α,ω-Heterotelechelic Poly(ϵ-caprolactone)s via Ring-Opening/Chain-Transfer Polymerization and Their Utility as Precursors to AB and ABC Block Copolymers†

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Introduction

A variety of catalysts have been investigated for the ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) to poly(ϵ-caprolactone) (PCL)[1] as PCL and its copolymers are useful due to their biodegradability and polymer blend compatibilization properties.[2] In a typical ROP of ϵ-CL, the growing chain propagates via the alkoxide end, and standard hydrolytic quenching yields the respective α-hydroxy-terminated PCL−OH. Several reports have documented a recent emphasis on the selective modification of the carboxylate ω-terminus using functionalized alcohols as chain-transfer agents. Representative examples include low molecular weight alcohols (R−OH)[1j,3] to yield α,ω-R−PCL−OH; diols and tetraols[4] to yield chain-reversed and star-shaped hydroxy-terminated PCLs; and oligomeric diols, e.g. PEG, to access α,ω-hydroxy-terminated HO−PCL−PEG−PCL−OH block copolymers.[5]

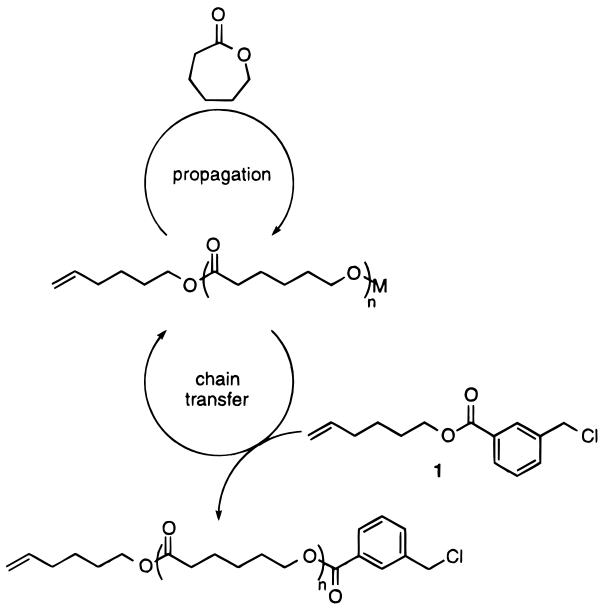
TEMPO[6,7] and 2,2,2-tribromoethyl[7] functionalized alcohols which are able to initiate the controlled free radical polymerizations of styrene and MMA have also been employed to yield hydroxy/TEMPO and hydroxy/tribromoethyl heterotelechelic PCLs and subsequent HO−PCL−PS and HO−PCL−PMMA block copolymers.[8] Extension to the synthesis of an ABC HO−PCL−P(butyl acrylate)−PMMA triblock copolymer was also reported.[9] The significance of ABC block copolymers has recently been demonstrated by Stadler and co-workers, who, following state-of-the-art sequential anionic polymerization techniques, prepared PS−PB−PCL[10] and PS−PE−PCL[11] ABC triblock copolymers[12a] with molecular weights (M_n) of 110 000−220 000 g/mol and polydispersities (PDI) of 1.15−1.47. The mechanical properties[12a,b] and unique morphologies[13] of these materials were governed by the sequence and physical nature of the blocks.

We report herein the development of a conceptually new approach to α,ω-*hetero*telechelic PCL which (a) significantly extends the variety of PCL end groups and (b) *independently* installs the two end groups at the α- and ω-termini of the resulting PCL chain. Moreover, choosing end groups for "living" polymerization methodologies enables the synthesis of new ABC triblock copolymers that are not otherwise possible from typical sequential anionic polymerization methods.

