Synthesis of Poly(ϵ-caprolactone) with a Stable Nitroxyl Radical as an End-Functional Group and Its Application to a Counter Radical for Living Radical Polymerization

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ABSTRACT: The quantitative synthesis of poly(ϵ-caprolactone) (PCL) with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at one chain end was attained through the anionic polymerization of CL by an aluminum tri(4-oxy-TEMPO), which was prepared by the reaction of triethylaluminum and 4-hydroxy-TEMPO. The TEMPO-supported PCL behaved as a polymeric counter radical for the radical polymerization of styrene, giving poly(CL-*block*-styrene) in quantitative efficiency. The radical polymerization was found to proceed in accordance with a living mechanism, because the conversion of styrene linearly increased over time, and the molecular weight was directly proportional to the reciprocal of the initial concentration of the PCL. The resulting copolymers had two glass transition temperatures due to the PCL block and polystyrene and one melting endotherm based on the crystalline phases of PCL. The TEM picture of the film obtained from the block copolymer demonstrated microphase segregation.

Introduction

Poly(ϵ-caprolactone) (PCL) is of industrial importance as a biodegradable and biocompatible material. For polymerization of the monomer ϵ-caprolactone (CL), several new initiators that are able to create new macromolecular architecture containing PCL segments have been discovered.[1−5] The studies on the polymerizations using these initiators involve investigating kinetics and mechanisms. Among such initiators, which are mainly metallic alkoxides, aluminum alkoxides have been the most widely studied.[6−10] The aluminum alkoxides are used to synthesize the designed polymers based on PCL. The designs concern the end-functionalization of PCL for preparing the halogeno-PCL, *tert*-amino-, and olefinic.[11] These functional groups, which are associated with the active alkoxy moiety of the aluminum alkoxide, are selectively attached to one chain end of PCL.

We have recently released a publication on the synthesis of polytetrahydrofuran (PTHF) with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at the chain end.[12] Whereas this polymer could be quantitatively obtained by the reaction of a living cationic PTHF and sodium 4-oxy-TEMPO, the TEMPO-supported PTHF acted as a polymeric counter radical for living radical polymerization of styrene, giving the poly(THF-*block*-styrene) in quantitative efficiency. The development of the method of this quantitative synthesis of the block copolymer has been based on numerous results, obtained by many investigators, concerning the styrene polymerization using TEMPO.[13−20] Our recent results can be included among this research.[21−26] In this recent study, it was found that the concentration of the growing polymer chain was identical to the initial concentration of TEMPO, with the result that all the polystyrenes obtained had the aminoxy moiety at their terminals.[22] This presence of the aminoxy moiety is significant if quantitative synthesis of polymers designed is required. We found the synthesis of PCL with TEMPO as an end-functional group at a terminal, and also the synthesis of a copolymer of CL and styrene through the living radical polymerization using the PCL as a counter radical. This paper describes the anionic polymerization of CL by TEMPO associated with an aluminum alkoxide as an initiator, and the application of the TEMPO-supported PCL to a polymeric counter radical for the radical polymerization of styrene. The morphology of a film obtained from the block copolymer is also described.

Experimental Section

Measurement. Gel permeation chromatography (GPC) was performed with a Toso HLC-802A instrument equipped with a Toso CP-8000 chromato processor. A combination of two polystyrene gel columns of Toso TSK gel G4000H_8 and G2000H_8 was used, with THF as the eluent at 42 °C. The molecular weight was determined by calibrating with polystyrene standards. Ultraviolet (UV) spectra were obtained with a Beckman DU-68 spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were also obtained with a Bruker ARX-500 NMR spectrometer. Gas chromatography (GC) was performed with a Shimadzu GC-6A. Differential scanning calorimetry (DSC) spectra were obtained with a Mac Science DSC-3100. Transmission electron micrography (TEM) was performed with JEM 1010.

Materials. CL was distilled over calcium hydride under a reduced pressure. 4-Hydroxy-TEMPO, which was prepared by the method reported previously,[27] was dried *in vacuo* for 30 min just before use. 4-Methoxy-TEMPO to be used for the calibration of UV absorption intensity was prepared by the method described previously.[28] Extrapure grade triethylaluminum, which is 15 wt% solution in toluene, was used without further purification. The 0.01 N aqueous solution of EDTA to be used for the extraction was prepared from a commercial grade 0.1 N aqueous solution of EDTA. Extrapure grade phenylhydrazine for ^{1}H NMR studies was used without further purification. Commercial grade

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styrene was washed with an aqueous alkaline solution and water, and distilled over calcium hydride. Benzoyl peroxide (BPO) was precipitated from chloroform and then recrystallized in methanol at 0 °C. Toluene was refluxed over sodium for 16 h, and then distilled just before use. THF was refluxed over sodium for several hours, and distilled.

