Ring-Opening Polymerization of ε-Caprolactone Initiated by Cyclopentadienyl Sodium

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ABSTRACT: Polymerization of ε-caprolactone had been investigated with cyclopentadienyl sodium as an initiator. The effects of reaction time, temperature, and concentration of the initiator on the yield and molecular weight of the polymer were discussed. It was shown that the high molecular weight of poly(ε-caprolactone) (13×10^4) was obtained with cyclopentadienyl sodium initiator, and the mechanism of polymerization was also discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1273–1276, 1998

Key words: ε-caprolactone; ring-opening polymerization; cyclopentadienyl sodium

INTRODUCTION

Polymerization of lactones is one of the most extensively studied types of ring-opening polymerization.[1,2] The ring-opening polymerization of ε-caprolactone (CL) has been of particular interest because of the biodegradability and permeability of poly(ε-CL) (PCL) for the potential use in drug delivery systems.[3] In general, polymerization of CL should be conducted in the presence of some initiators to get fast reaction and high molecular weight. Tin salts, such as tin(II)octoate or $SnCl_4$,[3–10] are the most widely used initiators for the polymerization of CL and other lactones. However, PCL free of heavy metal ions is preferable when it is used in medical and pharmaceutical applications. Therefore, there is a need to replace the tin-based initiators by using less poisonous ones.

Anionic polymerization of CL was studied by using alkoxide, alkyl lithium, and other organoalkali initiators.[11–20] But, during polymerization, the side reaction—such as chain transfer[21]—caused the reduction of the molecular weight of PCL. So, it was difficult to obtain high molecular weight of the polymer by present anionic polymerization mechanism. Based on the problems previously described, it is proposed to substitute heavy metal tin with a nontoxic counterpart (e.g., sodium) that should give a reasonable molecular weight. This article describes the anionic polymerization of CL initiated by cyclopentadienyl sodium (CpNa) and the characterization of resulting polymers.

EXPERIMENTAL

Materials

ε-CL from Aldrich Chemical Co. (Milwaukee, WI) was dried over calcium hydride and distilled under vacuum before use. Cyclopentadiene was prepared from dicyclopentadiene (purchased from Aldrich Chemical Co.) by heating and distilling at 180°C.

Toluene, benzene, and tetrahydrofuran (THF) was dried by refluxing over metal sodium and distilled under nitrogen atmosphere.

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Table I Solvent Effects on the Polymerization of CL

No.	Solvent	Yield (%)	$\bar{M}_v \times 10^{-4}$
1[a]	Toluene	98	11.6
2[a]	Benzene	96	10.7
3[a]	THF	Oligomer	—
4[b]	—	93	12.1

[a] 20°C, CL/initiator = 250 (molar ratio), 1 h, concentration of CL = 10% (w/w).
[b] In bulk (10 min).

CpNa was prepared by adding the freshly prepared cyclopentadiene to a dispersion of sodium in dried THF.

Polymerization

ε-CL polymerization was conducted by stirring in a flask previously flamed and purged with nitrogen CL, solvent, and initiator were added through a rubber septum with a syringe. When polymerization was completed, the reaction product was dissolved in $CHCl_3$, precipitated from a large amount of methanol, and dried at 40°C under a vacuum for 24 h.

Characterization

^{1}H-NMR spectrum were recorded on a Varian FT 80A NMR nuclear magnetic resonance (NMR) spectrometer at room temperature in $CDCl_3$, with trimethylsilane as the internal standard. Infrared (IR) spectra were recorded on a NICOLET MX-1 IR spectrometer, and the samples were prepared by casting from acetone solution onto KBr plates. Viscosity was measured with a ubbelohde viscometer at 25°C in THF. Molecular weight was calculated by the following equation[22,23]:

$$[\eta] = 1.09 \times 10^{-3} Mv^{0.6} \text{ (g dL}^{-1}\text{)}.$$

Table II Effects of CL/Initiator Molar Ratio on the Polymerization of CL[a]

No.	CL/Initiator (Molar Ratio)	Yield (%)	$\bar{M}_v \times 10^{-4}$
1	125	80	8.1
2	250	98	11.6
3	500	59	13.9
4	750	45	13.4
5	1000	38	12.3

[a] Conditions: 20°C, 1 h, toluene as the solvent, concentration of CL = 10% (w/w).

