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Well-Controlled Polymerization by Metalloporphyrin. Synthesis of Copolymer with Alternating Sequence and Regulated Molecular Weight from Cyclic Acid Anhydride and Epoxide Catalyzed by the System of Aluminum Porphyrin Coupled with Quaternary Organic Salt

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ABSTRACT: The system of (5,10,15,20-tetraphenylporphinato)aluminum chloride coupled with ethyltriphenylphosphonium bromide is a novel and efficient initiator for the living and alternating copolymerization of phthalic anhydride and epoxide. The "living" polyester thus formed initiates the copolymerization of phthalic anhydride and epoxide as well as the homopolymerization of epoxide, β-lactone, or ϵ-lactone to give the corresponding binary and/or ternary block copolymers of a desired block sequence with well-regulated chain length.

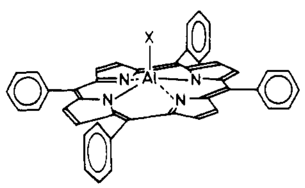
Introduction

In view of the great demand for elaborate molecular design of polymer molecules as required for materials of a desired function, one of the fundamental subjects of particular importance is to establish a facile and versatile procedure for the synthesis of well-defined macromolecules as to the sequence and the number of repeating units.

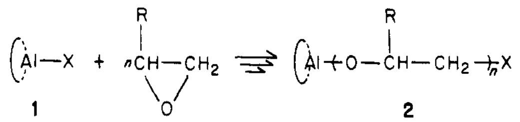
Since the first discovery of the formation of "living" polymer from styrene,[1] synthetic procedures for polymers with controlled molecular weight have been developed in the polymerization of nonpolar vinyl monomers under rather rigorous conditions.[2]

With respect to polar monomers, considerable side reactions with the polar substituent group are generally observed.[3] Thus, the control of molecular weight of the polymer has so far been achieved only in very limited cases, in very restricted combinations of monomer and catalyst.[4,5] Recently, the reaction of silyl ketene acetal with α,β-unsaturated carbonyl compounds was successfully extended to a novel synthetic procedure for the polymers with narrow molecular weight distribution from some acrylic and methacrylic esters.[6] However, limited applicability of the procedure was noted also in this case only to the polymerization of vinyl monomers with conjugated carbonyl groups.

In this paper, we describe the first achievement in a very high degree of regulation of the structure of copolymer as to the sequence and the number of repeating units, by using as a catalyst the system of aluminum porphyrin coupled with a quaternary organic salt,[7] particularly phosphonium salt. The reaction is the alternating copolymerization of phthalic anhydride and epoxide to give a polyester. This reaction has been reported to proceed by several catalyst systems such as tertiary amines, metal salts, and some organometallic compounds at a temperature higher than 100 °C[8] but the control of the molecular weight of the copolymer has never been achieved. The present finding is based on the applicability of aluminum porphyrin (1) as an effective catalyst for the polymerization of various types of monomers such as epoxide (eq 1)[9] and β-lactone (eq 2).[10] Of particular interest is the fact that the chain growth in both cases proceeds without any side reactions to afford polymers of controlled molecular weight with narrow distribution ("living" nature).[11,12] In these



(TPP)AlX (1)



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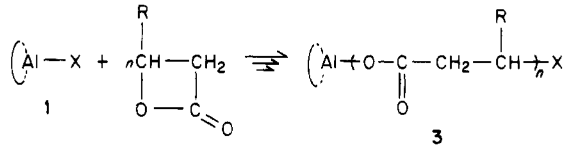

(2)

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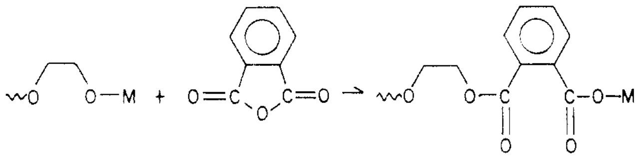
reactions, the structures of the reactive growing terminals are different from each other, an aluminum alkoxide and an aluminum carboxylate, respectively.[13,14] Thus, the copolymerization of phthalic anhydride and epoxide (eq 3 and 4), which is considered to involve growing species



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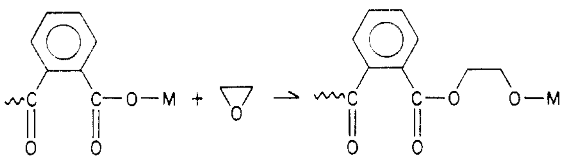


(4)

