

Study of a New Titanium Dual Initiator for the Synthesis of Poly(ϵ -caprolactone)-*b*-Polystyrene Block Copolymers by the Combination of Coordination and Nitroxide Mediated Polymerizations

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ABSTRACT: Poly ϵ -caprolactone-polystyrene block-copolymers (PCL-*b*-PSt) were synthesized using a modified titanium catalyst as the dual initiator. Alcoholysis of $\text{Ti}(\text{OPr})_4$ by 4-hydroxy 2,2,6,6 tetramethyl piperidinyloxy (HO-TEMPO) gave a bifunctional initiator $\text{Ti}(\text{O-TEMPO})_2$. Poly ϵ -caprolactone prepolymer end-capped with the nitroxide group was first prepared by ring opening polymerization of ϵ -caprolactone with this initiator at high conversion. The nitroxide-end-capped structure and molar mass (M_n) of the polymers were demonstrated by typical UV absorption band. This analytical technique indicates a near-quantitative nitroxide functionality and a M_n

in good agreement with size exclusion chromatography (SEC) ones. This polyester prepolymer was used to further initiate the radical polymerization with styrene and reach the block copolymers (PCL-*b*-PSt). All the prepolymers and block copolymers were characterized by SEC and NMR spectroscopy. Additionally, the preparation of star polymers bearing two kinds of arms (PCL and PSt) was envisaged and a preliminary result was given. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3491–3498, 2008

Key words: ring opening polymerization; block copolymers; nitroxide; dual initiator

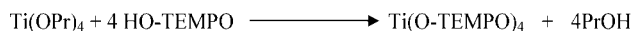
INTRODUCTION

Control of polymerization processes to give well-defined molecular weight and end-functionalized macromolecules has become an increasingly important aspect of polymer chemistry because these end-functionalized polymers can produce various types of block copolymers and networks.^{1–5}

Star-shaped polymers, which are composed of multiple polymer chains emanating from junction points, have received significant attention over the past decade. Because of their unique three-dimensional shape and highly branched structure, star-shaped polymers have shown lower viscosities than linear polymers of the same molecular weight.⁶ Their unique rheological behavior was a potential advantage during the polymer processing. Poly ϵ -caprolactone (PCL), is a widely used biocompatible and biodegradable polymer, suitable for numerous biomedical applications.^{7–10} The design concerning the end-functionalization of PCL is very attractive, including the PCL with reactive double bonds.¹¹

In the first step, by using multifunctional initiators,¹² we have prepared several poly ϵ -caprolactone-polystyrene block copolymers (PCL-*b*-PSt) with different lengths. On the second step, addition of divinylbenzene gave a star polymer. The present article deals with the modification of titanium propoxide by hydroxyl tempo (HO-TEMPO) with the aim to use it as bifunctional initiator in the copolymerization of styrene with ϵ -caprolactone. HO-TEMPO, a well-known controlled radical polymerization reagent, was associated with PCL, and the nitroxyl-terminated PCL could well control the propagation of the further radical polymerization. In the literature, many publications concern the alkoxyamine TEMPO terminated PCL. Mecerreyes et al. introduced PCL brushes at the surface of an electrically conducting material,¹³ Yoshida and Osagawa synthesized PCL block PS using aluminum tri(4-oxy-TEMPO) as initiator,³ Huang and coworkers prepared PCL-PS grafted PEO and PCL-*b*-poly(4-vinyl pyridine).^{4,5} It is important to indicate that among the mentioned articles, only aluminum initiator was used. We have synthesized here a new multifunctional titanium initiator. The ring opening polymerization of CL was performed and the TEMPO group was usefully introduced onto the terminal group of the PCL chain to further initiate the living radical polymerization of

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Scheme 1 Synthesis of dual initiator.

styrene and obtain a block polymer. Additionally, when divinylbenzene was added to styrene, it could give a star polymer microgel.

EXPERIMENTAL SECTION

Materials

Monomers (ϵ -Caprolactone (CL) and styrene) and solvents (Toluene, hexane, THF) purchased from Aldrich were dried over CaH_2 for 48 h and then distilled under reduced pressure prior to use. 4-Hydroxyl-2,2,6,6-tetramethylpiperidinyloxy (HO-TEMPO), benzoyl peroxide (BPO), and $\text{Ti}(\text{OPr})_4$ (from Aldrich) were used without further purification.

Synthesis of $\text{Ti}(\text{O-TEMPO})_4$

The multifunctional initiator $\text{Ti}(\text{O-TEMPO})_4$ was obtained by $\text{Ti}(\text{OPr})_4$ alcoholysis with HO-TEMPO according to the reaction of Scheme 1.

HO-TEMPO (1.0 g, 5.81 mmol) and $\text{Ti}(\text{OPr})_4$ (0.413 g, 1.45 mmol) were added in a 50-mL round-ground flask with a magnetic stirrer. The flask was placed in a preheated oil bath at 75°C and after 10 min, the vacuum was adjusted at about 80–100 mbar. The reaction mixture became solid after 5–10 min. The temperature was risen to 120°C and the vacuum decreased to 20 mbar for 5 min, before stopping the reaction, to get 1.092 g of product. The product was a light red solid at room temperature.

