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Facile Synthesis of ABC and CBABC Multiblock Copolymers of Styrene, *tert*-Butyl Acrylate, and Methyl Methacrylate via Room Temperature ATRP of MMA

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ABSTRACT: A detailed investigation of the atom transfer radical polymerization of methyl methacrylate (MMA) with the ethyl 2-bromoisobutyrate (2-EiBBr)/CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) catalyst system in anisole was performed at 30 °C. The number-average molecular weight of the PMMA was observed to increase gradually and linearly while the polydispersity index (PDI) remained narrow throughout the reaction time. The summary of these studies showed that PMMA with molecular weight up to 10^5 g/mol could be synthesized in a controlled fashion at room temperature. The new route developed was utilized to demonstrate the facile synthesis of ABC and CBABC multiblock copolymers of styrene, *tert*-butyl acrylate (tBA), and MMA. For this, the starting blocks of AB and BAB were synthesized by coupling different ATRP methods reported. The end-block consisting of PMMA was synthesized by the ATRP of MMA using the CuCl/PMDETA catalyst system (halogen exchange) with anisole as the solvent at room temperature. Gel permeation chromatography (GPC) was used to determine the M_n, M_w, and PDI of the polymers synthesized. The PDI of all the block copolymers is found to be low (1.1−1.4). ^{1}H NMR spectroscopy was used to determine the chemical composition of the block copolymers. Additional evidence for the blocky nature was also gained from FT-IR and thermal analysis.

Introduction

The recent experiments on block copolymers with three or more distinct types of blocks (ABC or ABCBA)[1,2] have revealed new exciting morphologies such as core−shell gyroid morphology,[3] unique knitting pattern,[4] and banana morphology.[5] This is due to the phase behavior of ternary systems, which is governed by two independent composition variables (f_A, f_B) and three interaction parameters (χ_{AB}, χ_{AC}, χ_{BC}), leading to richer phase diagrams. The experimental discovery of new morphologies in ternary systems has received considerable attention, not only from theoreticians[6] (to account for the domain shapes, dimensions, connectivity, and ordered symmetry) but also from experimentalists who are interested in studying phase transitions.[3] In contrast to block copolymers with two different monomers, the morphology of the ternary system is influenced not only by the overall molecular weight, the mole fraction of each of the block, and temperature but also by the sequence of the blocks,[7,8] chemical modification of one block,[4] and the solvent.[9] The ternary block copolymers can simultaneously exhibit different features in the microphase-separated state[10] (e.g., a lamella−cylinder combination phase, a lamella−sphere combination phase, etc.), which often have characteristics of one-, two-, and three-dimensional order simultaneously and can exhibit unique mechanical properties. Nanoporous polymeric materials with ultralow dielectric constants templated after these morphologies are also expected to have unusual electronic and transport properties.

In contrast to diblock copolymers, systematic studies on ternary systems (styrene−, butadiene/isoprene−, vinylpyridine−, methacrylate−, and PDMS) have been limited to those that can be polymerized either by anionic[11] or by group transfer polymerization.[12] The use of controlled radical polymerizations[13] [nitroxide-mediated radical polymerization (NMP) or atom transfer radical polymerization (ATRP) or reversible addition−fragmentation chain transfer (RAFT)] is proven to be an effective and more versatile method to prepare well-defined polymeric materials under mild conditions. ATRP[14−18] and RAFT[19] have been used to synthesize triblock copolymers. In contrast to other controlled radical polymerizations, ATRP[20] is known to impart good control on the polymerization of styrenic, acrylic, and methacrylic monomers. Few multiblock copolymers and especially triblock copolymers have been synthesized using ATRP techniques. Matyjaszewski and coworkers have demonstrated the ability of ATRP to prepare multiblock copolymers.[14,16] ABC triblock copolymers of poly(tBA-*b*-styrene-*b*-methyl acrylate)[15,16] and ABCBA multiblock copolymer of poly(4-vinylpyridine-*b*-MMA-*b*-tBA-*b*-MMA-*b*-4-vinylpyridine)[16] have been reported. The synthesis of an ABC triblock copolymer of poly(tBA-*b*-methyl acrylate-*b*-styrene)[17] using ATRP methods was also reported recently. Multiblock copolymers of methyl methacrylate and styrene were synthesized with broad molecular weight distribution regardless of the monomer sequence by ATRP.[18]

In recent years, there has been increasing interest in ATRP of hydrophobic[21−23] and hydrophilic[24] monomers at ambient temperature. Polymerization at lower temperature would have several advantages: spontaneous thermal polymerization and other side reactions are suppressed/eliminated. Lower polymerization temperatures can lead to better control over the polymerization reaction, which in turn can enable the facile synthesis of well-defined polymers. Haddleton et al.[21] described the relatively slow bulk polymerization of methyl methacrylate at 25 °C. In contrast, Matyjaszewski and coworkers[22] reported the rapid bulk polymerization of acrylates at 22 °C. In the latter case it was shown that

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the choice of ligand for the copper catalyst was critical for efficient polymerization. The ligands (*N*-alkyl-2-pyridylmethanimine[21] and Me_6[TREN][22]) used in the above studies should be synthesized especially for this purpose. It has also been demonstrated[25,26] that solvent polarity can be an important parameter in ATRP. Thus, the rate of polymerization of *n*-butyl acrylate in ethylene carbonate[25] and benzyl methacrylate in 1,2-diethoxyethane[26] showed an enhanced rate of polymerization compared to polymerization in the bulk or nonpolar/noncoordinating solvents. The increase in rate was ascribed to the solvation of the metal center, which results in a more active catalyst.[25,26] The facile synthesis of well-defined water-soluble polymers[24] and copolymers[27,28] via ATRP of water-soluble acrylate monomers in aqueous media at ambient temperature has also been reported. While this technique is useful for the preparation of water-soluble polymers and copolymers, it cannot be used to prepare hydrophobic polymers and copolymers. Thus, either the available ambient temperature ATRP polymerization routes require the synthesis of new ligands[21−23] or it is limited to hydrophilic monomers[24,27,28] with the degree of polymerization studied in the range 100−500.