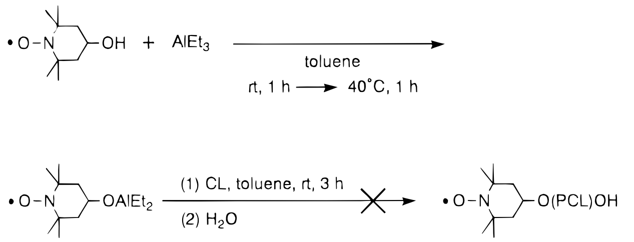
Anionic Polymerization of CL by an Aluminum Tri(4-oxy-TEMPO). Triethylaluminum of 15 wt% toluene solution (0.78 mL, 1.04 mmol) was added to 4-hydroxy-TEMPO (537 mg, 3.12 mmol) in 10 mL of THF at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h, and kept at 40 °C for 2 h under a nitrogen atmosphere, and then dried *in vacuo* for 1 h at 40 °C to remove the THF. To the resulting red-colored product was added 30 mL of toluene. After the mixture was kept at 40 °C for 1 h, it was cooled to room temperature. CL (3.0 mL, 27.1 mmol) was added to the mixture, and stirred. After the solution was kept for 3 h at room temperature under nitrogen, 1 mL of distilled water was added to it. The mixture was stirred for 10 min. After 20 mL of toluene was added to it, the toluene solution was washed three times with the 0.01 N aqueous solution of EDTA, and another three times with water. The toluene layer was dried over anhydrous magnesium sulfate and then evaporated to remove toluene. The product was purified by repeated precipitations from toluene into hexane, and dried *in vacuo* for several hours to yield 2.68 g of PCL (yield: 87%).

Radical Polymerization of Styrene in the Presence of the PCL. Styrene (1.0 mL, 8.73 mmol), BPO (10 mg, 0.0413 mmol), and PCL (P-1, 127 mg, containing 0.0536 mmol of TEMPO moiety) were placed in an ampule. After deaerating the contents, the ampule was sealed *in vacuo*. The polymerization was carried out at first for 3.5 h at 95 °C, and then continued for another 72 h at 125 °C. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitations from dichloromethane into hexane, and finally dried *in vacuo* for several hours to yield 733 mg of the block copolymer (yield: 75%). After addition of toluene as an internal standard, the dichloromethane solution was subjected to GC analysis to estimate the conversion of styrene.

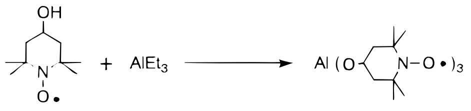
TEM Analysis. The film was prepared on a Cu grid with carbon substrate, by casting from the THF solution of the poly(CL-*block*-styrene). The film was dried in air for 30 min, and dyed for another 30 min in the presence of RuO_4aq in a laboratory dish. The film thus obtained was subjected to TEM analysis.

Results and Discussion

Scheme 1



Scheme 2



Synthesis of PCL with TEMPO as an End-Functional Group. An aluminum alkoxide with which TEMPO was associated, was prepared by reacting triethylaluminum with 4-hydroxy-TEMPO. In a preliminary attempt, a reaction of triethylaluminum was performed with an equimolar amount of 4-hydroxy-TEMPO to produce a diethylaluminum 4-oxy-TEMPO (Scheme 1). This compound, however, gave no PCL with TEMPO at a terminal because no signals originating from 4-hydroxy-TEMPO were observed in its ^{1}H NMR spectrum, although a small amount of PCL without TEMPO was obtained. Teyssié *et al.*[29] reported that diethylaluminum 2-hydroxyethyl methacrylate can initiate the CL polymerization to quantitatively give a methacryloyl-terminated PCL. The reason for the failure in our attempt may be that TEMPO cannot bear coexistence with a strong base of alkylaluminum. In fact, it has been found that TEMPO easily reacts with such strong bases of butyl lithium[30] and Grignard reagents,[31,32] converting into the corresponding alkoxyamines.

In a second approach, we attempted to use an aluminum tri(4-oxy-TEMPO), which was prepared by the reaction of triethylaluminum with three equimolar amounts of 4-hydroxy-TEMPO, as an initiator for the CL polymerization (Scheme 2). The reaction was carried out in toluene at room temperature for 1 h, and continued at 40 °C for another 1 h (Table 1, expt no. 1). While the polymerization was performed in toluene at ambient temperature for 3 h, the solution maintained the red color due to TEMPO. A polymer in a light red color was obtained, and its molecular weight (estimated by GPC calibrated with polystyrene standards) showed a unimodal curve. The polymer could be subjected to ^{1}H NMR measurement in the presence of phenylhydrazine because the TEMPO moiety is reduced into the corresponding hydroxylamine by this reagent. The ^{1}H NMR spectrum thus obtained is shown in Figure 1. It is clear that TEMPO was introduced into PCL because the signals originating from TEMPO were discerned at (a) 1.24, (b) 1.29, (c) 1.92, and (d) 1.95 ppm. These signals were assigned to two types of methyl protons, (a) axial and (b) equatorial, and to two methylene ones, (c) axial and (d) equatorial, respectively. The signal at 5.05 ppm also originates from TEMPO and is assigned to the methine proton. The signals at (h) 1.4, (g) 1.6, (f) 2.3, and (i) 4.1 ppm have all been attributed to the methylene protons of the PCL main chain. A signal was also discerned at (k) 3.64 ppm, originating from the methylene protons bonding to the hydroxy group, which is attached to another PCL terminal. The degree of introduction (DI) of TEMPO into the PCL was estimated to be 0.785 from the relative intensity of the terminal hydroxymethylene (k) and the tetramethyl (a and b) of TEMPO. The DI increased when the reaction was carried out in THF rather than in toluene (Table 1, expt no. 2). In particular, the time of the reaction at 40 °C in THF was extended to 2 h, with the result that a quantitative DI was achieved (expt no. 3). This result indicates that TEMPO associated with an aluminum alkoxide initiated the anionic polymerization of CL, selectively giving the PCL with TEMPO at a terminal. The DI was independent of the initial concentration of the initiator of aluminum tri(4-oxy-TEMPO), because