The presence of propanol obtained after distillation was estimated and analyzed by GC/MS. However, it was supposed that some unreacted $\text{Ti}(\text{OPr})_4$ and excess HO-TEMPO still remained in the mixture.

Both $\text{Ti}(\text{OPr})_4$ and HO-TEMPO could dissolve in hexane and it was chosen as the extraction reagent. A typical extraction procedure was as follows: 0.1 g $\text{Ti}(\text{O-TEMPO})_4$ crude product, and 3.4 g of hexane were added in a Pyrex-tube. The tube was placed on the Janke and Kunkel of IKA vibrated for 10 min, and then was placed in 60°C oil bath for another 20 min. At last the tube was centrifuged for 30 min. The solid, after filtration, was dried in vacuum at room temperature overnight until constant weight was reached. The product was obtained in 79% yield.

In the second part, we confirm the full site activity and four substitutions of the initiator propanol group by the hydroxyl TEMPO, by comparison the theoretical and experimental values of PCL polymer

mass obtained with this modified initiator by using $^1\text{H-NMR}$, SEC, and UV detection methods.

Polymerization of CL with $\text{Ti}(\text{O-TEMPO})_4$ as initiator

Polymerization was carried out in a sealed tube. A typically synthetic procedure is as follows: CL (1 g, 8.77 mmol), $\text{Ti}(\text{O-TEMPO})_4$ (0.016 g, 0.0219 mmol), and magnetic stirrer bar were added into a tube, put under vigorous stirring, to finally get a clear light red solution. Then the tube was immersed in an oil bath thermostated at the desired temperature. After suitable reaction time, the polymerization was stopped by freezing the tube in liquid nitrogen. The crude polymer samples were purified by pouring a polymer solution in THF into an excess of hexane or ethanol while stirring. The precipitate was collected by filtration and then dried in a vacuum oven at 45°C overnight. The conversion was calculated by gravimetry.

Block copolymerization styrene with TEMPO terminated PCL

A general synthetic procedure was as follows: PCL-TEMPO (0.15 g, $M_n = 8624 \text{ g mol}^{-1}$, $M_w/M_n = 1.3$, containing 0.0174 mmol of TEMPO moiety), styrene (0.6873 g, 6.61 mmol, degassed with N_2), and BPO (3.3 mg, 0.0134 mmol) were placed in a preheated tube. This solution was light red at first. After elimination of oxygen by nitrogen bubbling, the tube was sealed. The polymerization was carried out for 3.5 h at 85°C and the color became light yellow. Polymerization continued for another 20 h at 125°C and was stopped by cooling with liquid nitrogen. The product was purified by pouring a polymer solution in THF into an excess of methanol while stirring. The precipitate was collected by filtration and then dried in vacuum at 60°C overnight. Block copolymer was obtained in 85% yield.

Synthesis of star microgel based on PCL-TEMPO/divinyl benzene

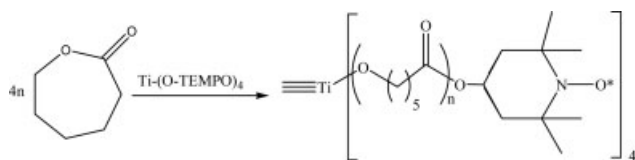
A solution of PCL-TEMPO ($M_n = 9967 \text{ g mol}^{-1}$, $M_w/M_n = 1.3$) 0.20 g ($2.01 \times 10^{-5} \text{ mol}$), divinylbenzene

TABLE I
DSC Data of Different TEMPO-Compounds

Reagent	Details of DSC ^{a,b}
HO-TEMPO	$T_{m1} = 76.5^\circ\text{C}$, $\Delta H_1 = 106.8 \text{ J/g}$
$\text{Ti}(\text{O-TEMPO})_4$ crude	$T_{m1} = 68^\circ\text{C}$, $\Delta H_1 = 13.2 \text{ J/g}$
$\text{Ti}(\text{O-TEMPO})_4$ purified	$T_{m1} = 68^\circ\text{C}$, $\Delta H_1 = 7.3 \text{ J/g}$

^a Temperature program of DSC: From ambient temperature to 160°C at a rate of 10°C/min .

^b Here, 1 refers to T_m or ΔH of HO-TEMPO.



Scheme 2 ϵ -caprolactone polymerization by using $\text{Ti}(\text{O-TEMPO})_4$.

(DVB) 0.10 g (7.91×10^{-4} mol), and BPO 3.8 mg in 3.80 g toluene was introduced into a Pyrex tube. After elimination of oxygen gas, the solution was placed in an oil bath at 85°C for 3.5 h and then further reacted at 110°C for 48 h. The resulting star microgel was precipitated from methanol to get a white powder which was dried in vacuum at 60°C overnight. Star polymer was obtained in 55% yield.

Characterization

Size Exclusion Chromatography (SEC) was performed on a Waters 515 with a Waters 7414 refractive index detector and a Waters model 440 absorbance detector using THF as solvent and eluent with a flow rate of 1.0 mL min^{-1} . The PCL or PS standards were used for the calibration curve. $^1\text{H-NMR}$ spectra were obtained on Bruker (400-MHz) spectrometer. CDCl_3 was the solvent and tetramethylsilane was the internal standard. FTIR and UV were recorded on a Nicolet NEXUS Fourier Transform Infrared and JASCO Spectrometers, respectively. DSC analyses were obtained with the Setaram DSC141 apparatus.