Synthesis of Heterotelechelic PCL

Alkali metal alkoxides and, in particular, alkali *tert*-butoxides are known to catalyze the ROP of ϵ-CL[14] (e.g., KO^{t}Bu yields PCL within seconds; $k_p = 120$ M^{-1} s^{-1} in THF at 0 °C).[14a] Problematic in these experiments, however, were intramolecular backbiting processes that led to PCL cyclics. Recent studies in our laboratory have demonstrated that KO^{t}Bu clusters are also excellent catalysts for the ester and carbonate interchange reactions (i.e., the acyclic version of the ring opening reaction). These catalysts have enabled the development of several synthetic protocols,[15] including the depolymerization of poly(bisphenolA carbonate) to homotelechelic polycarbonates.[16]

Scheme 1



Combining the knowledge that KO^{t}Bu is a good catalyst for the ROP of ϵ-CL and the acyclic ester interchange reaction, we present herein a new method for synthesizing α,ω-heterotelechelic PCL. Used in tandem, the ester interchange reaction should acylate a growing PCL alkoxide end group, while simultaneously generating a new acyclic ester-derived alkoxide to initiate the ROP of a new PCL chain. This strategy enables functionalized acyclic esters, effectively chain-transfer agents (CTA), to independently place, in one step, specific end groups at the α- and ω-termini of each PCL chain; hence the term heterotelechelic (Scheme 1). In this scenario, each catalyst initiates and terminates the synthesis of many polymer chains in a single experiment. To our knowledge, acyclic esters have not been previously utilized as chain-transfer agents for the ROP of lactones. Moreover, most current methods for the formation of heterotelechelic PCLs lead to at least one hydroxy terminus.

To demonstrate the utility of our methodology for the synthesis of heterotelechelic PCLs, and block copolymers derived therefrom, we have utilized CTAs **1**−**3** to generate several heterotelechelic PCL oligomers. The chlorobenzyl and chloroacetyl groups provide initiators for ATRP processes[17] while the unsaturated moieties provide useful spectroscopic and/or reactivity handles for additional manipulations of PCL functionality. The strong UV-absorbing character of the pyrene unit makes it a good spectroscopic probe.

† In Memory of Prof. Raimund Stadler.

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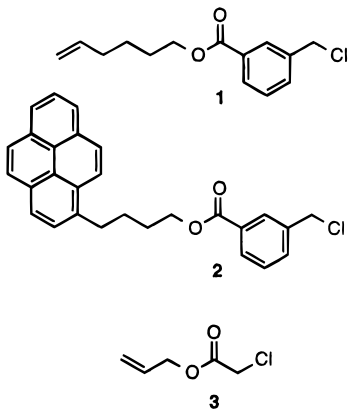
Table 1. Synthesis of α,ω-Telechelic PCL, PCL−PS, and PCL−PS−PMMA Block Copolymers

entry	CTA/ precursor	parameters	isolated yield (%)	M_n, g/mol calc	M_n, g/mol ^{1}H NMR	M_n, g/mol GPC	PDI
		cat:ϵ-CL:CTA					
1a	none	0.5:100:0	n.d.[a]	228 000	n.d.	30 700[d]	1.73
1b	**1**	0.5:100:10	30	2 500	3 500	2 600[d]	1.16
1c	**1**	0.5:100:4	63	6 000	5 500	3 700[d]	1.60
1d	**2**	0.5:100:10	83	2 700	6 100	9 800[d]	2.12
1e	**3**	0.5:100:4	46	5 800	3 500	3 700[d]	1.46
1f	**3**	0.5:100:2	47	11 500	9 400	9 300[d]	1.40
1g	**1c**	bromination	*b*		5 300	3 700[d]	1.54
1h	**1c**	halogen exchange	84[c]		5 800	3 700[d]	1.47
		ATRP of St					
2a	**1b**	CuCl/bipy			17 200	17 500[e]	1.33
2b	**1b**	$CuCl/N_4$			47 000	49 000[e]	1.30
2c	**1c**	$CuCl/N_3$			43 000	46 000[e]	1.44
2d	**1h**	$CuBr/N_4$			114 000	100 000[e]	1.40
2e	**1d**	$CuCl/N_4$			64 000	48 000[e]	1.28
		ATRP of MMA					
3a	**2c**	$CuBr/N_4$/110 °C[h]			123 000	73 000[e]	1.57
						87 000[f]	1.58
						77 000[g]	1.67
3b	**2b**	$CuBr/N_4$/90 °C[i]			270 000	150 000[e]	1.50
						180 000[f]	1.50
						169 000[g]	1.54
3c	**2d**	$CuCl/N_4$/90 °C[j]			279 000	239 000[e]	1.41
						287 000[f]	1.41
						167 000[g]	1.85

