{-5} mol), 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, an initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. After 14.5 h, a sample was dissolved in toluene, and GC analysis gave a monomer conversion of 57%. The polymer had a $M_n = 23\,980$ and a $M_w/M_n = 1.13$. The polymer was dissolved in about 50 mL of acetone, and then the solution was filtered through alumina to remove the copper catalyst. The polymer was precipitated into a 10-fold excess of MeOH and then isolated by vacuum filtration. Two additional precipitation cycles were performed. After drying under vacuum for 10 h, ¹H NMR analysis was performed in CDCl₃. The broad resonances for the aromatic protons of the p(St) were at $\delta = 6.5$ ppm and $\delta = 7.1$ ppm. The backbone proton resonances were visible at $\delta = 2.3$ and 1.9 ppm, along with a sharp singlet corresponding to the *tert*-butyl group at $\delta = 1.5$ ppm. The composition (32% p(tBA), 68% 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.

C. Symmetric ABA Triblock. a. Difunctional p(St). CuBr (0.372 g, 2.6×10^{-3} mol) and DMBHD (4.51 g, 1.30×10^{-2} mol) were added to a 50 mL rbf, which was sealed with a rubber septum, then degassed, and back-filled with nitrogen three times. Deoxygenated styrene (30 mL, 2.6×10^{-1} mol) and anisole (0.75 mL, as an internal standard) were added to the flask via purged syringes. Deoxygenated PMDETA (0.545 mL, 2.6×10^{-3} mol) was added, and the solution was allowed to stir to form the copper complex. The solution changed from cloudy and colorless to dark green but was heterogeneous. An initial sample was removed, and the flask was placed in an oil bath thermostated at 100 °C. After 100 min, a sample dissolved in THF showed the monomer conversion was 59%. The polymer had a corresponding $M_n = 1100$, with a $M_w/M_n = 1.17$. The reaction mixture was dissolved in approximately 150 mL of acetone, washed with the DOWEX MSC macroporous ion-exchange resin for about 1 h, and filtered two times through a column of alumina. The acetone was removed by evaporation, and the polymer was dissolved in about 100 mL of diethyl ether. After precipitating into a 10-fold excess of MeOH, the polymer was redissolved in diethyl ether and precipitated again. It was dried under vacuum for about 12 h. The yield of macroinitiator was 16.8 g. ¹H NMR (CDCl₃): $\delta = 7.1$, 6.9 ppm (aromatic protons), $\delta = 4.5$ (CHBr), $\delta = 3.3$ (methoxy protons from the initiator), $\delta = 1.0$ –2.8 ppm (backbone protons).

b. Block Copolymer. Difunctional bromo-terminated p(St) (2.08 g, 1.8×10^{-3} mol) and CuBr (0.128 g, 9.0×10^{-4} mol) were added to a 25 mL rbf, which was sealed with a rubber septum, then degassed, and back-filled with nitrogen three times. Deoxygenated tBA (18 mL, 1.26×10^{-1} mol) and acetone (6 mL) were added via purged syringes, and the polymer was dissolved. PMDETA (179 μ L, 9.0×10^{-4} mol) was added and the copper complex formed. An initial sample was removed. The solution was initially heterogeneous, but after heating at 60 °C for about 10 min, the solution became homogeneous. A sample removed at 22.5 h and dissolved in toluene had a monomer conversion of 96% and a $M_n = 14\,250$, with a $M_w/M_n = 1.14$. The purification was performed as in the case of a p(tBA) macroinitiator (section 3 of the Experimental Section).

After drying under vacuum for 12 h, ¹H NMR analysis was performed in CDCl₃. The aromatic proton resonances of the p(St) were at $\delta = 6.5$ ppm and $\delta = 7.1$ ppm. The resonances for the backbone protons were visible at $\delta = 2.3$ and 1.9 ppm, along with a sharp resonance corresponding to the *tert*-butyl group at $\delta = 1.5$ ppm. The composition (89% p(tBA), 11% 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.

D. ABC Triblock. The polymer described in section 4A of the Experimental Section was used as the macroinitiator for this block copolymerization. CuBr (4.1 mg, 2.8×10^{-5} mol), bromo-terminated p(tBA)-*b*-p(St) ($M_n = 18\,150$, 0.51 g, 2.8×10^{-5} mol), and DMB (66 mg, as an internal standard) were added to a 5 mL rbf, which was sealed with a rubber septum and degassed and back-filled with nitrogen three times. Deoxygenated methyl acrylate (1.0 mL, 1.1×10^{-2} mol) was added via a purged syringe, and the polymer was dissolved. PMDETA (5.8 μ L, 2.78×10^{-5} mol) was added and the copper complex formed. An initial sample was removed, and the flask was placed in an oil bath thermostated at 70 °C. After 3.5 h, the solution was dissolved in 3 mL of toluene. The monomer conversion was 23%. The polymer M_n was 24 790 with a $M_w/M_n = 1.10$. After washing with the DOWEX MSC macroporous ion-exchange resin for about 1 h, the solution was filtered to remove the resin, and the solvent was removed by evaporation. The polymer was dissolved in 10 mL of diethyl ether and precipitated into a 10-fold excess of MeOH. The precipitation cycle was repeated two more times, and then the polymer was dried under vacuum for 12 h. ¹H NMR analysis was performed in CDCl₃. The p(St) aromatic proton resonances were visible at $\delta = 6.5$ ppm and $\delta = 7.1$ ppm. The protons on the methoxy group of the p(MA) appeared at $\delta = 3.7$ ppm. The backbone proton resonances were at $\delta = 2.3$ and 1.9 ppm. The sharp *tert*-butyl was at $\delta = 1.5$ ppm. 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.

