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Alternating Copolymerization of Carbon Dioxide and Epoxide Catalyzed by the Aluminum Porphyrin–Quaternary Organic Salt or –Triphenylphosphine System. Synthesis of Polycarbonate with Well-Controlled Molecular Weight

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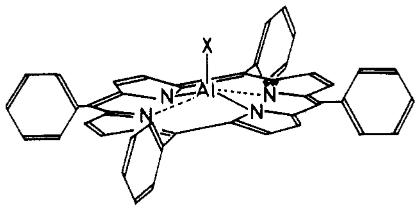
ABSTRACT: The first example of the formation of aliphatic polycarbonate with a narrow molecular weight distribution was demonstrated in the alternating copolymerization of carbon dioxide and epoxide by using as catalyst the system of aluminum porphyrin ((TPP)AlX (1), TPP = 5,10,15,20-tetraphenylporphinato) coupled with a quaternary ammonium or phosphonium salt. Novel AB- or ABA-type block copolymers consisting of polycarbonate and polyester chains with controlled molecular weight were also synthesized. The combination of triphenylphosphine with 1 was also effective as a catalyst.

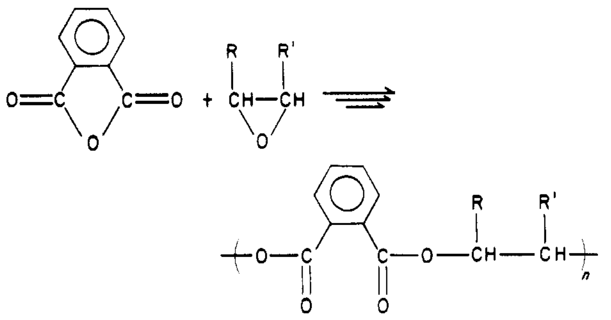
Introduction

Synthesis of copolymers with a well-defined structure is a subject of fundamental as well as practical importance. In this respect, control of sequence[1] as well as molecular weight[2] of copolymers is desirable.

In the previous paper, we reported the first successful example of the formation of an alternating copolymer with controlled molecular weight in the copolymerization of phthalic anhydride and epoxide by using as catalyst the combination of aluminum porphyrin ((TPP)AlX (1)) with a quaternary ammonium or phosphonium salt.[3] By taking advantage of the living nature of the copolymerization, we could successfully synthesize various block copolymers. Detailed spectroscopic investigations demonstrated that the chain growth simultaneously proceeds on both sides, respectively, of an aluminum porphyrin plane via aluminum alkoxide and aluminum phthalate as the growing species.[4] The combination of triphenylphosphine with aluminum porphyrin also gives the alternating copolymer with controlled molecular weight from phthalic anhydride and epoxypropane.[5] Thus, the aluminum porphyrin catalyst is characterized by wide applicability, by which the living polymerization of epoxide and β-lactone is also possible, taking place via aluminum alkoxide and aluminum carboxylate, respectively, as the growing species.[6-8]

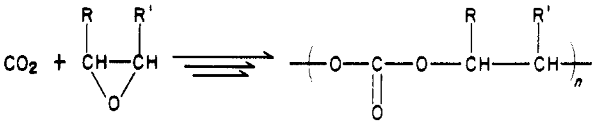


(TPP)AlX (1)



(1)

In this paper, we wish to report further development of the catalyst system of aluminum porphyrin coupled with a quaternary organic salt or triphenylphosphine for the copolymerization of carbon dioxide and epoxide. There has already been found a number of catalyst systems that give the alternating copolymerization of carbon dioxide and epoxide,[9] but no successful example has been reported with respect to control of the molecular weight of the copolymer. This paper describes the first achievement in the living and alternating copolymerization of carbon dioxide and epoxide, producing poly(alkylene carbonate) of controlled molecular weight with a narrow distribution.



$$\mathrm{CO_2} + \underset{\mathrm{O}}{\overset{\mathrm{R}\quad\mathrm{R'}}{\mathrm{CH{-}CH}}} \rightleftharpoons \left(\mathrm{O{-}\underset{\underset{O}{\|}}{C}{-}O{-}\overset{R}{CH}{-}\overset{R'}{CH}} \right)_n \qquad (2)$$

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[10] Commercial tetraethylammonium bromide (Et_4NBr) was recrystallized from ethanol. Triphenylphosphine (PPh_3) was recrystallized from ethyl ether. Ethyltriphenylphosphonium bromide ($EtPh_3PBr$) was prepared by the quaternization of PPh_3 with ethyl bromide at refluxing temperature and recrystallized from water.[11] Epoxyethane (ethylene oxide, EO), stirred with a mixture of potassium hydroxide and calcium hydride, was collected in a trap cooled with liquid nitrogen after three thaw-to-flow cycles. All other epoxides were distilled after refluxing or stirring with a mixture of potassium hydroxide and calcium hydride under a nitrogen atmosphere. Commercial high-purity carbon dioxide (CO_2) was used without further purification. Phthalic anhydride (PhthA) was purified by recrystallization from benzene. Dichloromethane (CH_2Cl_2), washed sequentially with concentrated sulfuric acid, water, and dilute aqueous sodium bicarbonate, was dried with calcium chloride, followed by distillation in a nitrogen atmosphere after refluxing with calcium hydride. Diethylaluminum chloride (Et_2AlCl) was fractionally distilled under nitrogen under reduced pressure.

