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Alcohol/Methylaluminum Diphenolate Systems as Novel, Versatile Initiators for Synthesis of Narrow Molecular Weight Distribution Polyester and Polycarbonate

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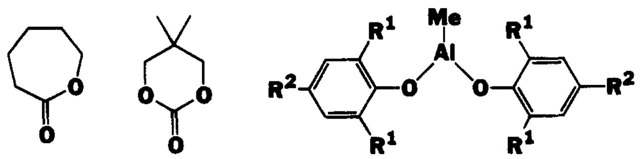
Introduction

Polyesters and polycarbonates are widely used polymer materials, and development of simple, convenient initiators for controlled ring-opening polymerization of cyclic esters and carbonates is important from practical as well as fundamental viewpoints. Although some excellent initiators have been reported for the living polymerization of these monomers,[1−3] some of them require special handling techniques such as high-vacuum conditions and all-glass apparatus and are not easy to use in a practical sense. Herein we report novel, convenient initiators composed of alcohols and methylaluminum diphenolates (**1a**−**1c**) for the living polymerization of ε-caprolactone (ε-CL) and 2,2-dimethyltrimethylene carbonate (DTC). We have recently reported that the basic concept of the Lewis acid-assisted, high-speed living polymerization of methacrylic esters[4] and epoxides[5] initiated with aluminum porphyrins is applicable to accelerate the *immortal* polymerization of epoxides in the presence of alcohol as a chain transfer agent.[6] In the course of the extension of this finding, ε-CL and DTC were found to be polymerized even in the *absence* of aluminum porphyrin initiators.

Results and Discussion

The polymerization of ε-caprolactone (ε-CL) with the methylaluminum bis(2,6-diphenylphenolate) (**1a**)−2-propanol (2-PrOH) system proceeded smoothly at room temperature (~22 °C) to give a narrow molecular weight distribution (MWD) polyester. For example, when a CH_2Cl_2 solution of **1a** was added under nitrogen to a CH_2Cl_2 solution of a mixture of 2-PrOH and ε-CL at the mole ratio $[\epsilon\text{-CL}]_0/[2\text{-PrOH}]_0/[\mathbf{1a}]_0$ of 50/1/0.3, the monomer conversion was increased to 46 and 100% in 1.0 and 2.5 h, respectively (run 1, Table 1). The final polymer, isolated by pouring the polymerization mixture into MeOH (isolated yield: ~90%), had an M_w/M_n ratio of 1.19 with an M_n value (6400)[7] close to $M_{n,\text{theory}}$ (5700) calculated from the monomer-to-alcohol mole ratio. When the initial mole ratio $[\epsilon\text{-CL}]_0/[2\text{-PrOH}]_0$ was increased from 50 to 300 (runs 2−5), the M_n of the produced polymer was increased from 6400 to 32 100 ($M_{n,\text{theory}}$ = 31 800), retaining the narrow MWD (M_w/M_n = 1.10−1.19). On the other hand, in the absence of 2-PrOH, the polymerization of ε-CL with **1a** alone under otherwise identical conditions to those of run 1 did not take place.



ε-CL DTC

1a: R^1 = Ph, R^2 = H
1b: R^1 = ^{tert}Bu, R^2 = Me
1c: R^1 = H, R^2 = ^{tert}Bu

MeOH was also usable for the present system (runs 6 and 7): At the mole ratio $[\epsilon\text{-CL}]_0/[\text{MeOH}]_0$ of 500 in the presence of **1a** (0.3 equiv with respect to MeOH), the polymerization of ε-CL at room temperature proceeded to 92% conversion in 42 h, giving a polymer with M_n and M_w/M_n, respectively, of 62 600 ($M_{n,\text{theory}}$ = 52 500) and 1.14 (run 7).

When methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**1b**) (run 8) or bis(4-*tert*-butylphenolate) (**1c**) (run 9) was used in place of **1a**, the polymerization of ε-CL also took place but gave a polymer with a slightly broader MWD (M_w/M_n > 1.2) than that with **1a**. On the other hand, an attempted polymerization by using Me_3Al[8] in place of **1** (run 10) resulted in the formation of a broad MWD polyester (M_w/M_n = 1.35).

The ROH/**1** systems were also applicable to the polymerization of 2,2-dimethyltrimethylene carbonate (DTC) (runs 11 and 12). For example, when **1b** (0.3 equiv with respect to ROH) was added at room temperature to a CH_2Cl_2 solution of a mixture of DTC and 2-PrOH ($[\text{DTC}]_0/[2\text{-PrOH}]_0$ = 50/1), the polymerization of DTC started and was complete within 2.5 h, affording a polycarbonate with M_n and M_w/M_n, respectively, of 6200[7] ($M_{n,\text{theory}}$ = 6500) and 1.18 (run 12). On the contrary, the epoxide 1,2-epoxypropane was not polymerized under similar conditions.[6]

The ^1H NMR spectrum of a poly(ε-CL) sample (run 1, 100% conversion) in $CDCl_3$ showed signals due to a terminal $(CH_3)_2CHO$ group of the polymer chain, while no signals characteristic of the aromatic end group originating from **1a** were detected.[9] The relative intensity of the signals due to OCH_2 in the polymer main chain to CH_3 in the terminal $(CH_3)_2CHO$ unit was 22.4, which is close to the initial mole ratio $[\epsilon\text{-CL}]_0/[2\text{-PrOH}]_0$ of 20.0. This was also the case for the poly(DTC) obtained in run 11.[10] Thus, in the polymerization of ε-CL and DTC with the ROH/**1** system, all the ROH molecules participate in the initiation step and are incorporated into the polymer terminal.