Table 1. Anionic Polymerization of CL[a] by Aluminum Tri4-oxy-TEMPO as an Initiator

expt no.	$[\text{initiator}]_0 \times 10^3$, mol/L	reaction conditions for preparing aluminum tri4-oxy-TEMPO	isolated yield, %	DI		Mn					content of TEMPO, mmol/g[h]
						NMR					
				NMR[b]	UV[c]	CH_2OH[d]	TEMPO[e]	UV[f]	GPC[g]	M_w/M_n[g]	
1	34.7	rt, 1 h + 40 °C 1 h (Tol)	84	0.785	0.913	2700	3410	2960	4550	1.42	0.338
2	34.7	rt, 1 h + 40 °C 1 h (THF) → rt, 2.5 h (Tol)	64	0.889	0.821	2920	3260	3560	3640	1.23	0.281
3	34.7	rt, 1 h + 40 °C 2 h (THF) → rt, 1 h (Tol)	87	0.981	1.01	3280	3220	3230	4710	1.33	0.309
4	69.4	rt, 1 h + 40 °C 2 h (THF) → rt, 1 h (Tol)	72	0.972	1.08	2550	2460	2370	3250	1.28	0.422
5	17.4	rt, 1 h + 40 °C 2 h (THF) → rt, 1 h (Tol)	58	1.00	0.983	4370	4200	4440	6740	1.29	0.225

[a] $[\text{CL}]_0 = 0.902$ mol/L. [b] Estimated by ^{1}H NMR based on the relative intensity of the terminal hydroxymethylene (-CH_2OH: $\delta H_k = 3.64$ ppm), and the tetramethyl of TEMPO (-CH_3: $\delta H_a = 1.24$ and $\delta H_b = 1.29$ ppm). [c] Calculated by UV spectroscopy based on the absorbance at 460 nm and the absolute molecular weight. [d] Estimated by ^{1}H NMR based on the relative intensity of the terminal hydroxymethylene and the methylene ($OC(O)CH_2$-: $\delta H_f = 2.3$ ppm) in the PCL main chain. [e] Estimated by ^{1}H NMR based on the relative intensity of the tetramethyl of TEMPO and the methylene ($OC(O)CH_2$-). [f] Estimated by UV spectroscopy based on the content of TEMPO. [g] Estimated by GPC based on polystyrene standards. [h] Calculated by UV spectroscopy based on the absorbance at 460 nm.

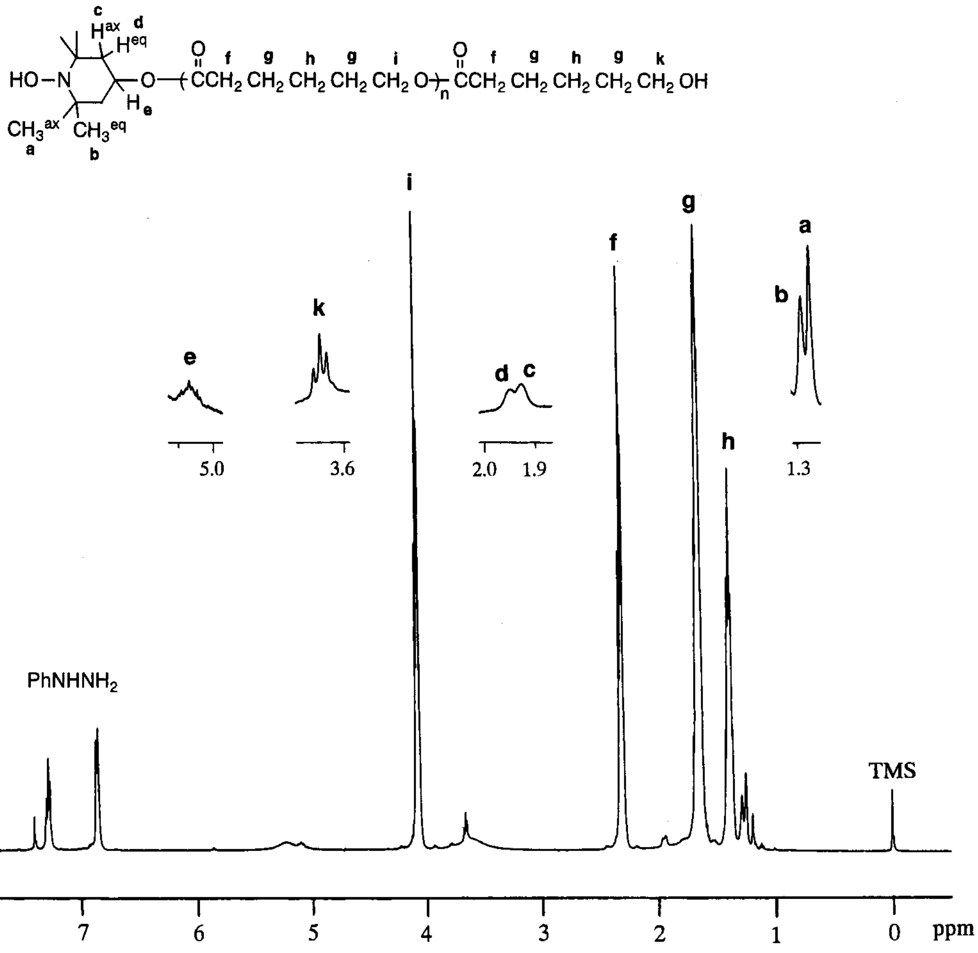


Figure 1. ^{1}H NMR spectrum of the PCL obtained by the anionic polymerization of CL by aluminum tri(4-oxy-TEMPO) (solvent: $CDCl_3$, in the presence of phenylhydrazine).