Procedures. Preparation of Catalyst Systems. A round-bottom flask (50 or 100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added by a hypodermic syringe in a nitrogen stream to dissolve the porphyrin. To this solution was added diethylaluminum chloride (1.2 mmol), and the mixture was stirred for 1 h. then volatile fractions were removed from the reaction mixture to leave (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl (1), X = Cl) as purple powder.[6] (5,10,15,20-Tetraphenylporphinato)aluminum alkoxide (1, $(TPP)Al(OCH(CH_3)CH_2)_nCl$, $n = 2$) was prepared by the oligomeriztion of 1,2-epoxypropane (propylene oxide, PO) with (TPP)AlCl, with the ratio $[PO]_0/[(TPP)AlCl]_0$ of 2 for several hours at room temperature.[6,12] Aluminum porphyrin thus obtained was dissolved in dichloromethane, and the solution was added

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by a hypodermic syringe under a nitrogen stream into a flask (50 or 100 mL) containing quaternary organic salt (Et_4NBr, $EtPh_3PBr$) (1 mmol) or PPh_3 (2 mmol) to give the catalyst solution.[3]

Copolymerization. A stainless steel autoclave (100 mL), dried under vacuum, was purged with nitrogen, and a catalyst solution (1 mmol/20 mL) was added by a hypodermic syringe. After the atmosphere of the system was replaced by carbon dioxide (CO_2), a prescribed amount of epoxide (100 mmol) was added by a hypodermic syringe. The reaction mixture was pressurized by carbon dioxide up to 50 kg·cm^{-2} and stirred magnetically at room temperature. After a definite time, the volatile fractions were removed from the reaction mixture at room temperature under reduced pressure and the residue was subjected to repeated reprecipitations from chloroform/methanol to leave a slightly colored polymeric product. The conversion of epoxide was calculated from the weight and the ^1H NMR spectrum (in $CDCl_3$) of the reaction mixture, from which the volatile fractions had been removed under reduced pressure (~20 mmHg) at room temperature. The composition of the product was determined by the ^1H NMR spectrum of the reaction mixture. For $(CH_2CH_2OCO_2)_x$, δ 4.4 (CH_2); $(CH(CH_3)CH_2OCO_2)_x$, δ 1.3 (CH_3), 4.2 (CH_2), 4.9 (CH); $(CH(CH_2CH_3)CH_2OCO_2)_x$, δ 1.0 (CH_3), 1.7 (CH_3CH_2), 4.3 (CH_2), 4.85 (CH); $(CH(CH_2OC_6H_5)CH_2OCO_2)_x$, δ 4.15 ($C_6H_5OCH_2$), 4.5 (CH_2), 5.2 (CH); in $CDCl_3$.

Block Copolymerization. At the first stage, the "living" copolymer of phthalic anhydride and 1,2-epoxypropane (25 mmol/25 mmol) was prepared in a round-bottom flask by the copolymerization with the (TPP)AlCl–$EtPh_3PBr$ or –Et_4NBr (1 mmol/1 mmol) system in CH_2Cl_2 at room temperature.[3] After the complete consumption of the comonomers, an aliquot of the reaction mixture was transferred by a hypodermic syringe to a stainless steel autoclave, in which the copolymerization of carbon dioxide and epoxide (the second stage of copolymerization) was carried out in a similar way as described above. Synthesis of the polyester–polycarbonate–polyester block copolymer (the third-stage copolymerization) was carried out by the addition of an equimolar mixture of phthalic anhydride and 1,2-epoxypropane to the final reaction mixture of the second stage from which the remaining, unreacted carbon dioxide had been released under atmospheric pressure. The reaction mixture after the removal of volatile fractions was weighed and examined by ^1H NMR to determine the conversion of the comonomers as well as the composition of products. For $(CH(CH_3)CH_2OCOC_6H_4COO)_x$: δ 1.4 (CH_3), 4.4 (CH_2), 5.4 (CH) in $CDCl_3$. A portion of the reaction mixture was also subjected to reprecipitation from chloroform/methanol to isolate the polymeric product.

