Macromolecules

Volume 32, Number 16 August 10, 1999

Unimolecular Combination of an Atom Transfer Radical Polymerization Initiator and a Lactone Monomer as a Route to New Graft Copolymers

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Received December 28, 1998; Revised Manuscript Received June 2, 1999

ABSTRACT: The synthesis, polymerization, and copolymerization of a new cyclic ester, γ-(2-bromo-2-methyl propionyl)-ϵ-caprolactone (**3**), containing a pendent-activated alkyl bromide functional group is described. This new compound serves as both a monomer for "living" ring-opening polymerization (ROP) as well as an initiator for the controlled atom transfer radical polymerization (ATRP). Three distinctive routes to poly(ϵ-caprolactone)−graft−poly(methyl methacrylate) copolymers were surveyed by either sequential or concurrent living polymerization procedures. The first approach involves the ROP of ϵ-caprolactone with various compositions of **3**, followed by the polymerization of methyl methacrylate via ATRP from the activated alkyl bromide sites along the polyester backbone. Alternatively, α-lactone functional methyl methacrylate macromonomers were prepared by ATRP of methyl methacrylate initiated from **3**. The macromonomers were copolymerized with ϵ-caprolactone via ROP to form the target graft copolymers. Finally, the graft copolymers could be prepared in a simple one-step approach by the concurrent polymerization of ϵ-caprolactone, **3**, and methyl methacrylate together with the appropriate initiator for the ROP and the catalyst for the ATRP. The new monomer enabled new graft copolymers having an aliphatic polyester backbone with poly(methyl methacrylate) grafts of controlled molecular weight and narrow polydispersities (∼1.3).

Introduction

The renewed interest in the macromolecular engineering of poly(lactones) and related polyesters stems from the discovery that many organometallic compounds are effective initiators/catalysts for controlled ring-opening polymerization (ROP),[1] allowing the preparation of functional oligomers, random and block copolymers, and polymers with unique topology or architectural control.[1−4] For instance, asymmetric functionality can be introduced in a controlled way through the use of aluminum alkoxide initiators bearing functional alkoxide groups [$Et_2Al(ORX)$, where X is any functional group]. After hydrolytic deactivation of the active aluminum alkoxide growing species, α-X-ω-hydroxy poly(lactone) telechelic chains are quantitatively and selectively recovered. The coupling of the telechelic macromonomers through block copolymerization provides a precise methodology to controlled macromolecular architecture.[2] Alternatively, dual "living" controlled polymerizations from a single initiating molecule without intermediate activation or transformation steps has been demonstrated with ROP of lactones, as well as other living procedures, with controlled free radical procedures, either nitroxide-mediated or atom transfer radical polymerization (ATRP), to form well-defined graft and block polymers.[5,6] The compatibility of these living controlled procedures allowed the polymerizations to be performed sequentially or concurrently.[6] The versatility of ROP as a means to macromolecularly engineer aliphatic polyesters and related structures has resulted in the synthesis of many new block and graft copolymers.

The introduction of controlled branching provides an alternative methodology to controlled macromolecular architectures. Dendrimers provide the ultimate example of the effects of branching on the physical and solution properties of polymers, whereas hyperbranched polymers are less perfect elaborations of such three-dimensional structures.[7] Noteworthy examples of dendritic polyesters have been reported by condensation methods.[8] However, the use of ROP methods to prepare polymers with unique topologies has been much less pervasive than other polymerization methods and has focused primarily on star polymers, and more recently,

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10.1021/ma982005a CCC: $18.00
Published on Web 07/23/1999

Kricheldorf[9] et al. have reported cyclic polyesters. The ROP of ϵ-caprolactone from the focal point of a fourth-generation dendron was reported to give a hybrid dendritic−linear block copolymer.[10] Likewise, we have reported the ROP of ϵ-caprolactone initiated from the peripheral surface functionality of dendritic molecules, such as dendrons, dendrimers, and hyperbranched polymers, derived from 2,2′-bis(hydroxymethyl) propionic acid, containing hydroxyl functionalities in the presence of stannous(II) 2-ethylhexanoate [$Sn(Oct)_2$]. This polymerization was found to be controlled, and accurate control of molecular weight, polydispersity, and end-group functionality was demonstrated, which permitted the synthesis of well-defined dendritic block and star polymers.

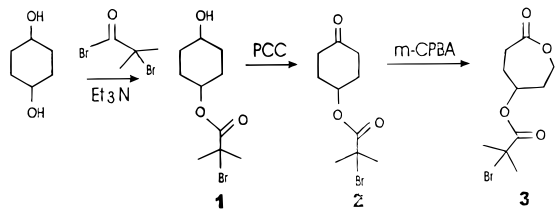
Among the many examples of the macromolecular engineering of aliphatic polyesters, only a few have focused on the modification of the cyclic lactones or lactides. Such monomers would be highly desirable for the fine tuning of properties such as T_g, degree of crystallinity, hydrophilicity, chemical reactivity, and so on. For instance, Albertsson and others[11] used multifunctional cyclic esters such as 2,2′-bis(ϵ-caprolactone-4-yl)propane and related monomers to crosslink aliphatic polyesters and impart elastomeric character. However, there are only limited examples of lactone or lactide monomers bearing functional groups.[12] For instance, Jérôme et al.[13] used 5-ethylene ketal caprolactone as a comonomer in the synthesis of aliphatic polyesters subsequent deacylation and reduction produced a hydroxyl functional polyester. These aliphatic polyester are hydrophilic and may be used for applications associated with this property including amphiphilic block polymers. Likewise, our interest is in the preparation of functional monomers as an alternative way to manipulate the properties and structure through controlled branching and block/graft copolymerization, as well as the semicrystalline morphology and polarity. In this article, the new functional lactone monomer that allows the preparation of well-defined graft copolymers will be described by a combination of ROP and ATRP of lactones and a variety of methacrylates (MA). Three synthetic routes to the target copolymers will be surveyed including a one-pot, one-step concurrent dual polymerization route and several sequential routes including a macromonomer approach and a grafting-from approach. The key attributes of each of these synthetic procedures will be discussed and compared. Moreover, this work constitutes the first example of lactone functional macromonomers and methacrylate-based copolymers with a polyester backbone.