RESULTS AND DISCUSSION

DSC was used to measure the melting point T_m of the product $\text{Ti}(\text{O-TEMPO})_4$. The results are listed in Table I.

These DSC values permit us to estimate the purity of the catalyst from the enthalpy of HO-TEMPO according to Scheme 1. Indeed, this compound is commercial and far more stable than $\text{Ti}(\text{O-TEMPO})_4$ which evolves with different parameters (time, moisture, purification methods . . .). So about 12.4% HO-

TEMPO was detected in crude $\text{Ti}(\text{O-TEMPO})_4$, reducing to 6.8% after extraction meaning an actual content of $\text{Ti}(\text{O-TEMPO})_4$ higher than 93%. On one hand the quantity of propanol collected and on the other hand the SEC and UV PCL analyses of polymer (see below) are in good agreement with this high purity.

Synthesis of PCL with nitroxide as an end-functional group

The initiator $\text{Ti}(\text{O-TEMPO})_4$ is a tetra functional initiator like $\text{Ti}(\text{OPr})_4$. The corresponding PCL has a four-arm structure (Scheme 2).

The theoretical degree of polymerization (DP_{th}) of each linear arm of the four-arm polymer was given by eq. (1):

$$\text{DP}_{\text{th}} = \frac{[\text{M}]_0}{4 \times [\text{I}]_0} \times C\% \quad (1)$$

where C is the CL monomer conversion determined by gravimetry; $[\text{M}]_0$ and $[\text{I}]_0$ are the molar concentrations of the initial monomer and initiator, respectively.

The theoretical molar weight $M_{n,\text{th}}$ of linear PCL was given by eq. (2):

$$M_{n,\text{th}} = (\text{DP}_{\text{th}} \times 114) + 171 \quad (2)$$

where 114 is the molar weight of the CL monomer and 171 is the molar weight of terminal group O-TEMPO .

Several SEC results of CL bulk polymerization at different temperatures are listed in Table II.

From the above data, it was clear that the molar mass (M_n) obtained by SEC test was in good agreement with the theoretical one. It means that the substitution of titanium ether by a TEMPO moiety did not affect the functionality of the initiator. However, Bounor-Legaré and coworkers¹⁴ showed that the substitution of propoxide to phenoxide ether in titanium compound influenced the average number of active sites per initiator and the kinetics of polymer-

TABLE II
Results of CL Bulk Polymerization Initiated by $\text{Ti}(\text{O-TEMPO})_4$

Sample	Conditions	Conversion (%)	$M_{n,\text{th}}^{\text{a}}$ (g mol ⁻¹)	$M_{n,\text{SEC}}^{\text{b}}$ (g mol ⁻¹)	M_w/M_n
PCL _{T-1}	130°C, 120 min	~ 100	6440	6600	2.0
PCL _{T-2}	130°C, 35 min	~ 100	5073	5300	1.83
PCL _{T-3}	130°C, 35 min	~ 100	11,230	11,500	1.72
PCL _{T-4}	110°C, 90 min	95	16,574	15,900	1.78
PCL _{T-5}	90°C, 160 min	64	11,160	9800	1.43
PCL _{T-6}	90°C, 25 min	27	4800	4600	1.20

^a $M_{n,\text{th}}$ was calculated according conversion.

^b The calibration curve was realized with PCL standards.

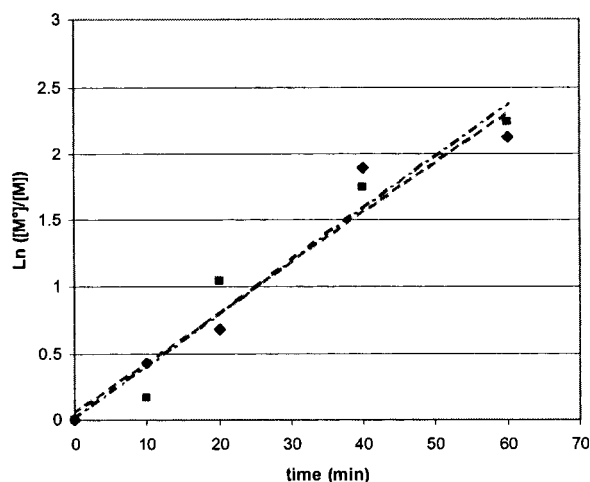


Figure 1 The semi-logarithmic plot of $\ln ([M]_0/[M])$ versus the reaction time for different bulk polymerization of ϵ -Caprolactone at 110°C ($[M]_0/4[I]_0 = 150$) using $\text{Ti}(\text{OPr})_4$ (■) or $\text{Ti}(\text{OTEMPO})_4$ (◆) as initiator. Linear regression (---).

ization. Table II indicates that the molecular weight of PCL was in a good agreement with the theoretical value. However, the obtained polymer has a broad M_w/M_n . This means that the bulk polymerization is not well controlled under the conditions that were used. It may be explained by the unavoidable presence, to high temperature and high conversion, of both inter- and intramolecular transesterification side reactions catalyzed by Titanium. As reported by Dubois et al.¹⁵, the number of transesterifications increases with temperature, reaction time, and type and concentration of catalyst or initiator. Besides, the relative reactivity of different metal alkoxide initiators towards chains already formed decreases in the following order: Sn, Ti, Zn, and Al.