[a] Not determined. [b] >98% conversion by in situ 500 MHz ^{1}H NMR. [c] >97% conversion by 300 MHz ^{1}H NMR. [d] Analyzed with UV detector, corrected for PCL with $K = 0.109$ mL/g, $\alpha = 0.60$. [e] Analyzed with UV detector, calculated for PS with $K = 0.014$ mL/g, $\alpha = 0.70$. [f] Analyzed with UV detector, calculated for PMMA with $K = 0.0104$ mL/g, $\alpha = 0.70$ [g] Analyzed with RI detector, calculated for PS. [h] Run in 40 wt % dry anisole for 8 h. [i] Run in 35 wt % dry anisole for 64 h; an aliquot removed after 17 h showed similar MWD. [j] See experimental.



The high ROP activity of KO^{t}Bu (0.5 mol %) toward ϵ-CL[14] yields telechelic PCLs with short reaction times (5 min, THF, ϵ-CL:CTA ratios of 10−50:1; Table 1).[18] The desired telechelics were isolated after precipitation/fractionation into pentane/MeOH in 46−83% yield (PDI 1.16−2.1). Particularly helpful in the characterization of the telechelic PCLs was electrospray mass spectrometry. Figure 1 shows the quadrupole ion trap electrospray ionization mass spectrum of **1b**, chemically deconvoluted to the +1 charge state.[19] The inset in Figure 1 shows a narrow mass range, higher resolution, spectrum obtained with a triple quadrupole mass spectrometer. The measured mass is within 0.04% of the expected mass for the 12-mer (ionization occurs by sodium ion attachment) and confirms the chemical structure of the expected heterotelechelic PCL. The minor envelope of peaks is most consistent with either cyclic PCL oligomers or a *tert*-butoxy-initiated chain.[20]

^{1}H NMR analysis of the well-separated unique resonances in the PCL spectra showed the expected 1:1 ratio

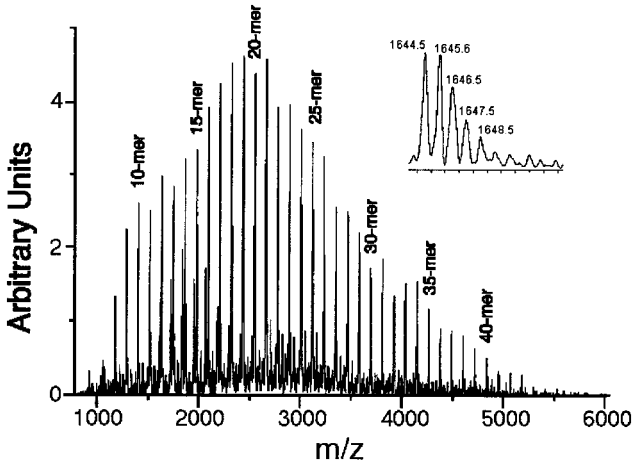


Figure 1. Electrospray mass spectra of PCL **1b** utilizing Na^+ ionization and chemical deconvolution to the +1 charge.[19] The inset represents a higher resolution triple quadrupole mass spectra of the 12-mer (see text).

of the two end groups and were completely consistent with the assigned structures. Molecular weights calculated from the relative ratio of end groups to the PCL methylene resonances agree with GPC data (universal calibration) and with the exception of **1d** are close to the theoretical values.

^{1}H NMR also proved helpful in analyzing end-functionalization experiments. For example, bromination of **1c** afforded the dibromohexyl-functionalized PCL **1g** as evidenced by the appearance of a characteristic new multiplet at 4.22 ppm and two doublet of doublets at 3.86 and 3.66 ppm with coincident loss of the olefinic resonances. Similarly, halogen exchange of **1c** with LiBr afforded the benzyl bromide-functionalized PCL **1h** as indicated by the expected upfield shift of the benzylic

