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Synthesis of Polyester–Polyether Block Copolymer with Controlled Chain Length from β-Lactone and Epoxide by Aluminum Porphyrin Catalyst

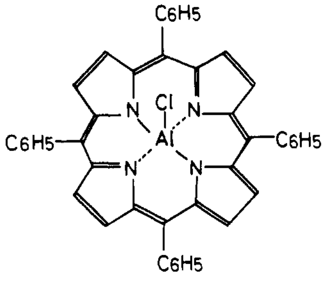
Tomokazu Yasuda, Takuzo Aida, and Shohei Inoue*

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. *Received December 29, 1983*

ABSTRACT: (5,10,15,20-Tetraphenylporphinato)aluminum chloride brings about the living polymerization of β-propiolactone and β-butyrolactone to give the corresponding polyester with narrow molecular weight distribution. Polyester-polyether or polyester–polyester block copolymers with narrow molecular weight distribution can be synthesized by adding epoxide or β-lactone as the second monomer to this living polyester. The chain lengths of the blocks can be regulated by changing the amount of the second monomer reacted.

Introduction

We have reported the living polymerization of epoxide such as ethylene oxide, propylene oxide, and 1,2-butene oxide catalyzed by (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1) proceeding with an aluminum alkoxide as propagating end group.[1,2] By the reaction of another epoxide with this living end, polyether–polyether block copolymer can be obtained.[3]



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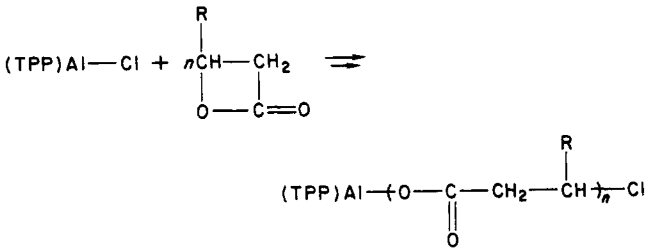
TPPAlCl

More recently, (TPP)AlCl has been found to exhibit high catalytic activity for the polymerization of β-propiolactone and β-butyrolactone to provide the corresponding polyester with well-controlled molecular weight and narrow molecular weight distribution.[4] The propagating end group in this polymerization has been established to be a (porphinato)aluminum carboxylate[5] (Scheme I).

In the present paper are described further details as to the living nature of the polymerization of β-lactone and its application to the synthesis of block copolymers having polyester–polyether or polyester–polyester sequence with narrow molecular weight distribution. There have been reported so far very limited examples as to the syntheses of polyester–polyether type block copolymer from β-lactone and epoxide[6] and of polyester–polyester type block copolymer from substituted β-lactones,[7] without detailed information about the molecular weight of the products.

Scheme I



Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ((TPP)H_2) was synthesized by the reaction of pyrrole with benzaldehyde.[8] Diethylaluminum chloride (Et_2AlCl) was distilled under reduced pressure in a nitrogen atmosphere. Dichloromethane, washed with sulfuric acid and then neutralized with sodium bicarbonate, was dried over calcium chloride for 1 night and then fractionally distilled over calcium hydride in a nitrogen atmosphere. β-Propiolactone and β-butyrolactone, dried by stirring with calcium hydride overnight at room temperature, were purified by fractional distillation under reduced pressure in a nitrogen atmosphere over calcium hydride. Ethylene oxide, after stirring with a mixture of potassium hydroxide and calcium hydride at room temperature, was degassed to remove air and then collected in a trap cooled at the liquid nitrogen temperature. Propylene oxide was purified by refluxing over a mixture of potassium hydroxide and calcium hydride and then distilled twice in a nitrogen atmosphere.