5. Hydrolysis. For a Typical Hydrolysis. P(tBA) (0.987 g, 7.7×10^{-3} mol ester) was added to a 10 mL rbf. Dioxane (3 mL) was added, and the polymer was dissolved. Concentrated HCl (1.0 mL, 3.2×10^{-2} mol) was added, the flask was covered with a condenser, and the solution was heated to reflux. After about 6 h, the solution was cooled, and the excess reagents were removed by evaporation under vacuum. ¹H NMR in D₂O revealed resonances at $\delta = 2.2$ and 1.6 ppm corresponding to the backbone protons. FT-IR (KBr pellet) showed the characteristic carboxylic acid absorbance from 2800 to 3600 cm⁻¹.

6. 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 tBA: isothermal run at 40 °C for 4 min; for St: 2 min at 100 °C followed by an increase to 180 °C and held for 2 min; for MA: 40 °C for 2 min followed by an increase to 180 °C and held for 2 min). Polymer molecular weights were estimated using a GPC system equipped with a Waters WISP 712 autosampler, Polymer Standards Service columns (guard, 10² Å, 10³ Å, 10⁵ Å), and a Waters 410 RI detector against linear polystyrene standards in THF (1 mL/min) at 35 °C. Toluene was used as an internal standard. ¹H NMR characterization was performed on a Bruker 300 MHz instrument. IR measurements were made on a Matteson ATI Infinity Series FTIR. Thermal analysis was performed using a Rheometric Scientific DSC equipped with a subambient temperature apparatus. The T_g was determined from the middle of the change in heat capacity at a heating rate of 10 °C/min.

Results

I. ATRP of *tert*-Butyl Acrylate: Kinetic Results. tBA has been successfully polymerized using several different methods, including anionic,^{25,26} nitroxide-medi-

Table 1. ATRP of TBA Using the CuBr/PMDETA Catalyst System, Initiated by Methyl 2-Bromopropionate under Various Conditions

entry	[M]/[I]	[Cu]/[I]	[L]/[I]	[Cu(II)]/[I]	solvent ^a	temp (°C)	time (min)	conv (%)	$M_{n,exp}$	$M_{n,theo}^b$	PDI
1	25	0.25	0.25	0		65	10	>95	NA ^c		NA ^c
2	25	0.25	0.25	0		55	18	>95	NA ^c		NA ^c
3	25	0.1	0.1	0		55	30	92	3150	3000	1.88
4	25	0.5	0.5	0		RT	160	89	3350	2850	1.59
5	25	0.1	0.1	0	50% benzene	55	120	30	1840	910	1.39
6	25	0.25	0.25	0	50% benzene	55	65	25	1640	800	1.54
7	50	0.5	0.5	0	20 mol % DMB ^d	RT	1060	77	5300	4900	1.33
8	50	0.5	0.525	0.025	20 mol % DMB ^d	60	120	86	6100	5500	1.21
9	50	0.5	0.55	0.05	20 mol % DMB ^d	60	120	94	5800	6000	1.21

^a Percent compared to volume of monomer added. ^b $M_{n,theo} = 128([tBA]_0/[I]_0 \times \text{conversion})$. ^c $M_{n,exp}$ and PDI were not measured for these samples due to the uncontrolled nature of the polymerization. ^d DMB = *p*-dimethoxybenzene.

ated,²⁷ and metallocene-mediated²⁸ reactions. ATRP has been used successfully for a variety of acrylate polymerizations, including methyl,¹³ *n*-butyl,¹⁴ and 2-hydroxyethyl.¹⁵ These polymerizations, however, utilized bipyridine ligands. This report focuses on using PMDETA as the ligand. As with any reaction, the conditions under which the reaction is performed must be optimized to achieve the desired results. ATRP is no exception.

A. Polymerizations in Nonpolar Solvents. The CuBr/PMDETA catalyst system is heterogeneous in bulk tBA monomer, unlike the analogous methyl acrylate system.¹⁶ This forced us to determine a new set of reaction conditions to use for the polymerization that would provide a reasonable rate of the reaction, controlled experimental molecular weights, and narrow molecular weight distributions. Several parameters were adjusted, including temperature, catalyst concentration, and solvent choice. Table 1 provides detailed information about the different reactions used to determine the optimal conditions for the polymerization.