Measurements. ^1H, ^{13}C, and ^{31}P NMR measurements were performed in $CDCl_3$ on a JEOL Type JNM GX-400 spectrometer operating at 399.7, 100.5, and 161.7 MHz, respectively. Chemical shift was determined with respect to $CHCl_3$ (δ 7.28) for ^1H NMR, $CDCl_3$ (δ 77.102) for ^{13}C NMR, and 80% aqueous H_3PO_4 (δ 0, in a capillary tube) for ^{31}P NMR. Infrared spectra of the reaction mixture were measured with a Hitachi 260-30 infrared spectrophotometer. Vapor pressure osmometry (VPO), for the determination of number-average molecular weight ($\bar{M}_n$) of polymer, was performed in benzene on Corona 117 molecular weight apparatus, using as standard polystyrene, $\bar{M}_n = 6200$, $\bar{M}_w/\bar{M}_n$ (ratio of weight-average molecular weight to number-average molecular weight) = 1.07, from Toyo Soda Manufacturing Co., Ltd. Gel permeation chromatography (GPC) of the reaction mixture, for the convenient estimation of the average molecular weight and the molecular weight distribution of polymer, was performed on a Toyo Soda Model 802A high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent. The flow rate was 1.1 mL·min^{-1}. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes (Toyo Soda Manufacturing Co., Ltd.) $\bar{M}_n = 107\,000$ ($\bar{M}_w/\bar{M}_n = 1.01$), $\bar{M}_n = 16\,700$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 6200$ ($\bar{M}_w/\bar{M}_n = 1.04$), $\bar{M}_n = 2800$ ($\bar{M}_w/\bar{M}_n = 1.05$), or standard poly(oxyethylenes) (Toyo Soda Manufacturing Co., Ltd.) $\bar{M}_n = 72\,000$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 39\,000$ ($\bar{M}_w/\bar{M}_n = 1.03$), $\bar{M}_n = 22\,000$ ($\bar{M}_w/\bar{M}_n = 1.14$) and standard poly(propylene glycols) (Lion Fat and Oil Co., Ltd.) $\bar{M}_n = 2000$ and $\bar{M}_n = 1000$ ($\bar{M}_w/\bar{M}_n \approx 1$).

Table I
Copolymerization of Carbon Dioxide (CO_2) and Epoxide with the (TPP)AlCl–Quaternary Organic Salt System[a,b]

run	epoxide	salt	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	epoxyethane[d]	$EtPh_3PBr$	5500	1.14
2	1,2-epoxypropane[e]	$EtPh_3PBr$	3500	1.09
3	1,2-epoxypropane[e]	Et_4NBr	4500	1.09
4	1,2-epoxycyclohexane	$EtPh_3PBr$	6200	1.06

[a] $[Epoxide]_0/[(TPP)AlCl]_0/[salt]_0 = 100/1/1$, $(P_{CO_2})_0 = 50$ kg·cm^{-2}, in CH_2Cl_2 (20 mL) at room temperature for 12–23 days; consumption of epoxide was approximately 100%. [b] The product was confirmed to be poly(alkylene carbonate) by NMR. [c] By GPC calibrated with standard polystyrenes. [d] $[Epoxide]_0/[(TPP)AlCl]_0/[salt]_0 = 160/1/1$; the reaction product contained 30% repeating oxyethylene units (δ 3.7 (CH_2), ^1H NMR in $CDCl_3$). [e] Cyclic carbonate was also formed.

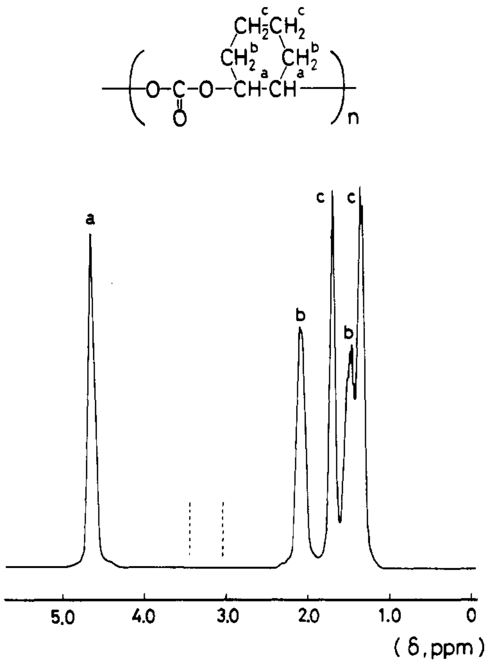


Figure 1. ^1H NMR spectrum of the reaction mixture in $CDCl_3$, in the copolymerization of carbon dioxide (CO_2) and 1,2-epoxycyclohexane (CHO) with the (TPP)AlCl-$EtPh_3PBr$ (1/1) system. Reaction conditions: $[CHO]_0/[cat.]_0 = 100$, $(P_{CO_2})_0 = 50$ kg·cm^{-2}, in CH_2Cl_2 (20 mL), at room temperature for 14 days, consumption of CHO = 100%.