similar to the above two types,[8] becomes the next target of the controlled polymerization by aluminum porphyrin catalyst. However, aluminum porphyrin (1) alone was found to exhibit little catalytic activity for the copolymerization.[15] In contrast, the combination of a quaternary organic salt (ethyltriphenylphosphonium bromide) with 1 was found very effective for the novel "living" and "alternating" copolymerization of phthalic anhydride and various epoxides, producing poly(alkylene phthalates) of controlled molecular weight with unusually narrow distribution. This is rather surprising, since the chain growth possibly involves three competing elementary steps, the reactions of alkoxide growing species with phthalic anhydride (eq 3) or epoxide, and phthalate growing species with epoxide (eq 4). Further development of this reaction to the synthesis of block copolymers was attempted by taking advantage of the living nature of the polymerization of various types of monomers catalyzed by aluminum porphyrin.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphyrin ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[16] Ethyltriphenylphosphonium bromide ($EtPh_3PBr$) was prepared by the quaternization of triphenylphosphine with ethyl bromide at refluxing temperature and recrystallized from water.[17] *cis-* and *trans*-2,3-epoxybutanes were synthesized respectively by the reaction of *cis-* and *trans*-2-butene with *N*-bromosuccinimide (NBS)[18] followed by the ring closure of the resulting bromohydrins in a concentrated aqueous solution of potassium hydroxide.[19] Epoxyethane, stirred with a mixture of potassium hydroxide and calcium hydride, was collected in a trap cooled with liquid nitrogen. All other epoxides were subjected twice to fractional distillation after stirring with a mixture of potassium hydroxide and calcium hydride in a nitrogen atmosphere with gentle heating or refluxing for 2–3 h. β-Butyrolactone and ϵ-caprolactone were allowed to keep stirring for 2 h with calcium hydride with gentle heating, followed by distillation in nitrogen under reduced pressure. Phthalic anhydride was purified by recrystallization from benzene. Dichloromethane was dried by refluxing over calcium hydride, followed by fractional distillation in a nitrogen atmosphere. Diethylaluminum chloride was fractionally distilled in 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. Diethylaluminum chloride (1.2 mmol) was added to this mixture, which was kept stirring for 1 h. Volatile fractions were removed from the reaction mixture to leave (5,10,15,20-tetraphenylporphinato)aluminum chloride (1, (TPP)AlCl[11]) as purple powder. (TPP)AlCl was redissolved in dichloromethane, and the solution was added by a hypodermic syringe in a nitrogen stream into a flask (50 or 100 mL) containing ethyltriphenylphosphonium bromide ($EtPh_3PBr$) (1 mmol) to give the catalyst solution ((TPP)AlCl–$EtPh_3PBr$).

Copolymerization Reaction. A 100-mL round-bottom flask fitted with a three-way stopcock containing phthalic anhydride (25 mmol) was purged with dry nitrogen, and dichloromethane (10 mL) and an epoxide (25 mmol) were added. To this mixture was then added the catalyst solution by a hypodermic syringe, and the reaction mixture was kept stirring magnetically in nitrogen at room temperature. After an appropriate reaction time, the volatile fractions were removed from the reaction mixture under reduced pressure, and the residue was subjected to repeated reprecipitation from chloroform/methanol to give slightly colored polymeric product. Conversion of phthalic anhydride was calculated from the intensities of the signals due to the phthalate group of alkylene phthalate and phthalic anhydride remained unreacted in the ^1H NMR spectrum of the reaction mixture. The composition of the product was also determined by ^1H NMR.

Block Copolymerization. The copolymerization of phthalic anhydride and an epoxide initiated by the living copolymer of phthalic anhydride and another epoxide (block copolymerization) was carried out by a similar procedure. An aliquot of the above copolymerization mixture, after the complete consumption of the comonomers (system I), was added to an equimolar mixture of phthalic anhydride and another epoxide (25 mmol/25 mmol). The block copolymerization of epoxide or lactone initiated by the living copolymer of phthalic anhydride and epoxide was performed under similar conditions by the addition of a prescribed amount of these monomers to system I. Ternary block copolymerization was carried out by a procedure similar to that described above.

Measurements. ^1H NMR spectra of the reaction mixture were measured in $CDCl_3$ by using a JEOL type JNM GX-400 spectrometer operating at 399.7 MHz. Chemical shifts were determined with respect to undeuterated chloroform (δ 7.28). Infrared spectra of the reaction mixture were measured with a Hitachi 260-30 infrared spectrophotometer. Vapor pressure osmometry (VPO), for the determination of the number-average molecular weight ($\bar{M}_n$) of the polymer, was performed in benzene on a Corona 117 molecular weight apparatus, using as a standard polystyrene: $\bar{M}_n = 2800$, $\bar{M}_w/\bar{M}_n$ (ratio of weight-average molecular weight to number-average molecular weight) = 1.05, from Toyo Soda Manufacturing Co., Ltd. Gel permeation chromatography (GPC) of the reaction mixture, for the convenient estimation of the 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 $mL{\cdot}min^{-1}$. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000–3000 (two), 3000 (one), and 2000 (one) Å. A molecular weight calibration curve was obtained by using standard polystyrenes: $\bar{M}_n = 107000$ ($\bar{M}_w/\bar{M}_n = 1.01$), $\bar{M}_n = 16700$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 6200$ ($\bar{M}_w/\bar{M}_n = 1.04$), and $\bar{M}_n = 2800$ ($\bar{M}_w/\bar{M}_n = 1.05$), from Toyo Soda Manufacturing Co., Ltd.