Initially, lower molecular weights were targeted. Entries 1, 2, and 3 show that although the rate of the reaction decreased with decreasing temperature and catalyst concentration, the high polydispersities indicate poor control over the polymerization. Lowering the temperature further to room temperature while increasing the catalyst concentration to compensate for the rate decrease (entry 4) also did not produce the desired results. Although the molecular weights agree quite well with the theoretical values, the polydispersity is rather high, indicating poor control. Addition of benzene did not help because it does not dissolve the catalyst. Slow initiation in both entries 5 and 6 contributed to the doubled experimental molecular weights when compared to the theoretical values. Targeting higher molecular weights with addition of a small amount of solvent decreased the concentrations of both initiator and catalyst, slowing down the reaction significantly (entry 7). Although the molecular weights agreed well with the theoretical value and the polydispersity was lower, the rate was unacceptably slow. An increase in temperature along with addition of a small amount of CuBr₂ (5% relative to Cu(I)) to moderate the rate seemed to be best for the reaction, producing polymers with controlled molecular weights and low polydispersities in a reasonable amount of time (entry 8). Increasing the concentration of Cu(II) 2-fold did not change the reaction rate, presumably because of a limited solubility of Cu(II) in the reaction mixture (entry 9).

Figure 1 is a semilogarithmic plot for the heterogeneous ATRP of tBA. The polymerization was initiated

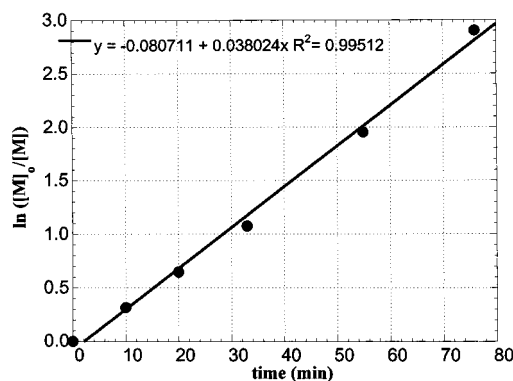


Figure 1. Plot of $\ln([M]_0/[M])$ vs time for ATRP of tBA at 60 °C in 20% *p*-dimethoxybenzene (DMB) with 5% added CuBr₂: $[tBA]_0 = 5.6$ M; $[\text{methyl 2-bromopropionate}]_0 = 0.11$ M; $[CuBr_2]_0 = 56$ mM; $[PMDETA]_0 = 58$ mM; $[CuBr_2]_0 = 2.8$ mM.

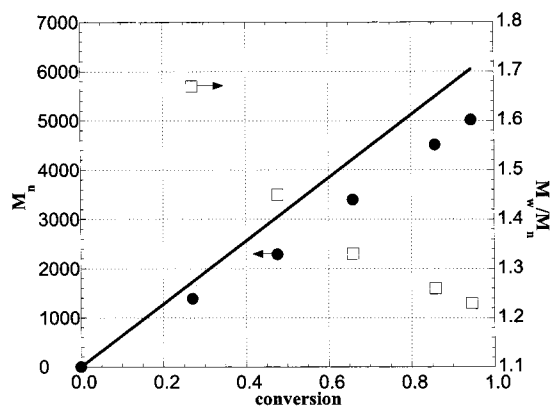


Figure 2. Plot of M_n and M_w/M_n vs conversion for ATRP of tBA at 60 °C in 20% *p*-dimethoxybenzene (DMB) with 5% added CuBr₂: $[tBA]_0 = 5.6$ M; $[\text{methyl 2-bromopropionate}]_0 = 0.11$ M; $[CuBr_2]_0 = 56$ mM; $[PMDETA]_0 = 58$ mM; $[CuBr_2]_0 = 2.8$ mM.

by methyl 2-bromopropionate (MBRP), catalyzed by CuBr/PMDETA, and run at 60 °C in 20% *p*-dimethoxybenzene (DMB) with 5% added CuBr₂ relative to Cu(I). The addition of Cu(II) was necessary to decrease the rate of polymerization and to lower the final polydispersities. The plot of $\ln([M]_0/[M])$ vs time is linear, indicating a constant number of propagating species throughout the reaction. The molecular weights increase linearly with conversion, and the molecular weight distributions decrease with conversion and at the end of the reaction are relatively narrow ($M_w/M_n = 1.23$, Figure 2). These polydispersities are not as low as in an analogous styrene polymerization, perhaps due to the larger rate constants of propagation for acrylate monomers.^{13,29,30}

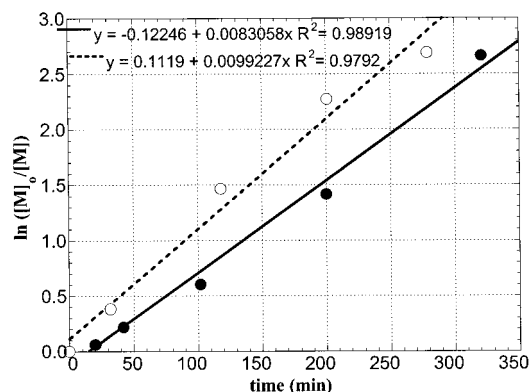


Figure 3. Plot of $\ln([M]_0/[M])$ vs time for ATRP of tBA at 60 °C in 25% acetone (solid circles) and DMF (open circles) with 5% added CuBr_2 : $[\text{tBA}]_0 = 5.2 \text{ M}$; $[\text{methyl 2-bromopropionate}]_0 = 0.11 \text{ M}$; $[\text{CuBr}]_0 = 53 \text{ mM}$; $[\text{PMDETA}]_0 = 56 \text{ mM}$; $[\text{CuBr}_2]_0 = 2.7 \text{ mM}$.