Experimental Section

Materials. Toluene was dried by refluxing over sodium and distilled under nitrogen prior to use, ϵ-caprolactone (ϵ-CL) was dried over CaH_2 and distilled under reduced pressure being stored under dry nitrogen atmosphere. The benzyl 2,2-bis(hydroxymethyl)propionate was synthesized as described elsewhere.[15] All other chemicals were purchased from Aldrich and used without further purification.

(4-Hydroxycycloheyl) 2-Bromo-2-methylpropionate, ***1***. 1,4-Cyclohexanediol (60.0 g, 519 mmol) and Et_3N (90.0 g, 780 mmol) were dissolved in THF (500 mL). 2-Bromoisobutyryl bromide (120 g, 519 mmol) were then slowly added. After 24 h of mixing, the THF was removed by evaporation. CH_2Cl_2 (1000 mL) was then

Scheme 1



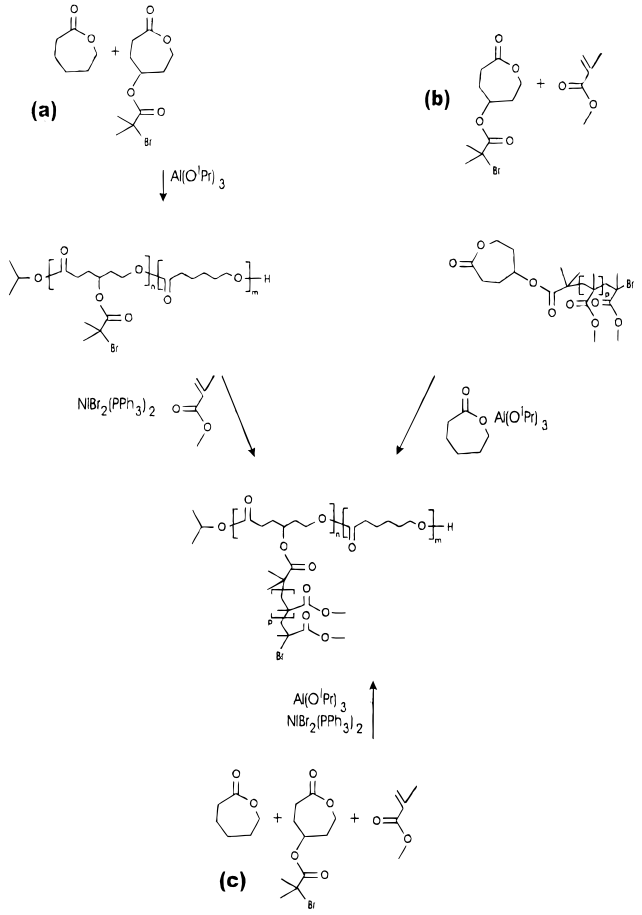
added, and the solution was washed three times with dilute HCl (1 M) and at last two more times with H_2O before it was dried over $MgSO_4$ and filtered. The product was purified using column chromatography (by silica gel using hexane/EtOAc gradient as eluent; the concentrations were 5, 10, 20, and 40 vol % of EtOAc). The product was followed and found with thin layer chromatography (TLC). After evaporating, the product came out as a orange liquid, which was further purified by distillation (140 °C, 10 mm Hg), giving a clear liquid. Yield: 72.0 g (40%). ^{1}H NMR ($CDCl_3$): δ 1.38−1.96 (m, 8H, $-CH_2-$), 1.84−1.87 (d, 6H, $-CH_3$), 3.67−3.77 (m, 1H, −CHOH−), 4.72−4.89 (m, 1H, −CHO−). ^{13}C NMR ($CDCl_3$): δ 27.27, 27.41, 30.37, 30.68, 31.39, 56.25, 56.33, 68.27, 71.09, 73.11, 171.0, 171.9.

(4-Ketocyclohexyl) 2-Bromo-2-methylpropionate, ***2***. Pyridinium chlorochromate (PCC) (69.0 g, 322 mmol) was added to a solution of **1** (71.0 g, 268 mmol) in CH_2Cl_2. After the mixture had been stirred for 3 h, anhydrous ethyl ether (300 mL) was added. The obtained mixture was filtered through silica gel. The yellow solution was then evaporated and purified using column chromatography (by silica gel using hexane/EtOAc gradient as eluent; the concentrations were 5, 10, 20, and 40 vol % of EtOAc). The product was a white crystalline powder. Yield: 48 g (68%). ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 6H, $-CH_3$), 2.02−2.69 (m, 8H, $-CH_2-$), 5.16−5.23 (m, 1H, −CHO−). ^{13}C NMR ($CDCl_3$): δ 29.92, 30.60, 36.96, 55.98, 69.87, 170.8.