Results and Discussion

Copolymerization of Phthalic Anhydride and Epoxide. Copolymerization of phthalic anhydride and 1,2-epoxypropane (25 mmol/25 mmol) by using the system of (TPP)AlCl (1) coupled with ethyltriphenylphosphonium bromide (1 mmol/1 mmol, (TPP)AlCl–$EtPh_3PBr$ system) as catalyst proceeded under mild conditions until the comonomers were completely consumed (Figure 1). The infrared spectrum of the reaction mixture showed a strong absorption at 1720 cm^{-1} due to the carbonyl group of phthalate units of the copolymer. Figure 2 shows the ^1H NMR spectrum of the reaction mixture at the final stage, in which the signals due to phthalic anhydride at δ 7.8 and 7.9 are hardly observed, while the signals due, respectively, to methyl (a, δ 1.4), methylene (b, δ 4.4), methine (c, δ 5.4), and phenylene protons of methylethylene phthalate units appear. Considering the absence of the signals corresponding to methylene and methine protons of the repeating oxymethylethylene units at about δ 3.4, these observations demonstrate the formation of alternating co-

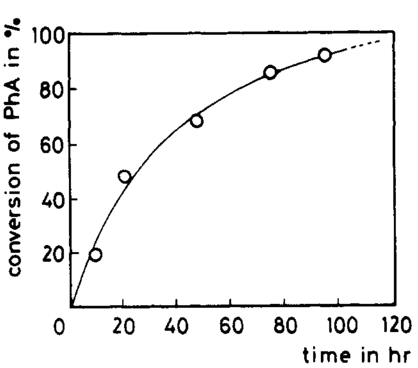


Figure 1. Copolymerization of phthalic anhydride (PhA) and 1,2-epoxypropane (PO) with the (TPP)AlCl–EtPh$_3$PBr system: time–conversion curve; $[PhA]_0/[PO]_0/[(TPP)AlCl]_0/[EtPh_3PBr]_0 = 25/25/1/1$ ($[(TPP)AlCl]_0 = 28.6$ mM), in CH$_2$Cl$_2$, 30 mL at room temperature.

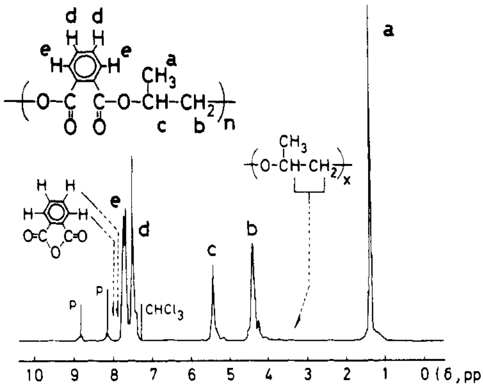


Figure 2. ^{1}H NMR spectrum of the reaction mixture in CDCl$_3$ in the copolymerization of phthalic anhydride and 1,2-epoxypropane with the (TPP)AlCl–EtPh$_3$PBr system; reaction conditions: see Figure 1; P, signals due to porphyrin.

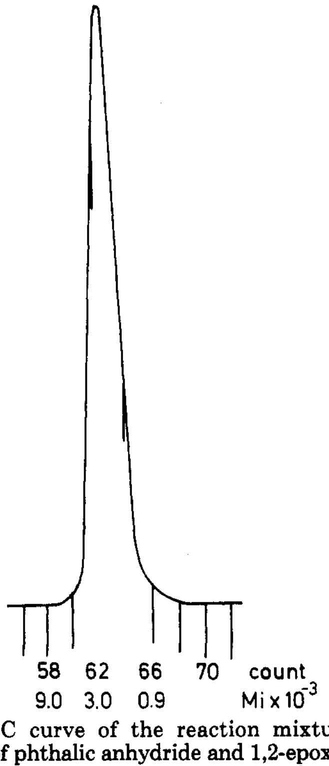


Figure 3. GPC curve of the reaction mixture in the copolymerization of phthalic anhydride and 1,2-epoxypropane with the (TPP)AlCl–EtPh$_3$PBr system; reaction conditions: see Figure 1, conversion ≈ 100%, $\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.09$.

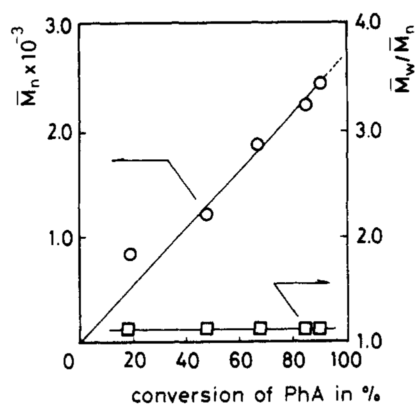


Figure 4. Copolymerization of phthalic anhydride (PhA) and 1,2-epoxypropane with the (TPP)AlCl–EtPh$_3$PBr system: relationship between $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (□)) of copolymer and conversion of PhA; reaction conditions: see Figure 1.

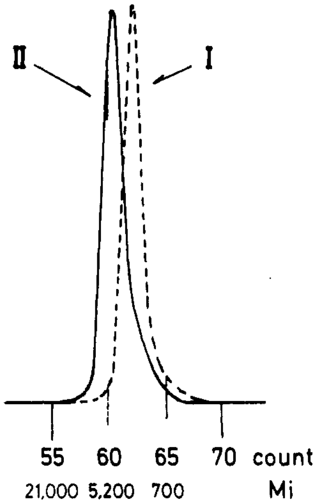


Figure 5. GPC profile of the copolymerization of phthalic anhyride (PhA) and 1,2-epoxypropane (PO) initiated by the copolymer of phthalic anhydride and 1,2-epoxypropane prepared with the (TPP)AlCl–EtPh$_3$PBr system; $[PhA]_0/[PO]_0/[\text{precopolymer}]_0 = 25/25/1$, in CH$_2Cl_2$ at room temperature, conversion ≈ 100%; peak I, starting copolymer, $\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.11$; peak II, reaction mixture finally obtained, $\bar{M}_n = 4200$, $\bar{M}_w/\bar{M}_n = 1.19$.