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Measurement. Gel permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-802 UR gel permeation chromatograph equipped with a differential refractometer detector using tetrahydrofuran as eluent: flow rate, 1.2 mL·min^{-1}; columns, 60 cm long with pore size 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). The molecular weight and the molecular weight distribution were estimated on the basis of the calibration curve obtained by using standard poly(propylene glycols) (PPG) for the lower molecular weight region and standard poly(ethylene oxides) (PEO) for the higher molecular weight region. Standard poly(ethylene oxides) were obtained form Toyo Soda Manufacturing Co., Ltd.: $\bar{M}_n = 22000$ ($\bar{M}_w/\bar{M}_n = 1.14$), $\bar{M}_n = 39000$ ($\bar{M}_w/\bar{M}_n = 1.03$), and $\bar{M}_n = 72000$ ($\bar{M}_w/\bar{M}_n = 1.02$). Standard poly(propylene glycols) were obtained from Lion Fat & Oil Co., Ltd.: $\bar{M}_n = 1000$ and 2000 ($\bar{M}_w/\bar{M}_n \simeq 1$).

Vapor pressure osmometry (VPO) was carried out on a Corona 117 vapor pressure osmometer using benzene as solvent at 50 or 40 °C (±0.1 °C). The number-average molecular weight ($\bar{M}_n$) of polymer of β-butyrolactone was calculated by the calibration curve obtained by using standard polystyrene of $\bar{M}_n = 10000$ ($\bar{M}_w/\bar{M}_n = 1.09$) or $\bar{M}_n = 43900$ ($\bar{M}_w/\bar{M}_n = 1.01$).

^{1}H NMR spectrum measurement was performed in dichloromethane or deuterated chloroform, using a JEOL Type 4H-A spectrometer operating at 100 MHz.

Preparation of Catalyst. (5,10,15,20-Tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1**) was prepared by the equimolar reaction between 5,10,15,20-tetraphenylporphine ((TPP)H_2) and diethylaluminum chloride (Et_2AlCl).[3] In a Pyrex tear-drop type flask (100 mL) equipped with a three-way stopcock, (TPP)H_2 (1 mmol) was purged with dry nitrogen gas, and then CH_2Cl_2 (20 mL) was introduced to dissolve the $TPPH_2$. To this solution was added Et_2AlCl (1.2 mmol, in 20% excess to (TPP)H_2) by syringe under a nitrogen atmosphere at room temperature with constant stirring. After a definite time, the volatile materials were removed from this reaction mixture under reduced pressure to give a purple solid with metallic luster. CH_2Cl_2 (20 mL) was introduced to this flask to dissolve the product, to obtain the catalyst solution.

Polymerization. To the catalyst solution under constant stirring was added the monomer by syringe at room temperature in a nitrogen atmosphere. After a definite time, a large excess of methanol was added to the reaction mixture to stop the polymerization, and then volatile materials were removed under reduced pressure to leave the product. The conversion was calculated by either of the following: (1) from the weight of the residue by subtracting the amount corresponding to the catalyst or (2) from the intensity ratio of the signals due to the monomer and the polymer in the ^{1}H NMR spectrum of the reaction mixture; for β-propiolactone, monomer 3.6 ppm (t, CH_2CO) and polymer 2.7 ppm (t, CH_2CO); for β-butyrolactone, monomer 1.5 ppm (d, CH_3) and polymer 1.2 ppm (d, CH_3).

In the case of β-propiolactone, the polymer was isolated as a slightly yellow-green powder by precipitation of the product from chloroform/methanol after shaking the chloroform solution with dilute hydrochloric acid. Anal. Calcd for $(C_3H_4O_2)_n$: C, 49.88; H, 5.59. Found: C, 49.77; H, 5.72.

Block Copolymerization. Prepolymer (homopolymer from the first monomer) was prepared by the polymerization of the corresponding monomer with (TPP)AlCl as described above, and then the second monomer was introduced to the prepolymer solution by trap-to-trap method[3] for ethylene oxide or by syringe for other epoxides and lactones. After a definite time, the conversion of the second monomer was determined by ^{1}H NMR spectroscopy of the reaction mixture: for ethylene oxide, monomer 2.4 ppm (s, CH_2) and polymer 3.4 ppm (s, CH_2); for propylene oxide, monomer 1.4 ppm (d, CH_3) and polymer 1.1 ppm (d, CH_3). To this polymerization mixture was added methanol to stop the polymerization, and the volatile materials were removed to leave the product.

