

Synthesis and Characterization of the Novel Block Copolymer Poly(ϵ -caprolactone)-*b*-Poly(4-vinyl pyridine) by the Combination of Coordination and Controlled Free-Radical Polymerizations

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ABSTRACT: A novel block copolymer, poly(ϵ -caprolactone)-*b*-poly(4-vinyl pyridine), was synthesized with a bifunctional initiator strategy. Poly(ϵ -caprolactone) prepolymer with a 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) end group (PCL_T) was first obtained by coordination polymerization, which showed a controlled mechanism in the process. By means of ultraviolet spectroscopy and electron spin resonance spectroscopy, the TEMPO moiety was determined to be intact in the polymerization. The copolymers were then obtained by the controlled radical polymerization

of 4-vinyl pyridine in the presence of PCL_T. The desired block copolymers were characterized by gel permeation chromatography, Fourier transform infrared spectroscopy, and NMR spectroscopy in detail. Also, the effects of the molecular weight and concentration of PCL_T on the copolymerization were investigated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2280–2285, 2004

Key words: diblock copolymers; radical polymerization; synthesis

INTRODUCTION

The preparation of block copolymers, a kind of useful polymer material, has attracted much interest in polymer chemistry.^{1–3} Recently, a large body of publications has reported a strategy to employ multifunctional initiators to initiate different polymerizations in sequence or concurrently to prepare block copolymers.^{4–7} In this way, the merits of various techniques can be combined, and more block polymers that can be hardly or trivially prepared via one mechanism become available. Because the applicable monomers have been expanded from the traditional styrene and its derivatives^{8,9} to acrylic esters¹⁰ and some amine-containing monomers, including dimethylacrylamide and vinyl pyridine,^{11,12} in recent years, nitroxide-mediated free-radical polymerization, typically with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the initiator, has become a versatile method for preparing polymers with well-controlled molecular weights and narrow polydispersities. Also, the technique can be successfully used to make block copolymers. In a previous work, we found that in the presence of the macroinitiator PEO with a TEMPO end group, the

polymerization of styrene could be carried out by controlled radical polymerization, and the molecular weight distribution was much narrower; even the molecular weight of polystyrene was as high as 10⁶.

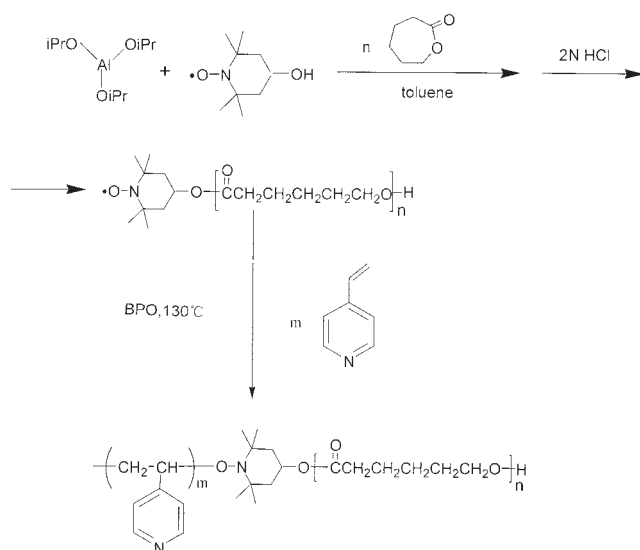
Here, we describe the preparation of a special diblock copolymer, poly(ϵ -caprolactone) (PCL)-*b*-poly(4-vinyl pyridine) [P(4-VP)], which has not been reported before. The copolymer PCL-*b*-P(4-VP) was obtained by a two-step procedure: first, a macroinitiator PCL with a TEMPO end group was prepared by the coordination polymerization of ϵ -caprolactone (CL); then, we initiated the polymerization of 4-vinyl pyridine (4-VP) by a controlled radical mechanism. This copolymer can be used in conducting materials and the coating industry; for example, it might be used as a promising pigment-dispersing agent in polyester powder coatings because PCL is compatible with polyesters and P(4-VP) has a high affinity with metal, so it should show strong interactions with TiO₂ fillers.^{13,14}

EXPERIMENTAL

Materials

Aluminum triisopropoxide was distilled *in vacuo* and dissolved in dry toluene and then stored at –12°C according to Duda's method.¹⁵ CL was dried over CaH₂ for 24 h and then distilled under reduced

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Scheme 1

pressure (114–116°C/6 mmHg). 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy was purified by recrystallization with hexane. Benzoyl peroxide (BPO) was recrystallized from ethanol twice before use. 4-VP was distilled under reduced pressure (59–61°C/6 mmHg) to remove the stabilizer. All of the other reagents were purified by common purification procedures.