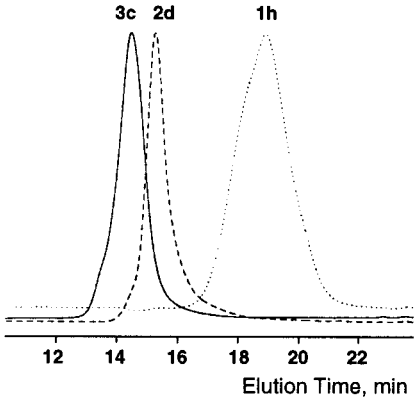


Figure 2. GPC chromatograms of PCL (**1h**), PCL-PS (**2d**), and PCL−PS−PMMA (**3c**).

hydrogens from 4.65 to 4.55 ppm (CD_2Cl_2). In each case, reactions proceeded to >97% conversion as assayed by ^{1}H NMR. HPLC analysis of **1c** and **1g** and deliberate mixtures thereof showed unique retention times for the peaks in **1g**, and the absence of peaks from **1c**, even though their respective GPC traces were superimposable.

PCL−PS AB Block Copolymers

Heterotelechelic PCLs **1b**−**d** and **1h** were employed as macroinitiators for the ATRP of styrene using heterogeneous[21] (**2a**) and homogeneous[22] (**2b**−**2e**) catalytic conditions to yield the PCL−PS AB diblock copolymers **2a**−**e** (Table 1). The resulting polystyrene blocks range in M_n from 15 000−100 000 g/mol as determined by integrating the PCL and PS regions in the ^{1}H NMR spectrum referencing to the known PCL MW. Gel permeation chromatography (GPC) of the precipitated polymers indicated that PS growth was well behaved as the polydispersities of the diblocks were only slightly increased relative to the macroinitiator. Extracting PCL−PS diblock **2b** with hot ethanol to remove unreacted starting material indicated a conversion efficiency of ∼86%, similar to literature protocols.[23]

PCL−PS−PMMA Block Copolymers

The PCL−PS diblock copolymers **2b**−**d** were utilized as macroinitiators for the ATRP of MMA to yield PCL−PS−PMMA triblock copolymers **3a**−**c** (Table 1). The added PMMA blocks range from 80 000 to 230 000 g/mol with an overall $M_{n,ABC}$ of 125 000−280 000 g/mol (as determined by ^{1}H NMR) and an overall PDI of ∼1.5. The MW of PS:PMMA blocks ranged from 40K:80K (**3a**), 40K:230K (**3b**), to 100K:180K (**3c**). Figure 2 depicts the GPC chromatograms of the sequence **1h** → **2d** → **3c**. In all cases, **3a**−**c**, initiator efficiencies for MMA polymerization by the PCL−PS macroinitiators were in the 65−85% region and are typical of Cu halide ATRP processes using benzyl halide-type initiators.[23] Also consistent with previous findings was the observation that the styryl bromide-terminated PCL−PS−Br **2d**/CuCl system gave improved initiation efficiencies over the styryl chloride end group/CuBr system.[24] Initiation also proved to be scale sensitive as large-scale reactions (entry **3a**, 0.07 mmol, 3.5 g) initiated well (82%) and gave monomodal GPC traces for the nonprecipitated polymer, while 0.01−0.005 mmol scale experiments (**3b**−**c**) initiated incompletely and yielded bimodal GPC traces. Repetitive selective reprecipitation of the dried ABC triblocks from ethyl acetate into cyclohexane/MeOH (12/1 v/v) and repetitive extraction of **3c** with hot isobutyl alcohol, however, effectively removed the traces of diblock precursor and homo PMMA present in the desired ABC triblock.

Summary

This paper outlines a new strategy for the synthesis of α,ω-functionalized heterotelechelic PCL by a repetitive ring-opening/chain-transfer protocol utilizing a readily available and inexpensive catalyst. This methodology has the advantage that each of the two end groups may be independently selected, and the products are not limited to those containing a hydroxy end group. This approach yields functionalized heterotelechelic PCLs capable of initiating the controlled radical polymerization of styrene and methyl methacrylate to yield PCL−PS and the as yet undescribed PCL−PS−PMMA ABC triblock copolymer.