B. Effect of Solvent. The evolution of the narrowing of the molecular weight distribution is rather slow for this reaction. This is attributed to the heterogeneous nature of the catalyst in DMB and the relatively low solubility of the deactivator in solution (supported by the above data in the table showing no rate difference between 5 and 10% added CuBr_2) as well as to the higher k_p .³⁰ In addition to the dependence on the rate constants of propagation and deactivation, the polydispersity is also a function of the concentration of deactivator in solution.²⁹ As this concentration increases, the polydispersity decreases. Equation 1 defines this relationship for a system with fast initiation and deactivation.²⁹

$$M_w/M_n = 1 + \frac{k_p[\text{RX}]_0}{k_d[\text{XCu(II)}]} \left(\frac{2}{p} - 1 \right) \quad (1)$$

Increasing the polarity of the solvent can affect the solubility of the catalyst.^{14,31} Specifically, the use of ethylene carbonate for ATRP of *n*-butyl acrylate¹⁴ or *N,N*-dimethylformamide (DMF) for ATRP of styrene³¹ enhanced the solubility of the both the Cu(I) and Cu(II)/2,2'-bipyridine complexes in the reaction mixture. This idea was extended to ATRP of tBA using the $\text{CuBr}/\text{PMDETA}$ catalyst system. Figure 3 is a plot of $\ln([M]_0/[M])$ vs time for ATRP of tBA using 25% acetone (solid circles) or 25% DMF (open circles) as the solvents. These reactions are homogeneous initially, which means that the concentration of deactivator in solution is higher than in the DMB reaction. The lower rate constants of polymerization for the reactions in acetone (solid circles) and DMF (open circles) compared to the reaction in DMB support this assumption. Figure 4 is a plot of M_n vs conversion for the acetone (solid circles) and DMF (open circles) reactions. The molecular weights increase linearly with conversion. Figure 5 is a comparison plot of M_w/M_n vs conversion for the three reactions. The decrease in the molecular weight distribution is clearly faster, and resulting polydispersities are lower for the reactions run using either acetone (solid circles) or DMF (open circles) rather than DMB (open squares) as the solvent.

Higher molecular weight polymers are also easily achieved with this catalytic system. The addition of CuBr_2 was unnecessary for these reactions. Simply lowering the initiator and catalyst concentrations de-

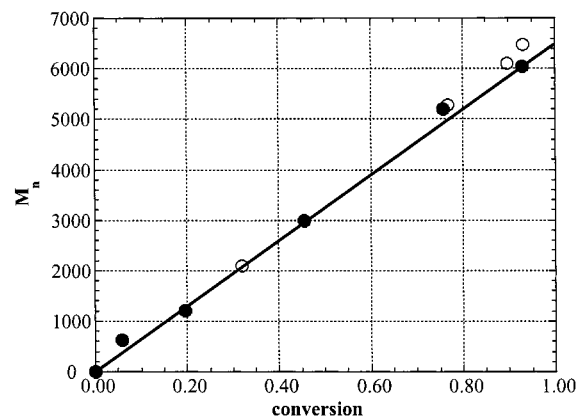


Figure 4. Plot of M_n vs conversion for ATRP of tBA at 60 °C in 25% acetone (solid circles) and DMF (open circles) with 5% added CuBr_2 : $[\text{tBA}]_0 = 5.2 \text{ M}$; $[\text{methyl 2-bromopropionate}]_0 = 0.11 \text{ M}$; $[\text{CuBr}]_0 = 53 \text{ mM}$; $[\text{PMDETA}]_0 = 56 \text{ mM}$; $[\text{CuBr}_2]_0 = 2.7 \text{ mM}$.

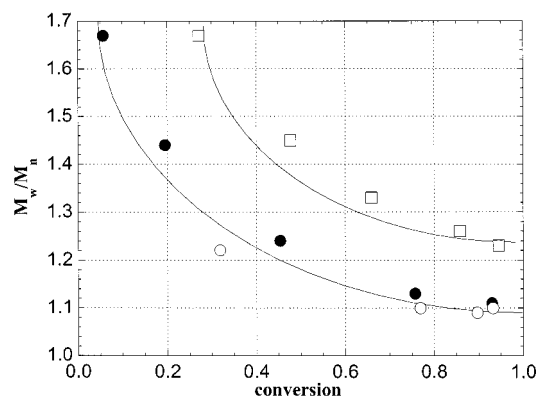


Figure 5. Comparison plot of M_w/M_n vs conversion for ATRP of tBA using 25% acetone (solid circles), 25% DMF (open circles), and 20% *p*-dimethoxybenzene (open squares) at 60 °C using $\text{CuBr}/\text{PMDETA}$ as the catalyst.