Preparation of the prepolymer of poly(ϵ -caprolactone) with a 2,2,6,6-tetramethylpiperidinyloxy end group (PCL_T)

To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (62 mg, 0.36 mmol) in 10 mL of toluene, 1 mL of a toluene solution of aluminum triisopropoxide (0.12 mol/L) was added in a reactor under a nitrogen atmosphere. The mixture was stirred at room temperature for 5 min, and the solvent was evaporated to dryness. Then, we repeated the process of adding 10 mL of toluene, stirring the mixture for 5 min, and evaporating the solvent. After three cycles of this procedure, 30 mL of dry toluene, followed by 4.0 mL of CL, were added to the reactor. The polymerization was kept at 25°C for a given time and was then stopped with excess aqueous HCl (2 mol/L). PCL_T was obtained by precipitation with hexane and was then purified twice by dissolution/precipitation with chloroform/ethanol.

Preparation of the block copolymer

A 100-mL ampule was charged with 0.02 mmol of PCL_T, 1 mL of 4-VP, and 3.7 mg of BPO. The mixture was sealed and degassed by three freeze–pump–thaw cycles. The vessel was immersed in a preheated oil

bath at 90°C for 3 h and then heated to 130°C, the temperature was kept throughout the reaction. The polymerization was quenched in liquid nitrogen after a given time. The resulting polymer was obtained by precipitation with diethyl ether and then extracted for 48 h by ethyl acetate to remove the unreacted PCL_T.

Measurements

¹H-NMR spectra were recorded on a DMX 500-MHz spectrometer (Bruker, Germany) with tetramethylsilane as the internal standard and chloroform-*d*₃ (CDCl₃) as the solvent. Gel permeation chromatography was performed on a PerkinElmer Series 200 (Beltsville, MD) with a refractive index detector with dimethylformamide as both the solvent and eluent and with standard polystyrene for the calibration. Measurement was performed at 70°C with a flow rate 1.0 mL/min. Ultraviolet (UV) spectra were taken on a 756 MC UV–visible spectrophotometer (Shanghai Third Analytical Instrument Factory, China). Electron spin resonance (ESR) spectra were recorded on a Bruker ER200D-SRC spectrometer (Bruker, Germany). IR spectra were obtained on a Magna-550 Fourier transform infrared spectrometer (Nicolet Analytical Instruments, Madison, WI).

RESULTS AND DISCUSSION

Preparation of PCL_T

It is well known PCL can be prepared by anionic technology¹⁶ and by diol with aluminum trialkoxides as the promoter.¹⁷ In this study, the active species was formed by the reaction of aluminum triisopropoxide with HTEMPO, as shown in Scheme 1; a light orange PCL_T was obtained. In the UV spectrum of PCL_T, the characteristic absorption at 430 nm among all of purified prepolymers with different molecular weights demonstrated the existence of the nitroxyl radical, which was consistent with a pioneering report.¹⁸ The TEMPO end group of the PCL_T was also detected by ESR spectroscopy, as shown in Figure 1. In benzene, three fine peaks were observed; the *g* value (the resonance

Figure 1 ESR spectrum of PCL_T.

TABLE I
PCL_T Data Obtained by the Coordination
Polymerization of CL

Prepolymer	M_n	M_w/M_n	Conversion (%) ^a
P-1	3900	1.17	42.7
P-2	5700	1.31	60.2
P-3	7300	1.31	82.5

M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Calculated by weighing the product.

positions of radical are expressed as a g value, it is a function of field strength and frequency) was 2.0064, and the hyperfine coupling constant (A) was 15.43 G, which was perfectly consistent with those of the standard 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy ($g = 2.0070$, $A = 15.88$ G).¹⁹

Table I indicates that the molecular weight of PCL_T increased with CL conversion, and in all cases, the polydispersity of the prepolymer was less than 1.35. Therefore, the coordination polymerization of CL in our system was actually a controlled process.