In this paper, we describe a simple method toward the synthesis of PMMA of relatively high molecular weight (10^5 g/mol) and relatively narrow PDI at room temperature and successfully demonstrate its utility toward the synthesis of ABC and CBABC multiblock copolymers starting from AB and BAB macroinitiators consisting of styrene and tBA as outlined in Scheme 1 and Scheme 2. Earlier, we had reported on the utility of this method toward the room temperature polymerization of MMA as well as block copolymers consisting of MMA, initiated from a silicon wafer surface to which a ATRP initiating moiety was anchored.[29] FT-IR, NMR, TGA, and GPC are used to characterize the block copolymers synthesized. To the best of our knowledge, the polymerization temperature reported here is the lowest for synthesizing multiblock copolymers based on organic soluble monomers by ATRP. Further, this work represents the first preparation of poly(styrene-*b*-tBA-*b*-MMA) and poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) multiblock copolymers in the sequence of styrene to acrylate to MMA by ATRP.

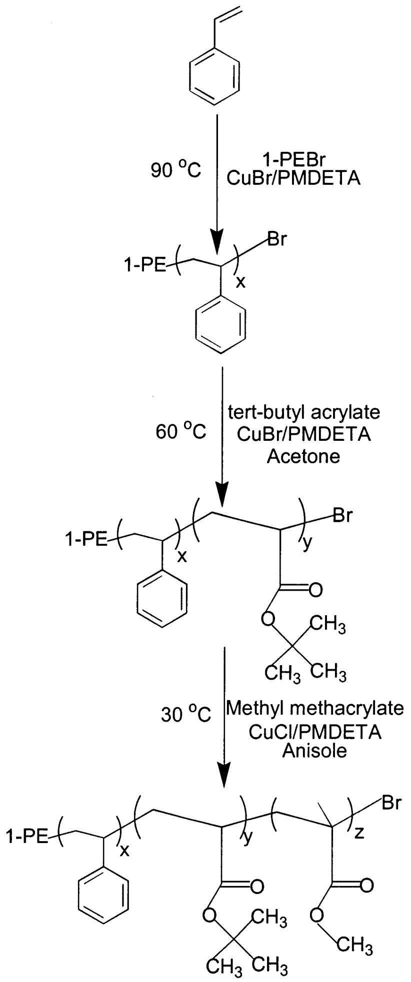
Experimental Section

1. Materials. Styrene (Fluka, ≥99.5%) and MMA (Fluka, ≥99.5%) were purified using an alumina column, distilled under reduced pressure from CaH_2, and stored under nitrogen at −20 °C. tBA (Fluka, ~ 99%) was rinsed with 5% NaOH and water in that order and dried over $CaCl_2$. It was then distilled under reduced pressure from $CaCl_2$ and stored under nitrogen at −20 °C. CuBr (98%), CuCl (98+%), PMDETA (99%), dimethyl 2,6-dibromoheptanedioate (DMDBHD, 97%), 1-phenylethyl bromide (1-PEBr, 97%), ethyl 2-bromoisobutyrate (2-EiBBr, 98%), anisole (99.7%), trifluoroacetic acid (TFA, 99+%), and DOWEX MSC-1 macroporous ion-exchange resin (20−50 mesh) were obtained from Aldrich and used without further purification. Acetone (≥99.5%), tetrahydrofuran (THF, ≥99.8%), methanol (technical grade), and hexane (technical grade) purchased from Fluka were used without further purification. Water was distilled twice before use.

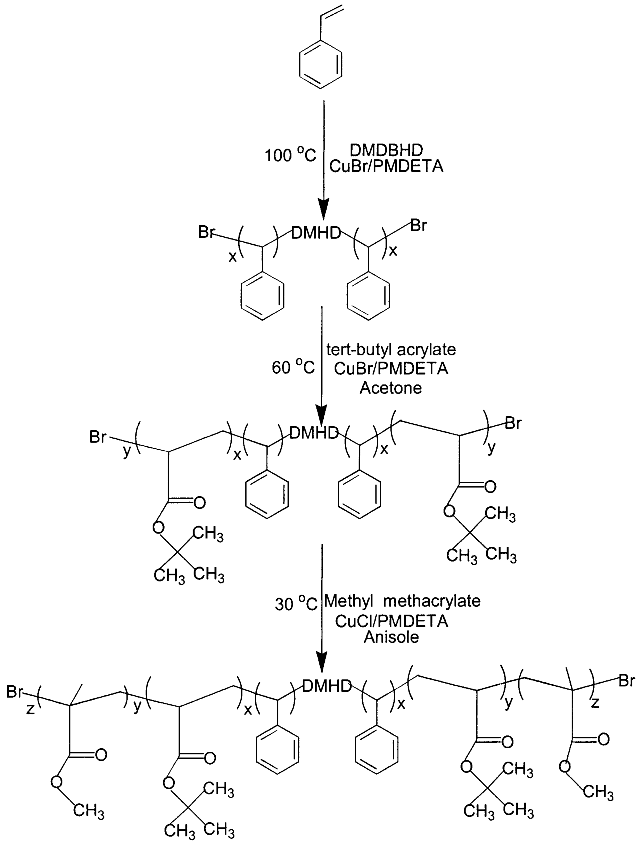
2. Methods. The FT-IR spectra of the polymers cast as a film from dichloromethane on a NaCl window (KBr pellet was prepared in the case of poly(acrylic acid)) were recorded using a Biorad Excalibur (U.S.A.) and JASCO FT-IR 410 (Japan) spectrometer at a resolution of 4 cm^{-1}. NMR spectra were recorded using a 250 MHz (for ^1H) Bruker Avance 250 (Germany) as well as 400 MHz (for ^1H) JEOL GSX-400 FT (Japan) spectrometer using deuterated solvents. GPC analysis was performed at room temperature using a Agilent GPC 1100 [Germany; Agilent pump equipped with Agilent 1100 series autosampler, three Polymer Standard Service 5 μm columns (8 × 300 mm) in series (guard column, two 100 Å and one 1000 Å columns of 8 × 300 mm) with a Agilent 1100 series RI detector]. Toluene (0.1 μL) was used as a flow marker. THF was used as the eluent at a flow rate of 1.0 mL/min. 0.2 wt % solutions of the polymer in THF (the polymer solutions were purified with alumina and DOWEX MSC macroporous ion-exchange resin to remove the residual copper complex before GPC analysis) were used for the measurements. Molecular weights were calculated with PSS software (PSS WinGPC scientific V 6.10) against linear low-polydispersity polystyrene (PS) as well as PMMA standards. However, the data measured with respect to PS standards alone are presented here. Thermal analysis was performed using a Mettler Toledo STAR^e (Switzerland) thermal analysis system between ambient and 800 °C at a heating rate of 20 °C/min under a flowing nitrogen atmosphere.