γ-(2-Bromo-2-methylpropionyl)-ϵ-caprolactone, ***3***. **2** (47.8 g, 182 mmol) was dissolved in 300 mL of $CHCl_3$ and added dropwise into a solution of 3-chloroperoxybenzoic acid (99.3 g, 407 mmol) in $CHCl_3$ (400 mL). The mixture was stirred for 24 h and then filtered over celite. The obtained yellow solution was washed twice with $NaHCO_3$ (2 M) and once with brine. The extracted product was then purified by column chromatography (by silica gel using hexane/EtOAc gradient as eluent; the concentrations were 5, 10, and 20% of EtOAc). The crude monomer was recrystallized from anhydrous ethyl ether to give the product as a white crystalline powder. Yield: 31.0 g (64%). ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 6H, $-CH_3$), 1.92−2.11 (m, $-CH_2-$), 2.47−3.02 (m, 2H, $-CH_2CO-$), 4.09−4.53 (m, 2H, $-CH_2O-$), 5.11−5.18 (m, 1H, −CHO−). ^{13}C NMR($CDCl_3$): δ 27.06, 28.26, 30.52, 33.45, 55.84, 63.15, 71.18, 170.4, 174.8. IR (cm^{-1}): 2948, 2974, 2925, 1723, 1445, 1283, 1234, 1176, 1063, 1024, 971, 888.

Polymerization Techniques. *ROP Using Al(O^{i}Pr)$_3$.* Homopolymerization and random copolymerization was carried out at 25 °C in dry toluene. **3** was dried by repeated azeotropic distillation (three times) of toluene just before polymerization. Then, solvent, ϵ-caprolactone (when needed), and initiator (solution in toluene) were successively added through a rubber septum with a syringe or stainless-steel capillary. After polymerization, an excess of 1 N HCl was added, and the polymer was recovered by precipitation in cold heptane.

Scheme 2



ROP Using Sn(Oct)$_2$. Copolymerizations were initiated with previously dried and distilled benzyl ester of bis-MPA using a catalytic amount of Sn(Oct)$_2$.[4e,f] The polymerizations were carried out in bulk at 110 °C for different times. The polymers were then dissolved in THF and precipitated in cold methanol.

The poly(caprolactone) macroinitiator and NiBr$_2$(PPh$_3$)$_2$ (20 mol %) were charged into the flask and evacuated and back-filled with nitrogen three times. The flask was placed in an oil bath heated to 80 °C, where the poly(caprolactone) melted. To this flask, methyl methacrylate or a mixture of methyl methacrylate and solvent was added. The polymerization times varied from several hours to overnight depending on the solids and catalyst contents. The polymers were dissolved in THF and isolated in either heptane or hexane and reprecipitated into methanol to afford a white powder.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrene of known molecular weight as the calibration standards. Four 5 μm Waters columns connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6 Å) were used with THF as solvent.

Results and Discussion

The synthesis of the new ATRP initiator functionalized lactone monomer **3** was performed in three steps (Scheme 1). 1,4-Cyclohexanediol was reacted with 0.8 equiv of 2-bromoisobutyryl bromide to yield the monofunctional intermediate product **1** in 40% yield. The isolated alcohol **1** was then oxidized into the corresponding ketone **2** by the use of pyridinum chlorochromate (PCC). Through a Bayer−Villiger oxidation, the ketone **2** was transformed into the corresponding cyclic ester **3** by using 3-chloroperoxybenzoic acid as a reagent.

This new monomer allows the synthesis of poly(ϵ-caprolactone)−graft−poly(methyl methacrylate) copolymers by three different synthetic routes. The first approach surveyed is the grafting-from technique, where initiating sites for ATRP are dispersed along the aliphatic polyester backbone (i.e., multifunctional "macroinitiator"), followed by the formation of poly(methyl methacrylate) grafts.[14] The second route to defined graft copolymers involves the preparation of methyl methacrylate macromonomers with lactone functionality by ATRP techniques, followed by the ROP with ϵ-caprolactone to yield the target graft copolymer. The final synthetic approach to the graft copolymers surveyed is a one-step, one-pot synthesis where the two polymerization procedures occur at the same time. The synthesis of these graft copolymers was accomplished by the use of a new compound that acts simultaneously as a monomer and an initiator for two different types of polymerization, ROP and ATRP ring-opening and controlled free radical. Previous investigations have described compounds that serve as "double headed" initiators for dual living polymerizations[6] and others that serve as initiators/chain terminators.[15] The three approaches to the graft copolymers are summarized in Scheme 2.