Polymerization of 4-VP by the initiation of PCL_T

The radical polymerization of 4-VP was performed in bulk with BPO as the initiator in the presence of PCL_T. The polymerization was carried out at 90°C first for 3 h for the decomposition of BPO, and the resulting radicals were fully trapped by PCL_T; no propagation reaction was observed in this stage. Next, the reaction temperature was increased to

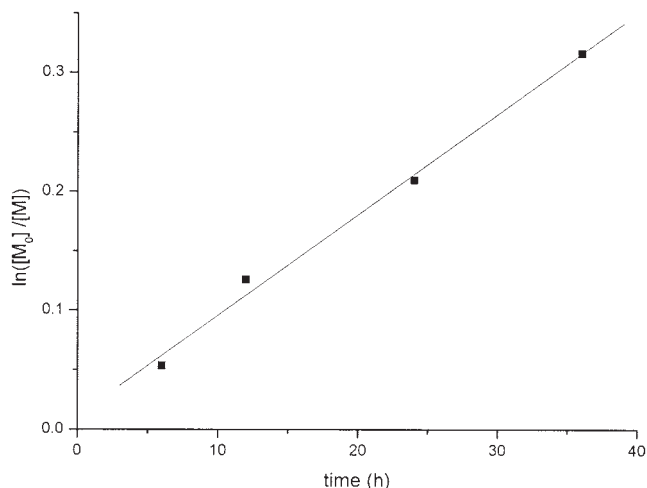


Figure 3 Relationship of molecular weight and polydispersity of the copolymers with 4-VP conversion. The polymerization conditions were as follows: [PCL_T] = 2.0×10^{-2} mol/L (P-1), [BPO]/[4-VP] = 1.3:1, and temperature = 130°C.

130°C and kept at this temperature for a required time. The relationship between the molecular weight and polydispersity of the resulting copolymers with monomer conversion is shown in Figure 2, in which the molecular weight was in proportion to the conversion. Figure 3 displays the plot of $\ln([M]_0/[M])$ versus polymerization time (where $[M]_0$ and $[M]$ stand for the original and current monomer concentrations, respectively); a perfect first-order relationship between these elements was observed. Therefore, the block copolymerization of 4-VP in the presence of PCL_T was a controlled process.

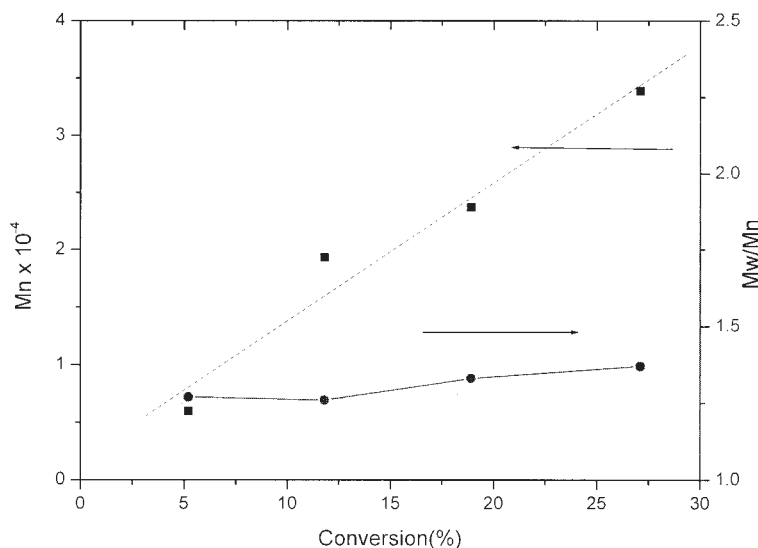


Figure 2 ¹H-NMR spectrum of the diblock copolymer recorded in CDCl₃. The polymerization conditions were as follows: [PCL_T] = 2.0×10^{-2} mol/L (P-1), [BPO]/[4-VP] = 1.3:1, and temperature = 130°C. M_n = number-average molecular weight and M_w = weight-average molecular weight.

TABLE II
Effect of PCL_T (P-2) Concentration on the Polymerization of 4-VP

[PCL _T] (× 10 ⁻² mol/L)	Time (h)	Conversion (%) ^a	M _n (×10 ⁻⁴)	M _w /M _n
1.0	12	19.7	2.78	1.38
	24	33.3	4.47	1.42
	36	47.8	7.28	1.54
2.0	12	14.4	2.40	1.35
	24	25.3	3.30	1.37
	36	37.7	5.19	1.47

Temperature = 130°C and [PCL_T]/[BPO] = 1.3:1.

^a Calculated by the gravimetric method.