all the DIs were quantitative in the three types of PCLs obtained from the three different concentrations of the initiator (expt nos. 3, 4, and 5). All the PCLs obtained had characteristic absorption λ_{max} at 460 nm, originating from the stable nitroxyl radical (Figure 2). The DI could also be calculated with the absorbance intensity at this wavelength and with absolute molecular weights of these PCLs. The intensity was calibrated using 4-methoxy-TEMPO. The DIs thus calculated were in close agreement with those estimated by ^{1}H NMR. The molecular weights were estimated by ^{1}H NMR based on the relative intensity of the terminal hydroxymethylene protons (k) at 3.64 ppm, and the methylene ones (f) at 2.3 ppm, the methylene bonding to the carbonyl carbon in the PCL main chain. Further, the molecular weights were estimated based on the content of TEMPO per gram of polymer, which was calculated by using the absorbance at 460 nm. For the PCLs obtained in the case that the reaction at 40 °C in THF was 2 h (expt nos. 3, 4, and 5), the molecular weights thus determined were in a good agreement with the absolute ones estimated by ^{1}H NMR. It was possible to estimate another molecular weight using the intensity ratio of the methylene protons (f) at 2.3 ppm to the

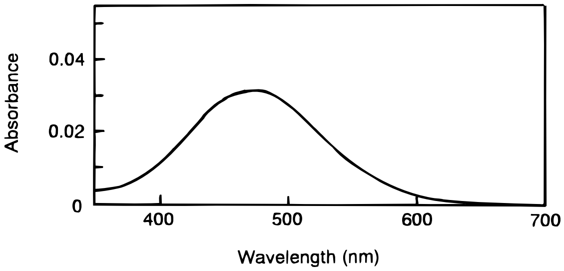


Figure 2. UV spectrum of the PCL (Table 1, expt no. 4) obtained by the anionic polymerization of CL by aluminum tri(4-oxy-TEMPO) (solvent: toluene).

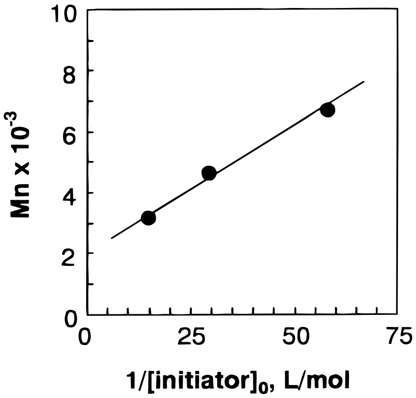


Figure 3. Plots of the molecular weight versus the reciprocal of $[\text{initiator}]_0$ in the polymerization of CL.

tetramethyl ones (a and b) of TEMPO at 1.24 and 1.29 ppm, respectively. For these PCLs, the molecular weights thus determined were also in close agreement with the absolute ones. These results indicate that TEMPOs are selectively attached to one chain end of the PCLs. In addition, the molecular weight for these three PCLs was directly in proportion to the reciprocal of the initial concentration of the initiator ($[\text{initiator}]_0$), as shown in Figure 3. This result suggests that the anionic polymerization proceeded in accordance with a living mechanism. The three PCLs demonstrated the presence of TEMPO attached to the PCL because the polymers manifested three sharp signals due to TEMPO in their electron spin resonance (ESR) spectra. Figure 4 illustrates a typical spectrum (Table 1, expt. no. 4). The g values of these polymers [2.00698 (expt no. 3), 2.00700 (no. 4), and 2.00707 (no. 5)] were near to, and the hyperfine coupling constants (A_N: 15.9 G, for all these polymers) were identical to those of 4-methoxy-TEMPO (g: 2.00698; A_N: 15.9 G). These results suggest that the stability of TEMPO attached to the PCL terminal was not affected by the polymer main chain under these conditions and, therefore, it is expected that these polymeric TEMPOs behave as counter radicals for living radical polymerization in the same manner as a monomeric TEMPO.

Living Radical Polymerization of Styrene Using PCL with TEMPO at the Terminal. A block copolymer of CL and styrene was synthesized by Teyssié *et al.*[33] by living anionic polymerization of CL using a metallic catalyst derived from the hydroxy-terminated polystyrene. Radical polymerization is a simple and convenient procedure. The radical polymerization of styrene was performed with BPO as an initiator, in the presence of the PCL. The polymerization was carried out in bulk at 125 °C, after being held at 95 °C for 3.5 h. It has been found that the rate of polymerization is much faster with TEMPO attached to a polymer than with TEMPO of low molecular weight, such as 4-methoxy-TEMPO.[12] This two-step procedure of heating has the potential to give block copolymers with narrow polydispersities, by dividing the initiation from the propagation. The results are shown in Table 2. The mixtures, which had an light red color due to TEMPO, turned light yellow after 3.5 h at 95 °C. The reaction was continued at 125 °C until the rotation of the stirrer bar stopped, with the result that highly viscous and colorless masses were obtained. The conversions of styrene, which were estimated by GC, were high in all cases. The molecular weights increased after the polymerization, and the polydispersities were slightly broadened. All the PCLs used had engaged in the polymerization, because the copolymers showed unimodal curves similar to the prepolymers of PCL and exhibited no peaks originating from the prepolymers in their GPCs. A typical GPC profile obtained from the product before precipitation is shown in Figure 5. This absence of peaks based on the prepolymers supports the quantitative formation of poly(CL-*block*-styrene) (Scheme 3).