polymer from phthalic anhydride and 1,2-epoxypropane in the present copolymerization reaction. High catalytic activity of the (TPP)AlCl–EtPh$_3$PBr system even at room temperature is noteworthy, since much higher temperature is usually required for the copolymerization of cyclic acid anhydride and epoxide by the catalyst systems so far reported.[8]

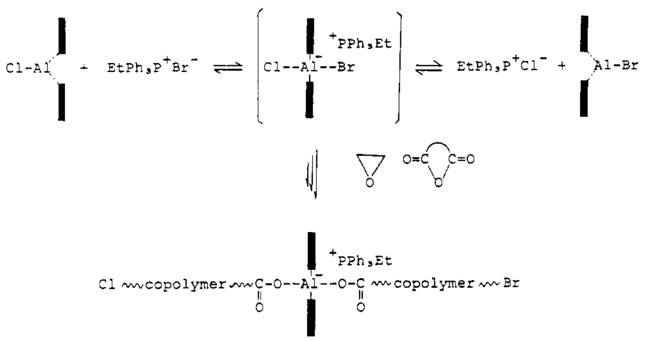
Another interesting observation of particular importance is the unusually narrow molecular weight distribution of the copolymer, as shown by the GPC curve of the reaction mixture (Figure 3). The number-average molecular weight ($\bar{M}_n$) of the copolymer linearly increased with the progress of the reaction, while the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$) remained almost constant close to 1 (Figure 4). These observations strongly indicate the rapid and quantitative initiation together with the absence of chain transfer and termination in the copolymerization of phthalic anhydride and 1,2-epoxypropane catalyzed by the (TPP)AlCl–EtPh$_3$PBr system. In order to confirm the living nature of the present copolymerization reaction, the comonomers (phthalic anhydride/1,2-epoxypropane = 25 mmol/25 mmol) were added further after the completion of the reaction. In the GPC profile shown in Figure 5, the peak (I) corresponding to the copolymer at the first stage disappeared, while a sharp elution curve (peak (II)) was observed at a higher molecular weight region. Thus, the

Table I
Copolymerization of Phthalic Anhydride (PhA) and Epoxide with the (TPP)AlCl-EtPh$_3$PBr System[a,b]

run	epoxide	$10^{-3}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[d]	N_p/N_{Al}[e]
1	epoxyethane[21]	(1.7)	1.16	(2.8)
2	1,2-epoxypropane	3.0 (2.5)	1.09	1.7 (1.9)
3	1,2-epoxybutane	(2.8)	1.11	(2.0)
4	1-phenyl-1,2-epoxyethane	2.7 (2.1)	1.14	2.5 (3.2)
5	1-phenoxymethyl-1,2-epoxyethane	3.6 (3.0)	1.08	2.1 (2.5)
6	*cis*-2,3-epoxybutane	3.3 (3.1)	1.11	1.7 (1.8)
7	*trans*-2,3-epoxybutane	3.4 (2.7)	1.09	1.6 (2.0)
8	1,2-epoxycyclohexane	4.0 (3.4)	1.17	1.5 (1.8)

[a] $[PhA]_0/[epoxide]_0/[(TPP)AlCl]_0/[EtPh_3PBr]_0 = 25/25/1/1$, in CH_2Cl_2 (30 mL) at room temperature for 4–16 days, conversion ≈ 100%.[20] [b] Product was confirmed to be the alternating copolymer (poly(alkylene phthalate)).[21] [c] By VPO; in parentheses, by GPC calibrated with standard polystyrene. [d] By GPC. [e] Number of polymer molecules per molecule of aluminum porphyrin. $N_p = Y_p\bar{M}_n^{-1}$; Y_p, yield of copolymer in grams; $\bar{M}_n$, number-average molecular weight of copolymer measured by VPO. In parentheses, the value based on $\bar{M}_n$ estimated by GPC.

Scheme I



copolymerization reaction at the second stage actually takes place from the reactive growing end of the copolymer formed at the first stage, confirming the living nature of the copolymerization of phthalic anhydride and 1,2-epoxypropane catalyzed by the (TPP)AlCl–EtPh$_3$PBr system.

This catalyst system was found also effective for the copolymerization of phthalic anhydride with epoxides other than 1,2-epoxypropane, as summarized in Table I. Various mono- and disubstituted epoxides copolymerized alternately under mild conditions with phthalic anhydride to afford the corresponding polyesters of well-regulated chain length.[21] Such a high regulation as to the sequence, as well as the number of the repeating units of copolymer (living and alternating copolymerization) is the first achievement in the field of polymer synthesis. The formation of copolymer molecules almost twice as many with respect to the molecules of aluminum porphyrin is observed in the reactions using various epoxides, as shown in the last column in Table I, where N_p and N_{Al} represent the numbers of the molecules of copolymer and aluminum porphyrin, respectively. This is in conformity with the proposed mechanism of the copolymerization reaction of phthalic anhydride and epoxide with the (TPP)AlCl–EtPh$_3$PBr system, in which the reaction proceeds simultaneously on both sides, respectively, of a metalloporphyrin plane (see Scheme I).[22]

Synthesis of Block Copolymers. The above finding prompted us to apply this excellent catalyst system, (TPP)AlCl–EtPh$_3$PBr, to the synthesis of novel block copolymers consisting of a wide variety of block sequences with controlled chain length.

