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Homopolymerization of ε-caprolactone Initiated by a Scandium Aryloxide

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Summary

Ring-opening polymerization of ε-caprolactone (CL) has been firstly achieved by a novel rare earth initiator of scandium tris(2,6-di-*tert*-butyl-4-methylphenolate), producing PCL with M_v of 75,700 in solution polymerization under mild conditions. Kinetics study indicates that the apparent activation energy is 58.0 kJ/mol. Mechanism study reveals that the monomer ring is opened via acyl-oxygen bond cleavage leading to a Sc-O active center.

Introduction

Ring-opening polymerization of lactone produces hydrolytically and biologically degradable aliphatic polymers, for which an intensive interest in exploring new and high active catalysts is paid. Catalysts for lactone polymerization are traditionally based on Sn, Al, Zn and lanthanide compounds[1~6]. Comparatively, the catalytic activities of scandium compound in polymerization have been seldom reported. Only $Sc(OTf)_3$ has been reported as catalyst for the ring-opening polymerization of lactide and lactone (ε-caprolactone and δ-valerolactone) in the presence of alcohol or H_2O[7-9]. We firstly found that scandium tris(2,6-di-*tert*-butyl-4-methylphenolate) ($Sc(OAr)_3$) is an effective single-component initiator for the CL polymerization. Characteristics of the CL polymerization initiated by $Sc(OAr)_3$ is reported in the paper.

Experimental

CL (Acros product, 99 %) was distilled under reduced pressure. $Sc(OAr)_3$ was prepared according to the literature[10]. Other chemicals were purified with standard methods. All polymerizations were carried out in 20 mL ampoules with Schlenk technique under inert atmosphere. The initiator was dissolved in toluene and introduced into monomer solution by a syringe. The polymerization was terminated by ethanol with 5 % HCl and the polymer was dried in vacuum to a constant weight.

The intrinsic viscosity of poly(ε-caprolactone) (PCL) was measured with Ubbelohde viscometer in DMF at 30.0 °C. The viscosity molecular weight of PCL was calculated according to Equation (1)[11].

$$[\eta](\mathrm{dL/g}) = 1.94\times10^{-4} M_v^{0.73} \quad (1)$$

GPC measurements based on commercial polystyrene standards were performed on a Waters 208 apparatus with Waters 2410 RI detector in THF (1.5 mL/min) at 30 °C. In order to compare with theoretic molecular weights, universal molecular weight calibration for PCL was calculated by

multiplying 0.45 on M_n (GPC) values[12]. ^1H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard.

Results and discussion

We have found for the first time that $Sc(OAr)_3$ alone is active for the ring-opening polymerization of CL. The polymerization of CL in toluene is effected by time and temperature. Raising temperature accelerates the reactions: to reach 60 % conversion needs more than 16 h polymerization at 0 °C, while at 20 °C or 40 °C or 60 °C needs 3 h or 40 min or 8 min respectively under the condition: $[CL]_0$=0.6 mol/L, $[CL]_0/[Sc(OAr)_3]$=500 ($[CL]_0$ is the initiatory concentration of CL and $[CL]_t$ is the concentration of CL during the reaction). Figure 1 reveals the steady polymerization at 0 °C. M_v of PCL increases with the conversion at the first 8 h, and then keeps almost constant suggesting the existing of transesterification.

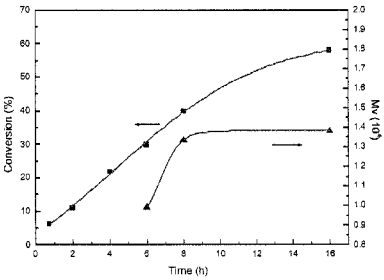

Figure 1. Effect of time on CL polymerization. Conditions: $[CL]_0$=0.6 mol/L, $[CL]_0/[Sc(OAr)_3]$=500, 0 °C, toluene.