Results and Discussion

Copolymerization of Carbon Dioxide and Epoxide. Copolymerization of carbon dioxide (CO_2) and epoxide by using the system of (TPP)AlCl (1, X = Cl) coupled with an equimolar amount of ethyltriphenylphosphonium bromide ($EtPh_3PBr$) or tetraethylammonium bromide (Et_4NBr) as catalyst proceeded at room temperature under a pressure of CO_2 (Table I). A typical example is shown by the copolymerization of carbon dioxide and 1,2-epoxycyclohexane with the (TPP)AlCl–$EtPh_3PBr$ system (run 4). The infrared spectrum of the reaction mixture after the complete consumption of epoxide showed two strong absorptions characteristic of a linear carbonate linkage at 1740 and 1280 cm^{-1}. In the ^1H NMR spectrum of the reaction mixture (Figure 1), the signal (a) assignable to the methine proton of the repeating oxycarbonyloxy(1,2-cyclohexene) units appeared at δ 4.7 ppm, while the signal corresponding to the repeating oxy(1,2-cyclohexene) units (δ 3.4, polyether) was hardly observed. These facts clearly indicate the quantitative formation of the alternating copolymer, poly(cyclohexene carbonate), from carbon dioxide and 1,2-epoxycyclohexane. Another observation of particular interest is a unimodal, sharp elution

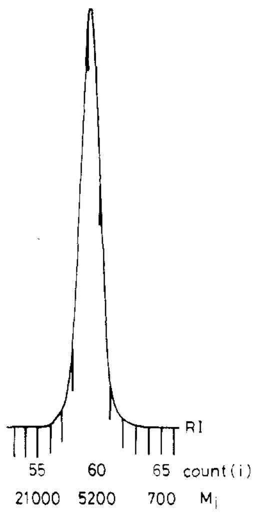


Figure 2. GPC curve of the reaction mixture in the copolymerization of carbon dioxide and 1,2-epoxycyclohexane with the (TPP)AlCl–EtPh$_3$PBr (1/1) system; reaction conditions, see Figure 1. Standard was polystyrene. M_i = molecular weight corresponding to count i.

curve in the GPC chromatogram of the reaction mixture (Figure 2). The ratio of weight-average molecular weight to the number-average molecular weight ($\bar{M}_w/\bar{M}_n$) was calculated from this chromatogram to be 1.06 ($\bar{M}_n$(GPC) = 6200, $\bar{M}_n$ (VPO) = 6800), indicating that the copolymer is of very narrow molecular weight distribution.

The copolymerization of carbon dioxide and other epoxides such as epoxyethane and 1,2-epoxypropane gave similar results (runs 1–3 in Table I). The GPC analysis of the reaction mixture clearly showed the formation of a copolymer with narrow molecular weight distribution. In the reaction of carbon dioxide and 1,2-epoxypropane, the infrared (1800 cm^{-1}) and NMR spectra indicated the concomitant formation of propylene carbonate, the one-to-one cyclic adduct between carbon dioxide and 1,2-epoxypropane.

When carbon dioxide and 1,2-epoxypropane were further added to the reaction mixture of the copolymerization corresponding to run 2 in Table I, a clear increase in the molecular weight of the copolymer was observed. The absence of the starting copolymer (peak I, $\bar{M}_n = 3500$, $\bar{M}_w/\bar{M}_n = 1.09$) in the final product (peak II, $\bar{M}_n = 8100$, $\bar{M}_w/\bar{M}_n = 1.10$) was confirmed by the GPC chromatogram of the reaction mixture (Figure 3), indicating the "living" nature of the copolymerization of carbon dioxide and epoxide catalyzed by the combination of (TPP)AlCl with EtPh$_3$PBr.

The copolymerization of carbon dioxide and 1,2-epoxypropane to form the alternating copolymer with narrow molecular weight distribution was also possible by using as catalyst the system of (TPP)AlOR (**1**, X = (OCH(CH$_3$)CH$_2$)$_n$Cl, n = 2) coupled with triphenylphosphine (PPh$_3$) ((TPP)AlOR–PPh$_3$ system). Furthermore, the number-average molecular weight ($\bar{M}_n$) of the copolymer could be successfully controlled by changing the mole ratio of 1,2-epoxypropane to the catalyst, as shown in Figure 4.

The formation of an alternating copolymer with narrow molecular weight distribution is rather surprising, since broadening of the molecular weight distribution is more likely in the copolymerization of comonomers with different structures, where the growing species of different reactivities are involved.

Synthesis of Block Copolymers. As described in the previous paper, the catalyst system from (TPP)AlX (**1**) and quaternary ammonium or phosphonium salt gives the "living" poly(alkylene phthalate) of controlled molecular weight with narrow distribution in the copolymerization of phthalic anhydride and epoxide.[3,4] The present work revealed that the same catalyst system is effective also for the "living", alternating copolymerization of carbon dioxide and epoxide. Since these two copolymerization reactions are considered to involve similar growing species, i.e., aluminum alkoxide and aluminum carboxylate, the synthesis of a novel AB- or ABA-type block copolymer consisting of polyester (A) and polycarbonate (B) blocks was attempted by the copolymerization of carbon dioxide and epoxide initiated by the "living" poly(methylethylene phthalate), the reaction mixture of the copolymerization of phthalic anhydride and 1,2-epoxypropane with the (TPP)AlCl (**1**, X = Cl)–EtPh$_3$PBr system. The results are summarized in Table II.