Block Copolymerization of Phthalic Anhydride and Epoxide. As can be expected from the result shown in Figure 5, the living copolymer formed from phthalic anhydride and 1,2-epoxypropane efficiently initiated the copolymerization of phthalic anhydride with epoxyethane or 1,2-epoxybutane to give the corresponding block copolymer with narrow molecular weight distribution. The living copolymer from phthalic anhydride and 1,2-epoxybutane also gave rise from its reactive growing end to the copolymerization of phthalic anhydride and 1,2-epoxypropane, producing the block copolymer with poly(ethylethylene phthalate) and poly(methylethylene phthalate) sequences of very narrow distribution as to the molecular weight (Table II). The contents of the repeating ethylethylene phthalate and methylethylene phthalate units were found to be almost equal at the final stage by ^{1}H NMR of the reaction mixture.

As exemplified by the GPC profile of the copolymerization of phthalic anhydride and 1,2-epoxypropane initiated by the living copolymer of phthalic anhydride and 1,2-epoxybutane (Figure 6), the quantitative initiation by the living, reactive growing end was demonstrated by the absence of the starting copolymer (peak I) in the final product (peak II). The length of the poly(methylethylene phthalate) chain was successfully controlled by changing the conversion of the second comonomers (Figure 7). These observations indicate the possible synthesis of block copolymers with a desired number of sequences of various poly(alkylene phthalate) blocks with well-controlled chain lengths.

Block Copolymerization of Epoxide. The addition of epoxide alone to the living poly(alkylene phthalate) also brought about a clear increase in the molecular weight of the product without broadening the molecular weight distribution. An example is shown by the GPC profile of the polymerization of 1,2-epoxypropane initiated by the living poly(methylethylene phthalate) (peak I) prepared from phthalic anhydride and 1,2-epoxypropane by using the (TPP)AlCl–EtPh$_3$PBr catalyst system (Figure 8). A sharp elution curve (peak II) at the higher molecular weight region with respect to the initial polyester (peak I) indicates the quantitative formation of a binary block copolymer consisting of polyester and polyether chains with well-regulated molecular weight, the contents of which were found to be 45% and 55%, respectively. Further-

Table II
Block Copolymerization of Phthalic Anhydride (PhA) and Epoxide from the Living Copolymer of Phthalic Anhydride and Epoxide

	precopolymer[a]			block copolymer[b]		
run	epoxide	$10^{-3}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	epoxide	$10^{-3}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	1,2-epoxypropane	2.4	1.12	epoxyethane[21]	3.3	1.18
2	1,2-epoxypropane	2.5	1.09	1,2-epoxybutane	4.6	1.17
3	1,2-epoxybutane	2.6	1.10	1,2-epoxypropane	4.6	1.08

[a] $[PhA]_0/[epoxide]_0/[(TPP)AlCl]_0/[EtPh_3PBr]_0 = 25/25/1/1$, in CH_2Cl_2 at room temperature, conversion ≈ 100%,[20] alternating copolymer (poly(alkylene phthalate)).[21] [b] $[PhA]_0/[epoxide]_0/[precopolymer]_0 = 25/25/1$, in CH_2Cl_2 at room temperature, conversion ≈ 100%,[20] alternating copolymer (poly(alkylene phthalate)).[21] [c] By GPC calibrated with standard polystyrene.

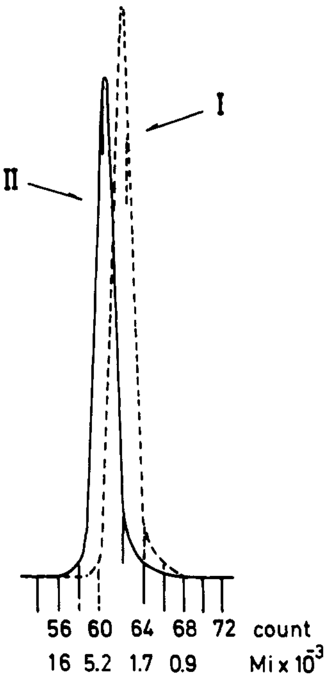


Figure 6. GPC profile of the block copolymerization of phthalic anhydride (PhA) and 1,2-epoxypropane (PO) initiated by the living copolymer of phthalic anhydride and 1,2-epoxybutane; $[PhA]_0/[PO]_0/[precopolymer]_0$ = 25/25/1, in CH_2Cl_2 at room temperature, conversion ≈ 100%; peak I, starting copolymer, $\bar{M}_n$ = 2600, $\bar{M}_w/\bar{M}_n$ = 1.10; peak II, reaction mixture finally obtained, $\bar{M}_n$ = 4600, $\bar{M}_w/\bar{M}_n$ = 1.08.