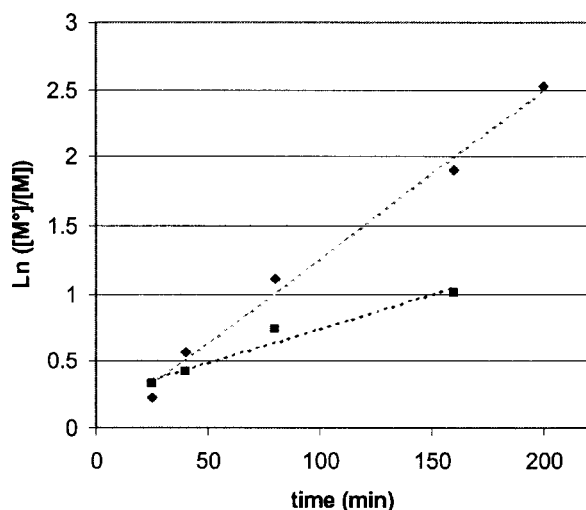


Figure 2 The semi-logarithmic plot of $\ln ([M]_0/[M])$ versus the reaction time for different bulk polymerization of ϵ -Caprolactone at 90°C ($[M]_0/4[I]_0 = 150$) using $\text{Ti}(\text{OPr})_4$ (◆) or $\text{Ti}(\text{OTEMPO})_4$ (■) as initiator. Linear regression (---).

Kinetics of polymerization of CL by modified and unmodified initiator

The controlled polymerization of caprolactone (CL) monomer initiated by $\text{Ti}(\text{O-TEMPO})_4$ was compared to the one initiated by common $\text{Ti}(\text{OPr})_4$. The kinetics of CL polymerization were carried out under two different temperatures (90 and 110°C) with a ratio $[M]_0/4[I]_0$ equal to 150.

Figures 1 and 2 show the plot of $\ln ([M]_0/[M])$ versus time at 110°C and 90°C , respectively. Figure 3 shows the evolutions of M_n and I_p with conversion.

The polymerization rate R_p follows a pseudo-first order time law, where k_{app} can be defined as the "apparent" rate constant:

$$R_p = -\frac{d[M]}{dt} = k_p[P^\circ][M] = k_{\text{app}}[M] \quad (3)$$

Integration of eq. (3) results in:

$$\ln \frac{[M]_0}{[M]_t} = k_p[P^\circ]t = k_{\text{app}}t \quad (4)$$

where $[P^\circ]$ represents the concentration of active centers.

The first-order time-conversion (Figs. 1 and 2) plot is a straight line with slope $k_{\text{app}} = k_p [P^\circ]$ meaning that the number of active centers is always constant which is an important proof of the living polymerization character. At 110°C $\text{Ti}(\text{OTEMPO})_4$ presents exactly the same activity as $\text{Ti}(\text{OPr})_4$. At lower temperature, 90°C , the living character is kept but k_{app} of modified initiator is divided by two with $\text{Ti}(\text{OTEMPO})_4$.

Moreover, the number-average molar weight is directly proportional to conversion (Fig. 3) at 110 and 90°C using $\text{Ti}(\text{OTEMPO})_4$ as initiator.

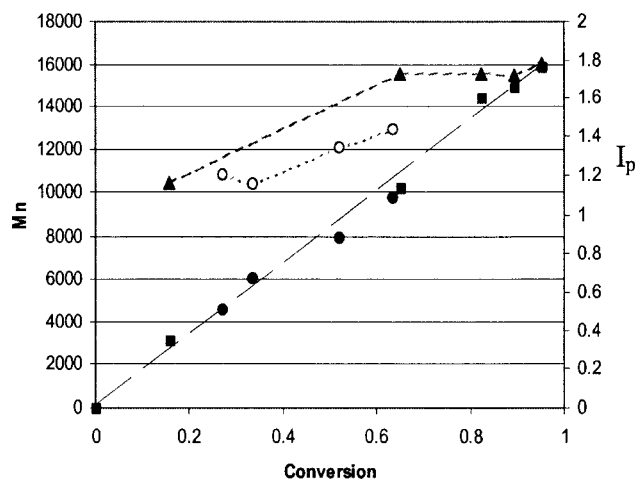


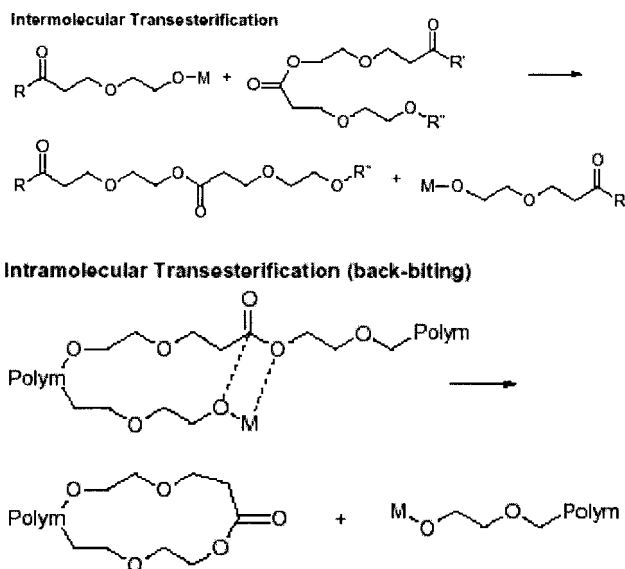
Figure 3 Evolution of M_n and I_p versus conversion of ϵ -Caprolactone initiated by $\text{Ti}(\text{OTEMPO})_4$ ($[M]_0/4[I]_0 = 150$) at $T = 110^\circ\text{C}$ (■ and ▲ respectively) and 90°C (● and ○ respectively). Theoretical M_n evolution (---).

