Synthesis of ABC 3-Miktoarm Star Terpolymers from a Trifunctional Initiator by Combining Ring-Opening Polymerization, Atom Transfer Radical Polymerization, and Nitroxide-Mediated Radical Polymerization

Tao He, Dejin Li, Xia Sheng, and Bin Zhao*

Department of Chemistry, University of Tennessee at Knoxville, Knoxville, Tennessee 37996

Received December 29, 2003; Revised Manuscript Received February 29, 2004

ABSTRACT: We report a new method to synthesize ABC 3-miktoarm star terpolymers by combining three different controlled/"living" polymerization techniques: ring-opening polymerization (ROP), atom transfer radical polymerization (ATRP), and nitroxide-mediated radical polymerization (NMRP). A trifunctional initiator bearing a hydroxy group, an ATRP initiator, and a NMRP initiator was designed and synthesized. The structure was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. ABC star terpolymers were then prepared from the trifunctional initiator by sequential ROP of ϵ-caprolactone, ATRP of methyl methacrylate, and NMRP of styrene. GPC and kinetic analysis indicated that the polymerizations were controlled. The 3-miktoarm star structure was further confirmed by cleavage of a star terpolymer.

Introduction

ABC 3-miktoarm star terpolymers are molecules composed of three different polymer chains emanating from a central junction point.[1−9] If all three arms are sufficiently long and the Flory−Huggins interaction parameters for all pairs are sufficiently large, microphase separation will occur, resulting in ordered morphologies comprised of nearly pure microdomains of each of the components. Unlike linear diblock and multiblock copolymers in which the junctions between different blocks are uniformly distributed over the interfaces between the domains, the junction points in ABC star terpolymers are restricted to periodically spaced parallel lines defined by the mutual intersection of the different domains due to the specific molecular architecture of star copolymers.[4,7−9] A wide variety of ordered morphologies of ABC miktoarm star terpolymers have been found using Monte Carlo simulations.[10,11] These include lamellar + sphere, polygonal cylinders, perforated layer, lamella + cylinder, columnar piled disk, and lamella in sphere. However, only a few experimental studies have been reported due to the difficulties in the synthesis.[1−9,12−18]

Several methods have been used to synthesize ABC star terpolymers. The first one is the chlorosilane approach.[1,2,5] 3-Miktoarm star terpolymers consisting of polyisoprene, polystyrene (PS), and polybutadiene were prepared using step-by-step substitutions of the chlorine atoms in trichloromethylsilane with living anionic polymers.[1,2] To overcome the difficulties in the incorporation of polymethacrylates by this method, Sioula et al. first coupled a living polyisoprene chain and a living polystyrene chain with trichloromethylsilane and then converted the third SiCl group to a sterically hindered anionic species, diphenylalkyl anion, followed by the polymerization of a methacrylate to form the third arm.[3] These polymers have been used in the morphology studies, and intriguing ordered phases have been discovered.[4,8] The second method is based on the nonhomopolymerizable macromonomer techniques. Nonhomopolymerizable macromonomers with 1,1-diphenylethylene groups at one end were reacted with a living polymer, producing an active species at the junction of diblock copolymers followed by the polymerization of the third monomer. Fujimoto et al. prepared star terpolymers of PS, poly(dimethylsiloxane), and poly(*tert*-butyl methacrylate) by this method.[6] Similar strategies were also used in the synthesis of star terpolymers of PS, polybutadiene, and poly(methyl methacrylate) (PMMA) (or poly(2-vinylpyridine))[12,13] and other star copolymers.[14]

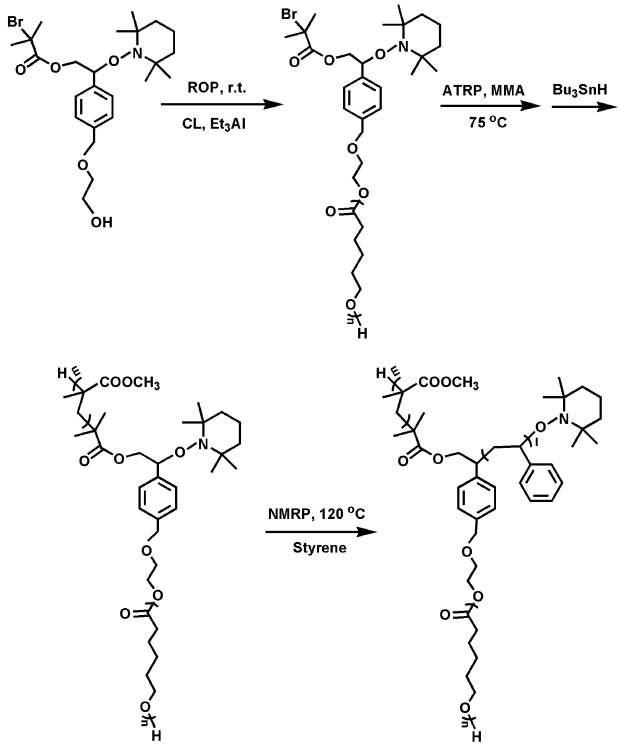
Other methods were also developed. To avoid the steric hindrance in the reactions between two polymeric species as in the first two methods, Lambert and coworkers developed a synthetic route with two successive initiation steps from a bifunctional macroinitiator, which was obtained by end-capping a living polymer with a difunctional small molecule, 1,1-diphenylethylene derivative.[15,16] Feng and Pan incorporated an atom transfer radical polymerization (ATRP) initiator into the junction of a diblock copolymer which was prepared by controlled cationic ring-opening polymerizations and synthesized the third arm by ATRP.[17] They also incorporated a maleic anhydride moiety into the junction of the diblock copolymer prepared by reversible addition−fragmentation chain transfer processes and obtained star terpolymers by reaction of the maleic anhydride moiety with poly(ethylene glycol).[18]

Here we report a new method to synthesize ABC 3-miktoarm star terpolymers. A trifunctional initiator bearing a hydroxy group, an ATRP initiator, and a nitroxide-mediated radical polymerization (NMRP) initiator was designed and used in the preparation of star terpolymers composed of poly(ϵ-caprolactone) (PCL), PMMA, and PS arms by sequential living ring-opening polymerization (ROP) of ϵ-caprolactone (CL), ATRP of MMA, and NMRP of styrene (Scheme 1). This approach is based on the recent progress in controlled/"living" polymerization techniques. A variety of diblock copolymers have been successfully synthesized from asymmetric difunctional initiators by combining either ATRP

* To whom correspondence should be addressed. E-mail: zhao@novell.chem.utk.edu.

10.1021/ma036010c CCC: $27.50
Published on Web 04/09/2004

Scheme 1. Synthesis of Star Terpolymers by Combining Ring-Opening Polymerization (ROP), Atom Transfer Radical Polymerization (ATRP), and Nitroxide-Mediated Radical Polymerization (NMRP) from a Trifunctional Initiator



and NMRP,[19,20] or NMRP and ROP,[21−26] or ATRP and ROP.[21−24,27−30] While the synthesis of diblock copolymers by ATRP and NMRP which are activated at different temperatures is a two-step process, the two polymerizations in the other methods can be carried out simultaneously in one pot.