By use of this convenient initiating system, we attempted the synthesis of a narrow MWD block copolymer from ε-CL and DTC. Thus, the first-stage polymerization was started from ε-CL by adding **1a** at room temperature to a mixture of ε-CL (50 mmol) and 2-PrOH ($[\epsilon\text{-CL}]_0/[2\text{-PrOH}]_0/[\mathbf{1a}]_0$ = 50/1/0.3, 100% conversion [2.5 h], M_n = 6400 [M_w/M_n = 1.19], Figure 1 (**I**)). Then a CH_2Cl_2 solution (10.4 mL) of DTC (130 equiv with respect to 2-PrOH) was added to this flask, whereupon the second-stage polymerization of DTC took place to give at 88% conversion (32 h) a polymer with M_n and M_w/M_n, respectively, of 20 000 and 1.17 (Figure 1 (**II**)). The absence of the ε-CL prepolymer in the final product, as observed by GPC, demonstrates the successful formation of a polyester−polycarbonate block copolymer. In this case, an attempted two-stage polymerization of these monomers in the reverse order (DTC [first stage: $[\text{DTC}]_0/[2\text{-PrOH}]_0/[\mathbf{1b}]_0$ = 50/1/0.3, 100% conversion in 2.5 h, M_n = 6200, M_w/M_n = 1.19] → ε-CL [50 equiv with respect to 2-PrOH]) was also

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Table 1. Polymerization of ϵ-CL and DTC Initiated with the Alcohol (ROH)/Methylaluminum Diphenolate (1) (1/0.3) Systems[a]

run	monomer	ROH	1	$[\text{monomer}]_0/[\text{ROH}]_0$	time/h	conv/%	M_n[b]	$M_{n,\text{theory}}$[c]	M_w/M_n[b]
1	ϵ-CL	2-PrOH	**1a**	50	1.0	46	4 000	2 700	1.16
					2.5	100	6 400	5 700	1.19
2		2-PrOH	**1a**	100	5.0	100	13 300	11 400	1.11
3		2-PrOH	**1a**	150	5.5	91	15 900	15 600	1.10
4		2-PrOH	**1a**	200	4.5	89	18 900	20 300	1.12
5		2-PrOH	**1a**	300	23.0	93	32 100	31 800	1.11
6		MeOH	**1a**	50	0.75	98	7 400	5 500	1.08
7		MeOH	**1a**	500	42.0	92	62 600	52 500	1.14
8		2-PrOH	**1b**	50	5.0	95	6 300	5 400	1.27
9		2-PrOH	**1c**	50	2.0	100	6 800	5 700	1.22
10		2-PrOH	Me_3Al	50	1.0	94	6 000	5 300	1.35
11	DTC	2-PrOH	**1b**	20	1.0	100	2 700	2 600	1.15
12		2-PrOH	**1b**	50	2.5	100	6 200	6 500	1.18

[a] In CH_2Cl_2 under N_2 at room temperature. [b] Estimated by GPC (see ref 7). [c] (Molecular weight of monomer) × ($[\text{monomer}]_0/[\text{ROH}]_0$) × (conv/100).

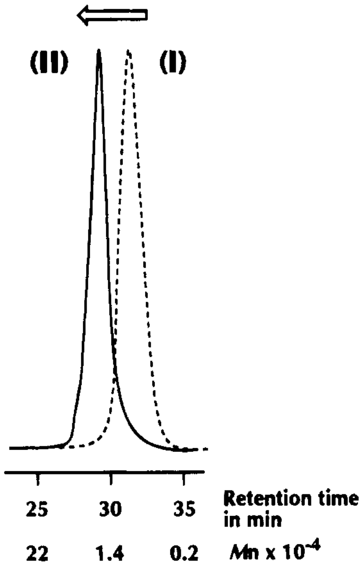

Figure 1. Two-stage polymerization from ϵ-caprolactone (ϵ-CL, 50 equiv) to 2,2-dimethyltrimethylene carbonate (DTC, 130 equiv) initiated with the 2-PrOH/**1a** (1/0.3) system in CH_2Cl_2 at room temperature. GPC chromatograms of the prepolymer of ϵ-CL ((**I**) M_n = 6400, M_w/M_n = 1.19, 100% conversion) and the block copolymer ((**II**) M_n = 20 000, M_w/M_n = 1.17, 88% conversion).