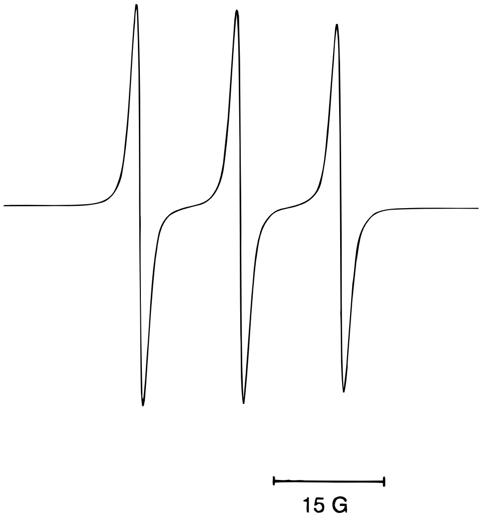


Figure 4. ESR spectrum of the PCL (Table 1, expt no. 4; solvent: benzene, at room temperature).

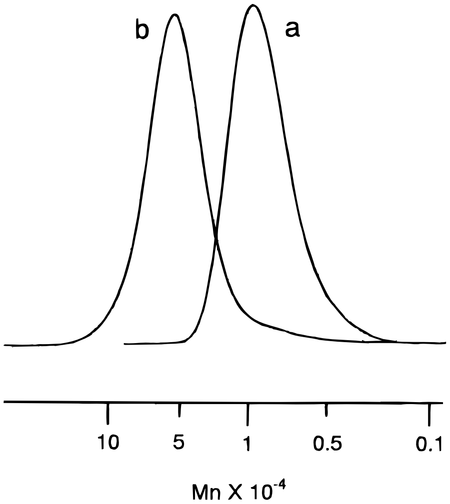


Figure 5. GPC profiles of (a) the prepolymer, P-3, and (b) the block copolymer (M_n, 26 200; M_w/M_n, 1.38).

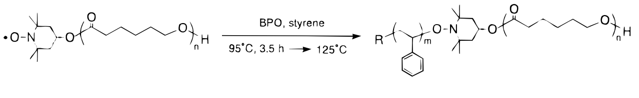
The block copolymer with lower molecular weight (conv., 41%; M_n, 5190; M_w/M_n, 1.35) was examined by

Table 2. Radical Polymerization of Styrene by BPO Using TEMPO-Supported PCL[a]

prepolymer			time, h	conv, %[c]	isolated yield, %	product		units[d]	
PCL	M_n[b]	M_w/M_n[b]				M_n[b]	M_w/M_n[b]	CL	St
P-1	3250	1.28	72	93	75	23 600	1.37	21	164
P-2	4710	1.33	80	89	74	19 900	1.42	27	143
P-3	6740	1.29	72	92	74	26 200	1.38	34	138

[a] [TEMPO-PCL]$_0$/[BPO]$_0$, 1.3 in all cases. [b] Estimated by GPC based on polystyrene standards. [c] Calculated by GC. [d] Estimated by ^{1}H NMR spectroscopy based on the relative intensity of the aromatic protons at 6.2−7.3 ppm and the methylene ones at 4.0 ppm (i) in the PCL main chain.

Scheme 3



^{1}H NMR to investigate the structure of the copolymer obtained. This copolymer was produced from the polymerization that was performed for 4 h at 125 °C using the PCL with the molecular weight of 3250. The ^{1}H NMR spectrum of this copolymer is shown in Figure 6. In addition to the signals due to CL, the signals originating from styrene were observed. The broad signals at 1.1−2.1 and 6.3−7.5 ppm were certainly assigned to the methylene and methine, and aromatic protons of styrene, respectively. The signals discerned at 1.29 and 1.32 ppm were assigned to the tetramethyl protons of TEMPO that connected the PCL segment to the polystyrene one. Signals were observed at 0.80 and 0.98 ppm, also originating from the tetramethyl protons. This observation invariably indicates that these two signals resulted from hindered rotation and ring inversion of TEMPO moiety. The axial and equatorial methylene protons of TEMPO were observed at 2.00 and 2.20 ppm, respectively. A signal was also discerned at 7.85 ppm, which was attributed to the aromatic protons at *ortho* position of the benzoyl group attached to the other polystyrene terminal. Further, the proton signals of methylene bonding to the benzoyl group and of the methine neighboring this methylene, were discerned at 4.7−5.4 and 2.5−3.0 ppm, respectively. The signal around 4.3 ppm was attributed to the methine proton, which was bonded to TEMPO supported on the PCL. This NMR analysis clarifies that the block copolymers have a structure in which the two different segments of PCL and polystyrene are connected by TEMPO.