Table 1. ROP of 3 and Copolymers of 3 and ϵ-Caprolactone

entry	reaction time (h)	yield (wt %)	mol fraction of **3** in feed: target	mol fraction of **3** in feed: measured	M_n theor[a]	M_n ^{1}H NMR[b]	M_n SEC[c]	M_w/M_n
4a	24	95	1	1	4 000	3800	4 800	1.24
4b	20	95	0.40	0.37	5 000	4750	12 300	1.15
4c	20	95	0.10	0.10	7 500	7500	8 700	1.30
4d	6	95	0.05	0.04	10 000	9500	19 200	1.14
4e	30	90	0.05	0.04	10 000	9000	14 000	1.38
4f	30	94	0.10	0.08	10 000	9200	16 300	1.44
4g	20	55	0.30	0.22	20 000		16 000	1.57
4h	30	77	0.40	0.34	7 700	6600	9 000	1.55

[a] Theoretical number-average molecular weight: $M_n = [\epsilon CL]/[init] \times 114 + MW_{init}$. [b] Experimental number-average molecular weight was measured by ^{1}H NMR. [c] M_n was determined by SEC (with polystyrene standards).

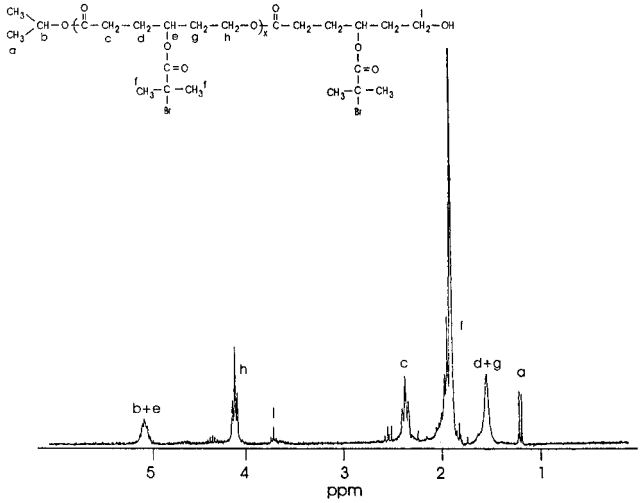


Figure 1. ^{1}H NMR spectrum of **4a**.

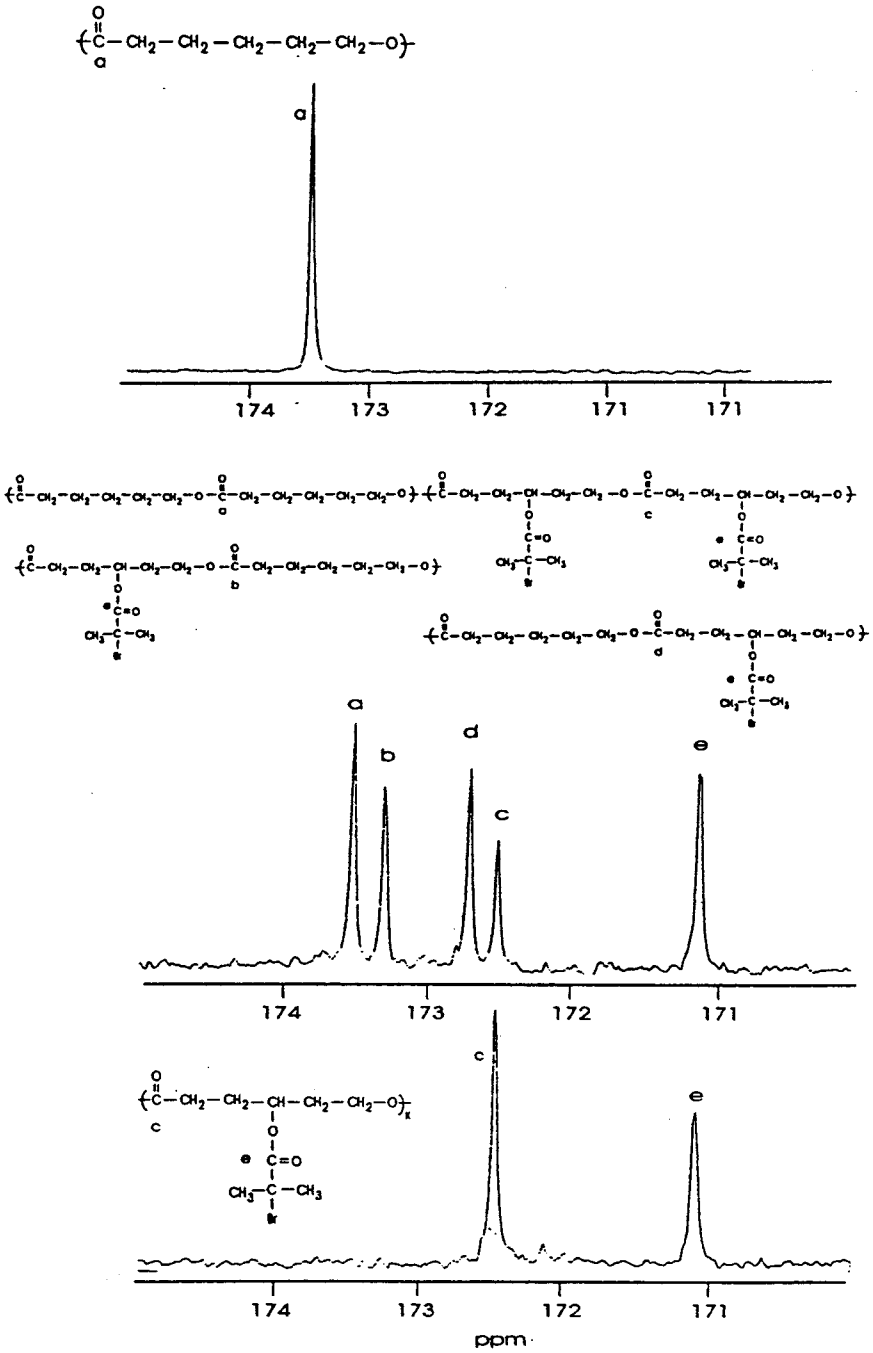


Figure 2. ^{13}C NMR spectrum of (a) poly(ϵ-caprolactone), (b) **4b**, and (c) **4a**.