Experimental Section

Materials. Most reagents were obtained from Aldrich and used as received. Allylchloroacetate, Et_3N, *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (N3), 1,1,4,7,10,10-hexamethyltriethylenetetramine (N4, Acros), and ϵ-caprolactone (99%) were distilled from CaH_2 prior to use. KO^{t}Bu was sublimed at least once and stored under inert atmosphere. Styrene and methyl methacrylate were passed through basic alumina prior to use. Solvents were purified by passing them through activated alumina.[25]

Characterization. ^{1}H NMR were obtained at 300 or 500 MHz using a minimum pulse delay of 10 s; ^{13}C NMR were recorded at 75 MHz. Molecular weights of PCL oligomers were determined by NMR (end group analysis), electrospray mass spectrometry, and gel permeation chromatography (GPC). Block copolymer composition was determined by GPC and by NMR based on end groups (for short blocks) and on the ratio of B or C blocks to the previously characterized PCL A block. The GPC used was a Hewlett-Packard 1100 liquid chromatograph equipped with a UV diode array detector running Caliber software (Polymer Labs.) and calibrated against polystyrene standards. The sample was eluded in THF at room temperature on a set of three Plgel 5 μm columns (mixed D, mixed D, 100 Å; Polymer Labs.). A Waters Alliance 2690 GPC with a refractive index detector and a column set of Styragel HR (Waters Corp.), 5 μm particle size 100 Å, 10^4Å, and 10^5Å with THF as solvent at 35 °C was also used. Melting points are uncorrected and were measured on a Thomas-Hoover capillary melting point apparatus. See ref 19 for details on the electrospray methodology.

Synthesis of Chain-Transfer Agents. 5-Hexenyl 3′-(chloromethyl)benzoate (1). 3-(Chloromethyl)benzoyl chloride (10 g, 0.053 mol) in 5 mL of dry THF was slowly added to a precooled (0 °C) stirring mixture of 5-hexen-1-ol (5.37 g, 0.054 mol), NEt_3 (7.35 mL, 0.054 mol), and catalytic quantity of DMAP in 50 mL of dry THF under inert atmosphere, and the mixture was stirred for 3 days at ambient temperature. The THF solution was then filtered through a short silica plug and the filtrate concentrated in vacuo to give a yellow oil which distilled at ∼104 °C/30 mTorr to yield 11.46 g (84%) of pure, colorless **1**. ^{1}H NMR ($CDCl_3$): δ 8.03 (t, *J* = 1.8 Hz, 1H), 7.98 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.57 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.80 (m, 1H), 5.04 (q, *J* = 1.8 Hz, 0.5H), 4.98 (m, 1H), 4.94 (m, 0.5H), 4.60 (s, 2H), 4.31 (t, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 6.6 Hz, 2H), 1.77 (m, 2H), 1.53 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 166.1, 138.3, 137.8, 133.0, 131.0, 129.6, 129.5, 128.9, 128.8, 114.9, 65.1, 45.5, 33.3, 28.1, 25.3.

4-(2′-Pyrenylbutyl) 3″-(chloromethyl)benzoate (2). 3-(Chloromethyl)benzoyl chloride (0.3 mL, 0.0021 mol) in 5 mL of dry THF was added to a precooled (0 °C) stirring mixture of 4-(2′-pyrene)butanol (429 mg, 0.0016 mol), NEt_3 (0.3 mL, 0.0022 mol), and a catalytic quantity of DMAP in 5 mL of dry THF under inert atmosphere, and the mixture was stirred for

46 h at room temperature. After workup as above, the solid material was dissolved in 2 mL of $CHCl_3$ and purified by running through a short silica column eluded with 3.5 L of $CHCl_3$/pentane (1:1 v/v) into four fractions. Fractions 2 and 3 were combined and concentrated in vacuo to give a yellow liquid that under high vacuum crystallized to give 721 mg (94%) of **2**; mp = 98−100 °C. ^{1}H NMR (CD_2Cl_2): δ 8.31 (d, J = 9.3 Hz, 1H), 8.04 (m, 10H), 7.57 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 4.61 (s, 2H), 4.40 (t, J = 6.3 Hz, 2H), 3.43 (t, J = 7.4 Hz, 1H), 1.98 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 166.2, 138.4, 137.0, 133.2, 131.8, 131.4, 131.2, 130.2, 129.8, 129.7, 129.2, 128.9, 127.8, 127.7, 127.5, 126.9, 126.2, 125.3, 125.2, 125.1, 125.0, 123.7, 65.26, 46.03, 33.32, 29.0, 28.47.

