

Ring-Opening Copolymerization of Trimethylene Carbonate and D,L-Lactide by Rare Earth Chloride

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ABSTRACT: Bulk copolymerization of trimethylene carbonate (TMC) and D,L-lactide (D,L-LA) was conducted at 80°C using rare earth chloride as catalyst. The copolymerization reaction showed an induction period. The effects of reaction time and temperature were examined. The polymerization activity of various rare earth chlorides was in the order: LaCl₃ > YCl₃, PrCl₃ > NdCl₃ >> DyCl₃. The copolymer was characterized by ¹H NMR. The reactivity ratios of TMC and D,L-LA were determined by the Fineman-Ross and Kelen-Tüdös methods.

KEY WORDS Ring-Opening Copolymerization / Trimethylene Carbonate / D,L-Lactide / Rare Earth Chloride /

Biodegradable materials are of great interest due to their versatile applications. Intensive research is being conducted in this field. Now the main target is to prepare biodegradable polymers with specified properties. Copolymerization can attain such an object and provide new materials.

Poly(lactide (PLA) is an important biodegradable material. In order to control its biodegradation rate and mechanical properties, D,L-lactide (D,L-LA) and L-lactide (L-LA) have been copolymerized with other monomers such as ε-caprolactone (CL), ethylene oxide,^{1,2} etc. The six member cyclic aliphatic carbonate is a relatively new biodegradable monomer.³ Copolymerization of D,L-LA and trimethylene carbonate (TMC) is expected to lead to new biodegradable material.

Our group has successfully developed the rare earth catalysts for the polymerization and copolymerization of a series of cyclic monomers, including epoxides, alkylene sulfides, lactones, etc.⁴⁻⁶ Recently, we found that the rare earth halides are good catalysts for polymerization of CL, TMC and copolymerization of CL and TMC.⁷⁻⁹ This article reports the copolymerization of D,L-LA and TMC in bulk using rare earth chloride as catalyst. The structure of the copolymer was characterized by GPC and NMR and the reactivity ratios of TMC and D,L-LA were determined.

EXPERIMENTAL

Materials

TMC was synthesized according to ref 10, then recrystallized from dried ethyl ether for three times. D,L-LA was prepared from D,L-lactic acid as described in ref 11 and recrystallized three times from dried ethyl acetate.

Rare earth chlorides: lanthanum chloride (LaCl₃), yttrium chloride (YCl₃), praseodymium chloride (PrCl₃),

neodymium chloride (NdCl₃), and dysprosium chloride (DyCl₃) were prepared from their oxides.¹² A γ-butyrolactone solution of rare earth chloride (0.15 M) was used as the polymerization catalyst.

Methylene chloride and methanol were of chemical grade and used as received. γ-Butyrolactone was refluxed over calcium hydride and distilled under reduced pressure.

Polymerization

All copolymerizations were carried out under dry nitrogen. Afterwards, the resulting copolymers were dissolved in methylene chloride and precipitated by methanol containing 5% HCl and washed with methanol several times, and then dried at 40°C *in vacuo* for 24 h.

Measurements

¹H and ¹³C NMR spectra were obtained on a Bruker400 spectrometer in CDCl₃ at room temperature with tetramethylsilane (TMS) as internal reference.

The molecular weight (MW) and molecular weight distribution (MWD) of the copolymer were determined by a Waters 150c GPC at 25°C and calibrated with polystyrene standards. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 ml min⁻¹.

Intrinsic viscosity of copolymer was determined in methylene chloride at 25°C by an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Characteristics of Copolymerization

Rare earth halides polymerize TMC at a temperature slightly higher than the melting point, which is about 50°C.⁷ However, D,L-LA can not polymerize in bulk or in solution under 80°C by rare earth chloride. A mixture of TMC and D,L-LA melts at 80°C. Therefore, the copolymerization was generally carried out at 80°C.

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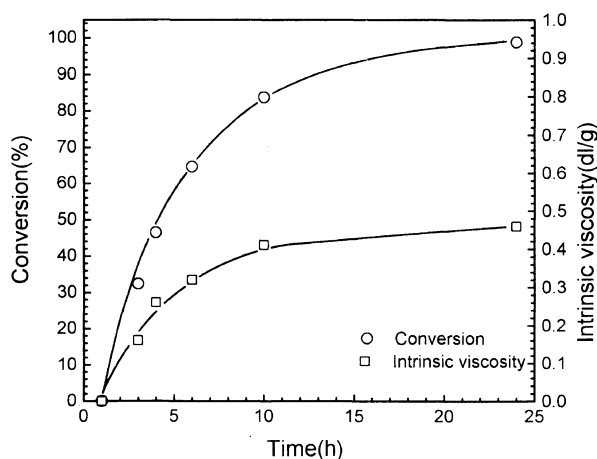


Figure 1. Conversion and intrinsic viscosity of a copolymer as a function of copolymerization time. Temperature, 80°C; catalyst, lanthanum chloride; $[M]/[C]=500$; TMC/D,L-LA = 50/50 (molar ratio in feed).