To confirm the structure of the resulting copolymer, several different techniques were used. All of the purified copolymers showed unimodal gel permeation chromatography profiles with narrow molecular weight distributions, as shown in Table II. Figure 4 shows the ¹H-NMR spectrum of copolymer; the chemical shifts for all of the protons in the copolymer were found. For example, the PCL segments of the copolymer were identified by the characteristic peaks of 2.30 and 4.06 ppm due to the —CH₂COO— and —COOCH₂— protons, respectively. Those peaks at 6.38 and 8.33 ppm were assigned to the protons at the pyridine ring of P(4-VP). The IR

spectrum of the samples (Fig. 5) exhibited absorptions at 2928, 1597, and 1414 cm⁻¹, which were assigned to the 4-VP segment, and the absorption at 1730 cm⁻¹ was due to the carbonyl group of the PCL segment.

Effects of the concentration and molecular weight of PCL_T on the copolymerization

Table II shows the effect of PCL_T concentration on the polymerization of 4-VP. Generally speaking, the higher the PCL_T concentration was, the higher the concentration of TEMPO radical was in the system. So the higher concentration of TEMPO exerted better control on the polymerization of 4-VP by the reversible termination of TEMPO with a propagating radical species. In this case, the amount of dormant formed by the coupling of the propagating species with TEMPO was high, so the remaining concentration of propagating species was low, leading to decreases in the polymerization rate, the molecular weight of the P(4-VP) block, and 4-VP conversion, but copolymers with a narrow polydispersity were obtained.²⁰

The effect of PCL_T molecular weight on the copolymerization was also investigated. When the PCL_T with lower molecular weight was used, the copolymer polydispersity was narrower and the conversion was

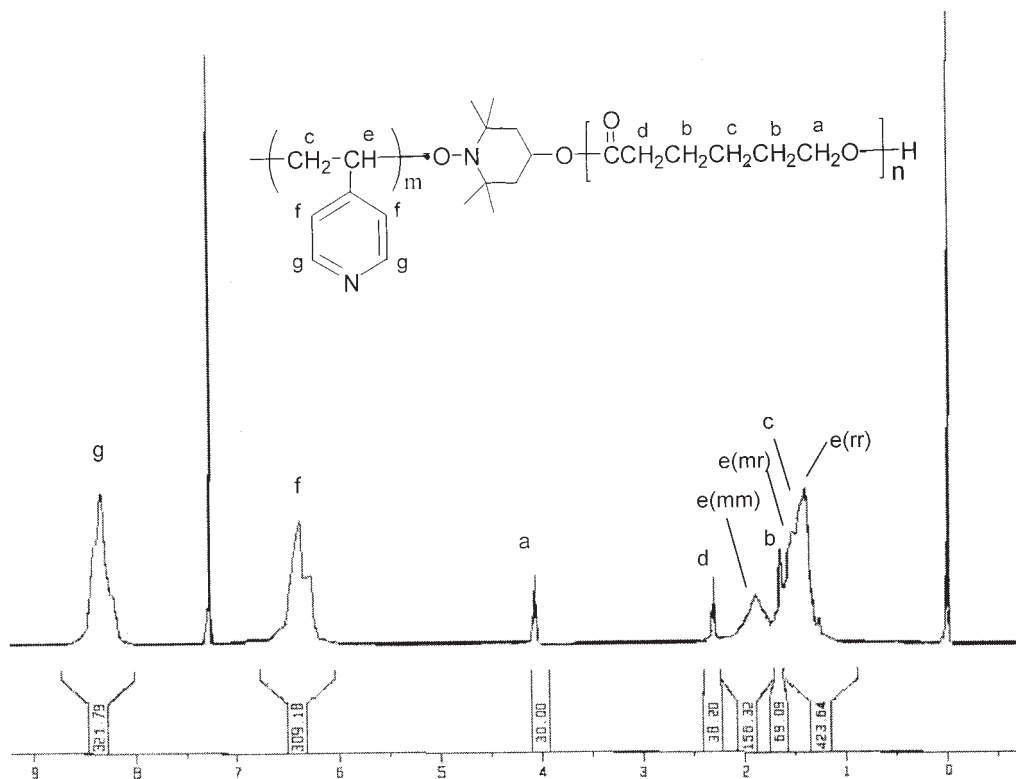


Figure 4 First-order time versus conversion plots in the radical polymerization of 4-VP. The polymerization conditions were as follows: [PCL_T] = 2.0 × 10⁻² mol/L (P-1), [BPO]/[4-VP] = 1.3:1, and temperature = 130°C.