According to the dynamics studies, we can conclude that the molar weight distribution became broader once raising the polymerization temperature or the conversion (Fig. 3 and Table II). For example in Figure 3, for a reaction temperature of 90°C and a reaction time of 25 min the conversion was about 27% and the molar weight distribution was only 1.20. But at 160 min, the conversion reached 63% and the distribution was 1.43. When the temperature was increased to 110°C the effect of time on molecular weight distribution was quite obvious. This may be put on account of the "ester exchange" effect reported by other researchers.¹⁵ It is well known from the ROP of lactones and lactides that the catalyst or initiator causes transesterification reactions (Scheme 3). Intermolecular transesterification reactions change the sequences of polycaprolactones. Intramolecular transesterification reactions, i.e., back-biting, cause degradation of the polymer chain, and the formation of cyclic oligomers. Both types of transesterification reaction broaden the molar weight distribution.

Determination of the molar mass (M_n) by UV absorption of end nitroxide functionality

The number-average molecular weight (M_n) of the polymers was calculated using Lambert-Beer's law. By measuring the absorbance at the absorption-maximum of a solution of the polymer, M_n can be calculated. Indeed, nitroxyl radical exhibits a characteristic UV absorption¹⁶ at 469 nm ($\pi-\pi^*$).

The intensity could be used to calculate the molar weight of PCL-TEMPO. Here, we used HO-TEMPO as standard calibration reagent. The linear relationship (Fig. 4) between the I_{469} and the molar concentration



Scheme 3 Reaction schemes for intermolecular and intramolecular transesterification reactions.

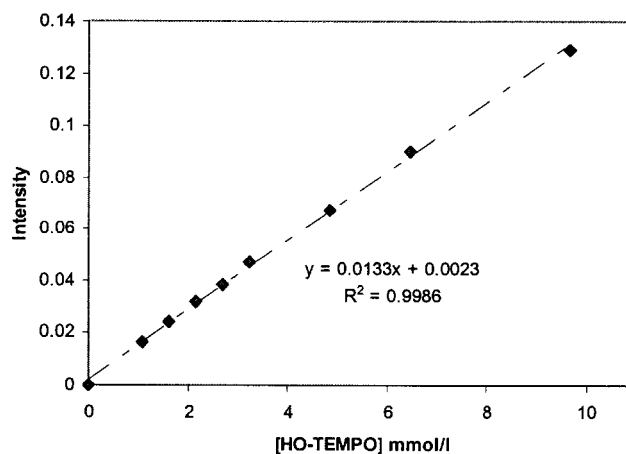


Figure 4 Absorption Intensity at 469 nm versus [HO-TEMPO] mmol/L.

of nitroxyl radical (HO-TEMPO) fitted well as eq. (5):

$$I_{469} = 13.039 \times [\text{HO} - \text{TEMPO}] + 0.003 \quad (5)$$

where I_{469} is the absorption intensity at 469 nm in toluene as solvent and [HO-TEMPO] is the molar concentration of nitroxide group.

The UV method can be used to measure the molar mass of PCL-TEMPO.

First, W_1 and W_2 represent the weight of PCL-TEMPO (density d_1) and the weight of toluene (density d_2) respectively. Then, assuming the polymer solution is an ideal solution, the total volume of the polymer solution was:

$$V_s = W_1/d_1 + W_2/d_2 \quad (6)$$

From the absorption intensity of PCL at 469 nm, eq. (7) gives the molar concentration of TEMPO:

$$[\text{TEMPO}] = (I_{469,P} - 0.003)/13.039 \quad (7)$$

The molar mass of PCL-TEMPO by UV ($M_{n,\text{UV}}$) was determined as follows:

$$M_{n,\text{UV}} = W_1/(V_s \times [\text{TEMPO}]) \quad (8)$$

Four PCL-TEMPO with different M_n were tested by UV and their results are listed in Table III.

TABLE III
The M_n of PCL-TEMPO Calculated by UV

Sample	W_1 (g)	W_2 (g)	$I_{469,P}$	$M_{n,\text{UV}}^a$ g mol ⁻¹	$M_{n,\text{SEC}}$ g mol ⁻¹
PCL _T -4	0.1834	3.7694	0.0375	15,340	15,900
PCL _T -7	0.2012	3.5513	0.0588	10,980	10,200
PCL _T -8	0.187	3.3897	0.068	9190	8200
PCL _T -9	0.1873	9.9899	0.0421	5330	4800

^a $I = 469$ nm, Toluene as solvent, $d_1 = 1.15$ g/cm³, $d_2 = 0.865$ g/cm³.