3. Polymerization Procedures. 3.1. Preparation of Monofunctional Bromo-Terminated Polystyrene. A Schlenk tube equipped with a 24/40 ground glass joint opening and a sidearm with a two-way stopcock (for gas flow regulation) was used in all the polymerizations. At first a magnetic stir bar was slid into the dry Schlenk tube, which was followed by the addition of CuBr (2.5 g, 1.7 × 10^{-2} mol) under a stream of dry nitrogen gas. The opening of the Schlenk tube was then sealed with the appropriate ground glass stopper, following which it was evacuated and back-filled with nitrogen three times. Following this deoxygenated styrene (40 mL, 3.5 × 10^{-1} mol) and PMDETA (3.0 g, 1.7 × 10^{-2} mol) were added via

Scheme 1



Scheme 2



gastight syringes (that had been previously purged with nitrogen) through the 24/40 opening under nitrogen flow. The mixture was stirred until a homogeneous solution of light green color was obtained (indicates the formation of the copper complex). After this, 1-PEBr (3.2 g, 1.7×10^{-2} mol) was added to the flask via the 24/40 opening under a stream of nitrogen. This mixture was carefully degassed through several freeze−thaw cycles to remove any dissolved oxygen, and the polymerization was carried out at 90 °C in an oil bath maintained at this temperature. Maximum yield: 95%.

3.2. Preparation of α,ω-Difunctional Bromo-Terminated Polystyrene.[30] A dry Schlenk tube (as used in the preparation of PS) equipped with a stir bar was charged with CuBr (2.5 g, 2.5×10^{-3} mol) under a flowing stream of nitrogen. It was then sealed with a ground glass stopper and was degassed and back-filled with nitrogen three times. Following this, deoxygenated styrene (30 mL, 2.6×10^{-1} mol) and PMDETA (2.5 g, 2.5×10^{-3} mol) were added via gastight syringes (that had been previously purged with nitrogen) through the 24/40 opening under nitrogen flow. The mixture was stirred until the formation of an essentially homogeneous solution. After this, DMDBHD (4.51 g, 1.3×10^{-2} mol) was added to the flask via the 24/40 opening under a stream of nitrogen. This mixture was carefully degassed through several freeze−thaw cycles to remove any dissolved oxygen, and the polymerization was carried out at 100 °C in an oil bath maintained at this temperature.

3.3. Purification[16] and Characterization of Polystyrene Macroinitiator. The product(s) obtained was diluted with acetone, stirred with DOWEX MSC macroporous ion-exchange resin for 5 min, and then filtered using Whatman filter paper. The filtrate was stirred with alumina until it turned colorless, filtered again, and then concentrated. The polymer was recovered from the filtrate by precipitating into excess methanol. The recovered polymer was redissolved in diethyl ether and precipitated using excess methanol twice, as reported before.[16] Finally, it was dried under vacuum (50 mTorr) for 12 h. GPC and NMR spectroscopy were used to characterize the polystyrene synthesized. Yield = 95%. ^{1}H NMR ($CDCl_3$) δ: 0.8−3.0 (broad m, $-CH_2$, −CH backbone protons and protons from the initiator), 4.1−4.6 (broad m, proton adjacent to the bromine end group), and 6.2−7.4 (m, aromatic protons from the initiator and polystyrene).

3.4. Polymerization of Methyl Methacrylate at Room Temperature. MMA polymerization was carried out in a Schlenk tube similar to the one employed in the polystyrene preparation. All MMA polymerizations were carried out in 50 vol % anisole solution at 30 °C (a few polymerizations were also performed at 90 °C). In a typical experiment, a dry Schlenk tube equipped with a magnetic stir bar was charged with CuBr (26 mg, 4.6 mmol) and was sealed with a ground glass stopper. It was subjected to evacuation followed by nitrogen filling as before. Following this, deoxygenated anisole and PMDETA (32 mg, 4.6 mmol) were added via gastight syringes (that had been previously purged with nitrogen) under a stream of nitrogen. Following the formation of a green homogeneous solution, MMA (18.5 g, 4.62 mol) was added via a gastight syringe under a stream of nitrogen. Finally, the initiator 2-EiBBr (35 mg, 4.6 mmol) was added via a gastight syringe under a stream of nitrogen, and the reaction vessel was sealed with the stopper. The polymerization mixture was carefully degassed through several freeze−thaw cycles to remove any dissolved oxygen and was placed in an oil bath maintained at 30 °C. The monomer conversion was determined from the amount of PMMA precipitated in hexane as a function of time. (The recovered polymer was weighed after drying for 24 h under high vacuum. The catalyst residue was taken into account in the calculation of monomer conversion.)

4. Block Copolymerizations. 4.1. Preparation of Poly(styrene-*b*-tBA). A dry Schlenk tube (as used in the homopolymerization experiments) equipped with a stir bar was charged with CuBr under a flowing stream of nitrogen. It was then sealed with a ground glass stopper and was degassed and back-filled with nitrogen three times. After this, bromo-terminated polystyrene was added to the Schlenk tube through the 24/40 opening under a stream of nitrogen. Deoxygenated acetone and tBA were added via gastight syringes (previously purged with nitrogen) under a stream of nitrogen. PMDETA was introduced via a gastight syringe under a stream of nitrogen. Upon the formation of a homogeneous solution (green in color) the reaction vessel was sealed with the stopper and was carefully degassed through several freeze−thaw cycles to remove any dissolved oxygen. Finally, the block polymerization was carried out at 60 °C in an oil bath maintained at this temperature for the desired time period as given in Table 1. Maximum yield: 68%.

4.2. Preparation of Poly(tBA-*b*-styrene-*b*-tBA). Poly(tBA-*b*-styrene-*b*-t-BA) was prepared using the same procedure as that used for poly(styrene-*b*-t-BA) except that α,ω-bromo-terminated poly(styrene) was used as the initiator. Maximum yield: 52%.