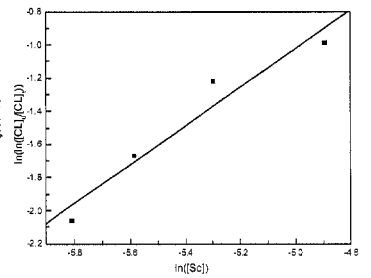

Figure 2. Kinetics study on CL polymerization at various $[Sc(OAr)_3]$. Conditions: $[CL]_0$=3.0 mol/L, 1 h, 0 °C, toluene. Correlative factors: 0.970, Slope: 1.17.

Table 1. Effect of $[CL]_0$ on CL polymerization.

$[CL]_0$ (mol/L)	Conv. (%)	$M_v \times 10^{-4}$
0.2	72.7	4.61
0.4	80.0	4.72
0.8	89.8	5.65
1.5	93.0	3.31
2.0	88.2	2.70

Conditions: $[CL]_0/[Sc(OAr)_3]$=500, 40 °C, 1.5 h, toluene.

Table 2. Effect of $[CL]_0/[Sc(OAr)_3]$ on CL polymerization.

$[CL]_0/[Sc(OAr)_3]$	Conv.(%)	$M_v \times 10^{-4}$
50	70.0	-
200	70.0	3.62
400	84.5	4.13
800	84.1	5.02
1000	78.9	7.57

Conditions: $[CL]_0$ =0.6 mol/L, 40 °C, 1.5 h, toluene.

Table 1 and Table 2 illustrate the influences of the monomer concentration ($[CL]_0$) and different molar ratio of $[CL]_0/[Sc(OAr)_3]$ on both conversion and molecular weight for 1.5 h polymerization at 40 °C. However, it is reasonable that higher molecular weight of PCL (75,700) was obtained with small amount of initiator. Figure 2 shows the influence of initiator concentration on the ring-opening polymerization at 0 °C. The slope is close to 1. The data indicate the CL polymerization obeys first

order reaction kinetics with initiator concentrations. Further more, according to Figure 3, it is seen clearly that the polymerization also belongs to first order reaction kinetics with monomer concentrations. Thus, the ring-opening polymerization reaction equation can be written as follows (Equation (2)):

$$-\frac{d[CL]}{dt} = k \cdot [Sc(OAr)_3] \cdot [CL] \quad (2)$$

The apparent rate constants (k) at 0 °C, 20 °C, 40 °C and 60 °C are calculated to be 0.796, 3.63, 22.2 and 70.5 $L \cdot mol^{-1} \cdot min^{-1}$ respectively. According to the Arrhenius equation (Equation (3)), it is found that the polymerization activation energy (ΔE_a) is 58.0 kJ/mol (Figure 4).

$$\ln k = \ln A - \frac{\Delta E_a}{RT} \quad (3)$$

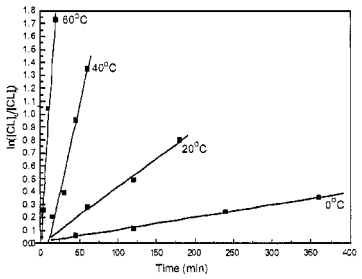

Figure 3. Kinetics study on CL polymerization at different temperatures. Conditions: $[CL]_0$=0.6 mol/L, $[CL]_0/[Sc(OAr)_3]$=500, toluene. Correlative factors: 0.997 (10 °C), 0.994 (20 °C), 0.984 (40 °C), 0.984 (60 °C).

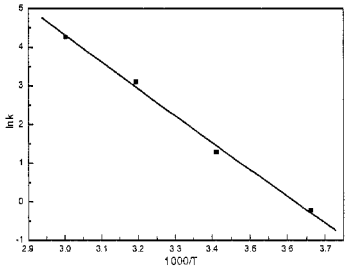

Figure 4. lnk versus 1000/T plot. Correlative factor: 0.998.