To confirm whether this radical polymerization proceeds in accordance with a living mechanism, further investigation was performed using the PCL with the molecular weight of 3250 and the polydispersity of 1.28 (Table 2, P-1). The first-order time conversion plots in the polymerization are shown in Figure 7. It is clear that ln[M]$_0$/[M] linearly increases over time, indicating that this polymerization proceeded in accordance with a living mechanism. On the other hand, a straight line was not obtained in the plots of the molecular weight of the copolymer versus conversion. The conversion−molecular weight and molar ratio of styrene to CL units in the copolymer are shown in Figure 8. The ratios were estimated by ^{1}H NMR, based on the relative intensity of the signals at 6.2−7.3 ppm originating from the aromatic protons, and those at 4.0 ppm due to the methylene bonding to the carboxyl group in the PCL main chain. It is likely, but not completely certain, that both the molecular weight and the ratio increase

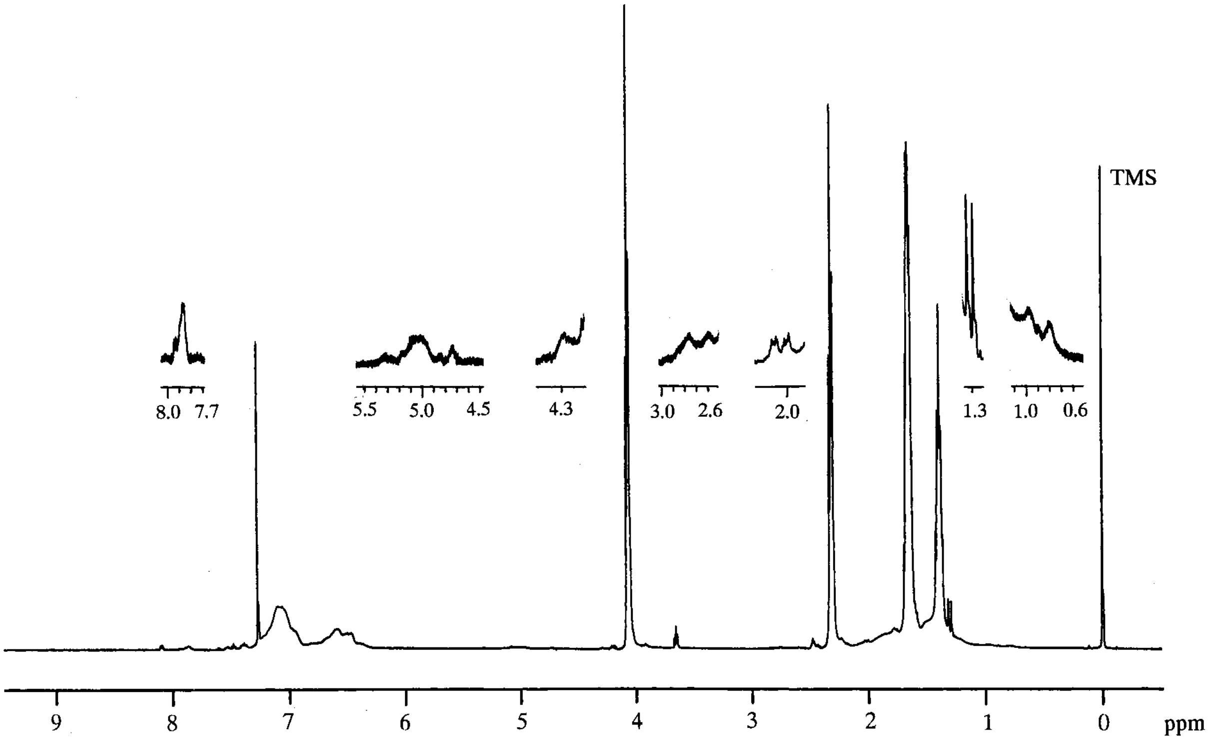


Figure 6. ^{1}H NMR spectrum of the copolymer (conv, 41%; M_n, 5190; M_w/M_n, 1.35), which was obtained by the radical polymerization of styrene by BPO using PCL (Table 2, P-1). The polymerization was carried out at 125 °C for 4 h, after being held at 95 °C for 3.5 h (solvent: CDCl$_3$).

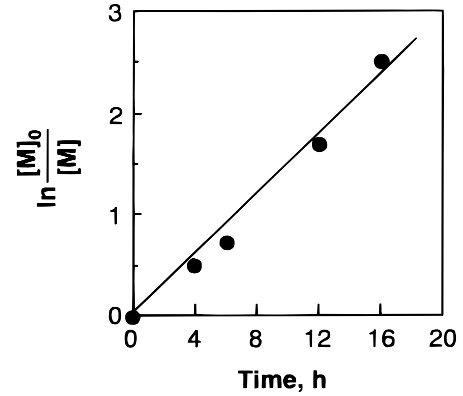


Figure 7. First-order time-conversion plots in the polymerization of styrene by BPO using the PCL (Table 2, P-1).