4.3. Purification and Characterization of the Diblock and Triblock Copolymers (AB and BAB) of Styrene and tBA. The procedure followed for purification of the block copolymers was the same as that described for homopolymers except that the nonsolvent used in this case was 1:1 v/v mixture of deionized water and methanol. IR (film, CH_2Cl_2) ν: 3024 (aromatic −C−H), 2976 (*tert*-butyl-C−H), 2929 (backbone −C−H), 1728 (ester −C=O), 1601 (aromatic −C=C), 1367 (*tert*-butyl-C−H), and 700 cm^{-1} (−C−H out-of-plane deformation of benzene ring). ^{1}H NMR ($CDCl_3$) δ: 1.5 (s, CH_3 *tert*-butyl), 1.9 and 2.2 (broad. $-CH_2$, −CH backbone protons), and 6.2−7.3 (m, aromatic protons from the initiator and the phenyl ring). ^{13}C NMR ($CDCl_3$) δ: 28, 37, 42 (backbone $-CH_3$, $-CH_2$, and −CH), 126, 128 (aromatic carbon from polystyrene), and 174 (−C=O). The TGA of the block copolymers showed two principal decompositions around 270 and 450 °C corresponding to tBA and polystyrene blocks.

4.4. Preparation of Styrene, tBA, MMA, and Triblock Copolymer (**ABC**)**.** The triblock copolymer preparation was also performed using a Schlenk tube similar to the one employed previously. At first, a magnetic stir bar was slid into the dry Schlenk tube following which CuCl was transferred under a stream of dry nitrogen gas. The opening of the Schlenk

Table 1. Summary of the Experimental Condition and Results Obtained from Block Copolymerization

experiment	macroinitiator	monomer	t (h)	M_n (SEC)	PDI	composition (mol % of S:tBA:MMA) from ^{1}H NMR
AB1[d]	p(St)Br[a]	tBA	26	15 200	1.12	20:80
AB2[d]	p(St)Br[a]	tBA	24	13 600	1.10	23:77
AB3[d]	p(St)Br[a]	tBA	8	4 200	1.31	49:51
AB4[e]	p(St)Br[b]	tBA	15	9 540	1.12	27:73
AB5[e]	p(St)Br[b]	tBA	6	4 400	1.19	43:57
AB6[f]	p(St)Br[b]	tBA	13	5 900	1.19	36:64
BAB1[g]	$p(St)_2Br$[c]	tBA	14	8 900	1.11	18:82
BAB2[g]	$p(St)_2Br$[c]	tBA	20	11 400	1.10	19:81
ABC1[h]	p(St-*b*-tBA)Br	MMA	14	47 700	1.40	5:16:79
ABC2[i]	p(St-*b*-tBA)Br	MMA	14	58 800	1.39	3:13:84
CBABC1[j]	p(St)-b-$[p(tBA)]_2$Br	MMA	14	38 400	1.34	4:12:84
CBABC2[j]	p(St)-*b*-$[p(tBA)]_2$Br	MMA	20	47 500	1.37	1:11:88

[a] Styrene:1-PEBr:CuBr:PMDETA = 20:1:1:1, bulk, T = 90 °C, time = 60 min, M_n(GPC) = 2100 and M_n(NMR) = 2500, M_w/M_n = 1.08. [b] Styrene:1-PEBr:CuBr:PMDETA = 20:1:1:1, bulk, T = 90 °C, time = 60 min, M_n(GPC) = 1900 and M_n(NMR) = 2200, M_w/M_n = 1.08. [c] Styrene:DMDBHD:CuBr:PMDETA = 20:1:0.2:0.2, bulk, T = 100 °C, time = 100 min, M_n(GPC) = 1300 and M_n(NMR) = 1600, M_w/M_n = 1.08. [d] tBA:p(St)Br[a]:CuBr:PMDETA = 83:1:0.5:0.5, 25% acetone, T = 60 °C. [e] tBA:p(St)Br[b]:CuBr:PMDETA = 72:1:0.5:0.5, 25% acetone, T = 60 °C. [f] tBA:p(St)Br[b]:CuBr:PMDETA = 36:1:0.5:0.5, 25% acetone, T = 60 °C. [g] tBA: p $(St)_2Br$[c]:CuBr:PMDETA = 94:1:0.5:0.5, 25% acetone, T = 60 °C. [h] MMA:AB2:CuCl:PMDETA = 513:1:1:1. [i] MMA:AB2:CuCl:PMDETA = 1000:1:1:1. [j] MMA:BAB2:CuCl:PMDETA = 982:1:1:1.

tube was then sealed with the appropriate ground glass stopper, following which it was evacuated and back-filled with nitrogen three times. Subsequently, bromo-terminated poly(styrene-*b*-tBA) diblock copolymer (AB) and degassed anisole were introduced under a stream of nitrogen. PMDETA was then added under nitrogen, and the mixture was stirred until a homogeneous solution (green color) was obtained. MMA monomer, previously purged with nitrogen, was then added via a gastight syringe, and the reaction vessel was sealed with the stopper. The polymerization mixture was carefully degassed through several freeze−thaw cycles and was placed in an oil bath maintained at 30 °C for the desired time period (details given in Table 1). After the desired time period the polymer solution was diluted with dichloromethane, stirred over alumina for 5 min, and filtered. The filtrate was concentrated, and the polymer was precipitated using excess hexane as the nonsolvent. It was then dried under dynamic vacuum (50 mTorr) for 12 h. Maximum yield: 40%. IR (film, CH_2Cl_2) ν: 3057 (aromatic-C−H), 2993 (asym C−H), 2950 (sym −C−H, PMMA), 1730 (−O−C=O), 1602 (aromatic C=C), and 702 cm^{-1} (aromatic −C−H out-of-plane def). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.6, (s, *tert*-butyl), 1.1, 1.2, and 2.0−2.4 (m, backbone CH, CH_2 protons), 3.8 (s $-OCH_3$, PMMA) and 6.3−7.5 (m, aromatic H, polystyrene). TGA (maximum decomposition) = 270 and 420 °C.

4.5. Preparation of MMA, tBA, and Styrene Pentablock Copolymer (CBABC). The preparation and purification of CBABC block copolymers were similar to the one described for the ABC triblock copolymer except that the initiator used was α,ω-bromo-terminated poly(tBA-*b*-styrene-*b*-tBA) triblock copolymer (BAB). The details of the preparation are given in Table 1. Maximum yield: 40%. IR (film, CH_2Cl_2) ν: 2981 (asym −C−H), 2950 (asym −C−H, PMMA), and 1730 cm^{-1} (−O−C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.6, (s, *tert*-butyl), 1.1, 1.2, and 2.0−2.4 (m, backbone CH, CH_2 protons), 3.8 (s, $-OCH_3$, PMMA), and 6.3−7.5 (m, aromatic H, polystyrene). TGA (maximum decomposition) = 270 and 420 °C.