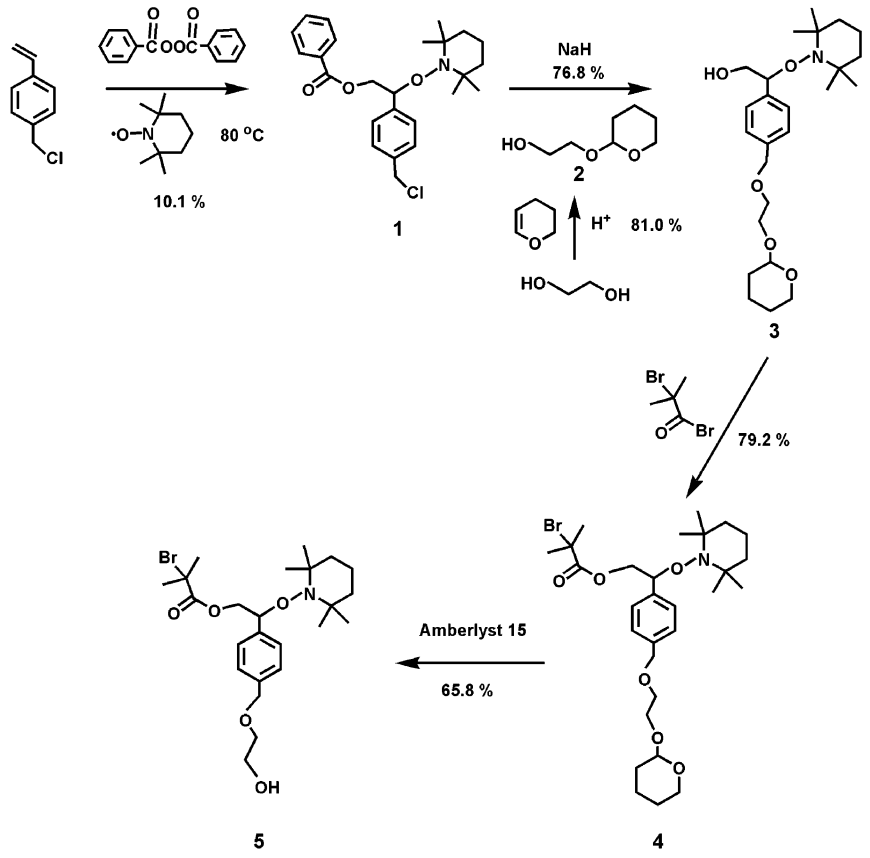
Results and Discussion

Design and Synthesis of a Trifunctional Initiator. Trifunctional initiator **5** bearing a hydroxy group, an ATRP initiator, and a NMRP initiator has been designed for the synthesis of ABC star terpolymers by combining living ROP, ATRP, and NMRP techniques. Living ROPs of CL are achieved using alcohols and triethylaluminum as initiation systems under strictly anhydrous conditions, producing polymers with narrow molecular weight distributions and predictable molecular weights.[31−35] ATRP and NMRP are two different controlled/"living" radical polymerization techniques and have been widely used in recent years in the synthesis of polymers with narrow polydispersities, controlled molecular weights, and various architectures.[22,36] In previous publications, we used ATRP and NMRP to fabricate mixed homopolymer brushes on silicon wafers by "grafting from" either mixed initiator-terminated self-assembled monolayers (SAMs)[37] or asymmetric difunctional initiator-terminated SAMs.[38] Trifunctional initiator **5**, 2-(4-(2′-oxa-4′-hydroxybutyl)phenyl)-2-(2″,2″,6″,6″-tetramethyl-1-piperidinyloxy)ethyl 2-bromo-2-methylpropionate, was prepared via a four-step procedure as illustrated in Scheme 2. 4-Vinylbenzyl chloride reacted with free radicals generated from benzoyl peroxide at 80 °C in the presence of 2,2,6,6-tetramethylpiperidinooxy produced **1** in a yield of 10.1%.[25,38] The reaction between THP-protected ethylene glycol **2** and **1** catalyzed by NaH afforded **3**, which was then reacted with 2-bromo-2-methylpropionyl bromide to incorporate the moiety of an ATRP initiator. Removing THP using dry Amberlyst 15 acidic resin produced the trifunctional initiator **5**. The structure was confirmed by the ^{1}H NMR spectrum shown in Figure 1, ^{13}C NMR, and mass spectroscopy. This compound was then used for the synthesis of ABC star terpolymers.

Synthesis of ABC 3-Miktoarm Star Terpolymers Composed of PCL, PMMA, and PS Arms. Although the first arm can be synthesized from the trifunctional initiator using any one of the three polymerization methods, we synthesized PCL first by living ROP of CL using triethylaluminum as catalyst because it is much easier to dry a small molecule than a macroinitiator. Rigorously anhydrous conditions are required to achieve a living polymerization of CL.[31−35] Considering that the activation of an ATRP initiator is a bimolecular process and the free radicals in NMRP are generated by thermal decomposition which is a unimolecular process, we synthesized the second arm by ATRP of MMA using PCL macroinitiator and NMRP of styrene to grow the third arm to minimize the possible steric hindrance encountered in the initiation of the third polymer chain. We confirmed that the NMRP initiator was stable at 75 °C under the typical ATRP conditions.[37,38] In a control experiment for the synthesis of mixed PMMA/PS brushes on silicon wafers,[38] we exposed a pure ATRP initiator-terminated SAM and a mixed SAM prepared from a toluene solution that contained an ATRP-initiator-terminated trichlorosilane and a NMRP initiator-terminated trichlorosilane with a molar ratio of 54.4:45.6 to the same NMRP conditions. A ∼2.0 nm PS film was observed on the pure ATRP initiator-terminated SAM, while a 19.1 nm PS brush was found on the mixed SAM. Presumably, the C−Br bond in the ATRP initiator was weak and acted as a chain transfer agent in NMRP. To eliminate the possibility of halogen atom-capped PMMA chains acting as a chain transfer agent in NMRP, we used tri(*n*-butyl)tin hydride to remove the halogen atoms from the PMMA chain ends in situ after ATRP.[38,39]

ROP of CL Initiated from the Trifunctional Initiator 5 in Toluene. As the first step in the synthesis of ABC 3-miktoarm star terpolymers composed of PCL, PMMA, and PS arms, ROP of CL was initiated from the trifunctional initiator **5** using triethylaluminum as catalyst in toluene at room temperature under a nitrogen atmosphere. Initiator **5** was first dried by azeotropic distillation using dry toluene at room temperature three times and further treated with a high vacuum at 35 °C for 8 h to completely remove any possible water followed by addition of 1.05 equiv of triethylaluminum via a syringe. The hydroxy group of the initiator **5** reacted with triethylaluminum, producing diethylaluminum monoalkoxide **6** (Scheme 3), which then initiated the polymerization via a "coordination−insertion" mechanism.[31−35] According to this proposed mechanism, the monomer is inserted into the aluminum−alkoxide bond with cleavage of the acyl−oxygen bond such that the binding of the growing chain to the aluminum through an alkoxide link is maintained. The polymerization was monitored by ^{1}H NMR spectroscopy, and the monomer conversion was determined by use of the peak at 4.03 ppm (the ester methylene group in the polymer) and the peak at 4.25 ppm (the methylene group in −COO-CH_2− in the monomer). The polymers were then purified and analyzed by GPC and ^{1}H NMR spectroscopy.