The preparation of the graft copolymers from the macroinitiator approach required that **3** polymerize by conventional ROP methods and that copolymerization with ϵ-caprolactone produces statistically random copolymers (polymer series 4, Table 1). Aluminum triisopropoxide was used to initiate the ROP of **3** and was homopolymerized and copolymerized with ϵ-CL in toluene (25 °C). The homopolymerization of **3** affords a polymer, **4a**, which has a narrow polydispersity ($M_w/M_n = 1.20$) and accurate molecular weight control, as judged from the initial monomer-to-initiator ratio and quantitative conversion of monomer to polymer (Table 1). The narrow polydispersity suggest that the ROP of **3** initiated from $Al(O^iPr)_3$ is controlled and is believed to proceed via a coordination-insertion mechanism from selective acyloxygen bond cleavage of the cyclic monomer. Shown in Figure 1 is the ^1H NMR spectra of **4a**. The spectra confirms the major peaks associated with the backbone, the presence of the isopropyl ester and a hydroxyl functional end group, and the absence of a monomer. In addition, the peaks associated with the activated alkyl bromide can be seen. Likewise, similar results were obtained for the copolymerizations of **3** with ϵ-caprolactone using the same experimental conditions (**4b**−**d**). The molecular weights agree with the values predicted from the monomer-to-initiator ratio, and the polydispersities are low, indicating the absence of transesterification reactions. Furthermore, the molar fraction of the respective components in the block copolymer, as measured by ^1H NMR, corresponds to the monomer feed, consistent with quantitative yields. ^{13}C NMR was used to assess the randomness of the aliphatic polyester copolymers. In particular, the signal of the carbonyl group is very sensitive to the nature of the adjacent

Table 2. Characteristics of Graft Copolymers Initiated from Macroinitiators 4

entry	macroinitiator	monomer	reaction time (h)	yield (wt %)	mol fraction of MMA in feed		M_n	M_n	M_n	
					target	measured	theor[a]	^{1}H-NMR[b]	SEC[c]	M_w/M_n
5a	**4d**	MMA	8	77	0.75	0.75	35 000	34 500	35 000	1.28
5b	**4c**	MMA	14	85	0.70	0.71	30 000	23 000	30 600	1.35
5c	**4h**	MMA	14[d]	95						
5d	**4h**	MMA	8		0.80	0.79	57 000		47 000	1.41
5e	**4d**	TMSEMA[e]	48	90	0.75	0.73	45 000	37 000	29 000	1.35

[a] Theoretical number-average molecular weight of the graft copolymer: $M_n = M_{n\ macro} + W_{Ma}/W_{Cl} \times M_{n\ macro}$. [b] Experimental number-average molecular weight was measured by ^{1}H NMR. [c] M_n was determined by SEC (with polystyrene standards). [d] A gel was obtained. [e] Trimethylsililoxy ethyl methacrylate.

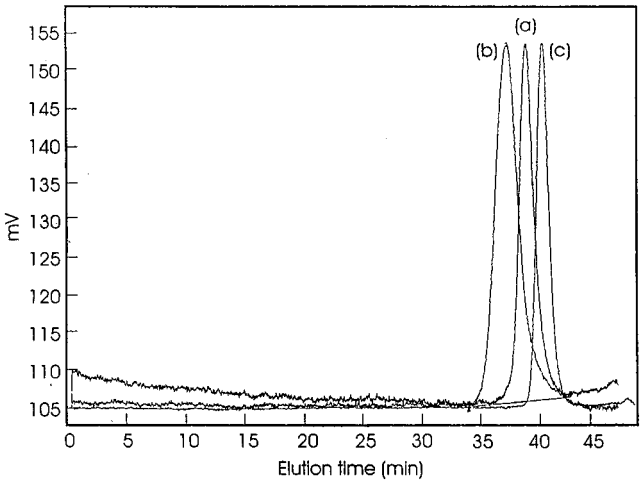


Figure 3. SEC traces for (a) **4d**, (b) **5a**, and (c) cleaved poly(methyl methacrylate) grafts.

units. Figure 2 shows a comparison of the carbonyl region of ^{13}C NMR spectra of both homopolymers and copolymer **4b** ($F_3 = 0.40$) where the signals of the four different diads are distinguished. From the relatively high intensity of the diads, the copolymers are assumed to possess a random instead of a block structure. Random copolymerizations were also carried out at 110 °C using $Sn(Oct)_2$ as a catalyst (entries **4e**−**h** of Table 1). Although the copolymerizations are successful, the control is somewhat compromised as evidenced by the broader molecular weight distributions ($M_w/M_n = 1.35$−1.60) and incomplete monomer conversions (entries **4g**,**h**). The ^{1}H NMR spectra shows the appearance of double bonds, consistent with products associated with the elimination of bromide as previously reported.[16]

The bromide functional polyesters were used as macroinitiators for the preparation of the graft copolymers (Scheme 2a). Fortuitously, methyl methacrylate is a good solvent for poly(caprolactone) allowing bulk polymerization conditions. However, THF was used in some cases to facilitate the miscibility and mediate the viscosity of the final copolymer.