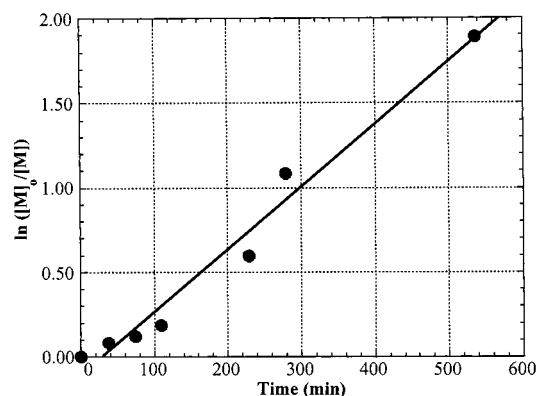


Figure 6. Plot of $\ln([M]_0/[M])$ vs time for ATRP of tBA at 70 °C in bulk: $[\text{tBA}]_0 = 6.8 \text{ M}$; $[\text{methyl 2-bromopropionate}]_0 = 16 \text{ mM}$; $[\text{CuBr}]_0 = 16 \text{ mM}$; $[\text{PMDETA}]_0 = 16 \text{ mM}$.

creased the rate of polymerization enough that the polydispersities were low. Figure 6 is a plot of $\ln([M]_0/[M])$ vs time for a reaction run at a monomer-to-initiator ratio of 400. The consumption of monomer increases linearly with time, indicating a constant number of active species throughout the reaction. Figure 7 shows the molecular weight and polydispersity as a function of conversion for the same reaction. The experimental molecular weights increase linearly up to about $M_n = 20\,000$, and then there is a slight curvature in the growth of the molecular weight with conversion. The

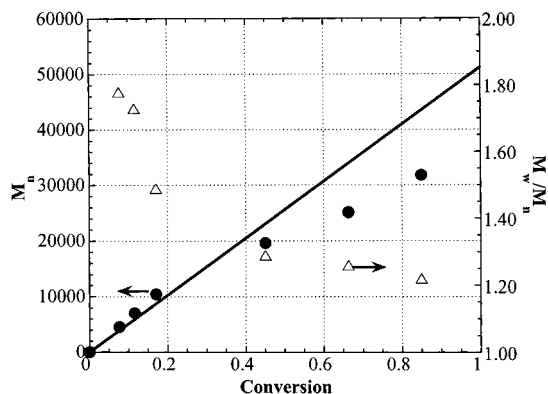
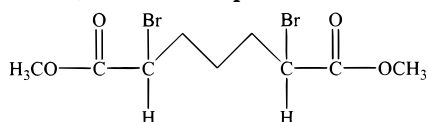


Figure 7. Plot of M_n and M_w/M_n vs conversion for ATRP of tBA at 70 °C in bulk: $[tBA]_0 = 6.8$ M; $[methyl\ 2-bromopropionate]_0 = 16$ mM; $[CuBr]_0 = 16$ mM; $[PMDETA]_0 = 16$ mM.

Scheme 2. Structure of Dimethyl 2,6-dibromoheptanedioate



molecular weight distributions evolve well as the reaction progresses, however, with a final $M_w/M_n = 1.22$, indicating transfer is not causing this deviation. This may suggest that at higher molecular weights differences in the hydrodynamic volumes between the p(tBA) and the linear polystyrene standards may lead to a nonlinear behavior.

C. Difunctional Initiation. A commercially available difunctional initiator, dimethyl 2,6-dibromoheptanedioate (DMDBHD), was also used to initiate ATRP of tBA. The initiator contains two bromine atoms capable of initiating a polymer chain as well as two ester groups, making it similar to the structure of the monomer (Scheme 2). The kinetic plots showed a small induction period initially. Several approaches were used to try to eliminate the induction period, including preparing separate catalyst and initiator solutions as well as vigorous deoxygenation of the initiator solution, but there was no improvement (Figure 8). 1H NMR analysis of the initiator did not show evidence of any impurities. Molecular weights increased linearly with conversion and final molecular weight distributions were low ($M_w/M_n < 1.25$) in all cases (Figure 9).

II. Hydrolysis of p(tBA). In contrast to other poly(alkyl acrylates), which generally have glass transition temperatures below room temperature, the T_g of p(tBA) with a $M_n = 5300$ and a $M_w/M_n = 1.33$ was measured at 36 °C. The polymer is a solid at room temperature and was easily isolated by repeated precipitations into a 50/50 v/v mixture of methanol and water.

The *tert*-butyl ester groups on purified p(tBA) were hydrolyzed using excess HCl in refluxing dioxane for 4–6 h. The resulting 1H NMR in D_2O showed the disappearance of the *tert*-butyl resonance at $\delta = 1.4$ and a shift in the methylene resonances in the backbone due to the presence of the acidic functionality (Figure 10). The acidic proton was not observed in the 1H NMR spectrum, due to exchange with the solvent, but FTIR analysis confirmed the presence of the acidic group. The broad absorbance characteristic of a carboxylic acid group is seen from 2800 to 3600 cm^{-1} , and the carbonyl stretch has shifted slightly, as expected (Figure 11, solid

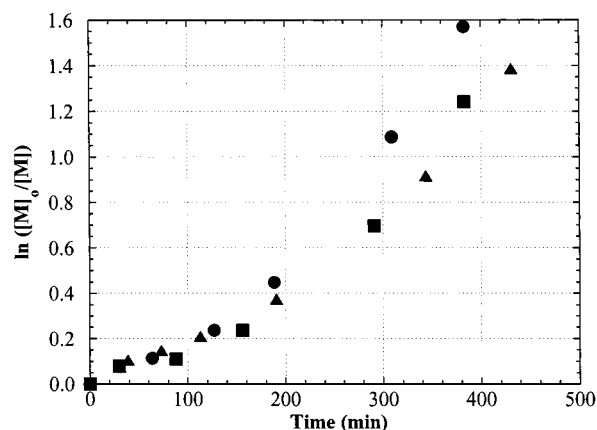


Figure 8. Plot of $\ln([M]_0/[M])$ vs time for ATRP of tBA at 60 °C in bulk: $[tBA]_0 = 6.8$ M; $[dimethyl\ 2,6-dibromoheptanedioate]_0 = 34$ mM; $[CuBr]_0 = 17$ mM; $[PMDETA]_0 = 17$ mM; (●) not separate solutions, (▲) separate initiator and catalyst solutions, (■×a8) separate initiator and catalyst solutions with a vigorous deoxygenation of the initiator solutions.