Scheme 2. Synthesis of Trifunctional Initiator 5



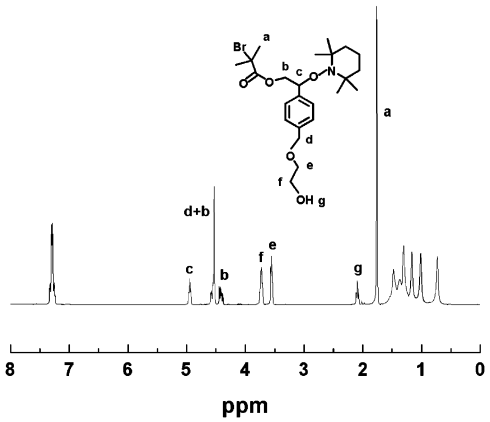


Figure 1. ^{1}H NMR spectrum of trifunctional initiator **5**.

The reaction conditions and the results are summarized in Table 1.

As shown in Table 1, the polymers obtained from the polymerizations that were stopped at conversions less than 100% exhibited relatively narrow polydispersities. These results are consistent with those reported in the literature using other alcohols and Et_3Al to polymerize CL.[31] A typical GPC curve (sample C-3 in Table 1) is shown in Figure 2 (curve a). As reported by Dubois et al.,[35] the molecular weight distributions broadened significantly when the polymerization time exceeded the time required for a complete monomer conversion. For instance, the polydispersity of sample C-4 in Table 1, which was isolated after 100% conversion, was 1.82, though a single peak was observed in GPC analysis. This is likely due to the intra- and intermolecular transesterification reactions promoted by the aluminum alkoxide catalyst.

To confirm that the polymerization of CL initiated from **6** is a living process, $\ln([M]_0/[M])$ vs time was plotted and shown in Figure 3. A linear relationship indicated that the polymerization was a first-order reaction with respect to the monomer concentration, and the number of the active growing chain ends was constant during the polymerization. Figure 4 shows the ^{1}H NMR spectrum of sample C-3 in Table 1. Besides the peaks from PCL, the peaks from the residual initiator moiety are clearly seen in the magnified area. The peaks located at 4.53 ppm corresponded to three protons of the initiator moiety as in the ^{1}H NMR spectrum of trifunctional initiator **5**—two from the benzyl group and one from −COOC*H*H−. Using these peaks and the ester methylene peaks of PCL located at 4.03 ppm, we calculated the number-average molecular weights of PCL; the results are summarized in Table 1. These values are reasonably close to those calculated on the basis of the ratio of the monomer to the initiator and the conversion. For instance, the M_n of sample C-1 determined using the peaks at 4.53 ppm as reference is 19 600, very close to 20 200 that was obtained on the basis of the conversion. This agreement suggested that the average number of active alkoxy groups per aluminum molecule was close to 1 under our experimental conditions, consistent with the report of Dubois and coworkers.[35] The molecular weights obtained by GPC analysis relative to polystyrene standards were much higher than those obtained from ^{1}H NMR analysis and the calculation based on the conversion.

ATRP of MMA Using PCL Macroinitiator. ATRP of MMA was then initiated from the PCL macroinitiator in anisole using pentamethyldiethylenetriamine (PMDETA) and CuCl as catalytic system to synthesize the second arm. The polymerization was monitored by ^{1}H

Scheme 3. Ring-Opening Polymerization of ϵ-Caprolactone Using Initiator 5 and $AlEt_3$

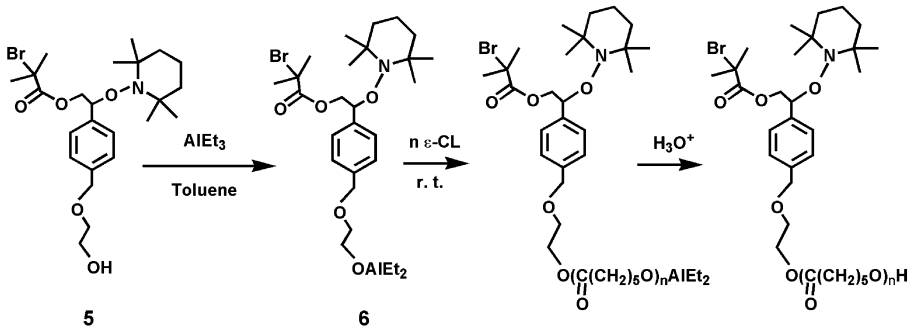


Table 1. Polymerization Conditions and Results of Ring-Opening Polymerization of ϵ-Caprolactone Using Trifunctional Initiator 5 and Et_3Al as the Initiation System in Toluene at Room Temperature under a N_2 Atmosphere

sample	$[M]_0/[I]_0$	conv (%)[a]	$M_{n,cal}$[b]	$M_{n,NMR}$[c]	$M_{n,GPC}$[d]	PDI[e]
C-1	200	88.7	20 200	19 600	48 400	1.35
C-2	217	64.5	16 000	18 100	39 700	1.37
C-3	135	60.2	9 300	11 400	26 800	1.34
C-4	150	100	17 100	NA	41 800	1.82

[a] Determined from ^{1}H NMR spectrum using the ester methylene peaks of poly(ϵ-caprolactone) (PCL) and ϵ-caprolactone. [b] Calculated by the ratio of the monomer to the initiator and the conversion. [c] Calculated from ^{1}H NMR spectrum of PCL. $M_{n,NMR} = (I_{4.03}/2)/(I_{4.53}/3) \times 114.1$, where $I_{4.03}$ and $I_{4.53}$ were integral values of the peaks located at 4.03 ppm (the ester methylene group of PCL, 2H) and 4.53 ppm (from the residual initiator moiety, 3H). [d] Determined by GPC using PS standards. [e] PDI = polydispersity index. Determined by GPC.

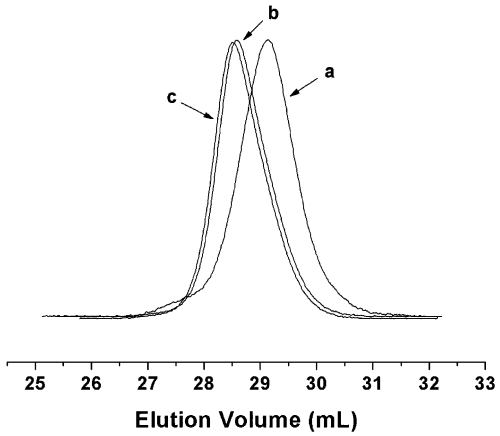


Figure 2. GPC curves of (a) a poly(ϵ-caprolactone) (C-3 in Table 1), (b) a poly(ϵ-caprolactone)-*b*-poly(methyl methacrylate) (CM-3 in Table 2), and (c) a star terpolymer (CMS-3 in Table 2).

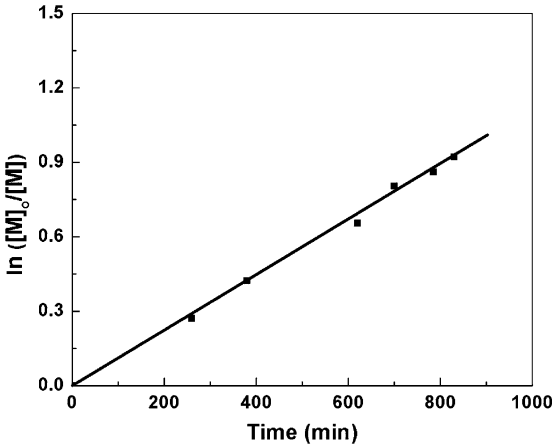


Figure 3. Relationship between $\ln([M]_0/[M])$ and the polymerization time in the ring-opening polymerization of ϵ-caprolactone using trifunctional initiator **5** and Et_3Al as the initiation system in toluene at room temperature. $[M]_0/[I]_0 = 135$; $[I]_0:[AlEt_3]_0 = 1:1.05$.