This general polymerization procedure was applied to each of the macroinitiators, and the characteristics of the graft copolymers prepared (copolymer series **5**) are shown in Table 2. For example, polymerization of methyl methacrylate from **4d** via ATRP-produced **5a** with a number-average molecular weight of 34 500 and a polydispersity of 1.28 in 80% conversion. Shown in Figure 3 are the SEC traces of **4d** and **5a**, where the copolymer shows the expected increase in molecular weight while maintaining a narrow polydispersity. ^{1}H NMR spectroscopy confirmed the structure with representative signals from both the caprolactone and methyl methacrylate components (Figure 4). The molar composition, calculated by comparison of the integrations of the separate signals, corresponds to the expected composition of the copolymer taking into account the charged composition and the conversion (Table 2). To further confirm the copolymer structure, the copolymer **5a** was dissolved in 1,4-dioxane (85 °C) and hydrolyzed with aqueous hydrochloric acid solution to give the cleaved poly(methyl methacrylate) grafts. Analysis of the product by ^{1}H-NMR clearly shows the disappearance of the resonances from **3** (Figure 3d), and comparison of the SEC traces (Figure 4) shows the grafts shifted to a lower molecular weight ($M_n = 13\ 600$) with a very low polydispersity index ($M_w/M_n = 1.06$). This constitutes further proof of the graft copolymer structure and characteristics of the graft. The macroinitiators with high contents of **3** gelled upon polymerization (**5c**), consistent with observations made by Hawker et al. on analogous systems because of the coupling reactions of radicals with the formation of a network.[17] To circumvent this problem and obtain high-density graft copolymers, the polymerizations were terminated at modest levels of conversion (**5d**), where termination coupling reactions are minimum. These results corroborate the validity of our strategy for the synthesis of the graft copolymers. It is worthwhile to remark that this method can be extrapolated to other monomers with interesting functionality. For instance, copolymer **5e** shows the synthesis of a poly(ϵ-caprolactone)-graft-poly(TMSEMA) copolymer that, after deprotection, leads to an amphiphilic copolymer.

The second synthetic approach to poly(ϵ-caprolactone)−graft−poly(methyl methacrylate) copolymers uses well-defined macromonomers, prepared by ATRP, to be used in a ROP synthesis. Although macromonomers containing a wide variety of polymerizable end groups have been synthesized and in some cases are commercial products, there are no reports on the synthesis of macromonomers bearing a polymerizable lactone end group. Our approach to the synthesis of graft copolymers using this technique is illustrated in Scheme 2b. The first step is the preparation of the new macromonomers that possess the caprolactone-type end group (Table 3). This was achieved by using **3** as initiator for the atom transfer polymerization of methyl methacrylate in the presence of $NiBr_2(PPh_3)_2$. The first entry corresponds to a bulk polymerization and affords a poly(methyl methacrylate), **6a**, with a molecular weight higher than that expected from the monomer-to-initiator ratio. The use of a small quantity of toluene as solvent, **6b** and **6c**, produced polymers with molecular weights that correlate well to the expected ones, and the polydispersities of the obtained poly(methyl methacrylate) are narrow, in good agreement with the controlled ATRP mechanism. Accordingly, ^{1}H NMR allows for the identification of the signals corresponding to the lactone end group (see Figure 5). Furthermore, the molecular weight