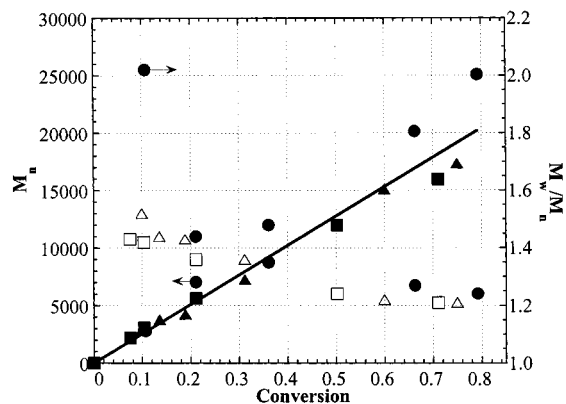


Figure 9. Plot of M_n (closed symbols) and M_w/M_n (open symbols) vs conversion for ATRP of tBA at 70 °C in bulk: $[tBA]_0 = 6.8$ M; $[dimethyl\ 2,6-dibromoheptanedioate]_0 = 34$ mM; $[CuBr]_0 = 17$ mM; $[PMDETA]_0 = 17$ mM; (●, ○×b0) not separate solutions, (▲, △×90) separate initiator and catalyst solutions, (■, □) separate initiator and catalyst solutions with a vigorous deoxygenation of the initiator solutions.

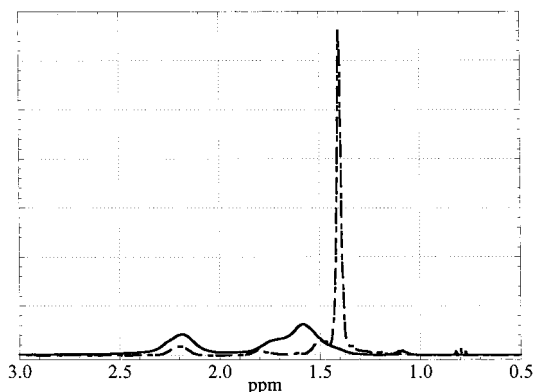


Figure 10. 1H NMR spectra of p(tBA) ($M_n = 5300$, $M_w/M_n = 1.33$) before (dotted line, $CDCl_3$) and after hydrolysis (solid line, D_2O). Both spectra were recorded at room temperature.

line). The original p(tBA) spectrum is shown for comparison (Figure 11, dotted line).

III. Block Copolymerization Using a p(tBA) Macroinitiator. Several block copolymers were prepared using p(tBA) macroinitiators. A bromo-terminated p(tBA) macroinitiator ($M_n = 6900$, $M_w/M_n = 1.19$) was

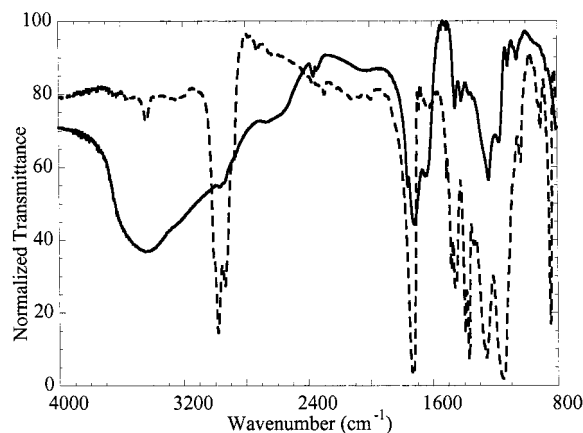


Figure 11. FT-IR of p(tBA) before (dotted line, $M_n = 5300$, $M_w/M_n = 1.33$) and after hydrolysis to poly(AA) (solid line) (both done as KBr pellets).