The copolymerization of carbon dioxide and 1,2-epoxypropane initiated by living poly(methylethylene phthalate) ($\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.11$), for example, proceeded at room temperature (Figure 5). The infrared spectrum of the reaction mixture showed a strong carbonyl absorption at 1740 cm^{-1} with a shoulder at 1720 cm^{-1}, corresponding to polycarbonate and polyester, respectively. The ab-

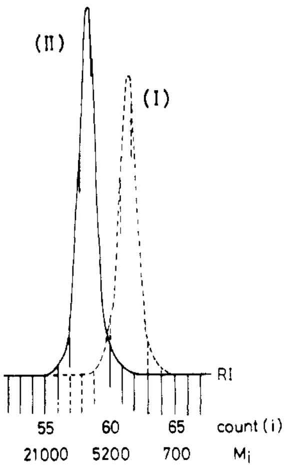


Figure 3. GPC profile of the copolymerization of carbon dioxide (CO_2) and 1,2-epoxypropane (PO) initiated by the "living" copolymer of CO_2 and PO prepared with the (TPP)AlCl–EtPh$_3$PBr (1/1) system; $[PO]_0/[cat.]_0 = 125$, $(P_{CO_2})_0 = 50$ kg·cm^{-2}, in CH_2Cl_2 (20 mL), at room temperature, consumption of PO = 100%; peak I, starting copolymer, $\bar{M}_n = 3500$, $\bar{M}_w/\bar{M}_n = 1.11$ ($[PO]_0/[cat.]_0 = 100$); peak II, final reaction mixture, $\bar{M}_n = 8100$, $\bar{M}_w/\bar{M}_n = 1.10$. Standard was polystyrene.

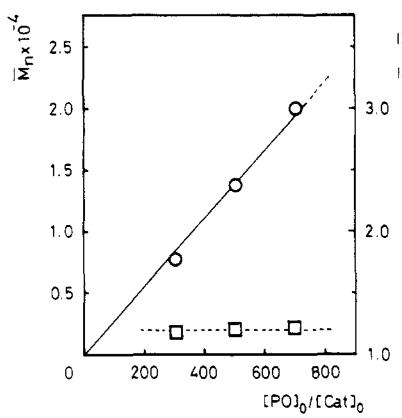


Figure 4. Copolymerization of carbon dioxide (CO_2) and 1,2-epoxypropane (PO) with the (TPP)AlOR (OR = (OCH(CH$_3$)CH$_2$)$_2$Cl)–PPh$_3$ (1/2) system: Relationship between $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (□)) of copolymer and $[PO]_0/[cat.]_0$; $(P_{CO_2})_0 = 50$ kg·cm^{-2}, in CH_2Cl_2 (20 mL), at room temperature for 7 days, conversion = 100%. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ by GPC calibrated with standard poly(oxyethylenes) and poly(propylene glycols).

Table II
Synthesis of AB- or ABA-Type Block Copolymers Consisting of Poly(epoxypropane-*alt*-phthalic anhydride) (A Block) and Poly(epoxide-*alt*-carbon dioxide) (B Block) by Using the (TPP)AlCl–EtPh$_3$PBr System[a]

	starting polyester (A)[b]		AB-type block copolymer[c]				ABA-type block copolymer[d]		
run	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	epoxide	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	cyclic carbonate,[f] %	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	content of polycarbonate (B),[f] %
1	2600	1.12	epoxyethane[g]	4400	1.10	~0	5700	1.14	
2	2300	1.13	1,2-epoxypropane	5900	1.11	18	8000	1.19	52
3	2500	1.16	1,2-epoxybutane[h]	7300	1.18				
4	2500	1.09	2,3-epoxypropyl phenyl ether	5600	1.12	43	8400	1.12	45
5	2500	1.09	1,2-epoxycyclohexane	6800	1.11	~0	8500	1.15	63

[a] In CH_2Cl_2 at room temperature, consumption of epoxide at each step ≈100%, polymeric product was confirmed to be the alternating copolymer by NMR. [b] $[\text{Phthalic anhydride}]_0/[\text{1,2-epoxypropane}]_0/[(\text{TPP})\text{AlCl}]_0/[\text{EtPh}_3\text{PBr}]_0 = 25/25/1/1$, for 5 days. [c] $[\text{Epoxide}]_0/[\text{cat.}]_0 = 113/1$, $(P_{CO_2})_0 = 50$ kg·cm^{-2} for 14 days. [d] $[\text{Phthalic anhydride}]_0/[\text{1,2-epoxypropane}]_0/[\text{cat.}]_0 = 35/35/1$, for 7 days. [e] By GPC calibrated with standard polystyrenes. [f] By ^{1}H NMR. [g] See footnote *d* in Table I. [h] $[\text{Epoxide}]_0/[\text{cat.}]_0 = 117/1$.