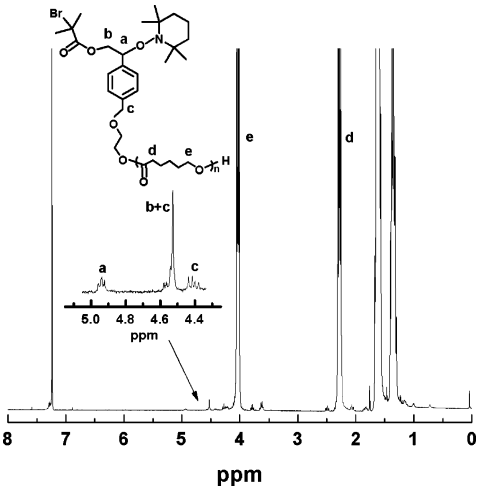


Figure 4. ^{1}H NMR spectrum of a poly(ϵ-caprolactone) (sample C-3 in Table 1).

NMR using the peaks located at 6.90−7.00 ppm, which belonged to the solvent anisole as the internal standard. The monomer conversion was determined by using the integral value of the peak located at 6.07 ppm (1H from the double bond of the monomer) at time *t* and the value of the same peak at time $t = 0$. After a desired conversion was reached, excess tri(*n*-butyl)tin hydride with respect to the initiator was injected into the mixture to remove the halogen atoms from the PMMA chain ends in situ. The polymerization conditions and the results of ^{1}H NMR and GPC analysis are summarized in Table 2. A typical GPC curve (CM-3 in Table 2) is shown in Figure 2 (curve b). The polydispersities of the diblock copolymers remained relatively low, less than 1.30. The peak shifted to a higher molecular weight compared to that of the PCL macroinitiator, and no shoulder peak was observed. Figure 5 shows the kinetic data of ATRP of MMA. An almost linear relationship between $\ln([M]_0/[M])$ and the reaction time suggests that the polymerization of MMA was controlled. A typical ^{1}H NMR spectrum of a diblock copolymer PCL-*b*-PMMA (CM-3 in Table 2) is shown in Figure 6. Using the peaks at 4.03 ppm (the ester methylene group of PCL) and the peak at 3.57 ppm (the ester methyl group of PMMA), the number-average molecular weight of PMMA were calculated and included in Table 2. These values are close to those calculated on the basis of the conversion

Table 2. Reaction Conditions and the Results of Atom Transfer Radical Polymerization (ATRP) of Methyl Methacrylate (MMA) Using Poly(ϵ-caprolactone) (PCL) Macroinitiators and Nitroxide-Mediated Radical Polymerization (NMRP) of Styrene Using PCL-*b*-PMMA Macroinitiators[a]

method	sample	initiator[b]	$[M]_0/[I]_0$	conv (%)[c]	$M_{n,cal}$[d]	$M_{n,NMR}$[e]	CL:MMA:St[f]	$M_{n,GPC}$[g]	PDI[g]
ATRP	CM-1	C-1	503/1	22.2	11 200	11 300		72 600	1.22
NMRP	CMS-1	CM-1	991/1	11.4	11 800	10 900	172:113:105	77 000	1.25
ATRP	CM-2	C-2	755/1	27.1	20 500	19 900		63 100	1.27
NMRP	CMS-2	CM-2	1106/1	19.6	22 600	23 600	159:199:227	69 200	1.35
ATRP	CM-3	C-3	605/1	21.2	12 800	9 600		46 100	1.26
NMRP	CMS-3	CM-3	957/1	12.1	12 000	13 600	100:96:131	49 700	1.31

[a] ATRPs of MMA were carried out at 75 °C under a N_2 atmosphere using PCL macroinitiators; NMRPs of styrene were carried out at 120 °C under a nitrogen atmosphere using PCL-*b*-PMMA macroinitiators. [b] Initiators C-1, C-2, and C-3 were from Table 1. [c] Conversions were determined by ^{1}H NMR spectroscopy using either the peaks of the solvent (in ATRP of MMA) or the ester methylene peaks of PCL as internal standard (in NMRP of styrene). [d] The number-average molecular weights of the new arm calculated from the ratio of the monomer to the initiator $[M]_0/[I]_0$ and the conversion. [e] The number-average molecular weights of the new arm calculated using PCL as reference. [f] The degrees of polymerizations of PCL:PMMA:PS calculated from ^{1}H NMR spectra. [g] The number-average molecular weight (M_n) and polydispersity index (PDI) of diblock copolymers or star terpolymers determined by GPC using PS standards.

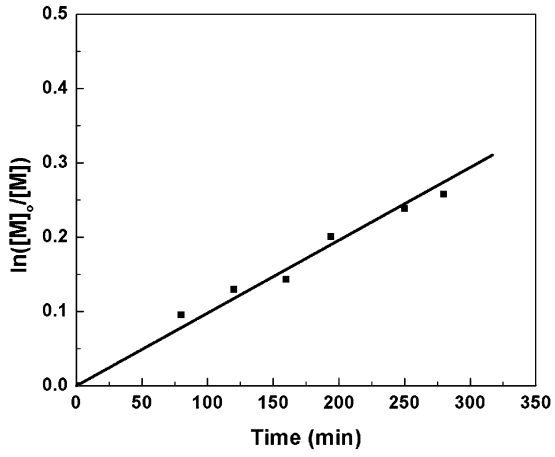


Figure 5. Relationship between $\ln([M]_0/[M])$ and the polymerization time for atom transfer radical polymerization of methyl methacrylate using poly(ϵ-caprolactone) macroinitiator in anisole at 75 °C. $[M]_0/[I]_0 = 605/1$; $[I]_0$:$[CuCl]_0$:[pentamethyldiethylenetriamine]$_0$ = 0.8:1:2.

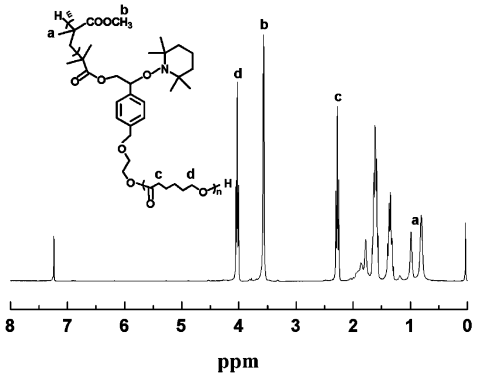


Figure 6. ^{1}H NMR spectrum of a poly(ϵ-caprolactone)-*b*-poly(methyl methacrylate) (CM-3 in Table 2).

and the ratio of the monomer to the macroinitiator. For instance, the calculated M_n of PMMA arm based on the conversion for sample CM-2 in Table 2 is 20 500, while the value calculated by ^{1}H NMR using the ester methylene peak of PCL as reference is 19 900. However, there was a large discrepancy between these two values if the reaction mixture was very viscous, leading to a gel effect.