5,6-Dibromohexyl 3′-(chloromethyl)benzoate. In a dry NMR tube, 29.6 mg (0.115 mmol) of **1** was dissolved in approximately 0.5 mL of CD_2Cl_2 cooled below room temperature, and 1.1 equiv of Br_2 in cold CD_2Cl_2 was added and the tube agitated. After 15 min quantitative conversion of the double bond into the dibromide had occurred as assayed by NMR and TLC (ether/pentane: 1/4 v/v). ^{1}H NMR (CD_2Cl_2): δ 8.07 (t, J = 1.8 Hz, 1H), 8.00 (dt, J = 7.5, 1.5 Hz, 1H), 7.61 (dt, J = 7.8, 1.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 4.65 (s, 2H), 4.34 (t, J = 6.3 Hz, 2H), 4.23 (m, 1H), 3.88 (dd, J = 10.4, 4.7 Hz, 1H), 3.68 (dd, J = 10.5, 9.3 Hz, 1H), 2.21 (m, 1H), 1.82 (m, 4H), 1.61 (m, 1H). ^{13}C NMR (CD_2Cl_2): δ 166.2, 138.4, 133.3, 131.4, 129.9, 129.7, 129.2, 65.1, 53.3, 46.1, 36.9, 36.1, 28.2, 23.9.

Synthesis of Heterotelechelic Polycaprolactone. A typical ROP/chain-transfer experiment for the synthesis of heterotelechelic PCL is given below.

1c. To 11.5 mL (0.11 mol) of ϵ-CL distilled freshly from CaH_2 was added 1.03 g (4 mmol) of 5-hexenyl 3′-(chloromethyl)-benzoate **1** in 40 mL of dry THF. To this rapidly stirring reaction was quickly added 61 mg (0.5 mmol) of sublimed KO^t-Bu in 2 mL of dry THF. After 5 min the yellow solution was precipitated into 600 mL of pentane/MeOH (2:1 v/v), filtered, washed with MeOH, and dried in vacuo at rt for 12 h to give 8.35 g (63%) of **1c**. ^{1}H NMR (CD_2Cl_2): δ 8.04 (t, J = 1.8 Hz, 1H), 7.98 (dt, J = 8.1, 1.4 Hz, 1H), 7.66 (dt, J = 7.8, 1.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 5.81 (m, 1H), 5.03 (q, J = 1.8 Hz, 0.5H), 4.96 (m, 1H), 4.92 (m, 0.5H), 4.65 (s, 2H), 4.30 (t, J = 6.5 Hz, 2H), 4.03 (t, J = 6.6 Hz, 44H), 2.28 (t, J = 7.5 Hz, 44H), 1.62 (m, 90H), 1.36 (m, 46H).

5,6-Dibromohexyl 3′-(chloromethyl)benzoate Heterotelechelic PCL 1g. A 29 mg (0.005 mmol) sample of **1c** was dissolved in an NMR tube in ∼0.5 mL of CD_2Cl_2 and cooled below room temperature, and 1.1 equiv of Br_2 in cold CD_2Cl_2 was added and agitated. After 60 min quantitative conversion of the double bond into the dibromide had occurred as assayed by 500 MHz ^{1}H NMR. HPLC chromatograms of **1c**, **1g**, and deliberate mixtures thereof (EA/hexanes, 25/75 gradient to 60/40 v/v in 90 min, on a CN-terminated silica column) showed a unique set of peaks for **1g** which did not overlap with those of **1c**. ^{1}H NMR (CD_2Cl_2): δ 8.04 (t, J = 1.5 Hz, 1H), 7.98 (dt, J = 8.1, 1.4 Hz, 1H), 7.61 (dt, J = 8.4, 1.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 4.65 (s, 2H), 4.30 (t, J = 6.6 Hz, 2H), 4.19 (m, 1H), 4.03 (t, 6.6 Hz, 44H), 3.86 (dd, J = 10.4, 4.4 Hz, 1H), 3.66 (dd, J = 10.5, 9.3 Hz, 1H), 2.28 (t, J = 7.5, 45H), 1.62 (m, 93H), 1.36 (m, 45H).