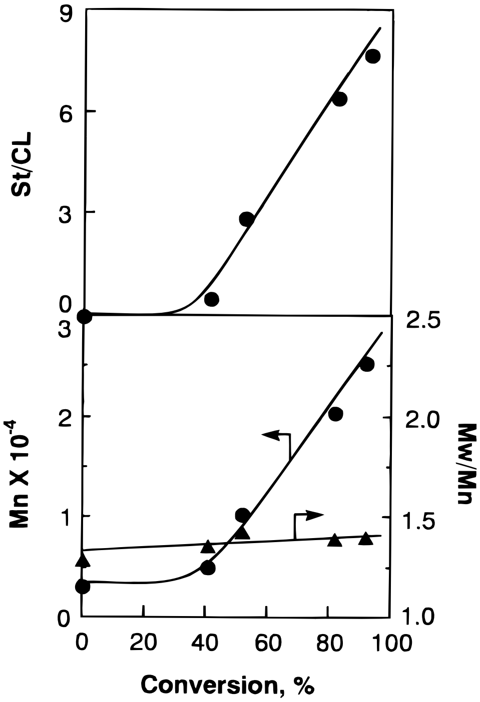


Figure 8. Plots of the molecular weight and molar ratio of styrene to CL units versus conversion in the polymerization of styrene by BPO using the PCL (Table 2, P-1).

linearly with an increase of the conversion when the conversion is >40%. This result has been observed in the polymerization of styrene using the PTHF that had TEMPO at the chain end as a counter radical.[12] Therefore, the result of the present study may also be accounted for by the fact that at <40% conversion, styrene was consumed for formation of the thermal initiator or thermal polymerization, when it is taken into consideration that a slight excess of amounts of the TEMPO moieties exists over those of BPO. Subsequently, the low molecular weight compounds thus produced were removed by drying *in vacuo*.

In living radical polymerization, the ultimate degree of polymerization ought to be determined by only two factors: the concentration of the monomer consumed and that of the growing polymer chain.[34] As described previously, we have already found in the living radical polymerization of styrene by BPO and 4-methoxy-TEMPO that the concentration of the growing polymer chain was identical to the initial concentration of 4-methoxy-TEMPO.[22] Therefore, it is expected that the molecular weight of the copolymer produced is in proportion to the reciprocal of the initial concentration of P-1 ([TEMPO-PCL]$_0$). The relation between the molecular weight and [TEMPO-PCL]$_0$ is shown in Table 3. All the conversions were high enough to compare the molecular weights. It is clear that the molecular weight and the molar ratios of styrene to CL units increase with a decrease in the amount of P-1; they were found to be directly proportional to the reciprocal of the [TEMPO-PCL]$_0$, as demonstrated in Figure 9. These results also support the same conclusion that this polymerization proceeds in accordance with a living mechanism.

These copolymers exhibited two glass transition and one melting endotherm in their DSC thermograms. The DSC thermograms of the PCL (Table 2; P-1), polystyrene (M_n, 20700; M_w/M_n, 1.15) and of the block copolymer (Table 2; M_n, 23600; M_w/M_n, 1.37) are illustrated in Figure 10. The PCL had a glass transition temperature of −56 °C and a melting endotherm at 45 °C, whereas the polystyrene showed a glass transition at 90 °C. It is clear that the copolymer has the glass transition temperatures for both the amorphous phases of PCL block (−70 °C) and the polystyrene block (76 °C). The melting endotherm (39 °C) for the crystalline PCL block can be also observed in the spectrum of the

Table 3. Radical Polymerization of Styrene by BPO and P-1

[TEMPO-PCL]$_0$, ×10^3 mol/L^a	time, h	conv, %^{b}	isolated yield, %	product		molar ratio
				M_n^{c}	M_w/M_n^{c}	St/CL^d
160	53	86	72	10 200	1.49	2.54
108	51	85	56	12 900	1.47	3.16
53.4	72	93	75	23 600	1.37	7.87
40.5	36	95	61	34 900	1.31	10.6

^{a} [TEMPO-PCL]$_0$/[BPO]$_0$, 1.3 in all cases. ^{b} Calculated by GC. ^{c} Estimated by GPC based on polystyrene standards. ^{d} Estimated by ^{1}H NMR spectroscopy based on the relative intensity of the aromatic protons at 6.2−7.3 ppm and the methylene ones at 4.0 ppm (i) in the PCL main chain.

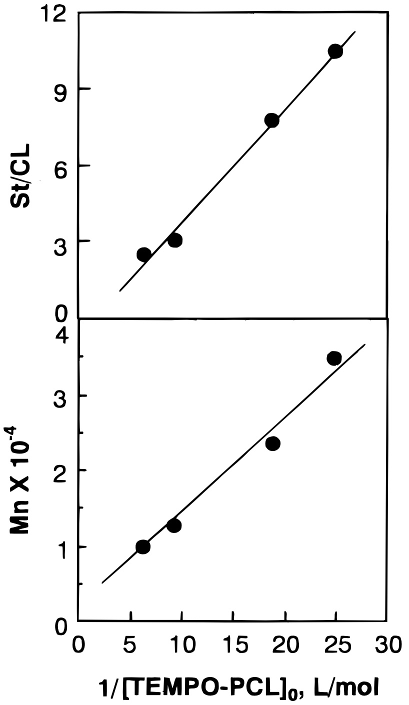


Figure 9. Plots of the molecular weight and molar ratio of styrene to CL units versus the reciprocal of [TEMPO-PCL]$_0$ in the polymerization of styrene by BPO using the PCL (Table 2, P-1).