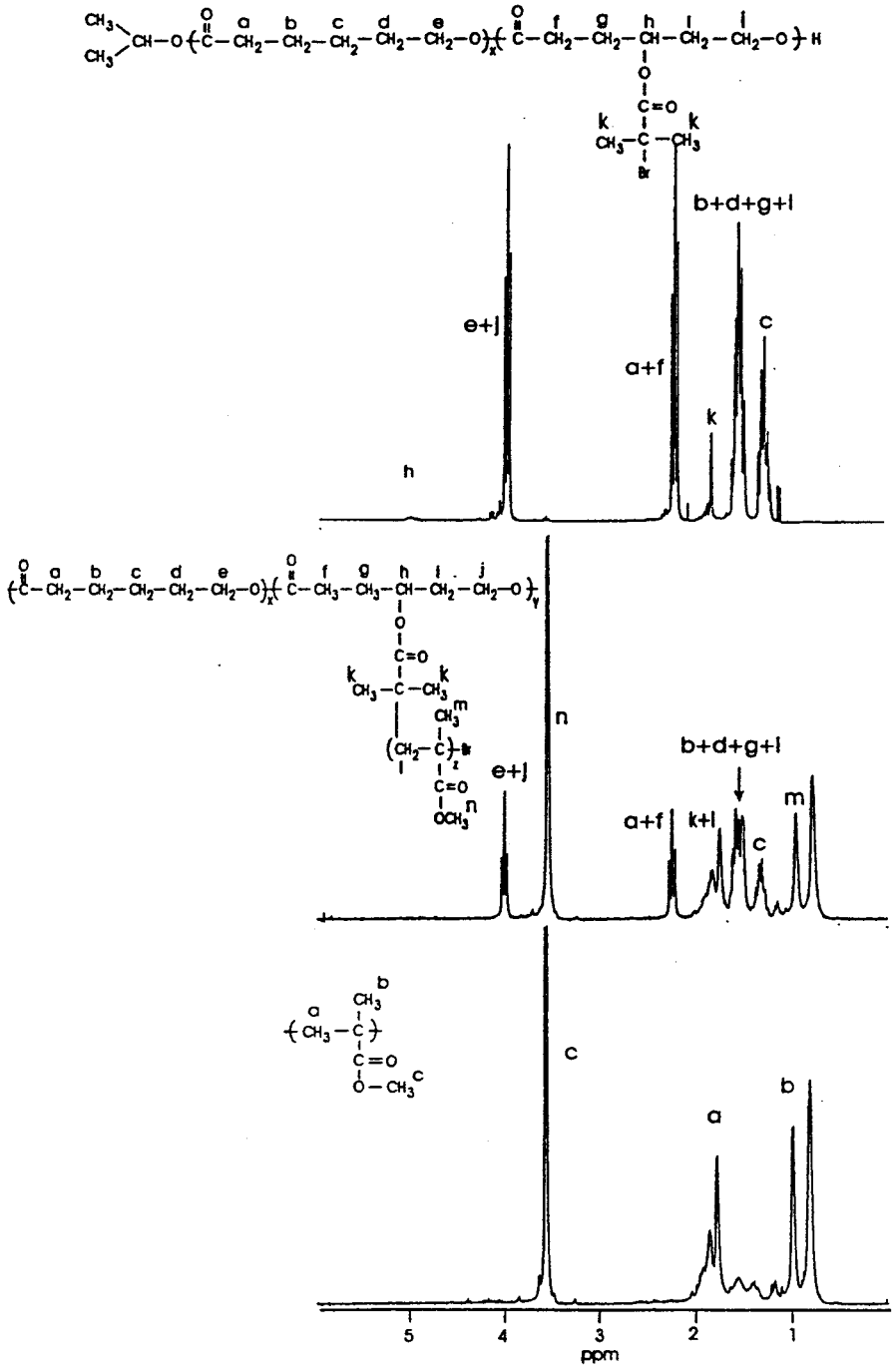


Figure 4. ^{1}H NMR spectrum of (a) **4d**, (b) **5a**, and (c) cleaved poly(methyl methacrylate) grafts.

Table 3. Characteristics of *a*-Lactone Functional Methyl Methacrylate Macromonomers

entry	reaction time (h)	yield (wt %)	M_n theor	M_n ^{1}H NMR	M_n SEC	M_w/M_n
6a	16	90	2000	2200	2100	1.16
6b	16	90	2000	2300	2000	1.15
6c	16	90	4000	3800	3500	1.22

calculated from comparison of the integration of the signals corresponding to the methyl methacrylate units with the signals from the lactone end group is in good correlation with the molecular weight measured by SEC. This suggests a quantitative functionalization of the poly(methyl methacrylate) chains.

Copolymerization of the ϵ-caprolactone functional methyl methacrylate macromonomers with ϵ-caprolac-

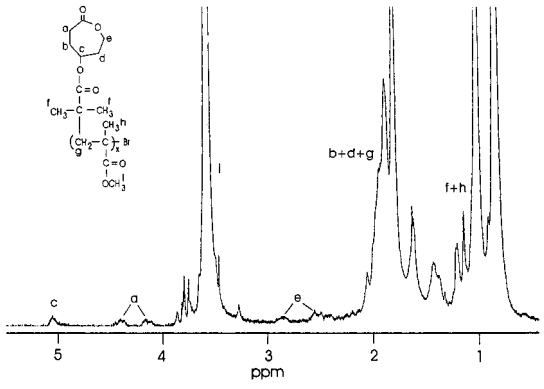


Figure 5. ^{1}H NMR spectrum of **6c**.

Table 4. Characteristics of Graft Copolymer Prepared from Macromonomer Route

entry	macro-monomer	reaction time (h)[a]	mol fraction of macromonomer in the field: target	mol fraction of macromonomer in the field: measured ^{1}H NMR	yield (wt %)	M_n SEC[b]	M_w/M_n
7a	6b	14	0.52	0.53	96	8 900	1.45
7b	6b	14	0.69	0.62	94	11 500	1.50
7c	6c	14	0.68	0.6	92	16 000	1.81
7d	6c	14	0.82	0.82	80	8 900	1.44
7e	6b	48	0.33	0.27	95		
7f	6b	48	0.47	0.49	95	18 000	1.70

[a] Reaction conditions: toluene, [monomer] are at 85 °C. [b] M_n was determined by SEC (with polystyrene standards).