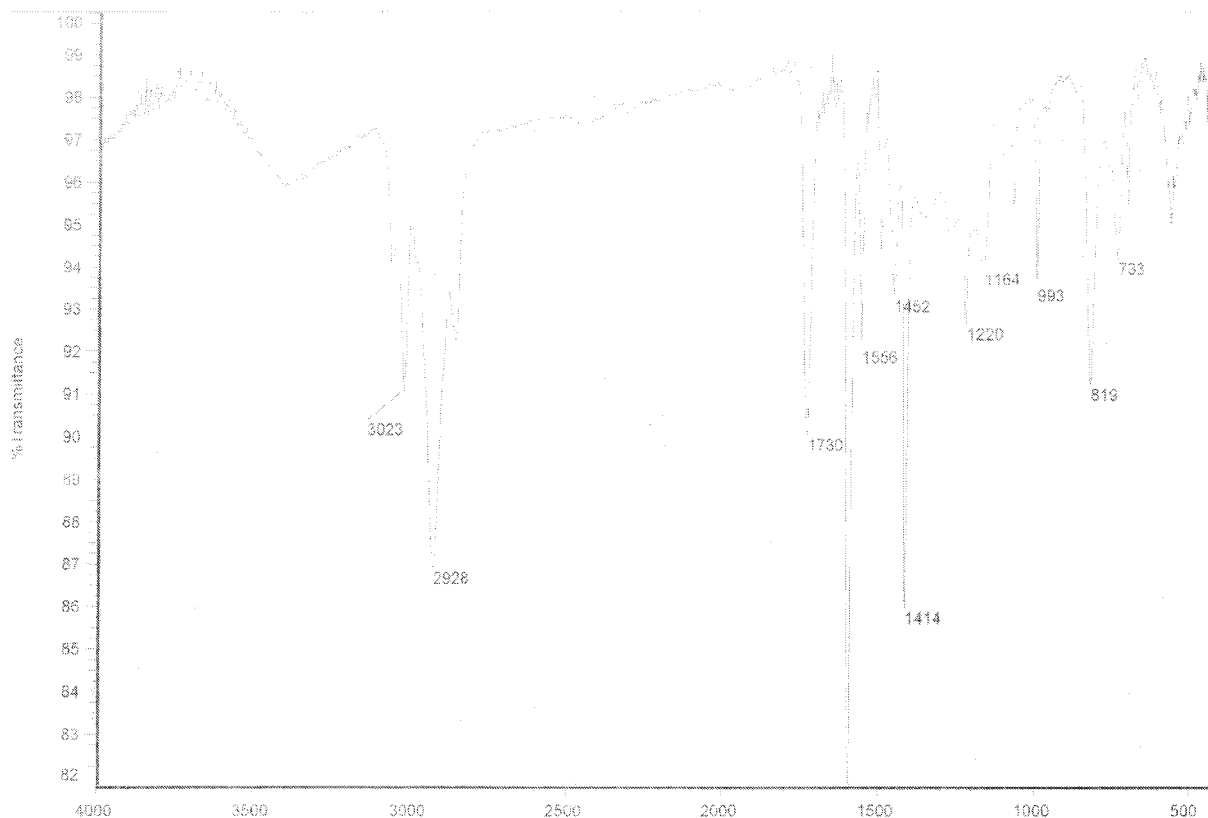


Figure 5 IR spectrum of the diblock copolymer. The polymerization conditions were as follows: $[PCL_T] = 2.0 \times 10^{-2}$ mol/L (P-1), $[BPO]/[4-VP] = 1.3:1$, and temperature = 130°C .

lower, as shown in Table III. We suggest that when the molar concentration was the same, the PCL_T with a lower molecular weight showed a relatively higher diffusion ability and a lower system viscosity, and the dormant was easy to form, so the remaining concentration of propagating species was low, leading to a low polymerization rate, low molecular weight, and low conversion.

CONCLUSIONS

A novel block copolymer, $PCL-b-P(4-VP)$, was synthesized by the polymerization of 4-VP initiated by

TABLE III
Effect of PCL_T Molecular Weight on the Polymerization of 4-VP

Prepolymer	Time (h)	Conversion (%) ^a	M_n ($\times 10^{-4}$)	M_w/M_n
P-1	12	11.8	1.93	1.26
	24	18.9	2.37	1.33
	36	27.1	3.39	1.37
P-3	12	15.7	2.64	1.32
	24	28.9	3.94	1.44
	36	44.2	7.45	1.58

Temperature = 130°C , $[BPO]/[4-VP] = 1.3:1$, and $[PCL_T] = 2.0 \times 10^{-2}$ mol/L.

^a Calculated by the gravimetric method.

the macroinitiator PCL_T . We confirmed that the TEMPO moiety of PCL was intact in the polymerization and that the copolymers were obtained by controlled radical polymerization. The molecular weight and concentration of PCL_T affected the copolymerization.

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