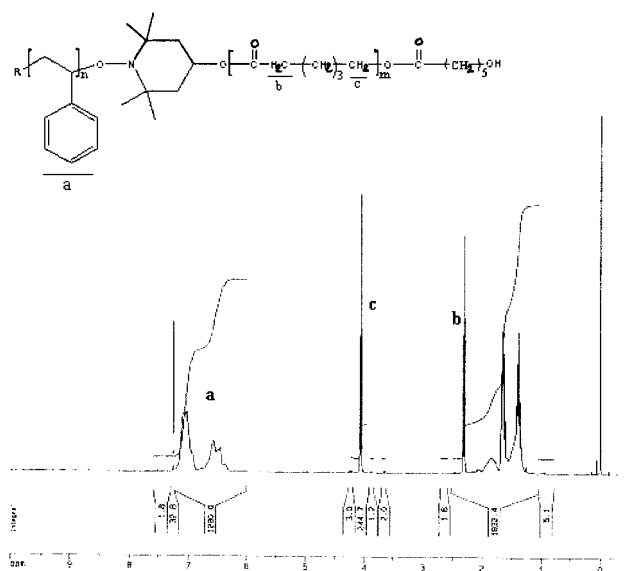


Figure 5 $^1\text{H-NMR}$ spectrum of one copolymer PCL-*b*-PSt (sample B3).

It shows that the molar weights thus determined by UV are in a good agreement with the ones estimated by SEC. So, it was possible to estimate M_n of PCL-TEMPO by using UV spectroscopy. These results are consistent with a living character because polymers with nitroxide chain end functionality are obtained quantitatively.

Nitroxide mediated polymerization of styrene using PCL-TEMPO as radical macroinitiator

The radical polymerization of styrene was performed in bulk with BPO as initiator in the presence of PCL-TEMPO. The polymerization was carried out at 85°C first for 3.5 h for the decomposition of BPO, and resulting radicals were fully trapped by macronitroxide PCL-TEMPO. No propagation reaction was observed in this stage. The solution, which had a light red colour due to free nitroxide, turned light yellow after 3.5 h at 85°C . Then, the reaction temper-

ature was increased to 125°C and kept at this temperature for 24 h.

Several block polymers were synthesized (Fig. 5) and their characterizations are gathered in Table IV.

Table IV shows the effect of $[\text{St}]/[\text{TEMPO}]$ feed ratio on block polymerization. For the same prepolymer PCL-T-2 and the same reaction time, two different feed ratios, 156 and 276, were used. The lower ratio meant the higher concentration of TEMPO radical group. A higher concentration of TEMPO exerted better control on the polymerization of styrene by reversible termination of TEMPO with propagating radical species. In this case, the amount of dormant species formed by the coupling of the propagating species with TEMPO was high, so the remaining concentration of propagating species was low. This led to the decrease in the polymerization rate and the conversion of styrene, but copolymer with a narrow polydispersity was obtained.

A typical SEC image is shown in Figure 6 (PCL-T-3 as prepolymer). Almost all the PCL-TEMPO used was involved in the polymerization because the SEC patterns of the copolymers showed unimodal curves and exhibited no peaks originating from the prepolymers.

Kinetics of polymerization of styrene using PCL-TEMPO as radical macroinitiators

To confirm whether this radical polymerization proceeds in accordance with a living mechanism, further dynamics studies were performed using the PCL-TEMPO with $M_n = 4600 \text{ g mol}^{-1}$, $M_w/M_n = 1.2$. From Figure 7 a first-order linear relationship is observed between $\ln[M]_0/[M]$ and reaction time. It confirms that the polymerization of styrene in the presence of PCL-TEMPO is a controlled process.

Preliminary study on the Synthesis of star microgel copolymer based on PCL-TEMPO

As satisfactory control of molar mass and molecular architecture can be achieved by "living" radical

TABLE IV
Radical Polymerization of Styrene by BPO with PCL-TEMPO^a

Block	Prepolymer		$[\text{St}]/[\text{R-NO}^*]$	Conversion (%) ^c	Block polymer		Units ^d	
	M_n^b	M_w/M_n^b			M_n^b	M_w/M_n^b	CL	$\text{St}_{\text{th}}/\text{St}_{\text{NMR}}$
B-1	PCL-T-2		156	49.1	17,170	1.5	45	77//101
B-2	5300	1.8	276	75.2	30,850	1.7	45	208//211
B-3	PCL-T-3		620	32.5	55,720	1.4	100	201//207
B-4	11,500	1.7	633	94.5	85,890	1.6	100	598//599

^a $[\text{PCL-TEMPO}]_0/[\text{BPO}]_0 = 1.3$ in all cases.

^b Estimated by SEC based on PCL standard.

^c Conversion yield calculated by gravimetry after 24 h of reaction.

^d Units of CL based on SEC, units of St_{th} estimated based on the conversion and ratio of $[\text{St}]/[\text{PCL-TEMPO}]$, $\text{St}_{\text{th}} = ([\text{St}]/[\text{PCL-TEMPO}]) \times \text{conversion}\%$, St_{NMR} units of styrene estimated by $^1\text{H-NMR}$ (Fig. 5) based on the relative integral of the aromatic protons at 6.2–7.2 ppm to the methylene protons at 4.0 ppm in the PCL main chain.