Table III Effects of Temperature on the Polymerization of CL[a]

No.	Temperature (°C)	Yield (%)	$\bar{M}_v \times 10^{-4}$
P_1	0	50	5.2
P_2	10	84	9.4
P_3	15	94	10.8
P_4	20	98	11.6
P_5	30	96	11.1
P_6	40	92	10.1

[a] Conditions: CL/initiator = 250 (molar ratio), 1 h, toluene as the solvent, concentration of CL = 10% (w/w).

RESULTS AND DISCUSSION

Polymerization of ε-CL initiated by CpNa could be conducted either in bulk or in solution (as recorded in Table I). The reaction was found to be conducted easily and controllably. It can be seen from Table I that, PCL with relatively low molecular weight, was obtained when polymerizations were conducted in polar solvents (e.g., THF). However, high molecular weight PCL could be obtained in nonpolar solvents (e.g., toluene benzene). It also can be seen from Table I that it took a relatively short time for polymerization of CL in bulk in comparison with solution polymerization. This indicated that the high concentration of CL increased the reaction velocity. In this article, polymerization of CL in toluene solution will be discussed.

Table IV Effects of Reaction Time on the Polymerization of CL[a]

No.	Reaction Time (min)	Yield (%)	$\bar{M}_v \times 10^{-4}$
Q_1	15	84	7.9
Q_2	30	96	9.2
Q_3	60	98	11.6
Q_4	120	92	13.1
Q_5	180	84	12.9
Q_6	240	76	11.4

[a] Conditions: CL/initiator = 250 (molar ratio), 20°C, toluene as the solvent, concentration of CL = 10% (w/w).

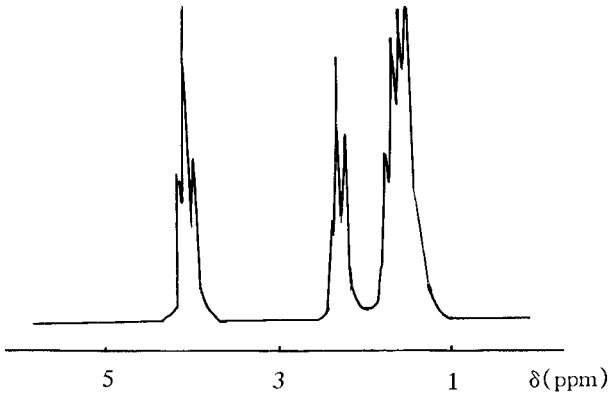


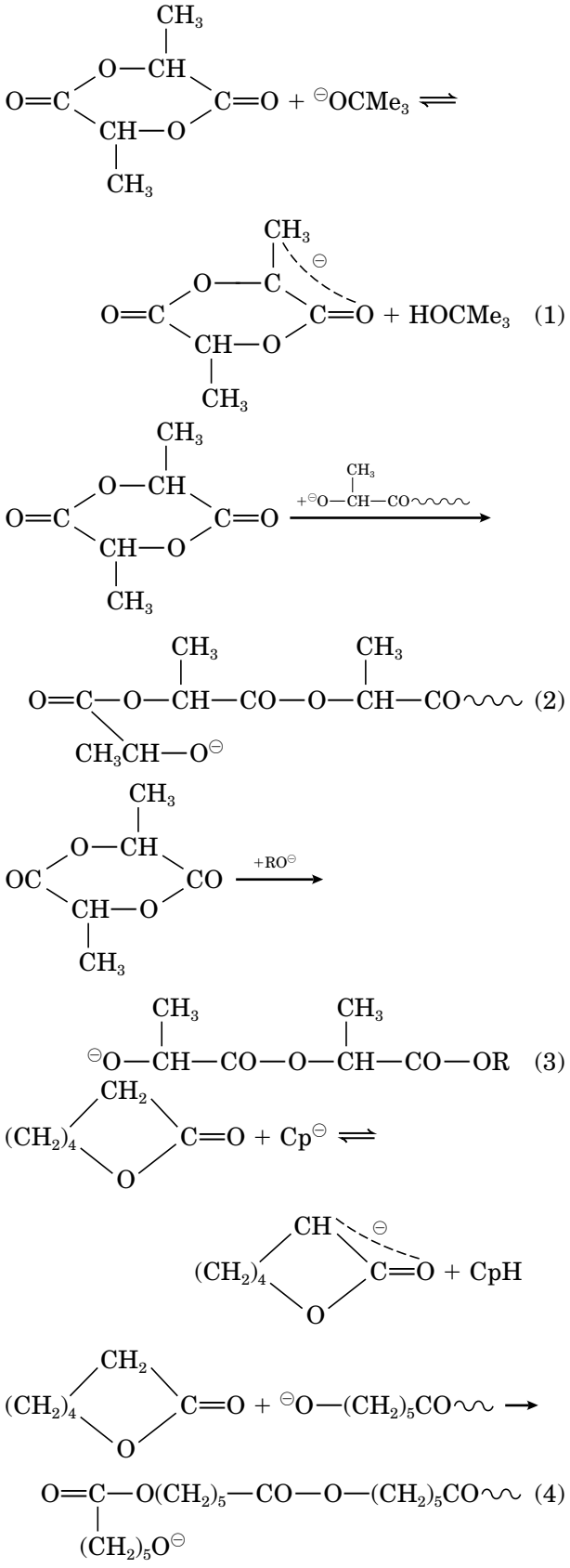
Figure 1 80 MHz ^{1}H-NMR spectrum of PCL.