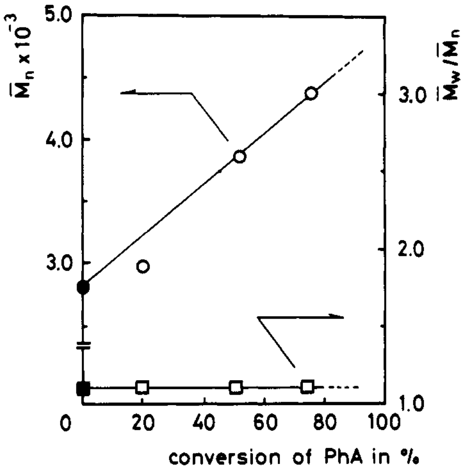


Figure 7. Block copolymerization of phthalic anhydride and 1,2-epoxypropane initiated by the living copolymer of phthalic anhydride and 1,2-epoxybutane: dependence of $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (□)) upon conversion; ● and ■ represent respectively $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the starting living copolymer; reaction conditions: see Figure 6.

more, a polyester–polyether–polyester (ABA) type of ternary block copolymer (polyester, 65%; polyether, 35%) could be synthesized by the successive addition of an equimolar mixture of phthalic anhydride and 1,2-epoxypropane to the reaction system of the above binary copolymerization (peak II), from which the residual, unreacted 1,2-epoxypropane had been removed by evacuation. GPC of the final reaction mixture after the complete consumption of the comonomers showed a sharp elution curve (peak III) without peak II due to the starting binary block copolymer, indicating the persistence of the living nature of the first stage of the copolymerization in the subsequent stages.

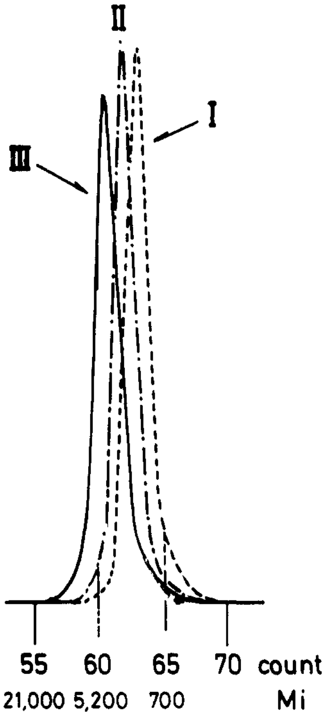


Figure 8. GPC profile of the block copolymerization of 1,2-epoxypropane (PO), followed by the mixture of phthalic anhydride (PhA) and 1,2-epoxypropane, initiated by the living copolymer of phthalic anhydride and 1,2-epoxypropane. $[PO]_0/[precopolymer]_0$ = 100, in CH_2Cl_2 at room temperature for 7 days, conversion = 31% (at the second stage); $[PhA]_0/[PO]_0/[prepolymer]_0$ = 25/25/1, in CH_2Cl_2 at room temperature for 7 days, conversion ≈ 100% (at the third stage); peak I, precopolymer, $\bar{M}_n$ = 2100, $\bar{M}_w/\bar{M}_n$ = 1.15; peak II, reaction mixture at the second stage, $\bar{M}_n$ = 3100, $\bar{M}_w/\bar{M}_n$ = 1.10; peak III, reaction mixture at the third stage, $\bar{M}_n$ = 4900, $\bar{M}_w/\bar{M}_n$ = 1.12.

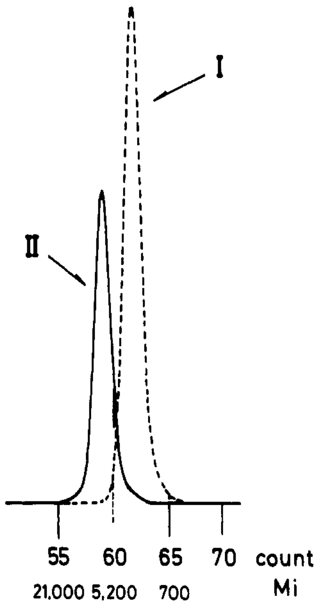


Figure 9. GPC profile of the block copolymerization of β-butyrolactone (BL) initiated by the living copolymer of phthalic anhydride and 1,2-epoxypropane,[25] $[BL]_0/[precopolymer]_0$ = 100, in CH_2Cl_2 at room temperature for 3.6 days, conversion = 100%; peak I, precopolymer, $\bar{M}_n$ = 3000, $\bar{M}_w/\bar{M}_n$ = 1.07; peak II, reaction mixture, $\bar{M}_n$ = 6.800, $\bar{M}_w/\bar{M}_n$ = 1.07.

Block Copolymerization of Lactone. The block copolymerization of β-butyrolactone (four-membered ring) or ε-caprolactone (seven-membered ring) was attempted by using the reaction system of the copolymerization of phthalic anhydride and epoxide containing the living polyester. In the case of β-butyrolactone, the product was

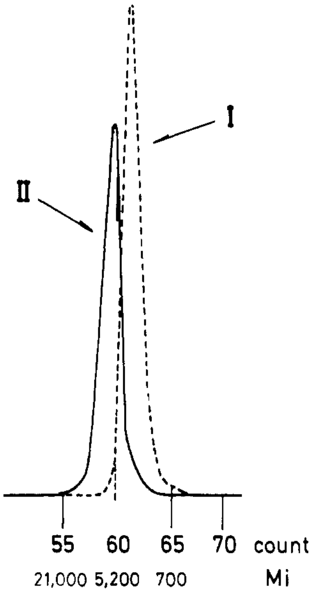


Figure 10. GPC profile of the block copolymerization of ϵ-caprolactone (CL) initiated by the living copolymer of phthalic anhydride and 1,2-epoxypropane, reactive end group of which was allowed to react with 1,2-epoxypropane prior to the addition of CL,[26] $[\mathrm{CL}]_0/[\mathrm{precopolymer}]_0 = 100$, in CH_2Cl_2 at room temperature for 7 days, conversion = 62%; peak I, precopolymer, $\bar{M}_n = 3300$, $\bar{M}_w/\bar{M}_n = 1.08$; peak II, reaction mixture, $\bar{M}_n = 6000$, $\bar{M}_w/\bar{M}_n = 1.15$.