NMRP of Styrene Using PCL-*b*-PMMA Macroinitiator. To synthesize the third-arm PS, NMRPs of styrene were carried out using PCL-*b*-PMMA macroinitiators in chlorobenzene at 120 °C. A ratio of the monomer to the initiator of ∼1000 was used, and the

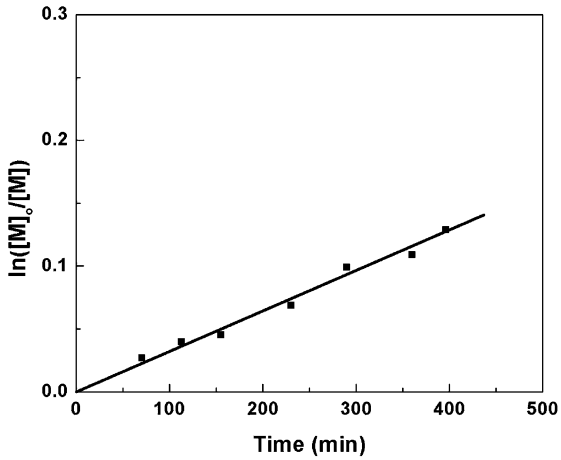


Figure 7. Relationship between $\ln([M]_0/[M])$ and the polymerization time for nitroxide-mediated radical polymerization of styrene using a poly(ϵ-caprolactone)-*b*-poly(methyl methacrylate) macroinitiator in chlorobenzene at 120 °C. $[M]_0/[I]_0 = 957/1$.

polymerization was stopped at monomer conversions less than 20% to avoid the gel effect. During the polymerization, samples were taken from the reaction mixture at a desired time via a syringe for ^{1}H NMR analysis. Using the peak at 4.03 ppm (the methylene group of $-COOCH_2-$ in PCL) as the internal standard, the conversion was determined by comparing the integral value of the peaks at 5.72 ppm to that of the same peaks in the original sample. The polymerization conditions and the results of ^{1}H NMR spectroscopy and GPC analysis are summarized in Table 2. GPC analysis (see Figure 2c) showed a single peak shifting to a higher molecular weight compared to that of the diblock copolymer macroinitiator, and the polydispersity remained relatively low. Kinetic analysis showed an almost linear relationship between $\ln([M]_0/[M])$ and the reaction time (Figure 7), suggesting that the polymerizations were controlled and the concentration of the growing chains was a constant. Figure 8 shows the ^{1}H NMR spectrum of a star terpolymer (CMS-3 in Table 2). The peaks in the range 6.25−7.21 ppm belong to the aromatic protons of PS. The molecular weights of PS calculated using these peaks and the ester methylene peaks of PCL are close to those calculated on the basis of the monomer conversion and the ratio of the monomer to the initiator. For example, the M_n of PS in sample CMS-1 determined using PCL as reference is 10 900, very close to 11 800 obtained on the basis of the conversion. The increases in M_n of star terpolymers

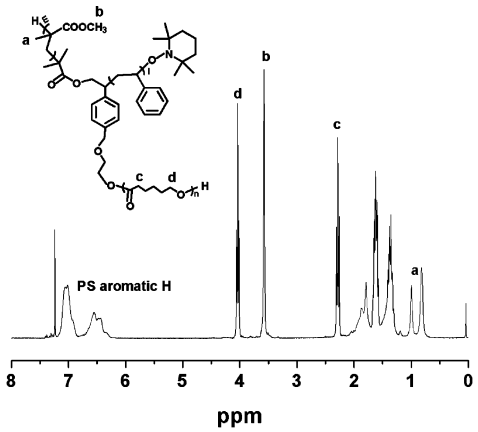


Figure 8. ^{1}H NMR spectrum of a star terpolymer composed of poly(ϵ-caprolactone), poly(methyl methacrylate), and polystyrene arms (CMS-3 in Table 2).

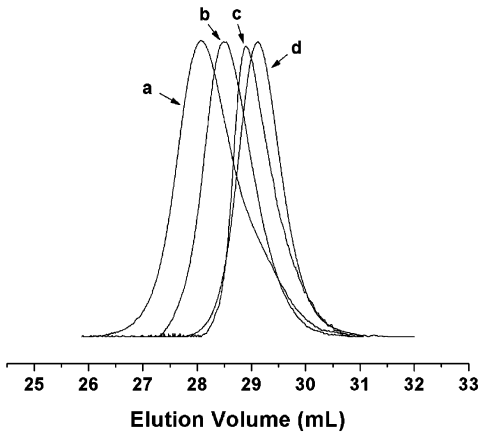


Figure 9. GPC analysis of the polymers obtained in arm cleavage experiments: (a) a star terpolymer (CMS-2); (b) the polymer obtained after reaction for 4 h; (c) poly(methyl methacrylate) obtained after reaction for 4 days and removal of polystyrene by extraction with cyclohexane for 3 h; (d) polystyrene obtained after reaction for 4 days and extraction with cyclohexane for 3 h.

relative to the macroinitiators obtained by GPC are much lower than those calculated from ^{1}H NMR and the conversion. The compact structure of the star terpolymers should be responsible for this. To confirm that the PS chains were connected to the PCL-*b*-PMMA macroinitiator, we used cyclohexane to extract star terpolymer CMS-3 in a Soxhlet extractor. No homopolymer of styrene was found in cyclohexane, and the ^{1}H NMR spectrum showed no changes in the ratios of PS to PCL and PMMA, indicating that the polystyrene chains were grown from the junction points of PCL-*b*-PMMA.

Arm Cleavage of a Star Terpolymer (CMS-2). To further confirm the structure of ABC 3-miktoarm star terpolymers that were synthesized by this method, we cleaved the arms off the star terpolymer CMS-2 using sodium methoxide in a mixed solvent of THF and methanol.[40,41] Sodium methoxide was chosen in order to keep the ester group of PMMA intact but to cleave other ester bonds. It was observed in the experiments that the ester groups of PCL were cleaved much faster than the ester linkage between PMMA and PS arms, which was originally from trifunctional initiator **5**. ^{1}H NMR spectroscopy was used to determine the minimum reaction time that was required to completely degrade PCL chain. Under the conditions described in Experimental Section, it took ~4 h to completely degrade PCL chain. A portion of the reaction mixture was then taken for GPC analysis (curve b Figure 9), and the rest of the mixture was continued refluxing for 4 days to completely cleave the ester bond between PS arm and PMMA arm. The resultant mixture of PS and PMMA was separated by extraction with cyclohexane. ^{1}H NMR spectra showed that a complete separation of PS and PMMA was achieved after extraction with cyclohexane for 3 h and 100% pure PS and PMMA were obtained. GPC analysis showed that the molecular weight of PS arm (M_n = 23 800, curve d in Figure 9) was close to the value determined from the ^{1}H NMR analysis (22 600 based on the conversion and 23 600 based on the peaks of PCL), and the polydispersity was 1.34. The molecular weight of PMMA obtained by GPC analysis (M_n = 26 300, M_w/M_n = 1.29, curve c in Figure 9) was also close to that of PMMA (M_n = 28 300, M_w/M_n = 1.26) obtained by cleavage of the PCL-*b*-PMMA macroinitiator. Since PS standards were used for calibration, there was a discrepancy between the values obtained by GPC and ^{1}H NMR analysis (M_n = 19 900). Although the percentage of the ester bond between PS and PMMA arms that was cleaved after reaction for 4 h was unknown, GPC analysis indicated a very high percentage of PS-*b*-PMMA was maintained after 4 h reaction. The number-average molecular weight of PS-*b*-PMMA was 46 000 with a polydispersity of 1.29, close to the sum of the molecular weights of PS and PMMA (M_n = 50 100, GPC results) obtained after the complete cleavage. Arm cleavage experiments confirmed the structure of star terpolymers that were synthesized by this new method.