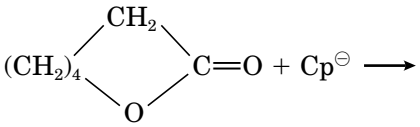
Table II shows the results of CL polymerization with different CL/initiator molar ratios. It showed that a high yield of PCL was obtained at a low CL/initiator molar ratio. But the molecular weight decreased owing to increasing number of active species. High molecular weight PCL can be obtained at a high CL/initiator ratio.

Table III summarizes the results of the polymerization of CL at different temperatures. Data show that the yield and molecular weight of PCL increased with the increase of reaction temperature within the range of 0°C ~ 20°C. But, when the temperature was above 20°C, the yield and molecular weight of PCL got slight reductions. Thus, the maximum yield and molecular weight of PCL were obtained at 20°C.

We can see from Table IV that the yield and molecular weight of PCL reached a maximum after 1 h; after further reaction, the yield and molecular weight of PCL dropped due to the possible side reaction occurring. It was demonstrated by Gross and colleagues[24] and Kricheldorf and Boettcher[25] that *t*-BuOk and *n*-butyl-Li can initiate anionic polymerization of lactide in toluene. They found that the polymerization of lactide reacted by the deprotonation of monomers [eqs. (1) and (2)] and by the direct nucleophilic attack of monomer onto a carbonyl group [eq. (3)]. Similar to that, we suggested that polymerization of CL initiated with CpNa be as described.

Polymerization of CL with CpNa possibly caused the following equilibriums [eqs. (4) and (5)]:





$$^{\ominus}O—[CH_2]_5—CO—O—[CH_2]_5—COCp \quad (5)$$

To study the true equilibrium of polymerization, we characterized the structure of PCL with IR and ^{1}H-NMR. The IR spectrum of PCL showed that the absorption bands at 1756 cm^{-1}, 2946 cm^{-1}, and 1173 cm^{-1}, are due to —C═O, C—H of —CH_2 and C—O stretch, respectively. The absorption band at 3510 cm^{-1} is assigned to terminal hydroxy groups. This is in accordance with ref. 26. From the IR spectrum of PCL, no cyclopentadienyl end groups were found. The ^{1}H-NMR spectrum of PCL (Fig. 1) shows the peaks at —$(CH_2)_4$—, —CO—CH_2—, and —OCH_2— methylene protons, respectively. The ^{1}H-NMR spectrum of PCL with CpNa is in accordance with ref. 27. Also, no cyclopentadienyl end groups were found from the ^{1}H-NMR spectrum of PCL. It indicated that ring-opening polymerization of CL initiated by CpNa was mainly through the deprotonation of the monomer Eq. (4) and not quite through direct nucleophilic attack onto a carbonyl group of monomers. The single active center produced during polymerization is the effective starting point from which high molecular weight PCL was obtained. However, in other anionic polymerization, both ways of chain propagations coexist.[25]

In conclusion, CpNa is an effective initiator for the polymerization of CL, and the initiator is nontoxic and convenient to prepare. High molecular weight PCL (10×10^4) can be obtained by using CpNa as an initiator.

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