Table 3 summarizes the molecular weights and molecular weight distributions of PCL obtained at various conditions. In low conversions, theoretic molecular weights calculated from Equation (4) are close to the calibrated GPC values (M_n) indicating that every scandium metal initiated one polymer chain. At moderate convsersions (≥ 50%), the MWD broadened and the calibrated GPC values (M_n) are far less than the theoretic molecular weights, which shows that the cyclization occurred in the later stage of polymerization and led to broader molecular weight distributions of PCL.

$$M_n = 114 \times Conversion \times \frac{[CL]}{[Sc(OAr)_3]} \quad (4)$$

Table 3. Molecular weights and molecular weight distributions of PCL

Temp (°C)	Time	Conv. (%)	$M_n^a \times 10^{-4}$	$M_n^b \times 10^{-4}$	MWD
0	2 h	10.9	0.62	0.93	1.83
0	16 h	58.0	3.30	0.50	2.34
20	1 h	24.5	1.40	1.27	1.78
20	6 h	89.1	5.08	2.29	2.15
40	15 min	18.6	1.06	0.91	1.72
40	2 h	87.1	4.96	2.72	1.94
60	4 min	21.8	1.24	1.08	1.74
60	20 min	80.5	4.59	1.04	2.11

Conditions: $[CL]_0$=0.6 mol/L, $[CL]_0/[Sc(OAr)_3]$=500, toluene.

[a] Theoretic molecular weights.

[b] Calibrated GPC values.

Table 4. Effect of solvent on CL polymerization.

Solvent	Time (h)	Conv. (%)	$M_v \times 10^{-4}$
Toluene	3	88.6	2.40
Dichloromethane	5	46.1	3.05
Tetrahydrofuran	5	33.6	1.42
Nitrobenzene	24	-	-

Conditions: $[CL]_0$=0.6 mol/L, $[CL]_0/[Sc(OAr)_3]$=500, 40 °C.

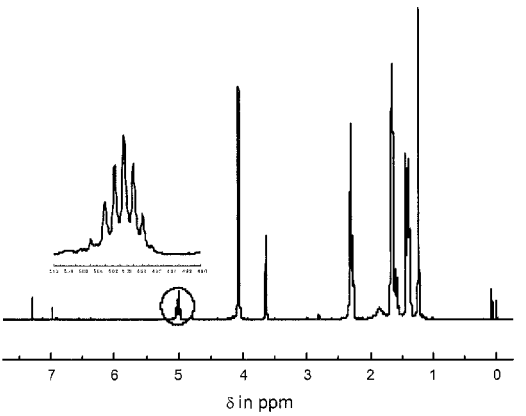

Figure 5. ^{1}H NMR spectrum of PCL with the end unit of isopropyl, initiated by $Sc(OAr)_3$.

Compared with toluene, the polar solvents such as tetrahydrofuran and dichloromethane are no good to the ring-opening polymerization of CL (Table 4). The conversions of CL reached 33.6 % after 5 h in tetrahydrofuran and 46.1 % after 5 h in dichloromethane. As to stronger polar solvent such as nitrobenzene, there was no reaction occurred even after 24 h under the same conditions. These facts suggest that the polymerization proceeds via a coordination mechanism rather than an ionic mechanism. For further investigation of ring-opening mode, a PCL sample of low molecular weight terminated by isopropanol had been prepared and characterized by ^{1}H NMR (Figure 5), in which a doublet peak at 1.23 ppm, a septette peak at 5.00 ppm assigned to isopropyl group bonded with acyl-end, i.e. -COOC**H**$(CH_3)_2$ structure, and a triplet peak at 3.82 ppm assigned to –CH_2OH structure in the other chain end appeared. No signals at 3.3~3.7 ppm for –$CH_2OCH(CH_3)_2$ structure distinguished from the alkyl-oxygen bond cleavage. Therefore, the monomer is believed to insert into living chain via the break of acyl-oxygen bond. As a conclusion, $Sc(OAr)_3$ initiating CL polymerization performs an acyl-oxygen bond cleavage anionic coordination mechanism going along with the same pathway as $Ln(OAr)_3$ initiators[4].

Acknowledgements

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