Conclusions

ABC star terpolymers composed of PCL, PMMA, and PS arms were successfully synthesized from a trifunctional initiator using living ROP of CL, ATRP of MMA, and NMRP of styrene in a three-step process. GPC and kinetic analysis demonstrated that all three types of polymerization were controlled, leading to relatively low polydispersities. The structure of ABC star terpolymers was further confirmed by cleavage of arms off a star terpolymer. This strategy can be extended to the synthesis of a variety of star terpolymers with controlled molecular weights and low molecular weight distributions as living ROP can be extended to the monomer lactide and ATRP can be applied to a variety of methacrylates and acrylates, providing a great flexibility in tailoring the compositions and the molecular weights of star terpolymers.

Experimental Section

Materials and Characterization. 4-Vinylbenzyl chloride (90%, Acros), 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 98%, Acros), benzoyl peroxide (BPO, 97%, Aldrich), and sodium hydride (NaH, 60% dispersion in mineral oil, Acros) were used as received. ϵ-Caprolactone (99%, Aldrich), methyl methacrylate (99%, Acros), and styrene (99%, Aldrich) were dried with calcium hydride and distilled under reduced pressure before use. Toluene and tetrahydrofuran (THF) were distilled from sodium and benzophenone under nitrogen atmosphere just prior to use. Triethylaluminum (1.9 M solution in toluene) was purchased from Aldrich and used as received. All other chemical reagents were purchased from either Acros or Aldrich and used without further purification.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer using $CDCl_3$ as the solvent and the residual solvent proton as the internal standard. Mass spectroscopy was performed in the Mass

Spectroscopy Center in the Chemistry Department at the University of Tennessee at Knoxville on a Micromass Quattro II tandem electrospray spectrometer run in the positive ion electrospray mode. Gel permeation chromatography (GPC) was carried out at room temperature using a modular Knauer GPC system with a HPLC K-501 pump, a UV-K2501 detector, a RI-K2301 refractive index detector, and 5 μm PSS−SDV gel, 10^2−10^5 Å 60 cm, and 100 Å 60 cm columns. The data were processed using Polymer Standards Service software (PSS WinGPC). Tetrahydrofuran (THF) was used as the carrier solvent at a flow rate of 1.0 mL/min, and toluene was used as internal standard. Standard monodisperse polystyrenes (Polymer Laboratories) were used for calibration.

Synthesis of 1. Benzoyl peroxide (5.0 g, 21 mmol) and 4-vinylbenzyl chloride (47.3 g, 0.31 mol) were added into a 250 mL three-necked flask. The mixture was stirred under N_2 atmosphere in an ice bath, and 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 9.07 g, 58.2 mmol) was added slowly. The flask was then placed in an oil bath with a preset temperature of 80 °C. After the reaction proceeded for 20 h, excess 4-vinylbenzyl chloride was removed under reduced pressure, and the crude product was purified by column chromatography using a mixture of methylene chloride and hexanes with a volume ratio of 3:1 as eluent to give **1** (1.81 g, 10.1%). ^{1}H NMR δ (ppm): 0.74, 1.04, 1.17, 1.33 (each br s, 12H, C*H*$_3$), 1.26−1.56 (m, 6H, −C*H*$_2$C*H*$_2$C*H*$_2$−), 4.49 (dd, 1H, −OC*H*H−), 4.56 (s, 2H, −C*H*$_2$-Cl), 4.79 (dd, 1H, −COOCH*H*−), 5.03 (dd, 1H, −C*H*−), 7.35−7.71 (complex m, 7H, Ar*H*), 7.87−7.91 (m, 2H, Ar*H*). ^{13}C NMR δ (ppm): 15.09, 20.37, 34.06, 40.35, 46.08, 60.11, 66.61, 83.55, 127.86, 128.29, 128.30, 129.52, 130.07, 132.86, 136.67, 140.96, 166.26. Mass spectrum 430.14.

Synthesis of 2. Ethylene glycol (148.0 g, 2.387 mol), 3,4-dihydro-2*H*-pyran (10.0 g, 0.119 mol), and tetrahydrofuran (20 mL) were added into a 250 mL flask. After the mixture was stirred in an ice bath for 15 min, 2 drops of concentrated HCl were added. The reaction proceeded at room temperature for 15 h. After removal of THF by rotavapor, methylene chloride (50 mL) was added. The mixture was washed with water five times (5 × 30 mL) and then dried with anhydrous sodium sulfate. After removal of methylene chloride by rotavapor, the crude product was distilled under reduced pressure to give **2** as a colorless liquid (13.98 g, 81.0%). ^{1}H NMR δ (ppm): 1.42−1.82 (m, 6H, −CHC*H*$_2$C*H*$_2$C*H*$_2$−), 2.95 (s, 1H, −O*H*), 3.42−3.51 (m, 1H, −OC*H*HCH$_2$CH$_2$−), 3.61−3.76 (m, 4H, −OC*H*$_2$C-*H*$_2$O−), 3.81−3.92 (m, 1H, −OCH*H*CH$_2$CH$_2$−), 4.51 (m, 1H, −OC*H*O−). ^{13}C NMR δ (ppm): 19.85, 25.12, 30.66, 62.09, 63.09, 70.56, 99.98.

Synthesis of 3. Dry THF (20 mL), **2** (3.72 g, 25.5 mmol), and NaH (1.54 g, 38.5 mmol) were added into a 100 mL three-necked flask. The mixture was stirred under a nitrogen atmosphere for 30 min followed by the addition of a solution of **1** (2.2 g, 5.1 mmol) in THF (10 mL) in a dropwise fashion. The mixture was stirred at room temperature overnight. The solvent was removed by a rotavapor, and the residue was partitioned between water (20 mL) and methylene chloride (20 mL). The aqueous phase was neutralized by a 2 N HCl solution and was extracted by methylene chloride (3 × 20 mL). The organic extracts were combined and dried over anhydrous sodium sulfate. After the removal of methylene chloride by a rotavapor, the crude product was purified by column chromatography using hexanes/ethyl acetate (1:1, v/v) as eluent to afford **3** (1.71 g, 76.8%). ^{1}H NMR δ (ppm): 1.12, 1.19, 1.31, 1.47 (each br s, 12H, −C*H*$_3$) 1.32−1.84 (m, 12H, −CHC*H*$_2$C*H*$_2$-C*H*$_2$− and −CC*H*$_2$C*H*$_2$C*H*$_2$C−), 3.45−3.49 (m, 1H, −OC*H*HCH$_2$-CH$_2$−), 3.59−3.70 (m, 4H, HOC*H*HCHON and −O*CH*$_2$C*H*HO−), 3.81−3.89 (m, 2H, −OCH*H*CH$_2$CH$_2$− and −OCH$_2$CH*H*O−), 4.18 (dd, 1H, HOCH*H*-), 4.55 (s, 2H, ArC*H*$_2$O−), 4.62 (t, 1H, −OC*H*O−), 5.27 (dd, 1H, −HOCH$_2$C*H*−), 5.83 (br s, 1H, −O*H*), 7.31 (m, 4H, Ar*H*). ^{13}C NMR δ (ppm): 17.08, 19.41, 20.34, 20.66, 25.39, 30.52, 32.69, 34.57, 40.13, 40.33, 60.31, 61.65, 62.16, 66.63, 69.37, 69.65, 72.82, 83.36, 98.87, 126.78, 127.65, 138.07, 138.14.