Determination of Molecular Weight. A part of the obtained product was dissolved in tetrahydrofuran, the insoluble part (the catalyst residue) was filtered off using a Teflon filter with pore size 0.45 μm, and the solution was subjected to GPC analysis.

For the homopolymer of β-butyrolactone (BL), the polymer was subjected to VPO analysis after isolation by either of the following two methods. In one of the procedures, the obtained product was dissolved in chloroform and shaken with hydrochloric acid, and the solution was evaporated to leave the residue which was again dissolved in chloroform. This solution was subjected to gel permeation chromatography using chloroform as eluent: column, 60 cm long with pore size 8000 Å (one); flow rate, 11 mL·min^{-1}, to give the polymer as a slightly brown viscous liquid. In the other procedure, the obtained product was dissolved in a small amount of chloroform, diluted by a large amount of methanol, and added to hydrochloric acid. To this solution was added *n*-hexane (the same volume as methanol) with vigorous stirring, and a small amount of diethyl ether was added to this mixture to precipitate the polymer. Recovered polymer was dissolved in a small amount of chloroform, and the above operation was repeated twice to give the polymer as a slightly brown viscous liquid. The GPC curve of the polymer thus obtained showed no differences from the corresponding product before purification.

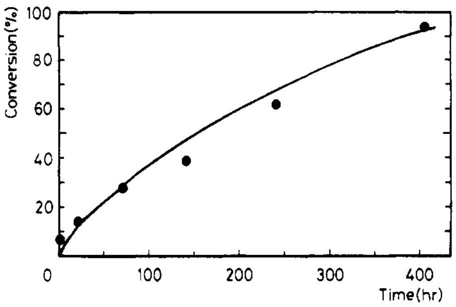


Figure 1. Time–conversion curve for the polymerization of β-propiolactone (PL) with (TPP)AlCl at room temperature in CH_2Cl_2. $[PL]_0/[(TPP)AlCl]_0 = 300$; $[(TPP)AlCl]_0 = 20.4$ mM.

The obtained product, after removal of volatile materials from the reaction mixture, may be directly subjected to VPO measurement without any further treatment, since the propagating end group in the polymerization of β-lactone was found to be sufficiently stable in air at room temperature. This procedure was applied to the polymer of β-butyrolactone (BL) obtained at $[BL]_0/[(TPP)AlCl]_0 = 200$.

The number of polymer molecules *N* was calculated by the following equation, where $[\text{monomer}]_0$ represents the initial amount of monomer in moles, conv the conversion in percent, and $\bar{M}_n$(VPO) the number-average molecular weight of polymer measured by VPO.

$$N = [\text{monomer}]_0 \times \frac{\text{conv}}{100} \times \frac{1}{\bar{M}_n(\text{VPO})}$$

Results and Discussion

Polymerization of β-Lactone Catalyzed by (TPP)AlCl. The polymerization of β-propiolactone catalyzed by (TPP)AlCl at room temperature proceeded more rapidly than that of β-butyrolactone[5] to give poly(β-propiolactone) quantitatively (Figure 1). The gel permeation chromatogram (GPC) of the resulting polymer showed the characteristics of the narrow molecular weight distribution as indicated by the ratio of the weight-average molecular weight to the number-average molecular weight ($\bar{M}_w/\bar{M}_n = 1.26$, $\bar{M}_n = 3.5 \times 10^3$). During the polymerization, the number-average molecular weight of the polymer increased linearly with conversion, keeping the molecular weight distribution narrow (Figure 2). As shown in Figure 3, a linear relationship was observed between the initial mole ratio of the monomer to the catalyst ($[\text{monomer}]_0/[\text{catalyst}]_0$) and the number-average molecular weight of the polymer obtained at 100% conversion.