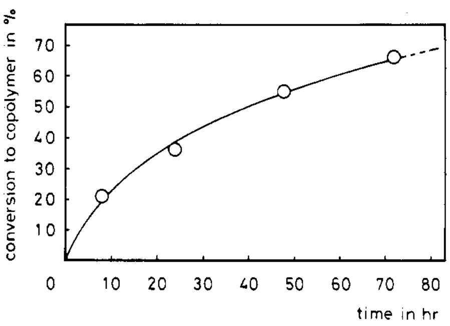


Figure 5. Copolymerization of carbon dioxide (CO_2) and 1,2-epoxypropane (PO) initiated by the "living" copolymer of phthalic anhydride (PhthA) and PO prepared with the (TPP)AlCl–EtPh$_3$PBr system ($[\text{PhthA}]_0/[\text{PO}]_0/[(\text{TPP})\text{AlCl}]_0/[\text{EtPh}_3\text{PBr}]_0 = 25/25/1/1$, conversion = 100%). Conversion to copolymer vs. time: $[\text{PO}]_0/[\text{cat.}]_0 = 95$, $(P_{CO_2})_0 = 50$ kg·cm^{-2}, in CH_2Cl_2 (30 mL), at room temperature.

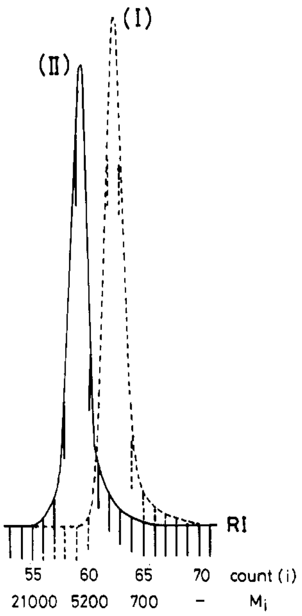


Figure 6. GPC profile of the copolymerization of carbon dioxide and 1,2-epoxypropane (PO) initiated by the "living" copolymer of phthalic anhydride (PhthA) and PO prepared with the (TPP)AlCl–EtPh$_3$PBr (1/1) system: peak I, starting PhthA–PO copolymer, $\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.11$; peak II, reaction mixture at 66% conversion, $\bar{M}_n = 5800$, $\bar{M}_w/\bar{M}_n = 1.07$. Reaction conditions, see Figure 5. Standard was polystyrene.

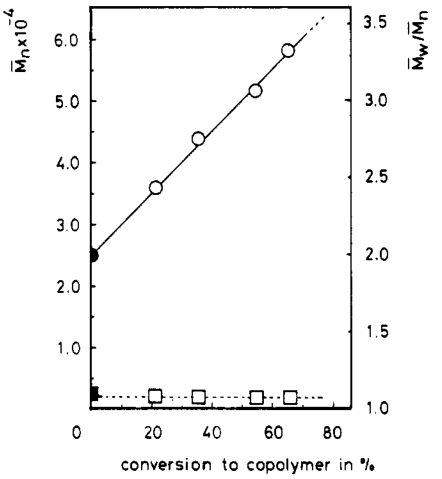


Figure 7. Copolymerization of carbon dioxide and 1,2-epoxypropane (PO) initiated by the "living" copolymer of phthalic anhydride (PhthA) and PO prepared with the (TPP)AlCl–EtPh$_3$PBr (1/1) system. Relationship between $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (□)) of block copolymer and conversion of comonomers to methylethylene carbonate unit. (●) and (■) represent $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the starting PhthA–PO copolymer, respectively. Reaction conditions: see Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ by GPC calibrated with standard polystyrenes.

sorption at 1800 cm^{-1} was also observed, indicating the formation of a small amount of cyclic carbonate. Successful formation of a polyester–polycarbonate block copolymer was demonstrated by a unimodal, sharp chromatogram of the reaction mixture without peak I, corresponding to the starting poly(methylethylene phthalate) ($\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.11$). An example is shown by the GPC curve of the reaction mixture obtained after 72 h (66% conversion) (peak II in Figure 6, $\bar{M}_n = 5800$, $\bar{M}_w/\bar{M}_n = 1.07$). The polycarbonate content (72%) as determined by NMR and that estimated from the number-average molecular weights of polyester and polycarbonate blocks (67%) were in good agreement with each other. The molecular weight of the polycarbonate block linearly increased with the progress of reaction, while the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$) remained almost constant (1.07–1.09) (Figure 7).

Copolymerization of carbon dioxide and epoxyethane, 1,2-epoxybutane, 2,3-epoxypropyl phenyl ether (glycidyl phenyl ether), or 1,2-epoxycyclohexane also affords the corresponding polyester–polycarbonate block copolymer with controlled block lengths (runs 1 and 3–5 in Table II). The unfavorable formation of cyclic carbonate was remarkable in the case of the reaction of carbon dioxide with 2,3-epoxypropyl phenyl ether (44%). On the other hand, in the copolymerization of carbon dioxide and 1,2-epoxycyclohexane a quantitative conversion of comonomers to polycarbonate block was obtained (run 5). The contents of polyester and polycarbonate in the block copolymer