Synthesis of 4. Methylene chloride (15 mL), **3** (1.70 g, 3.91 mmol), and triethylamine (2.40 g, 23.8 mmol) were added into a flask. The reactor was then placed in an ice bath followed by addition of a solution of 2-bromo-2-methylpropionyl bromide (3.83 g, 15.6 mmol) in methylene chloride (10 mL) in a dropwise fashion. The reaction mixture was stirred at room temperature for 8 h, then washed with water (4 × 20 mL), and dried over anhydrous sodium sulfate. After the removal of methylene chloride using a rotavapor, the crude product was purified by column chromatography with 8:1 hexanes/ethyl acetate as eluent to afford **4** (1.81 g, 79.2%). ^{1}H NMR δ (ppm): 0.72, 1.00, 1.16, 1.30 (each br s, 12H, −C*H*$_3$), 1.22−1.84 (m, 12H, −CC*H*$_2$C*H*$_2$C*H*$_2$C− and −CHC*H*$_2$C*H*$_2$C*H*$_2$−), 1.75 (s, 6H, C*H*$_3$−CBr−C*H*$_3$), 3.44−3.50 (m, 1H, −OC*H*HCH$_2$CH$_2$−), 3.57−3.63 (m, 3H, −OC*H*$_2$C*H*HO−), 3.80−3.89 (m, 2H, −OCH$_2$-CH*H*O− and −OCH*H*CH$_2$CH$_2$−), 4.40 (dd, 1H, −COOC*H*H-CHON), 4.53−4.63 (m, 4H, −OC*H*O−, ArC*H*$_2$O−, and −COOC-H*H*CHON), 4.93 (dd, 1H, −C*H*ON), 7.28 (m, 4H, Ar*H*). ^{13}C NMR δ (ppm): 17.07, 19.40, 20.34, 25.39, 30.52, 30.68, 33.98, 40.30, 55.55, 60.11, 62.11, 66.57, 67.48, 69.26, 72.87, 83.29, 98.81, 127.27, 127.56, 137.66, 139.49, 171.31. Mass spectrum: 584.3.

Synthesis of 2-(4-(2′-Oxa-4′-hydroxybutyl)phenyl)-2-(2″,2″,6″,6″-tetramethyl-1-piperidinyloxy)ethyl 2-Bromo-2-methylpropionate (5). Compound **4** (1.80 g, 3.1 mmol), dry Amberlyst 15 ion-exchange resin (0.60 g), and methanol (10 mL) were added into a 50 mL flask. The mixture was stirred under N_2 at 35 °C overnight. The Amberlyst 15 resin was filtered off, and the solvent was removed by a rotavapor. The crude product was purified by column chromatography with 2:1 hexanes/ethyl acetate as eluent to give **5** (1.02 g, 65.8%). ^{1}H NMR δ (ppm): 0.73, 1.02, 1.17, 1.30 (each br s, 12H, −C*H*$_3$), 1.21−1.54 (m, 6H, −C*H*$_2$C*H*$_2$C*H*$_2$−), 1.76 (s, 6H, C*H*$_3$−CBr−C*H*$_3$), 2.10 (t, 1H, −O*H*), 3.54−3.57 (m, 2H, −OC*H*$_2$CH$_2$OH), 3.71−3.76 (m, 2H, −OCH$_2$C*H*$_2$OH), 4.42 (dd, 1H, −COOC*H*H−), 4.53−4.59 (m, 3H, ArC*H*$_2$O− and −COOCH*H*−), 4.95 (dd, 1H, −C*H*ON), 7.24−7.33 (m, 4H, Ar*H*). ^{13}C NMR δ (ppm): 17.07, 20.35, 30.69, 34.05, 55.55, 60.14, 61.84, 67.48, 71.27, 73.02, 83.25, 127.39, 127.68, 137.79, 171.32. Mass spectrum: 500.2.

ROP of CL from Trifunctional Initiator 5. A typical procedure for ROP of CL is as follows. Trifunctional initiator **5** (0.105 g, 0.21 mmol) was added into a dry 25 mL two-necked flask followed by capping of the flask with a rubber septum. The flask was then degassed and back-filled with nitrogen three times followed by injection of dry toluene (2.0 mL) via a syringe. After the initiator was dissolved, a high vacuum was used to remove toluene at room temperature. This process was repeated two more times. The flask was then placed in an oil bath at 35 °C and evacuated for 8 h. The flask was then removed from the oil bath and filled with nitrogen. Dry toluene (3.0 mL) was added followed by injection of the solution of triethylaluminum in toluene (0.116 mL of 1.9 M solution, 0.22 mmol) via a syringe under a nitrogen atmosphere. (*Caution*: the solution of triethylaluminum in toluene should be handled with great care as it can catch fire in air.) The mixture was stirred under a N_2 atmosphere at room temperature for 2 h, and then dry toluene (7.0 mL) and CL (3.0 mL, 28 mmol) were injected via syringes. Samples were taken from the reaction mixture via syringes at a desired time interval for ^{1}H NMR analysis. The polymerization was stopped at a conversion of 60.2% by addition of excess glacial acetic acid with respect to the aluminum catalyst (0.2 mL). The reaction mixture was diluted with methylene chloride, passed through a short neutral aluminum oxide column, and precipitated in methanol. The polymer was purified by precipitation in methanol three times followed by treatment with a high vacuum to give a dry polymer (1.55 g, 50.2%). The polymer was analyzed by GPC relative to PS standards. M_n = 26 800; M_w/M_n = 1.34.

ATRP of MMA Using PCL Macroinitiator. A typical procedure for ATRP of MMA is as follows. Anisole (14.80 g) and MMA (4.78 g, 47.8 mmol) were added into a flask containing a PCL macroinitiator (0.90 g, 0.079 mmol). After PCL was completely dissolved, CuCl (10.0 mg, 0.101 mmol) and pentamethyldiethylenetriamine (34.2 mg, 0.198 mmol) were added. The mixture was degassed by freeze−pump−thaw for three times and then placed in an oil bath with a preset temperature of 75 °C. By use of the peaks at 6.90−7.00 ppm,

which belonged to the solvent anisole as the internal standard, the conversion of the monomer was determined by ^{1}H NMR analysis of the sample taken at a desired time interval using the peak located at 6.07 ppm, which was assigned to one proton in the double bond of MMA. After polymerization for 280 min, tri(*n*-butyl)tin hydride (0.18 mL, 0.67 mmol) was injected, and the reaction continued for 30 min. The mixture was then opened to air and cooled to room temperature. The catalyst was removed by passing the polymer solution through a short aluminum oxide column. The crude polymer was purified by precipitation in methanol three times and dried under high vacuum (1.53 g, 13.2%). The block copolymer was analyzed by GPC against PS standards. $M_n = 46\,100$; $M_w/M_n = 1.26$. ^{1}H NMR analysis showed that the ratio of degrees of polymerization of PCL and PMMA was 1:0.96.