5. Hydrolysis of the Poly(tBA).[17] A dry 100 mL round-bottom flask fitted with a stir bar was charged with the respective block copolymer, which was then dissolved in dichloromethane. Trifluoroacetic acid (TFA) (5-fold molar excess when compared to the concentration of *tert*-butyl ester group) was then added, and the mixture was stirred at room temperature for 24 h. In the case of the di- and triblock copolymers (AB and BAB) of styrene and tBA the product of hydrolysis separates out of the solvent. It was then filtered, rinsed with dichloromethane, and thoroughly dried (light brown in color). In the case of ter- and pentablock copolymers the product of hydrolysis was soluble in dichloromethane. Therefore, in this case, after 24 h of reaction, the dichloromethane solution was concentrated at room temperature, and the viscous concentrate was precipitated in excess hexane. The glassy light brown solid was then rinsed well with hexane and dried under vacuum. The hydrolysis of copolymers was confirmed by FT-IR and TGA analysis.

Results and Discussion

The two important factors in the synthesis of well-defined block copolymers by ATRP are (1) the reactivity of the chain end-functionality and (2) the cross-propagation efficiency,[16] which can be achieved by a careful choice of suitable catalytic system and the order of block copolymer synthesis as well as by selecting different synthetic methodologies (i.e., halogen-exchange technique[31]). The facile syntheses of poly(styrene-*b*-tBA-*b*-MMA) (ABC) and poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) (CBABC) were carried out by using a copper halide as the transition-metal catalyst and PMDETA as the complexing ligand. Different polymerization conditions such as a couple of different reaction mediums and halogen exchange were utilized to achieve the desired well-defined block copolymers. The terpolymer and pentablock copolymer were synthesized in three steps. In the first step, monofunctional and bifunctional bromine-terminated polystyrene were synthesized.[16,30] In the second step AB and BAB block copolymeric macroinitiators were synthesized. Finally, the newly developed room temperature copolymerization of MMA with the AB diblock and the BAB triblock copolymer resulted in the desired multiblock copolymers. As a first step, the kinetics of MMA polymerization at room temperature was studied. The GPC analysis of the homopolymers and block copolymers synthesized revealed the molecular weight characteristics and the blocking efficiency. ^{1}H NMR analysis was used to determine the composition of the resulting polymers.

ATRP of Methyl Methacrylate: Kinetic Results. MMA polymerization was carried out in anisole using a CuBr/PMDETA catalytic system. 2-EiBBr was used as the initiator, and the polymerization was carried out at 90 °C as reported in the literature.[32] Polymerization at 90 °C resulted in a conversion of 70% within 90 min. The number-average molecular weight evaluated by GPC was 72 000, and the PDI was 1.12 (data not shown). After 90 min, an increase in molecular weight distribution was observed, indicating the significance of the side reaction beyond 90 min. The first-order

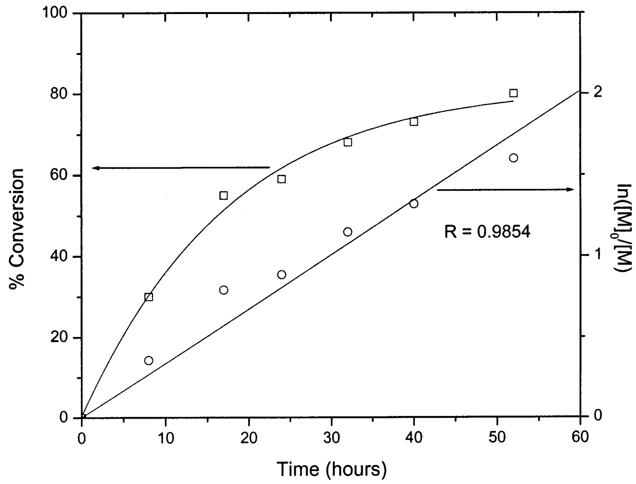


Figure 1. Conversion vs time plot for the ATRP of MMA at 30 °C (50% anisole, MMA:2-EiBBr:CuBr:PMDETA = 1000:1:1:1).

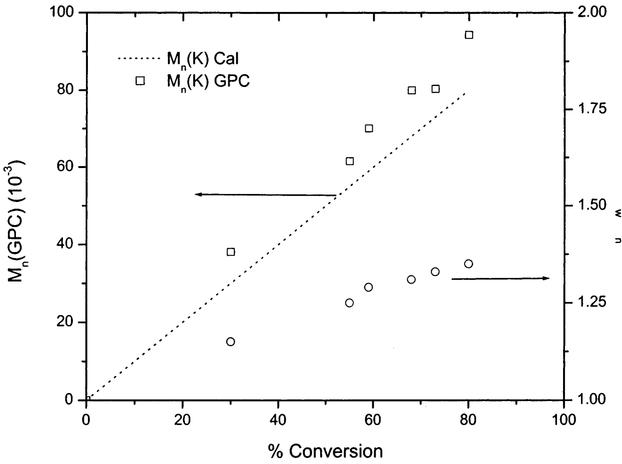


Figure 2. M_n and PDI vs monomer conversion for the ATRP of MMA at 30 °C (50% anisole, MMA:2-EiBBr:CuBr:PMDETA = 1000:1:1:1).

kinetic plot showed a significant curvature (Supporting Information) consistent with the observation of Matyjaszewski and co-workers.[32] The rapid increase in MMA conversion prompted us to investigate the system further to achieve PMMA with controlled molecular weights and narrow molecular weight distributions. Several parameters can be varied (temperature, catalyst concentration, and solvent) to achieve controlled radical polymerization. The polymerization at ambient temperature was observed to result in controlled radical polymerization, the kinetics of which is discussed below.