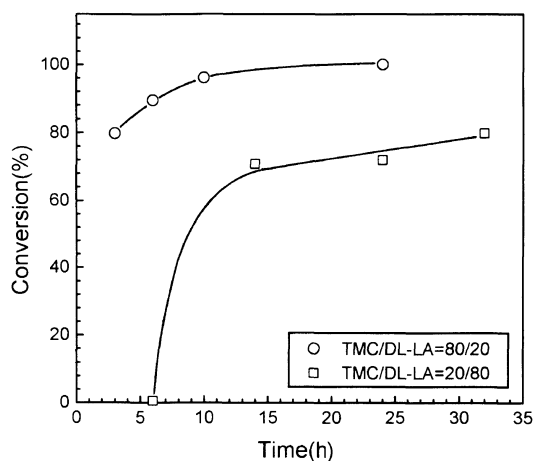


Figure 2. Conversion of a copolymer as a function of copolymerization time. Effects of various comonomer ratios. Polymerization conditions as Figure 1.

The copolymerization characteristics was shown in Figures 1 and 2. Figure 1 depicts the conversion and intrinsic viscosity of the copolymer as a function of polymerization time. From the data, it can be seen that both conversion and intrinsic viscosity of the copolymer increase with the elongation of polymerization time and there is an induction period of the polymerization, which decreases with increasing TMC in the feed (Figure 2).

Temperature affects polymerization. As indicated in Table I, the higher the temperature, the faster the copolymerization rate. A mixture of TMC and D,L-LA only partially melts at 60°C, and this may be the reason for a low conversion. At 150°C with a long polymerization duration (8 h), the conversion and MW of copolymer were dropped, possibly due to transesterification inducing degradation of macromolecular chain and formation of oligomer,¹⁵ which is proved by GPC in Figure 3. When the copolymerization took place at 120°C, the conversion attained 94% and copolymer with MW 2.75×10^4 and MWD 1.52 was prepared (Table I, No. 4).

The catalytic activity of various rare earth chlorides for copolymerization followed the order: $\text{LaCl}_3 > \text{YCl}_3$,

Table I. Effects of temperature on copolymerization of TMC and D,L-LA

No.	1	2	3	4	5	6
$T/^\circ\text{C}$	60	80	100	120	120	150
t/h	10	10	10	1	8	8
Conv/%	2	84	94	94	90	85
$[\eta]^a$	—	0.41	0.44	0.44	0.41	0.29
MW ^b ($\times 10^3$)	—	26.8	—	27.5	28.6	12.3
MWD ^c	—	1.49	—	1.52	1.50	1.44

Catalyst, LaCl_3 ; $[M]/[C]=500$; TMC/D,L-LA = 50:50 (molar ratio in feed). ^aIntrinsic viscosity at 25°C in CH_2Cl_2 . ^bWeight average MW, GPC data at 25°C in THF. ^cGPC data at 25°C in THF.

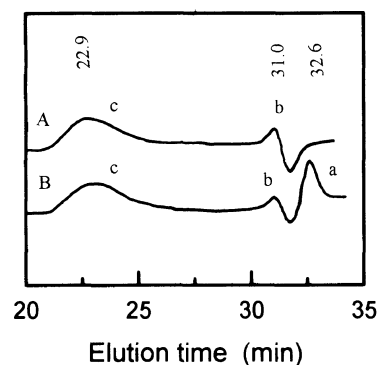


Figure 3. GPC curves of (A) reaction sample of TMC and D,L-LA after 8 h at 150°C, (B) (A) plus comonomer mixture of 50:50 (molar ratio) TMC and D,L-LA. a, peak of monomer; b, peak of oligomer; c, peak of polymer.

Table II. Comparison of various rare earth compounds on polymerization activity

No.	1	2	3	4	5
Catalysts	YCl_3	LaCl_3	PrCl_3	NdCl_3	DyCl_3
Conv/%	70	84	69	52	2

Conditions, 80°C; $[M]/[C]=500$; TMC/D,L-LA = 50:50 (molar ratio in feed), 10 h.

$\text{PrCl}_3 > \text{NdCl}_3 \gg \text{DyCl}_3$ as shown in Table II. LaCl_3 , showing the highest activity, is a good catalyst, because it is cheap, stable and easy to prepare. DyCl_3 is much less active than others. The composition of the copolymers prepared by the above rare earth chlorides was the same as that produced by lanthanum chloride.

NMR of Copolymer

^1H NMR spectra of the resulting copolymer, which justifies the structure of TMC and D,L-LA copolymer, are shown in Figures 4 and 5.