found to be virtually the block copolymer consisting of poly(alkylene phthalate) and poly(β-butyrolactone) sequences, although a small portion of the prepolymer unfavorably remained unreacted. On the other hand, the block copolymer could hardly be obtained from ϵ-caprolactone even in a prolonged reaction. These results are considered closely related to the fact that (porphinato)aluminum carboxylate cannot initiate the polymerization of ϵ-caprolactone but gives rise effectively to the polymerization of β-butyrolactone,[23] while a quite reverse preference for ϵ-lactone and β-lactone is observed for (porphinato)aluminum alkoxide.[24]

On the other hand, the structure of the reactive end group of the living copolymer obtained from the equimolar mixture of phthalic anhydride and epoxide, at the final stage of the reaction as detected by NMR, is a (porphinato)aluminum carboxylate.[7] However, the existence of a trace of a (porphinato)aluminum alkoxide may not be excluded (see eq 3 and 4 and Scheme I). In order to convert the structure of the reactive end group of the living copolymer completely into a (porphinato)aluminum carboxylate, the reaction system containing the living copolymer was allowed to react with excess molar equivalents of phthalic anhydride with respect to aluminum porphyrin.[25] Attempted block copolymerization of β-butyrolactone using living prepolymer (poly(ethylethylene phthalate)) after the above treatment resulted in a quantitative initiation leading to successful formation of the block copolymer with narrow molecular weight distribution. The absence of unreacted prepolymer in the product was confirmed by the GPC curve of the reaction mixture (Figure 9), and the contents of poly(ethylethylene phthalate) and poly(β-butyrolactone) blocks by the ^1H NMR analysis were 20% and 80%, respectively.

In contrast, the block copolymerization of ϵ-caprolactone was initiated quantitatively when the living copolymer had been allowed to react with an excess of 1,2-epoxypropane prior to the addition of ϵ-caprolactone.[26] The block copolymer of poly(ethylethylene phthalate) and poly(ϵ-caprolactone) thus obtained showed a unimodal and sharp elution curve (Figure 10), indicating the narrow molecular weight distribution of each block. In this case, the quantitative conversion of the terminal structure of the living copolymer into a (porphinato)aluminum alkoxide by the reaction with epoxide is considered responsible for the change in the reactivity of the living copolymer toward ϵ-caprolactone. The content of the repeating units from ϵ-caprolactone was found to be 60%.

Conclusion

The first example of a high degree of regulation as to the sequence as well as the molecular weight of copolymer was realized by using the system of aluminum porphyrin coupled with a quaternary organic salt as catalyst in the copolymerization of phthalic anhydride and epoxide. This is rather surprising since the copolymerization reaction involves two different elementary reaction steps, by which the broadening of the molecular weight distribution is more likely to occur.

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(15) The copolymerization of phthalic anhydride and 1,2-epoxypropane by (TPP)AlX (X = Cl, OR) took place very slowly to give the copolymer rich in ether linkages in a very low yield upon prolonged reaction.
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(20) By ^1H NMR spectrum of the reaction mixture, based on the signals corresponding to phthalic anhydride and the phthalate unit in the copolymer.
(21) The absence of repeating ether units in the copolymer was confirmed by the ^1H NMR spectrum of the reaction mixture. In the case of ethylene oxide, the reaction mixture contained 20% repeating oxyethylene units.
(22) In the copolymerization reaction of phthalic anhydride and 1,2-epoxypropane by using the system of (TPP)AlCl coupled with $Et_4N^+Br^-$ as catalyst, the terminal residues of the copolymer carrying chlorine and bromine were detected by the ^{13}C NMR spectrum of the reaction mixture.[7]
(23) The "living" polymer of β-butyrolactone with a (porphinato)aluminum carboxylate growing end (3 in eq 2) gives rise to the block copolymerization of β-propiolactone[12] but not to that of ϵ-caprolactone.
(24) The "living" polymer of 1,2-epoxypropane with a (porphinato)aluminum alkoxide growing end (2 in eq 1) gives rise to the block copolymerization of ϵ-caprolactone but not to that of β-butyrolactone.[12]
(25) Eight molar equivalents of phthalic anhydride with respect to aluminum porphyrin was added to the copolymerization system after the completion of the first stage of the co-

polymerization, and the mixture was stirred overnight at room temperature.

(26) Ten molar equivalents of 1,2-epoxypropane with respect to aluminum porphyrin was added to the copolymerization system after the first stage of the copolymerization, and the mixture was stirred overnight at room temperature, followed by evacuating the reaction system to remove 1,2-epoxypropane that remained unreacted.