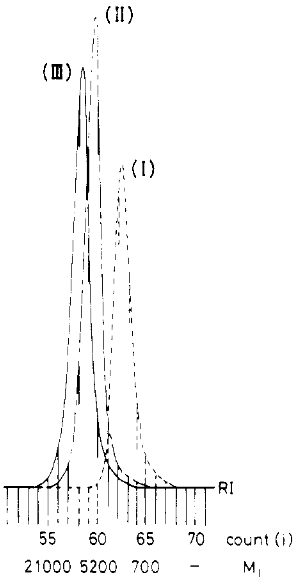


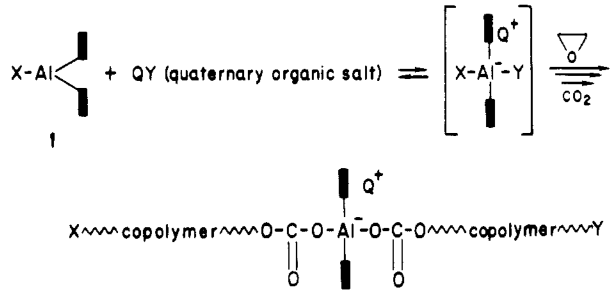
Figure 8. GPC profile of the formation of polyester–polycarbonate–polyester block copolymer in the copolymerization by the (TPP)AlCl–EtPh$_3$PBr (1/1) system: peak I, poly(methylethylene phthalate), $\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.09$; peak II, poly(methylethylene phthalate)–poly(cyclohexene carbonate) block copolymer, $\bar{M}_n = 6800$, $\bar{M}_w/\bar{M}_n = 1.11$; peak III, poly(methylethylene phthalate)–poly(cyclohexene carbonate)–poly(methylethylene phthalate) block copolymer, $\bar{M}_n = 8500$, $\bar{M}_w/\bar{M}_n = 1.15$. Reaction conditions: see Table II, run 5. Standard was polystyrene.

estimated by the NMR analysis (19% and 81%, respectively) were in good agreement with the calculated values from the amounts of the starting polyester and 1,2-epoxycyclohexane employed for the reaction.

Furthermore, a polyester–polycarbonate–polyester (ABA-type) ternary block copolymer could be synthesized by the reaction of an equimolar mixture of phthalic anhydride (PhthA) and 1,2-epoxypropane (PO) with the reaction system of the above binary block copolymerization. As shown in the last column in Table II, all the reaction mixtures obtained after the complete consumption of the comonomers showed a clear increase in the molecular weight, keeping the molecular weight distribution narrow. When the copolymerization was initiated from the reactive growing end of poly(cyclohexene carbonate) linked to poly(methylethylene phthalate) (run 5 in Table II), the final product exhibited the GPC profile shown in Figure 8. The content of polycarbonate (62%) estimated from the molecular weights of polyester and polycarbonate blocks was in excellent agreement with that determined by the NMR analysis of the reaction mixture (63%).

Thus, the living and alternating nature of the copolymerization of phthalic anhydride and epoxide with the (TPP)AlX–quaternary organic salt system was successfully followed by the subsequent copolymerization of carbon dioxide and epoxide and then further copolymerization of phthalic anhydride and epoxide, producing AB- and ABA-type block copolymers.

Mechanism of Copolymerization. As reported previously, aluminum porphyrin alone is not a very good catalyst for the copolymerization of carbon dioxide and epoxide, since it gives a rather low content of the carbon dioxide units in the resulting copolymer.[13] It should be also noted here that quaternary ammonium or phosphonium salt alone did not bring about the reaction between carbon dioxide and epoxide under similar conditions. Thus, the living and alternating nature of the copolymerization of carbon dioxide and epoxide is realized only when aluminum porphyrin is coupled with quaternary organic salt. The formation of AB- and ABA-type block copolymers by the copolymerization of phthalic anhydride and epoxide with the aluminum porphyrin–quaternary organic salt system followed by the copolymerization of carbon dioxide and epoxide, etc., strongly indicates that the mechanism of the copolymerization of carbon dioxide and epoxide is similar to that of the copolymerization of phthalic anhydride and epoxide. Similarity between these two copolymerization reactions was also observed in the fact that the system of aluminum porphyrin coupled with quaternary organic salt gives twice as many copolymer molecules as molecules of aluminum porphyrin; the number-average molecular weight ($\bar{M}_n$) of poly(cyclohexene carbonate) (run 4 in Table I) as measured by vapor pressure osmometry was found to be 6900, corresponding to about half the calculated value by assuming the formation of one polymer molecule per one molecule of aluminum porphyrin. Thus, the chain growth is considered to proceed simultaneously on both sides of an aluminum porphyrin plane, similar to the mechanism proposed for the copolymerization of phthalic anhydride and epoxide[4]



(3)