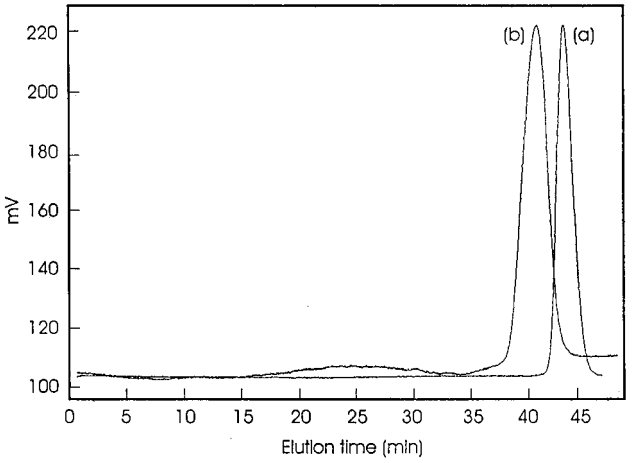


Figure 6. Comparison of the SEC traces for macromonomers (a) **6b** and (b) **7e**.

tone was accomplished using $Sn(Oct)_2$ as the catalyst and the benzyl ester of bis-MPA as the initiator. The polymerization of ϵ-caprolactone under these conditions has been demonstrated to be nearly quantitative and controlled.[2i] The reaction conditions and the characteristics of copolymer series **7** are listed in Table 4. The graft copolymers were purified from residual trace amounts of unreacted monomer/macromonomers by precipitation in hexanes and extraction with methanol. Examination of the ^{1}H NMR spectrum of the graft copolymers reveals resonances for both the methyl methacrylate and ϵ-caprolactone components, suggesting the incorporation of the macromonomers into the polymeric backbone. The ratio of incorporation was determined by comparison of the discrete resonance at 4.10 ppm with the resonance at 3.75 ppm, which compares favorably with the feed ratio in all cases. Graft copolymer formation was corroborated by the comparison of the SEC traces of macromonomer **6b** with those of graft copolymer **7e** (Figure 6). The SEC trace of the graft copolymer shows the expected increase in molecular weight and the absence of any unreacted macromonomer. These results demonstrate the validity of our second pathway for the synthesis of copolymers series **7**. It is worthwhile to remark that this is simply one example of a graft system from a specific monomer set, but in principle, this approach is applicable to other cyclic monomers such as other lactones and lactides as well as other (meth)acrylic or styrenic functional and nonfunctional monomers.

The last route to the targeted graft copolymer is the concurrent or dual living polymerization approach. The new compound, **3**, was used simultaneously as a monomer and initiator for two different types of polymerization, ring-opening and controlled radical, at the same time. $Al(O^iPr)_3$ was the initiator for the ROP of ϵ-caprolactone, and $NiBr_2(PPh_3)_2$ was used as the catalyst for ATRP of methyl methacrylate. The polymerizations were performed in the bulk at 90 °C, and after 14 h, the product as dissolved in THF and precipitated in hexanes. The graft copolymer, **8**, was isolated in 92% yield and had a number-average molecular weight by SEC of 12 000, relative to polystyrene standards. The polydispersity of **8** was somewhat broader than those prepared sequentially and was 2.30 in 92% yield. Although the degree of control over the copolymer parameters was partially compromised, it is the simplicity of this approach compared to the other ones described that sets it apart.

Summary

The synthesis of a new functionalized cyclic ester, **3**, is described that served as a monomer amenable toward living ROP of cyclic esters as well as an initiator for the ATRP of methyl methacrylate. The new monomer/initiator enabled poly(ϵ-caprolactone−graft−poly(methyl methacrylate) copolymers by three distinctive routes. New activated bromide functional macroinitiators were prepared that allowed the growth of methyl methacrylate grafts to form the requisite graft copolymers. Alternatively, lactone functional methyl methacrylate macromonomers were prepared and used as comonomers in the ROP of ϵ-caprolactone to form the target graft copolymers. Finally, the graft copolymers could be prepared in a one-step approach by the concurrent polymerization of ϵ-caprolactone, **3**, and methyl methacrylate together with the appropriate initiator for the ROP of the lactones, together with the catalyst for ATRP. Each of the three synthetic routes to the graft copolymers surveyed produced somewhat different results. The most pronounced difference was between the one-pot, one-step concurrent polymerization procedure and the macromonomer route in which the polymerizations were conducted sequentially. The control of molecular weight and polydispersity was clearly compromised in the one-step procedure. The differences between the sequential polymerization routes were subtle. The graft copolymers prepared from the poly(ϵ-caprolactone)s containing pendent-activated bromides or initiating sites for ATRP produced graft copolymers with controlled molecular weight and narrow polydispersities. This grafting-from technique offered more control than the macromonomer route in which lactone functional methyl methacrylate functional macromonomers were employed in a lactone synthesis. Such substituted lactones are known to polymerize somewhat slower than their unsubstituted analogues. Although there have been numerous reports of poly(ϵ-caprolactone)-based diblock and graft copolymers, this example constitutes the first that contains poly(ϵ-caprolactone) as the backbone and the synthesis and polymerization of a lactone functional macromonomer. Moreover, the versatility of the functional lactone permitted the comparison of a grafting-from versus a macromonomer route to graft copolymers.

Acknowledgment. Financial support by the NSF Materials Research Science and Engineering Center on Polymer Interfaces and Macromolecular Assemblies under Cooperative Agreement NSF DMR 9400354 is

acknowledged. D.M. thanks the Bask government for a fellowship.

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MA982005A