The ATRP of MMA was performed at 30 °C as described in the Experimental Section. The linear time dependence of ln([M]$_0$/[M]) (Figure 1) is consistent with a controlled polymerization, which is first-order with respect to the monomer. The dependence of molecular weight and polydispersity on the MMA conversion is illustrated in Figure 2. The linear dependence of M_n with conversion is in agreement with a controlled process with a constant number of growing chains. The molecular weight of the resulting PMMA increased linearly with conversion, but the measured molecular weights were slightly higher than the calculated values (dotted line in Figure 2). The initiation efficiency ($f = M_{n,cal}/M_{n,GPC}$) was calculated from the experimental M_n and the expected M_n as reported before.[33] Thus, a "f" value of 0.87 is observed for the present system. This value is comparable to that reported earlier[32] using the same system and is superior to the reported value of 0.75 for MMA polymerization performed using 2-EiBBr/NiBr$_2$(PPh$_3$)$_2$ in toluene at 85 °C.[33] The higher initiation efficiency of 0.87 indicates that less side reactions have occurred. As can be seen from Figures 1 and 2, in about 20 h, a reasonably high conversion (60%), a high molecular weight (65 000), and a relatively low PDI (~1.25) are observed with this room temperature polymerization. The reported results using the same system at 90 °C[32] indicated that at 60% MMA conversion a number-average molecular weight of ~16 000 and a PDI of 1.15 is achieved, while that reported using the 2-EiBBr/NiBr$_2$(PPh$_3$)$_2$ system for the same monomer conversion[33] are $M_n \sim 30\,000$ and PDI ~ 1.25. Thus, the results reported here clearly indicate that, under the very mild room temperature ATRP conditions developed, high molecular weight PMMA can be formed with minimal side reactions when compared with that reported at 90 °C.[32]

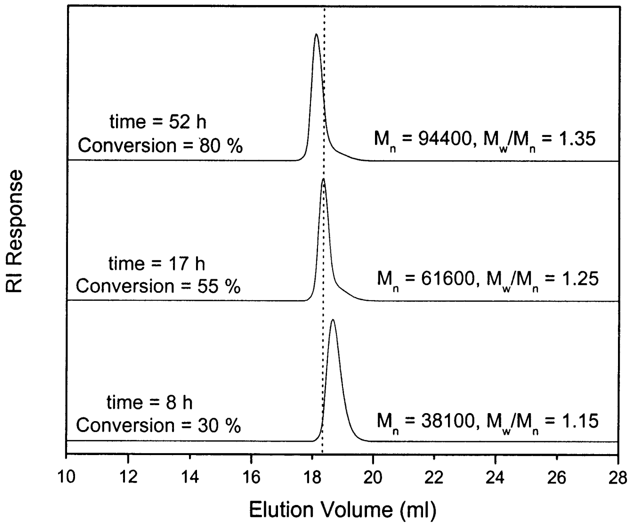


Figure 3. Evolution of the GPC chromatograms with conversion and time for MMA polymerization at 30 °C (50% anisole, MMA:2-EiBBr:CuBr:PMDETA = 1000:1:1:1).

The PDI was observed to increase from 1.15 to 1.35 after a very long polymerization time of 52 h. The low PDI observed initially is probably due to fast activation. Although the PDI increase with time was small, it still indicated that the lowering of the polymerization temperature significantly reduces the rate of chain termination/transfer reaction but does not eliminate it totally. The increase of polydispersity with conversion (time) can also be due to the dramatic increase in viscosity that occurs at high conversion, which is expected to change the rate of exchange between the active and the dormant species. The gel permeation chromatograms of few PMMA samples synthesized are shown in Figure 3. The kinetic studies[34] clearly demonstrate that narrow dispersed, high molecular weight PMMA can be synthesized in a facile manner at room temperature. This result was therefore used to evaluate the synthesis of ABC and CBABC block copolymers from suitably designed AB and BAB block copolymeric macroinitiators with MMA as the "C" block, at room temperature.

Synthesis of Macroinitiators. Bromo-terminated monofunctional polystyrene macroinitiator was synthesized using 1-phenylethyl bromide as the initiator and the CuBr/PMDETA catalytic system. α,ω-Bifunctional

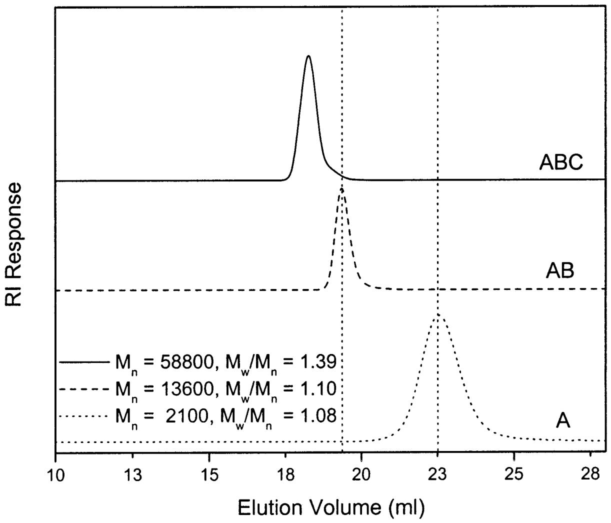


Figure 4. GPC traces of bromo-terminated polystyrene (A, dotted line), poly(styrene-*b*-tBA) (AB, dashed line), and poly(styrene-*b*-tBA-*b*-MMA) (ABC, solid line).

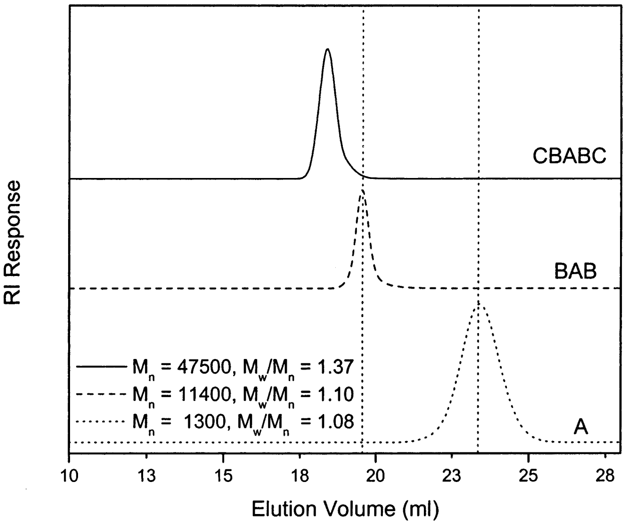


Figure 5. GPC traces of α,ω-dibromo-terminated polystyrene (A, dotted line), poly(tBA-*b*-styrene-*b*-tBA) (BAB, dashed line), and poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) (CBABC, solid line).

bromo-terminated polystyrene was prepared similarly but utilizing the commercially available bifunctional initiator, DMDBHD. The procedure of Davis and co-workers[16,30] was slightly modified for the synthesis of the polystyrene macroinitiators. The footnote under Table 1 summarizes the results of the macroinitiator synthesis. The molecular weights of the macroinitiators determined by GPC and ^{1}H NMR were similar and comparable within experimental error (±4 DP). The final polydispersities were also low. It must be mentioned here that the universal calibration curve used for evaluating the molecular weight deviates from linearity in this molecular weight range of the macroinitiators synthesized, and therefore the PDI values reported are not accurate. The GPC traces of the macroinitiators are shown in Figures 4 and 5. These reactions were designed to produce low molecular weight polystyrene, as the high viscosity of the macroinitiator can cause a problem in the subsequent steps.