As to the activity of the aluminum porphyrin–triphenylphosphine (PPh$_3$) system for these copolymerization reactions, the copolymerization system of phthalic anhydride and 1,2-epoxypropane with the (TPP)AlOR–PPh$_3$ system was investigated by NMR, and propenyltriphenylphosphonium salt ($CH_3CH{=}CHP^+Ph_3$) was detected as a single phosphorus species after the completion of reaction; the reaction mixture in CDCl$_3$ showed a singlet signal at δ 17.1 in ^{31}P NMR, a doublet signal at 109 (J = 87.9 Hz) and a singlet signal at 159 in ^{13}C{^{1}H} NMR, assignable to $C{=}CHP^+Ph_3$ and $CH{=}CHP^+Ph_3$, respectively.[14] This fact indicates a quantitative quaternization of PPh$_3$ by the reaction with 1,2-epoxypropane in the copolymerization system with carbon dioxide or phthalic anhydride. Since (2-phenoxyethyl)triphenylphosphonium bromide is known to be readily converted into vinyltriphenylphosphonium bromide with the release of phenol upon refluxing in ethyl acetate,[15], the intermediate for the formation of propenyltriphenylphosphonium species in the reaction of phthalic anhydride, 1,2-epoxypropane, and triphenylphosphine in the presence of aluminum porphyrin is tentatively considered as $OCOC_6H_4COOCH(CH_3)CH_2P^+Ph_3$. In the absence of aluminum porphyrin, no quaternization occurred under similar conditions. Thus, the mode of the copolymerization reaction catalyzed by the aluminum porphyrin–triphenylphosphine system is considered essentially the same as in reaction 3.

Conclusion

The system of aluminum porphyrin coupled with quaternary organic salt or triphenylphosphine is an effective catalyst for the alternating copolymerizations of carbon dioxide and epoxide as well as of cyclic acid anhydride and epoxide to give copolymers with controlled molecular weight. The facile synthesis of multiblock copolymers consisting of polycarbonate and polyester chains is possible by taking advantage of the living nature of the copolymerizations.

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(5) The copolymerization of phthalic anhydride and 1,2-epoxypropane (50 mmol/50 mmol) with the (TPP)AlOR (1, X = OR)–PPh_3 (1 mmol/2 mmol) system in CH_2Cl_2 (60 mL) at room temperature for 24 h gave the alternating copolymer in a quantitative yield: $\bar{M}_n = 3000$, $\bar{M}_w/\bar{M}_n = 1.1$. On the other hand, in the absence of PPh_3 under similar conditions for 1 month, the copolymer containing 53% ether linkages and 47% ester linkages ($\bar{M}_n = 5500$, $\bar{M}_w/\bar{M}_n = 1.1$) was formed with the complete consumption of epoxide (unpublished results).

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Thermally Depolymerizable Polycarbonates. 2. Synthesis of Novel Linear Tertiary Copolycarbonates by Phase-Transfer Catalysis

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ABSTRACT: The first synthesis of copolycarbonates containing a tertiary diol structure has been achieved by using a solid–liquid phase-transfer-catalyzed polycondensation of the bis(carbonylimidazolide) of 2,5-dimethyl-2,5-hexanediol with various other diols in the presence of powdered potassium carbonate. The solubility and physical properties of the copolycarbonates are affected by the nature of the diol used in the polycondensation. Higher melting polymers are obtained when the diol structure incorporates an aromatic ring while increased solubility results from increased steric crowding or the incorporation of less symmetrical or aliphatic structures in the diol component. The copolycarbonates decompose cleanly upon heating to approximately 200 °C with liberation of volatile materials, leaving no solid residue. For example, the copolycarbonate of 2,5-dimethyl-2,5-hexanediol and *p*-benzenedimethanol is stable to 200 °C, and then undergoes rapid thermolysis with formation of carbon dioxide, *p*-benzenedimethanol, and a mixture of three dienes corresponding to all the possible dehydration products of 2,5-dimethyl-2,5-hexanediol. The thermal lability of the polycarbonates allows their analysis by gas chromatography–mass spectroscopy using direct solid sample injection.

Introduction

The synthesis of novel polymeric materials that can be modified by physical processes such as heating, irradiation, and/or changes in pressure is of great interest as these materials are finding numerous applications as coatings, additives for postreaction within preformed polymers, cross-linking agents, blowing agents, adhesives, etc. We have recently described the synthesis of poly[*p*-((*tert*-butyloxycarbonyl)oxy)styrene][2] and its α-methylstyrene analogue[3] as useful polymeric precursors to the corresponding poly(*p*-hydroxystyrene) and poly(*p*-hydroxy-α-methylstyrene). The *tert*-butyloxycarbonyl (t-Boc) protecting group was chosen for these syntheses, as it afforded stable yet easily removable protection for the phenolic groups of *p*-hydroxystyrene while allowing for easy and controlled polymerization. Although the t-Boc protecting group has been used mainly for the protection of amino groups in applications such as the synthesis of polypeptides,[4] we have demonstrated recently[5] its general applicability to the protection of alcohol, phenol, enol, and thiol functionalities. The t-Boc group is particularly interesting in these applications, as it can be removed under mild conditions.[4,6,7] Several polymers containing thiol pendant groups have been prepared by thermolysis of solutions of their thiocarbonate derivatives.[8] In the case of t-Boc-protected phenolic polymers,[1,2] we have found that removal of the protecting groups is best achieved[1] by heating the polymers, in the solid state, to approximately 190 °C. When followed thermogravimetrically, the deprotection reaction is characterized by no measurable loss of mass until the critical temperature is reached, whereupon virtually instantaneous and quantitative loss of the elements of the t-Boc protecting group (carbon dioxide and 2-methylpropene) is observed. The thermal deprotection

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