Recyclable Polymer-Bound Lanthanide Diene Polymerization Catalysts

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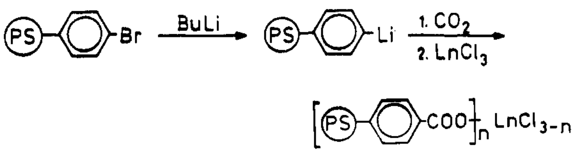
ABSTRACT: Divinylbenzene cross-linked polystyrene bound neodymium and cerium catalysts that polymerize butadiene stereospecifically to form *cis*-1,4-polybutadiene in the presence of organoaluminum reagents are described. These immobilized catalysts can be recycled without significant loss of activity or selectivity. Neodymium chloride was also attached to carboxylated polyethylene to form a polyethylene-bound neodymium carboxylate that formed a homogeneous diene polymerization catalyst in solutions of aromatic solvents in the presence of triethylaluminum and ethylaluminum dichloride. Polybutadiene was successfully separated from the precipitated polyethylene-bound catalyst at room temperature after dilution of the reaction mixture with additional solvent but the activity of these polyethylene-entrapped catalysts was not significantly better than the activity of the polystyrene-bound catalysts.

Lanthanide salts in the presence of organoaluminum reagents are known to be useful as catalysts in stereospecific polymerizations of butadiene and isoprene.[1-4] Generally these catalysts are used in the form of suspensions in hydrocarbon solvents although homogeneous polymerizations can be carried out with lanthanide carboxylates instead of lanthanide halides as catalyst precursors.[5] These catalysts have not proven to be reusable. In this paper, we describe our initial efforts to develop recyclable lanthanide diene polymerization catalysts which have led to the preparation of reusable polymer-bound catalysts for these polymerization reactions.

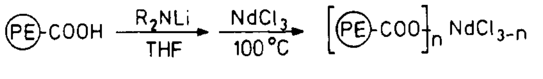
Although polymer-supported catalysts have seen widespread use in other reactions,[6,7] there are fewer examples of polymer-supported diene polymerization catalysts. Ziegler-type catalysts for diene polymerization have been anchored onto polymers,[8] but there are no reports in which lanthanide catalysts have been used in this fashion. In order to develop recyclable lanthanide polymerization catalysts, we had to first bind such catalysts to a suitable insoluble polymer. Since several sorts of insoluble carboxylated polymers are readily available and since lanthanide carboxylates were reported to function as useful lanthanide diene polymerization catalyst precursors, our initial studies focused on polymeric carboxylate salts of cerium and neodymium. The studies reported in this paper describe polystyrene-bound and polyethylene-bound carboxylate salts of neodymium and their use in diene polymerization.

Carboxylated DVB-cross-linked polystyrene (2% divinylbenzene cross-linking) was obtained by literature procedures[9] and exchanged with either neodymium chloride or cerium chloride (eq 1). The resulting resins mainly contained $Nd(O_2C{-}PS)_3$ and $Ce(O_2C{-}PS)_3$, which had Nd and Ce loadings of 0.86 and 1.19 mmol of Nd and Ce/g of polymer, respectively, as determined by combustion of these polymers and analysis of the ash. Each of these polystyrene-bound lanthanide carboxylates contained some residual chloride based on analysis for halogen using a Volhard titration. The chloride content of the Nd resin was 0.3% and the Ce resin contained 0.34% chloride (0.08 and 0.10 mmol of Cl/g of polymer, respectively). We presume that the exchange process by which the lanthanide salts are incorporated into the polystyrene did not result in quantitative exchange of chloride from the lanthanide precursor. Such a result is perhaps expected because of the increasing amount of cross-linking that occurs as the resin-bound carboxylates displace chloride from the lanthanide metal. We were unable to ascertain from IR spectroscopy if small amounts of $PS{-}CO_2Li$ remained unreacted in any of these catalyst precursors. However, flame tests of these polymers failed to detect lithium.



(1)

Neodymium derivatives of carboxylated polyethylene were obtained from commercially available oxidized polyethylene (0.5 mequiv of CO_2H/g of polymer) by the procedure of eq 2. Analysis of the resulting polymer for neodymium and chloride indicated that a mixture of neodymium chlorocarboxylates of average stoichiometry $(PE{-}CO_2)_{2.3}NdCl_{0.7}$ had formed. A band at 1710 cm^{-1} in the neodymium-containing polyethylene indicated either that some unreacted carboxylic acid groups or that other carbonyl groups remained in this polymer.[10]



$$\text{PE-COOH} \xrightarrow[\text{THF}]{R_2NLi} \xrightarrow[100\,^{\circ}C]{NdCl_3} [\text{PE-COO}]_n NdCl_{3-n} \qquad (2)$$

Polymerizations of dienes were carried out by first forming the catalyst and then adding the diene to be polymerized. In a typical procedure, 0.02 g of the neodymium-containing carboxylated polystyrene resin (0.017 mmol of Nd) and 1.7 mL of a benzene solution that was 0.41 M in i-Bu_3Al and 0.22 M in $AlEt_2Cl$ were added to a 20-mL glass tube and allowed to stand at room temperature for 3 h. Then 4.8 mL of butadiene in benzene (0.15 g of C_4H_6/mL) was added and the glass tube was sealed. The reactions were allowed to stir using a magnetic stirring bar for 2 days. Workup consisted of addition of 10 mL of additional dry benzene to dilute the viscous reaction solution followed by centrifugation and forced

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