Reactivity Ratios of Comonomers

The Fineman–Ross and Kelen–Tüdös methods,^{13,14} both based on the Mayo–Lewis equation, were used to determine the reactivity ratios r_1 and r_2 . Copolymerization was carried out with LaCl_3 at 80°C in bulk. The composition of the copolymer was determined from ^1H NMR spectra using distinct peaks of $\delta = 5.04$ (PLA) and $\delta = 4.21$ (poly(trimethylene)carbonate) (PTMC).

The data by Fineman–Ross method (eq 1) are shown in Table III. The reactivity ratios of r_1 (TMC) and r_2

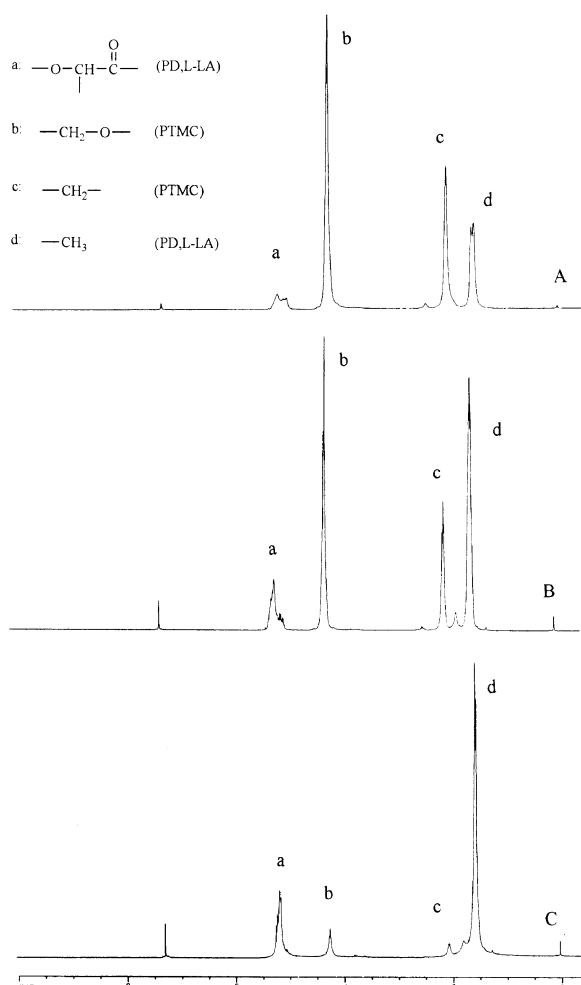


Figure 4. ^1H NMR of poly(TMC-co-D,L-LA). A, TMC/D,L-LA = 80/20 (molar ratio in feed); B, TMC/D,L-LA = 50/50 (molar ratio in feed); C, TMC/D,L-LA = 20/80 (molar ratio in feed).

Table III. Determination of r_1 and r_2

No.	1	2	3	4	5
x^a	4.302	3.116	1.587	0.960	0.644
y^b	0.389	0.260	0.131	0.0705	0.0425
G	-6.757	-8.869	-10.528	-12.657	-14.509
F	47.576	37.344	19.226	13.072	9.758
η	-0.0978	-0.151	-0.258	-0.366	-0.463
ζ	0.688	0.634	0.472	0.378	0.312

Catalyst, LaCl_3 ; temperature, 80°C ; $\alpha = 21.546$. ^a Molar ratio in the feed. ^b Molar ratio of monomer units in the copolymer, NMR data. Refer to text for the codes of G , F , η , and ζ .

(D,L-LA) were 0.19 and 15.4, respectively with a correlation coefficient of 0.962.

$$G = r_1 \cdot F - r_2 \quad (1)$$

where

$$G = \frac{x(y-1)}{y} \quad F = \frac{x^2}{y} \quad x = \frac{m_1}{m_2} \quad y = \frac{dm_1}{dm_2}$$

m_1 : mole fraction of TMC in feed
 m_2 : mole fraction of D,L-LA in feed
 dm_1 : mole fraction of TMC in polymer
 dm_2 : mole fraction of D,L-LA in polymer
 r_1 : reactivity ratio of TMC
 r_2 : reactivity ratio of D,L-LA

Kelen-Tüdös method (eq 2) was used for comparison. The same r_1 (0.19) and r_2 (15.5) were obtained (Table III). The correlation coefficient was 0.989 by this method.

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \zeta - \frac{r_2}{\alpha} \quad (2)$$

where

$$\eta = \frac{G}{\alpha + F} \quad \zeta = \frac{F}{\alpha + F} \quad \alpha = \sqrt{F_{\min} F_{\max}}$$

D,L-LA is thus more active than TMC under the present conditions and block-like copolymer was prepared. The copolymerization mechanism is now under investigation.

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