5-Hexenyl 3′-(bromomethyl)benzoate Heterotelechelic PCL 1h. A 3 g (0.55 mmol) sample of **1c** and 500 mg (5.7 mmol) of LiBr were dissolved in 50 mL of acetone and refluxed for 2 h and isolated (2.85 g), and the process was repeated. The resulting acetone solution was precipitated into 500 mL of MeOH/water (4/1 v/v), washed with MeOH/water (1/1 v/v), filtered, washed again with MeOH/water (1/1 v/v), and dried in vacuo to yield 2.49 g (83%) of **1h** with ≥98% functionalization. ^{1}H NMR (CD_2Cl_2): δ 8.05 (s, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 5.81 (m, 1H), 5.04 (q, 1.8 Hz, 0.5H), 4.97 (m, 1H), 4.93 (m, 0.5H), 4.56 (s, 2H), 4.30 (t, J = 6.6 Hz, H), 4.03 (t, J = 6.7 Hz, 100H), 2.28 (t, J = 7.6 Hz, 100H), 1.62 (m, J = 7.8 Hz, 200H), 1.36 (m, 100H).

Synthesis of PCL−PS and PCL−PS−PMMA Block Copolymers. The experimental setup followed general ATRP protocols of styrene and methyl methacrylate as published elsewhere.[21−24]

PCL−PS 2d. A 14.6 mg (0.1 mmol) sample of CuBr, 23.3 mg (0.1 mmol) of N4, and 3 g of styrene added were placed into a dry Schlenk flask and sonicated for 5 min. A 365 mg (0.1 mmol) sample of **1h** dissolved in 3.03 g of styrene (58 mmol total) was added to the Schlenk flask, and the contents were subjected to three freeze−pump−thaw cycles. Upon sealed under vacuum, the vessel was placed in an oil bath (105 °C) for 20 h. After the addition of 50 mL of THF to dissolve the polymer, the green solution was filtered through silica and precipitated into a mixture containing 1000 mL of MeOH and 50 mL of water. The precipitate was filtered, washed with MeOH, and dried in vacuo to yield 1.58 g of polymer (160 mg of filtrate). To remove unreacted starting material, the dry polymer was suspended three times in 100 mL of hot ethanol and filtered to ultimately yield 1.24 g of purified **2d** (the filtrate gave 90, 13, and 1 mg of solids, respectively). An attempt to further purify the material by dissolving it in 25 mL of ethyl acetate and precipitating into 400 mL of pentane did not change MWD and resulted in the recovery of 1.15 g of **2d** (filtrate: 45 mg of solids). Reaction temperatures and times for the other PCL−PS block copolymers were as follows: **2a**, 130 °C/19 h; **2b**, 100 °C/16 h; **2c**, 110 °C/8 h; **2e**, 110 °C/24 h.

PCL−PS−PMMA 3c. A 400 mg (0.004 mmol) sample of **2d** was transferred into a dry Schlenk flask. Catalyst solution (190 μL, 0.004 mmol of CuCl, 0.004 mmol of N4, 1.7 mmol of MMA) obtained from a stock solution containing CuCl (5.5 mg, 0.055 mmol), N4 (13.2 mg, 0.057 mmol), and MMA (2.4 g, 24 mmol) was syringed into the Schlenk flask along with additional MMA (610 μL, 5.7 mmol). After three freeze−pump−thaw cycles the vacuum-sealed flask was placed in a 90 °C oil bath for 16 h. The resulting polymer was dissolved in 10 mL of THF, filtered through alumina, and precipitated into 100 mL of water. The solids were filtered, washed, and dried in vacuo to yield 790 mg of product **3c** (36 mg in filtrate). To remove starting diblock, 600 mg of **3c** was dissolved in 14 mL of ethyl acetate and precipitated into 150 mL of cyclohexane and 10 mL of MeOH. The procedure was repeated and yielded 350 mg of **3c**. Repetitive stirring of the dried polymer in ^{i}BuOH at 70 °C (a selective solvent for PMMA) overnight and subsequent filtering removed some, but not all, of a low molecular weight tail.

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References and Notes

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