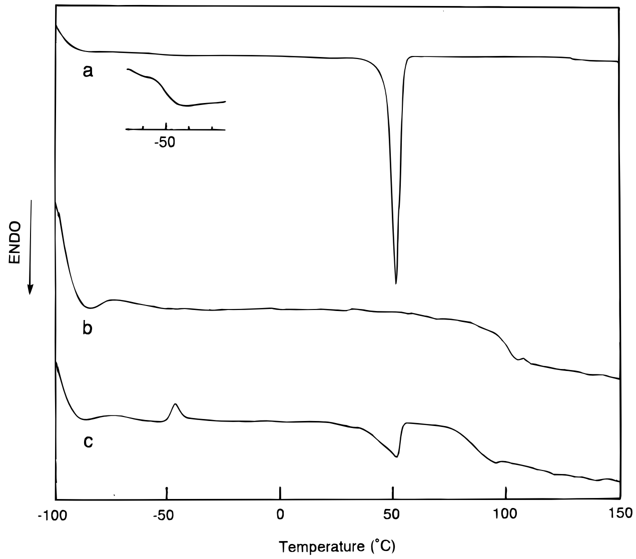


Figure 10. DSC spectra of (a) the PCL (Table 2, P-1), (b) polystyrene (M_n, 20 700; M_w/M_n, 1.15), and (c) the copolymer (M_n, 23 600; M_w/M_n, 1.37), which was obtained from the polymerization of styrene by BPO using the PCL (Table 2, P-1).

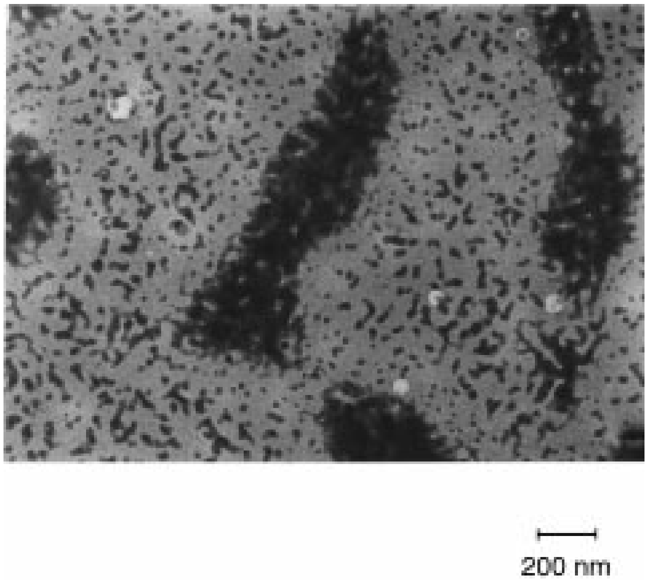


Figure 11. A TEM picture of the copolymer (M_n, 23 600; M_w/M_n, 1.37), which was obtained from the polymerization of styrene by BPO using the PCL (Table 2, P-1). The film was prepared by casting from the THF solution of the copolymer and dying with RuO_4.

copolymer. The glass transition and melting endotherm were in close agreement with those characteristics based on each of the homopolymers. The copolymer showed an exotherm at −50 °C, originating from cold crystallization of the amorphous PCL. This observation suggests that the crystallinity was reduced at low temperature in the block copolymer, with the result that the PCL block was in amorphous condition rather than in crystallized condition. This result means that the polystyrene blocks prevented the PCL blocks from crystallizing. These results are indicative of the complete immiscibility in the two components; therefore, the components are expected to promote microphase segregation. The film prepared by casting from THF solution of this polymer was subjected to TEM analysis, after the film was dyed with ruthenium tetraoxide. The TEM picture is shown in Figure 11. The domains dyed black originate from the polystyrene blocks. As expected, the two components of PCL and polystyrene promoted microphase segregation.

Conclusions

The quantitative synthesis of PCL with TEMPO at the terminal was attained by the anionic polymerization of CL with an aluminum tri(4-oxy-TEMPO) as an initiator. The TEMPO attached to the PCL behaved as a counter radical for the radical polymerization of styrene, giving the poly(CL-*block*-styrene) in quantitative yield. This polymeric TEMPO was found to wholly engage in the polymerization, based on the fact that no prepolymer of the PCL was observed in GPC of the copolymer. This absence of the prepolymer suggests that the anionic polymerization of CL completely proceeded in accordance with a living mechanism. The TEMPO-supported PCL would not have been quantitatively produced if this polymerization had involved undesirable side reactions, including a backbiting attack and an attack of the growing species on the other main chains, and, therefore, the prepolymer should remain after the radical polymerization. The radical polymerization also proceeded in accordance with a living mechanism, because the conversion of styrene linearly increased over time and the molecular weight was directly proportional to the reciprocal of the initial concentration of the PCL. When these results and discussion are taken into account, 4-hydroxy-TEMPO can be regarded as a transforming agent from living anionic to living radical polymerization. We have already reported that sodium 4-oxy-TEMPO derived from 4-hydroxy-TEMPO acts as a transforming agent from living cationic to living radical polymerization.[12] These results mean that 4-hydroxy-TEMPO can be used for both the transforming agents from living anionic and cationic polymerizations to living radical.

The resulting copolymers had two glass transition temperatures due to PCL block and polystyrene, and one melting endotherm based on the crystalline phases of PCL. The copolymer also had an exotherm based on cold crystallization of the amorphous PCL, which means that the crystallinity was reduced in the copolymer at low temperature as a result of the polystyrene blocks preventing the PCL ones from crystallizing. These results indicate that the components of PCL and polystyrene blocks are completely immiscible. In fact, the TEM picture of the film obtained from the block copolymer exhibited microphase segregation. These results are indicative of formation of a new material that consists of biodegradable and nonbiodegradable polymer blocks.

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