successful to give at 94% conversion (1.5 h) a polycarbonate–polyester block copolymer with M_n and M_w/M_n, respectively, of 13 400 and 1.20. In both cases, the heterodiad sequences (ϵ-CL → DTC, DTC → ϵ-CL), possibly formed as a result of transesterification, were not detected by ^{13}C NMR.[11]

In the ^1H NMR spectrum in C_6D_6 at 22 °C after 10 min upon mixing 2-PrOH[12] and **1b**[13] (1/0.13), the singlet signal due to the Me–Al group was observed to shift from δ −0.01 to 0.39 without a decrease in intensity, while a set of new signals due to 2,6-di-*tert*-butyl-4-methylphenol[14] and a multiplet signal assignable to Me_2CHO–Al (δ 4.58, 2H with respect to Me–Al) were observed in addition to the trace signals due to **1b**. Thus, the actual initiating species is an aluminum alcoholate, formed by the ligand exchange of the phenolic group of **1b** with 2-PrOH. Considering the fact that the degree of polymerization of the produced polymer agrees with the mole ratio $[\text{monomer}]_{\text{reacted}}/[\text{ROH}]_0$ and the MWD is narrow (Table 1), the growing alcoholate species exchanges with ROH reversibly and much more rapidly than the chain growth, and consequently all the ROH molecules participate in initiating the polymerization (*immortal* character).

In conclusion, a novel, simple initiating system composed of alcohol and methylaluminum diphenolate (**1**) was developed for the controlled polymerization of cyclic ester and carbonate, which enables the facile synthesis of narrow MWD polyester, polycarbonate, and their block copolymer with controlled molecular weight.

Experimental Section

Materials. Solvents, alcohols (MeOH and 2-PrOH), and Me_3Al, used for the polymerization,[4,6] and ϵ-caprolactone (ϵ-CL)[2a] were purified as reported previously. Phenols were recrystallized from hexane. 2,2-Dimethyltrimethylene carbonate (DTC) was synthesized from the corresponding glycol and ethyl chloroformate in THF and recrystallized from benzene/hexane. **1a** was prepared as follows: To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing 2,6-diphenylphenol (1.28 g, 5.2 mmol) at 0 °C under nitrogen were successively added CH_2Cl_2 (8.7 mL) and Me_3Al (0.25 mL, 2.6 mmol), and the mixture was stirred for 2 h at room temperature. The resulting solution was used for the polymerization. **1b** and **1c** were synthesized by the method described previously.[4]

Polymerization. Polymerization was carried out under nitrogen at room temperature in a 50-mL round-bottomed flask fitted with a three-way stopcock. For isolation of the produced polymer, the polymerization mixture was poured into MeOH, and the white precipitates formed were collected by filtration and dried in vacuo at room temperature.

Measurements. ^1H and ^{13}C NMR spectra (270 MHz) were recorded in $CDCl_3$ or C_6D_6, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28 for ^1H, δ 77.1 for ^{13}C) or C_6H_6 (δ 7.40 for ^1H) as internal standard. Gel permeation chromatography (GPC) was performed at 40 °C using THF as eluent at a flow rate of 1.0 mL·min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes.[7]

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(7) Molecular weights (M_n and M_w), estimated by GPC calibrated by using polystyrene standards, were multiplied by 0.6 and 0.53 for poly(ϵ-CL) and poly(DTC) samples, respectively, based on the ^{1}H NMR end group analyses.

(8) R_2AlOR', prepared by the reaction of R_3Al with R'OH, has been reported to be effective for the living polymerization of ϵ-CL, but isolation of R_2AlOR' by a special distillation technique is required to realize a narrow MWD of the product (see ref 2c).

(9) ^{1}H NMR in $CDCl_3$: δ 1.42 ($OCH_2CH_2CH_2$), 1.6–1.8 ($CH_2CH_2CH_2CH_2CH_2$), 2.33 ($C(O)CH_2$), 4.10 (OCH_2) [main chain]; δ 1.26 (CH_3), 5.01 (CH) [terminal $(CH_3)_2CHO$ group].

(10) ^{1}H NMR in $CDCl_3$: δ 1.00 (CH_3), 3.98 (CH_2) [main chain]; δ 1.33 (CH_3), 4.89 (CH) [terminal $(CH_3)_2CHO$ group].

(11) In the CH_2O region, only two signals assignable to the homodiad sequences (ϵ-CL → ϵ-CL [δ 64.2], DTC → DTC [72.5]) were observed, while signals assignable to the heterodiad sequences (ϵ-CL → DTC [δ 67.8], DTC → ϵ-CL [68.9]; see ref 3c) were not detected.

(12) ^{1}H NMR in C_6D_6 at 22 °C: δ 1.24 (d, Me), 4.04 (m, CH), 1.39 (d, OH).

(13) ^{1}H NMR in C_6D_6 at 22 °C: δ −0.01 (s, Me–Al), 1.84 (s, *t*-Bu), 2.55 (s, *p*-Me), 7.42 (s, *m*-Ph–H).

(14) ^{1}H NMR in C_6D_6 at 22 °C: δ 1.62 (s, *t*-Bu), 2.49 (s, *p*-Me), 7.30 (s, *m*-Ph–H), 5.03 (OH).

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