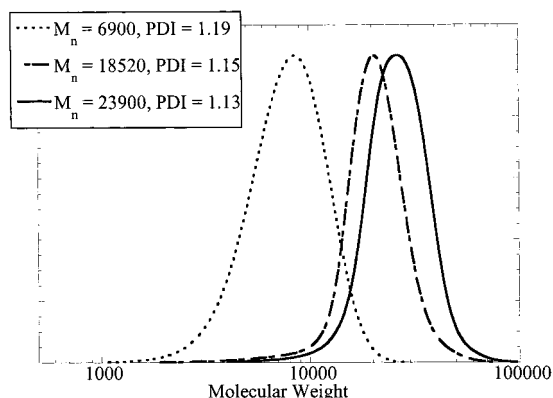


Figure 12. GPC traces of p(tBA) (dotted line), p(tBA)-b-p(St) (dashed line), and p(tBA)-b-p(St)-b-p(tBA) (solid line) in THF.

used to initiate ATRP of styrene using an equimolar amount of the CuBr/PMDETA catalyst system (relative to the number of moles of initiating groups) at 100 °C in bulk. The resulting AB diblock copolymer ($M_n = 18\,520$, $M_w/M_n = 1.15$) was subsequently used to initiate a third block of tBA to prepare an unsymmetric ABA triblock copolymer ($M_n = 23\,900$, $M_w/M_n = 1.13$). The copolymer was then hydrolyzed to yield an amphiphilic block copolymer containing the hydrophobic portion in the middle of the chain. Figure 12 shows the GPC traces of the macroinitiator, the AB diblock copolymer, and the ABA triblock copolymer. Relatively high blocking efficiency was achieved on the basis of the movement of the entire trace to higher molecular weight for each block. Figure 12 also indicates that cross-propagation between p(St) and p(tBA) was efficient regardless of the nature of the end group.

Results from Bednarek et al. indicate that p(tBA) prepared using the CuBr/PMDETA catalyst system will progressively lose functionality with increasing conversion.^{17,18} In their experiments, however, they used a 2–4-fold excess of the amine ligand compared to Cu(I) for the polymerization, as opposed to the one equivalent used in these reactions. This could lead to a side reaction that may eliminate the terminal halide,³² which does not appear to be occurring for the equimolar amount of CuBr:PMDETA. When lower degrees of polymerization of p(tBA) were targeted (DP = 10), the reactions were performed in bulk at a 1:1 ratio of initiator:CuBr, with 0.5 equiv of PMDETA at 60 °C.¹⁷ The reaction reached 80% monomer conversion in 35 min, indicating a

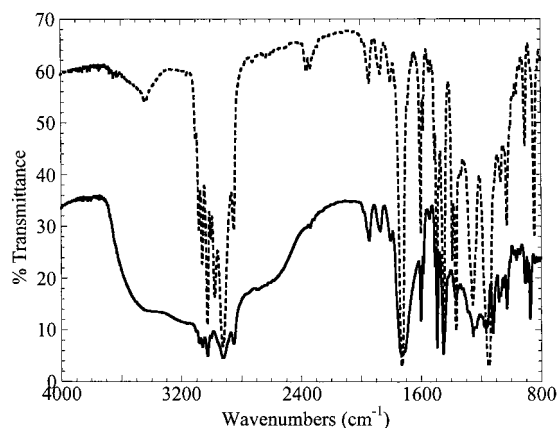


Figure 13. IR spectra of p(tBA)-b-p(St)-b-p(tBA) before (dotted line) and after hydrolysis (solid line) (done as a KBr pellet).

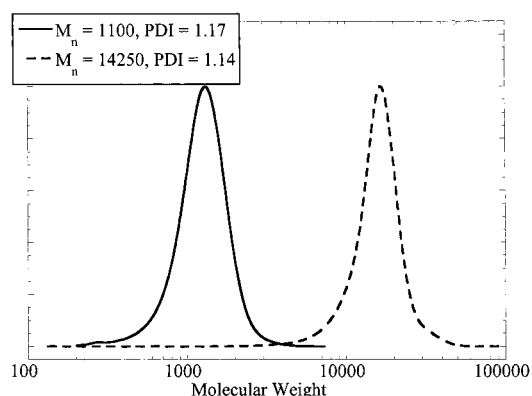


Figure 14. GPC traces of difunctional p(tBA) (solid line) and ABA triblock copolymer p(St)-b-p(tBA)-b-p(St) (dashed line) in THF.

relatively high concentration of radicals and excess termination. In addition, the CuBr/PMDETA complex is heterogeneous in tBA, especially at this high catalyst concentration. This could also promote the elimination reaction if uncomplexed ligand is present in solution. As demonstrated here, choosing the proper conditions for the polymerizations can prevent this elimination reaction and allow the preparation of block copolymers with a high degree of blocking efficiency.

Figure 13 shows the IR spectra of the ABA triblock copolymer before and after hydrolysis. The peaks observed between 2800 and 3200 cm^{-1} are due to both the p(St) and the p(tBA) blocks. After hydrolysis, the acid functionality is clearly visible as the broad absorbance from 2800 to 3800 cm^{-1} . The ^1H NMR shows complete disappearance of the *tert*-butyl resonance, as in the homopolymer spectra shown in the preceding section. These copolymers have some interesting solubility properties. The p(St) portion makes the copolymer insoluble in water. The poly(acrylic acid) portion causes the polymer to swell in chloroform, and both blocks are soluble in pyridine, the solvent chosen for ^1H NMR analysis.