NMRP of Styrene Using the Block Copolymer PCL-*b*-PMMA Macroinitiator. A typical procedure of NMRP of styrene using a PCL-*b*-PMMA macroinitiator is as follows. Chlorobenzene (5.32 g) and styrene (4.48 g, 43.1 mmol) were added into a flask containing the diblock copolymer macroinitiator (0.95 g, 0.045 mmol). The mixture was degassed by three freeze−pump−thaw cycles and then placed in an oil bath with a preset temperature of 120 °C. During the polymerization, samples were taken from the reaction mixture at a desired time via a syringe for ^{1}H NMR analysis. Using the peak at 4.03 ppm (the methylene group of $-COOCH_2-$ in PCL) as the internal standard, the conversion was determined by comparing the integral value of the peaks at 5.72 ppm to that of the same peaks in the original sample. After polymerization for 400 min, the mixture was cooled to room temperature and opened to air. The polymer was purified by precipitation in methanol for three times. Treatment with a high vacuum gave a dry polymer (1.13 g, 4.0%). The star copolymer was analyzed by GPC against PS standards. $M_n = 49\,700$; $M_w/M_n = 1.31$. ^{1}H NMR analysis showed that the ratio of degrees of polymerization of PCL and PMMA and PS was 1:0.96:1.31.

Cleavage of a PCL-*b*-PMMA (CM-2). A solution of sodium methoxide (20.0 mg, 0.37 mmol) in a mixed solvent of THF (5.0 mL) and methanol (0.2 mL) was added into a flask containing a solution of a diblock copolymer PCL-*b*-PMMA (CM-2, 0.20 g) in THF (15 mL). The reaction mixture was refluxed at 70 °C for 5 h. After removal of solvents, the polymer was dissolved in methylene chloride and precipitated in methanol. The polymer was then analyzed by ^{1}H NMR and GPC. $M_n = 28\,300$, $M_w/M_n = 1.26$.

Cleavage of an ABC Star Terpolymer (CMS-2). A solution of sodium methoxide (27.5 mg, 0.51 mmol) in a mixed solvent of THF (5.0 mL) and methanol (0.3 mL) was added into a 50 mL flask containing a solution of a star terpolymer (CMS-2 in Table 2, 0.40 g) in THF (20 mL). The mixture was refluxed at 70 °C. The degradation of PCL was monitored by ^{1}H NMR. As soon as the peaks at 4.03 ppm completely disappeared (after ∼4 h), a portion of the reaction mixture (3.0 mL) was taken, and the solvent was removed by a rotavapor. The polymer was redissolved in methylene chloride and precipitated in methanol. The rest of the reaction mixture was refluxed for 4 days. After removal of the solvents, the polymer was precipitated in methanol, dried with a high vacuum, and then extracted with cyclohexane using a Soxhlet extractor for 3 h. Both the polymer that remained in the thimble of the extractor and the polymer that was extracted into cyclohexane were analyzed by ^{1}H NMR and GPC. The M_n and polydispersity of PMMA were 26 300 and 1.29, respectively. The M_n and polydispersity of PS were 23 800 and 1.34, respectively.

Acknowledgment. The authors thank the University of Tennessee at Knoxville (start-up funds) and the American Chemical Society Petroleum Research Funds (PRF# 40084-G7) for supporting this research.

References and Notes

(1) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649−4651.
(2) Hadjichristidis, N.; Iatrou, H.; Behal, S. K.; Chludzinski, J. J.; Disko, M. M.; Garner, R. T.; Liang, K. S.; Lohse, D. J.; Milner, S. T. *Macromolecules* **1993**, *26*, 5812−5815.
(3) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 1518−1520.
(4) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 8429−8432.
(5) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857−871.
(6) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208−2213.
(7) Okamoto, S.; Hasegawa, H.; Hashimoto, T.; Fujimoto, T.; Zhang, H.; Kazama, T.; Takano, A.; Isono, Y. *Polymer* **1997**, *38*, 5275−5281.
(8) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 5272−5277.
(9) Yamauchi, K.; Takahashi, K.; Hasegawa, H.; Iatrou, H.; Hadjichristidis, N.; Kaneko, T.; Nishikawa, Y.; Jinnai, H.; Matsui, T.; Nishioka, H.; Shimizu, M.; Furukawa, H. *Macromolecules* **2003**, *36*, 6962−6966.
(10) Dotera, T. *Phys. Rev. Lett.* **1999**, *82*, 105−108.
(11) Gemma, T.; Hatano, A.; Dotera, T. *Macromolecules* **2002**, *35*, 3225−3237.
(12) Hüchstädt, H.; Abert, V.; Stadler, R. *Macromol. Rapid Commun.* **1996**, *17*, 599−606.
(13) Hüchstädt, H.; Göpfert, A.; Abert, V. *Macromol. Chem. Phys.* **2000**, *201*, 296−307.
(14) Quirk, R. P.; Yoo, T.; Lee, B. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 911−926.
(15) Lambert, O.; Reutenauer, S.; Hurtrez, G.; Riess, G.; Dumas, P. *Polym. Bull. (Berlin)* **1998**, *40*, 143−149.
(16) Lambert, O.; Reutenauer, S.; Hurtrez, G.; Dumas, P. *Macromol. Symp.* **2000**, *161*, 97−102.
(17) Feng, X.-S.; Pan, C.-Y. *Macromolecules* **2002**, *35*, 2084−2089.
(18) Feng, X.-S.; Pan, C.-Y. *Macromolecules* **2002**, *35*, 4888−4893.
(19) Tunca, U.; Karliga, B.; Ertekin, S.; Ugur, A. L.; Sirkecioglu, O.; Hizal, G. *Polymer* **2001**, *42*, 8489−8493.
(20) Tunca, U.; Erdogan, T.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2025−2032.
(21) Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R.; Hedrick, J. L.; Hawker, C. J.; Malmstrom, E. E.; Trollsas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1274−1276.
(22) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(23) Hawker, C. J.; Hedrick, J. L.; Malmstrom, E. E.; Trollsas, M.; Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R. *Macromolecules* **1998**, *31*, 213−219.
(24) Jérôme, R. *Macromol. Symp.* **2002**, *177*, 43−59.
(25) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1997**, *30*, 7050−7055.
(26) Weimer, M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425−8428.
(27) Smith, A. P.; Fraser, C. L. *Macromolecules* **2002**, *35*, 594−596.
(28) Hedrick, J. L.; Trollsas, M.; Hawker, C. J.; Atthoff, B.; Heise, C. A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, Ph. *Macromolecules* **1998**, *31*, 8691−8705.
(29) Ydens, I.; Degee, P.; Dubois, P.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromol. Chem. Phys.* **2003**, *204*, 171−179.
(30) Mayer, U.; Palmans, A. R. A.; Loontjens, T.; Heise, A. *Macromolecules* **2002**, *35*, 2873−2875.
(31) Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 977−981.
(32) Jacobs, C.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1991**, *24*, 3027−3034.
(33) Dubois, Ph.; Degéé, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 2730−2735.
(34) Dubois, Ph.; Barakat, I.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 4407−4412.
(35) Dubois, Ph.; Ropson, N.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 1965−1975.
(36) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(37) Zhao, B. *Polymer* **2003**, *44*, 4079−4083.
(38) Zhao, B.; He, T. *Macromolecules* **2003**, *36*, 8599−8602.
(39) Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 66−70.
(40) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762−6768.
(41) Johnson, R. M.; Corbin, P. S.; Ng, C.; Fraser, C. L. *Macromolecules* **2000**, *33*, 7404−7412.

MA036010C