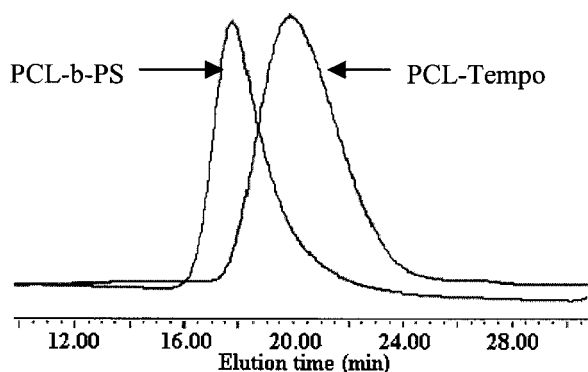


Figure 6 SEC profiles of the prepolymer (PCL_{T-3}, $M_n = 11500 \text{ g mol}^{-1}$, $M_w/M_n = 1.7$) and block copolymer ($M_n = 85900 \text{ g mol}^{-1}$, $M_w/M_n = 1.6$).

polymerization, the formation of star microgel polymer was investigated. Herein, we describe the synthesis of a star polymer based on PCL-TEMPO/Divinylbenzene reagent and also using PCL-PS diblock instead of PCL-TEMPO (Fig. 8). Several polymerization results are listed in Table V.

Figure 9 shows the SEC profiles of the star polymer and the prepolymer PCL-TEMPO; it is obvious that the product has a much higher M_n than that of the prepolymer. The star polymer produces two peaks, the first ranging from 16 to 19 min and the second ranging from 19 to 24 min. The second may be ascribed to the linear prepolymer.

Once PCL-*b*-PS was used as prepolymer, it formed a high crosslinking microgel, and thus, no SEC data were obtained. Especially for PCL-PS-gel-2, the solution was slightly cloudy and even gel could be observed.

FTIR was used to study the difference between the prepolymer and the resulting gel (Fig. 10). The

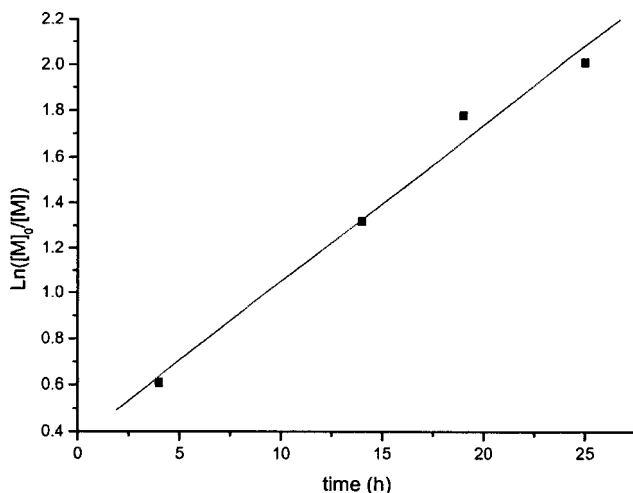


Figure 7 The semi-logarithmic plot of $\ln([M]_0/[M])$ versus the reaction time for bulk polymerization of styrene under PCL-TEMPO nitroxide co-initiation with BPO. Linear regression (—).

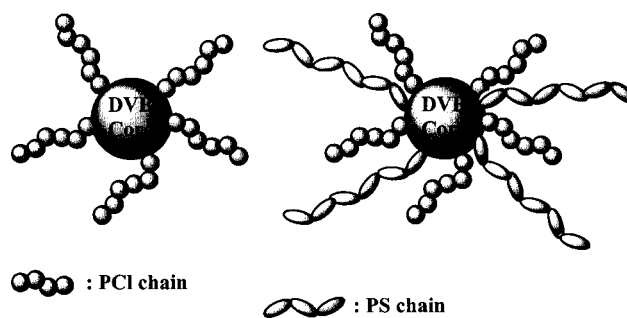


Figure 8 Schematic structure of PCL-TEMPO/DVB (left) and PCL-PS/DVB (right) star polymers.

absorption at 1600 cm^{-1} was assigned to aromatic rings of styrene and DVB. The comparison of the relative value of the intensity at 1740 cm^{-1} (C=O) to that at 1600 cm^{-1} , showed that the gel was in much greater amount than the prepolymer. It means that the DVB reacted with PCL-PS.

The content of DVB in the gel was estimated from FTIR data (defined as G). Wavelengths between $1768\text{--}1654 \text{ cm}^{-1}$ (Fig. 10) belong to C=O of PCL, but it overlaps with the peak of PS aromatic ring and the wavelength range may have drifted when different block or gel samples were tested. If the effect of PS is not eliminated, there may be an error on the determined value.

Then, the wavelengths of $1631.5\text{--}1560.2 \text{ cm}^{-1}$ were defined as the transmission of aromatics (A_{PS}). The wavelengths from 1996.0 to 1637.3 cm^{-1} were defined as the transmission of A_1 , which includes the transmission of C=O of PCL and contribution of PS aromatics. The true $A_{C=O}$ can be determined by eq. (9):

$$A_{C=O} = A_1 - A_{PS}/k \quad (9)$$

where k is a calibration factor and is equal to 1.64, which is the ratio $A_{PS1631-1560}/A_{PS1996-1637}$ of pure PS.