In addition, difunctional p(St) prepared using DMD-BHD ($M_n = 1100$, $M_w/M_n = 1.17$) was used as a macroinitiator for block copolymerization with tBA ($M_n = 14\,250$, $M_w/M_n = 1.14$) to prepare a symmetric ABA triblock copolymer in two steps rather than three. Again, the GPC traces indicate a high blocking efficiency with no remaining macroinitiator (Figure 14). Anal-

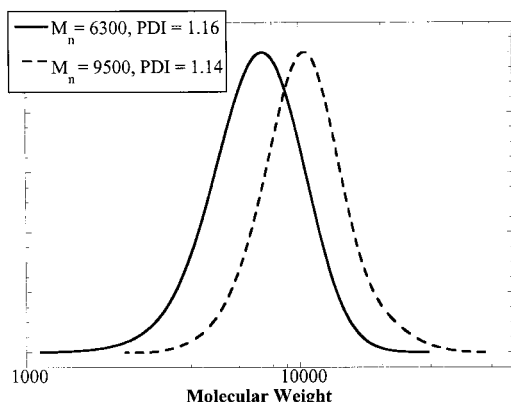


Figure 15. GPC traces of difunctional p(St) (solid line) and ABA triblock copolymer p(tBA)-b-p(St)-b-p(tBA) (dashed line) in THF.

Table 2. Results of Block Copolymerizations

entry	macroinitiator	monomer	$M_{n, \text{expt}}^g$	M_w/M_n
1	p(tBA) ^a	MA ^b	15 720	1.11
2	p(tBA) ^a	DMAEMA ^c	20 800	1.30
3	p(tBA) ^d	St ^e	18 150	1.11
4	p(tBA)-b-p(St)	MA ^f	24 790	1.10

^a $M_n = 6890$, $M_w/M_n = 1.19$. ^b Ratio of M:I:Cu:L = 200:1:0.5: 0.5, bulk, 70 °C. ^c Ratio of M:I:Cu:L = 200:1:1:1, 50% anisole, 90 °C. ^d $M_n = 7300$, PDI = 1.11. ^e Ratio of M:I:Cu:L = 100:1:1:1, bulk, 100 °C. ^f Ratio of M:I:Cu:L = 400:1:1:1, bulk, 70 °C. ^g Determined against linear PSt standards.

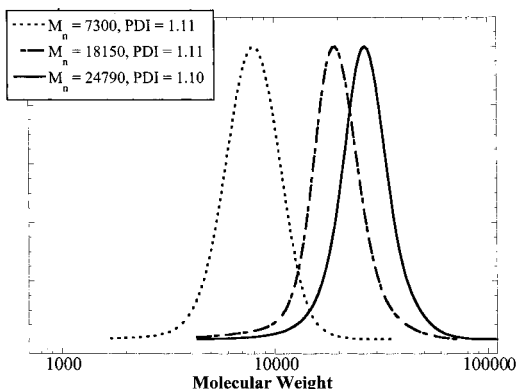


Figure 16. GPC traces of p(tBA) (dotted line), p(tBA)-b-p(St) (dashed line), and p(tBA)-b-p(St)-b-p(MA) (solid line), taken in THF.

gously, difunctional p(tBA) was synthesized ($M_n = 6300$, $M_w/M_n = 1.16$) and used to initiate ATRP of styrene ($M_n = 9500$, $M_w/M_n = 1.14$) to prepare an ABA triblock copolymer with the alternate order of blocks (Figure 15).

Block copolymers were also prepared using a monofunctional p(tBA) macroinitiator with poly(methyl acrylate) (MA) and poly((dimethylamino)ethyl methacrylate) (DMAEMA). Both reactions were successful, and the resulting polymers had molecular weights that were close to the theoretical values with low polydispersities. The reaction conditions used for the chain extension of p(tBA) with MA were similar to those used for the synthesis of higher molecular weight p(tBA). For the chain extension with DMAEMA, previous work by Zhang and Matyjaszewski showed that utilizing a mixed halogen system enhanced initiation over propagation, resulting in a higher blocking efficiency.³³ Table 2 (entries 1 and 2) provides the details about these reactions.

A bromo-terminated p(tBA)-b-p(St) diblock copolymer was also used to initiate ATRP of methyl acrylate to make an ABC triblock copolymer by controlled radical polymerization (Table 2, entries 3 and 4). The GPC traces of the macroinitiator, diblock copolymer, and triblock copolymer are shown in Figure 16. All the blocks were prepared using the CuBr/PMDETA catalyst system had controlled molecular weights and low polydispersities. ¹H NMR analysis in CDCl₃ indicated a composition of 30% p(tBA), 53% p(St), and 18% p(MA).

Conclusions

tert-Butyl acrylate was successfully polymerized using the CuBr/*N,N,N',N'',N''*-pentamethyldiethylenetriamine catalyst system with both monofunctional and difunctional alkyl halide initiators. Polymers with various molecular weights and narrow molecular weight distributions were prepared. For lower molecular weights, the addition of small amounts of Cu(II) decreased the rate of polymerization and lowered the polydispersities of the final polymers. In addition, increasing the polarity of the solvent lowered the polydispersities further by increasing the concentration of deactivator in solution. Hydrolysis of the *tert*-butyl ester group provided poly(acrylic acid). Several block copolymers were synthesized using both monofunctional and difunctional poly(*tert*-butyl acrylate) as the macroinitiator. Upon hydrolysis, amphiphilic block copolymers resulted. Finally, an AB diblock copolymer of poly(*tert*-butyl acrylate)-b-poly(styrene) was used to initiate ATRP of methyl acrylate to afford an ABC triblock copolymer.

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