The monofunctional and bifunctional bromo-terminated polystyrene macroinitiators were used to initiate the ATRP of tBA to produce AB and BAB block copolymeric macroinitiators. Here again, the procedure of Davis and co-workers was slightly modified for the synthesis of the block copolymers.[30] The experimental conditions used for the block copolymerization as well as the results obtained are summarized in Table 1. All the block copolymerizations were conducted using acetone as the solvent with CuBr/PMDETA as the catalyst at 60 °C.

Several AB diblock copolymers were prepared using polystyrene macroinitiator as shown in Table 1. The GPC trace of the AB diblock copolymer of poly(styrene-*b*-tBA) is shown in Figure 4. The evolution of GPC traces as a function of time (Supporting Information) suggests the complete disappearance of the peak due to the macroinitiator as the time of polymerization increases and thus confirms the formation of the AB diblock copolymer. The α,ω-difunctional bromo-terminated polystyrene (M_n = 1300, M_w/M_n = 1.08) was used for the subsequent block copolymerization with tBA, resulting in BAB diblock copolymers summarized in Table 1. The GPC trace of the BAB triblock copolymer is shown in Figure 5. Here again, the evolution of GPC traces as a function of time (Supporting Information) suggests the complete disappearance of the macroinitiator, as the time of polymerization increases and confirms the formation of the ABA triblock copolymer. The blocky nature of the di- and triblock copolymers was further confirmed by FT-IR, ^{1}H NMR, and TGA measurements (data shown in Experimental Section and Supporting Information).

ABC and CBABC Multiblock Copolymers. For efficient synthesis of block copolymers of complex architecture, the following three factors are important:[16] (1) the monomer to be added must have a high equilibrium constant favoring polymerization compared to the monomer constituting the end of the macroinitiator (the equivalent usage in living polymerization is the rate of initiation must be greater than or equal to the rate of propagation), (2) essentially all the chain ends of the macroinitiator must possess the halide end group, and (3) halogen exchange must be employed, if necessary, to facilitate initiation rate of the block copolymerization (halogen exchange) to be higher than that of propagation. The first two principles are aptly satisfied by the choice and the method of synthesis of the bromo-terminated tBA block copolymer for MMA polymerization. Efficient halogen exchange was achieved by the use of CuCl and the linear PMDETA ligand with bromo-termianted tBA block copolymer initiator, thus fulfilling the third condition. Thus, the complete system deviced is ideal for the synthesis of the complex block copolymer architecture desired.

ABC Triblock Copolymer. The AB diblock copolymer of poly(styrene-*b*-tBA) (M_n = 13 600, M_w/M_n = 1.10, AB2 as shown in Table 1) was chain extended with methyl methacrylate, using CuCl/PMDETA catalytic system with anisole as the solvent at 30 °C to produce ABC triblock copolymer. The details of experimental condition as well as the results of molecular weight and molecular weight distribution are summarized in Table 1. The GPC trace of the ABC triblock copolymer obtained from the AB diblock macroinitiator (M_n = 13 600 and PDI = 1.10) is presented in Figure 4. The increase in molecular weight (M_n = 47 700, M_n = 58 800) indicates the formation of the ABC triblock copolymer. The observation of a small tail (~5% of the total peak area) indicates that all the AB diblock

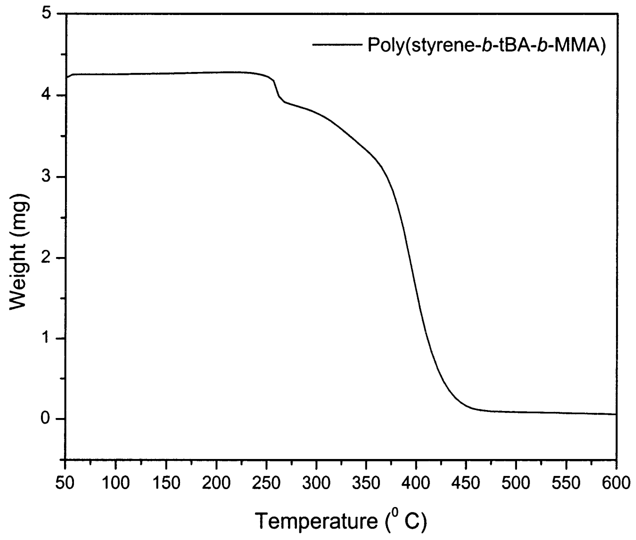


Figure 6. TGA of poly(styrene-*b*-tBA-*b*-MMA) block copolymer (M_n = 47 700, M_w/M_n = 1.40).

macroinitiator may not have been consumed completely although the cross-propagation efficiency is very high.

The ^{1}H NMR of the triblock copolymer (Supporting Information) in $CDCl_3$ showed a new peak at 3.8 ppm corresponding to the $-OCH_3$ group of the PMMA, confirming the formation of the block copolymer. This along with the characteristic resonances due to poly(tBA) and polystyrene confirmed the formation of the ABC triblock copolymer. The ^{1}H NMR compositional analysis of the ABC triblock copolymer calculated on the basis of the ratio of the area for the methoxy protons of PMMA to the total area of the block copolymer supports the presence of major amount (80%) of PMMA in the block copolymer. The FT-IR of the triblock copolymer shows a new band at 2950 cm^{-1}, which is characteristic of the alkyl $-C-H$ stretching from MMA. This along with the other characteristic vibrational bands due to poly(tBA), and polystyrene further supports the presence of the three monomers in the block copolymer. The TGA of the block copolymers (Figure 6) shows a decomposition around 270 °C corresponding to the tBA block and a broad transition occurring from 320 to 420 °C corresponding to the decomposition of both the PS and the PMMA constituents, further supporting the blocky nature. The composition determined (ABC 1, Table 1) on the basis of the weight loss showed 12% for tBA and 88% for styrene + MMA. The compositions determined by TGA are very close to the composition determined by ^{1}H NMR.