TABLE V
Star Polymers Obtained by Using PCL-TEMPO or PCL-PS with DVB

Sample	Prepolymer		Yield (%) ^a
PS-gel-1 ^b	PCL-TEMPO	$M_n = 9967$ $M_w/M_n = 1.43$	55
PCL-PS-gel-1 ^c	PCL ₇₄ PS ₁₂₆	$M_n = 21,500$, $M_w/M_n = 1.71$	53
PCL-PS-gel-2 ^b	PCL ₄₀ PS ₃₁₄	$M_n = 37,200$, $M_w/M_n = 1.45$	50

^a Yield calculated by gravimetric conversion of DVB.

^b Weight ratio of PCL-TEMPO, DVB, BPO, toluene [2 : 1 : 0.038 : 30]; 85°C for 3.5 h and then 125°C for 48 h.

^c Weight ratio of PCL-*b*-PS, DVB, BPO, toluene [2 : 1 : 0.038 : 8]; 125°C for 48 h.

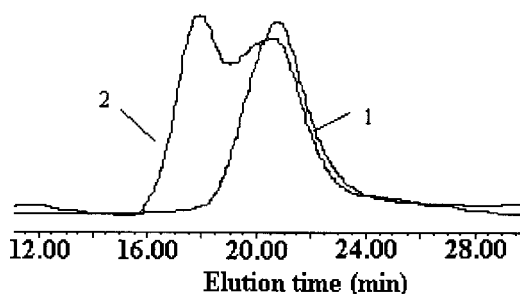


Figure 9 SEC profiles of the prepolymer PCL-TEMPO (1) and star polymer (2).

Blends of prepolymers and PDVB were prepared respectively as FTIR calibration and the weight ratio were both 1 : 2 (PDVB : prepolymer).

Then, G can be calculated approximately by using eq. (10):

$$G = \frac{A_{\text{PS}/\text{A}_{\text{C}=\text{O}} \text{ of gel} - A_{\text{PS}/\text{A}_{\text{C}=\text{O}} \text{ of prepolymer}}{A_{\text{PS}/\text{A}_{\text{C}=\text{O}} \text{ of blend} - A_{\text{PS}/\text{A}_{\text{C}=\text{O}} \text{ of prepolymer}} \times \frac{1}{3} \quad (10)$$

where 1/3 takes in account the PDVB content in the blend.

The data are listed in Table VI. It shows that the experimental value is slightly higher than the theoretical one.

CONCLUSIONS

Block copolymers and star polymers were synthesized by polymerization of lactone and unsaturated monomer in presence of a Titanium dual initiator by combination of coordination and nitroxide mediated polymerizations. $\text{Ti}(\text{O-TEMPO})_4$ was successfully synthesized by reaction of HO-TEMPO with $\text{Ti}(\text{OPr})_4$. $\text{Ti}(\text{O-TEMPO})_4$ was used for the controlled ring-opening polymerization of ϵ -caprolactone and

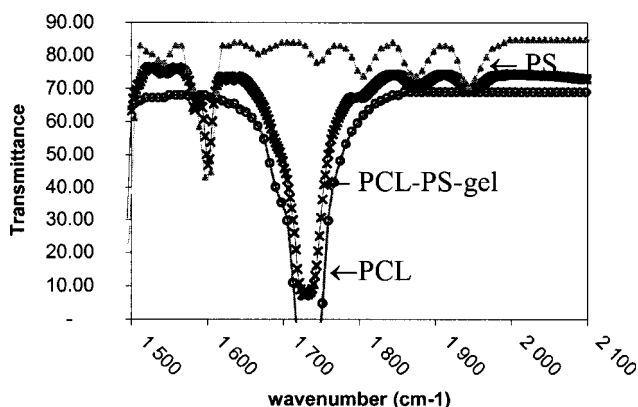


Figure 10 FTIR spectrum of poly (ϵ -Caprolactone) (○), polystyrene (▲), and PCL-PS-gel (×) between 1500 and 2100 cm^{-1} .

TABLE VI
Weight Content of PDVB in Gel

Sample	$A_{\text{PS}}/A_{\text{C}=\text{O}}$	G_{FTIR}	G_{theory}
Prepolymer-1	0.378	29.7%	20.8%
PCL-PS-gel-1	0.498		
Blend-gel-1 ^a	0.534		
Prepolymer-2	0.093	25.7%	20.0%
PCL-PS-gel-2	0.172		
Blend-gel-2 ^a	0.182		

^a Blend was prepared by prepolymers and PDVB, the weight ratio was 1 : 2 (PDVB : prepolymer) G_{theory} was calculated by the weight conversion of DVB.

introducing the TEMPO radical on the terminal of PCL chain. Both polymerizations of ϵ -caprolactone and styrene were achieved. The TEMPO moiety was shown to be intact after the ring opening polymerization of ϵ -caprolactone, in spite of high polydispersity (~ 1.2 to 2), and further to initiate radical polymerization of styrene to obtain the PS-*b*-PCL copolymers. By introducing DVB reagent as a crosslink "core," star polymers have also been successfully prepared. In the future, after mixture of the elaborate copolymer in a matrix, it should be possible to synthesize *in situ* star polymers by addition of DVB to modify the properties of the matrix.

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