CBABC Triblock Copolymer. CBABC pentablock copolymers were synthesized using the BAB triblock copolymer [with M_n = 11 400 and M_w/M_n = 1.10 (BAB2 as shown in Table 1)] as the macroinitiator, and the chain was extended using MMA. The polymerization was carried out using CuCl/PMDETA catalytic system with anisole as the solvent at 30 °C. The GPC traces of both the BAB macroinitiator and the CBABC block copolymer are shown in Figure 5. The gel permeation chromatograms of the CBABC polymer indicated an increase in molecular weight, confirming the formation of the desired block copolymer. The essentially complete consumption of the macroinitiator indicates a very high cross-propagation efficiency. The chromatogram of the CBABC block copolymers, however, shows the presence of a small low molecular weight tail. This could be due to less than 100% consumption of the macroinitiator, or it could also be due to a similar feature seen in the case of the homopolymerization of MMA, as revealed in Figure 3. More details about the polymerization condition and the molecular weight characteristics are summarized in Table 1.

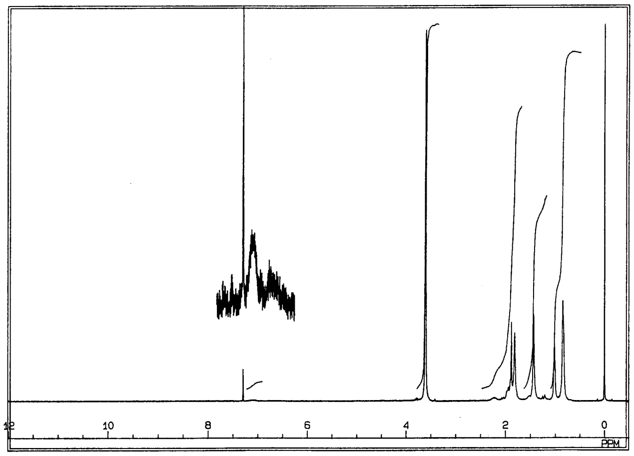


Figure 7. ^{1}H NMR of poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) block copolymer (M_n = 47 500, M_w/M_n = 1.37).

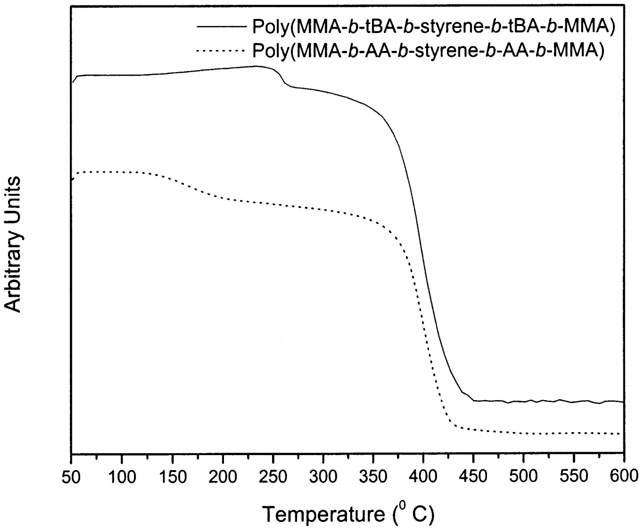


Figure 8. Comparison of the TGA curves of poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) before hydrolysis (solid line) and after hydrolysis (dotted line).

The ^{1}H NMR analysis (Figure 7) of the CBABC block in $CDCl_3$ showed a new peak at 3.8 ppm corresponding to $-OCH_3$ group of the PMMA, confirming the formation of the block copolymer. The proton NMR compositional analysis of the CBABC multiblock copolymer calculated on the basis of the ratio of the area for the methoxy protons of PMMA to the total area of the block copolymer supports the presence of major amount (85%) of PMMA in the block copolymer. The FT-IR of the pentablock showed a new band at 2950 cm^{-1}, which is characteristic of alkyl $-C-H$ stretching in PMMA. This along with other characteristic vibrational bands due to poly(tBA) and polystyrene confirms the presence of all the three monomers in the block copolymer. The TGA of the block copolymer (Figure 8) showed decomposition around 270 °C corresponding to the tBA block (Supporting Information) and a broad transition occurring from 320 to 420 °C corresponding to the decomposition of both the PS and the PMMA constituents, further supporting the blocky nature. The composition determined (CBABC2, Table 1) on the basis of weight loss showed 12% for tBA and the remaining 88% for styrene + MMA. The compositions determined by TGA are very close to the composition determined by ^{1}H NMR.

Hydrolysis of the Multiblock Copolymer. The copolymers were hydrolyzed using a previously reported procedure[17] to yield amphiphilic block copolymers. The selective cleavage of the *tert*-butyl ester in the presence of the methyl ester group was achieved using anhydrous TFA as the hydrolyzing agent. The FT-IR analysis of the resulting block copolymer confirmed the presence of acid functionality (Supporting Information), as revealed by the formation of broad carboxylic band between 2800 and 3750 cm^{-1}, overlapping with the vibrational bands from the polymer backbone between 2800 and 3200 cm^{-1}. The thermal analysis of the hydrolyzed multiblock copolymer (Figure 8) shows a broad transition between 320 and 420 °C. This along with the appearance of a new transition at 150 °C characteristic of poly(acrylic acid) [p(AA)] and the absence of the degradation around 270 °C indicates the complete conversion of the *tert*-butyl ester to the acid functionality (Supporting Information).

Conclusion

In conclusion, relatively narrow dispersed high molecular weight PMMA and relatively low dispersed ABC triblock and CBABC pentablock copolymers of styrene, tBA, and methyl methacrylate are synthesized by ATRP. The kinetic results of the MMA polymerization illustrate that the polymerization at room temperature proceeds effectively with narrow PDI and a good control over the number-average molecular weight. The ABC and CBABC block copolymers are synthesized from the AB and BAB block for the first time under mild conditions (room temperature polymerization). The GPC chromatograms confirm that the chain-end functionality is high, and is active as well, as evidenced by the essentially complete consumption of the macroinitiator in all the block copolymerizations with the molecular weight distributions remaining relatively narrow even after the last block has been added (indicating that termination is negligible). The FT-IR, NMR, and TGA analyses along with the GPC data confirm the block copolymer formation. The hydrolysis of the *tert*-butyl ester groups resulted in the formation of amphiphilic block copolymers, comprising of polystyrene−PMMA (hydrophobic) and p(AA) (hydrophilic) segments.

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Supporting Information Available: Kinetic plot for MMA polymerization at 90 °C, GPC, FT-IR, ^{1}H NMR, and TGA of homopolymers and selected block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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