The linear relationship between $\bar{M}_n$ (measured by VPO) and the initial mole ratio of the monomer to the catalyst was also observed in the polymerization of β-butyrolactone (Figure 4). The number of polymer molecules is calculated to be almost equal to the number of catalyst at any initial mole ratio of the monomer to the catalyst, as shown in Figure 5. Thus, the polymerization of β-lactones catalyzed

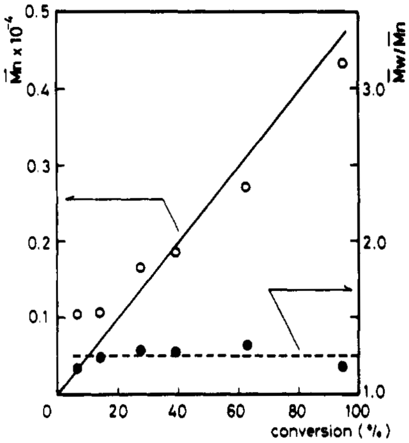


Figure 2. Polymerization of β-propiolactone (PL) with (TPP)AlCl. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and conversion. $[PL]_0/[(TPP)AlCl]_0 = 300$; $[(TPP)AlCl]_0 = 20.4$ mM. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC calibrated with PEO and PPG.

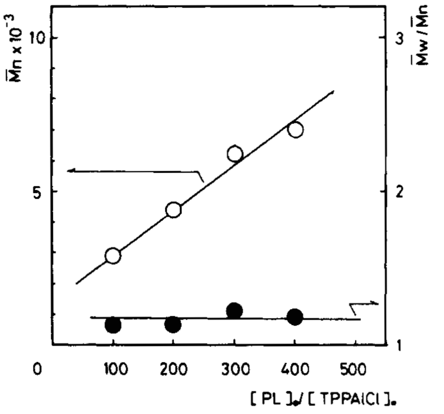


Figure 3. Polymerization of β-propiolactone (PL) with (TPP)AlCl. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and the initial mole ratio of PL to (TPP)AlCl. Conversion ≃ 100%. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

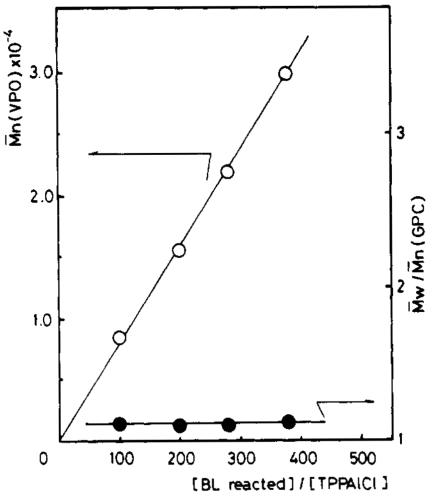


Figure 4. Polymerization of β-butyrolactone (BL) with (TPP)AlCl. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and the mole ratio of BL reacted to (TPP)AlCl. $\bar{M}_n$ as measured by VPO. $\bar{M}_w/\bar{M}_n$ as estimated by GPC.

by (TPP)AlCl is confirmed to proceed with a living nature. Thus, it is possible to control the molecular weight by changing the initial mole ratio of the monomer to the catalyst or by selecting a certain conversion, keeping a narrow molecular weight distribution.

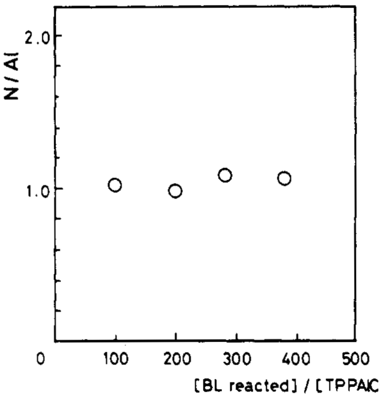
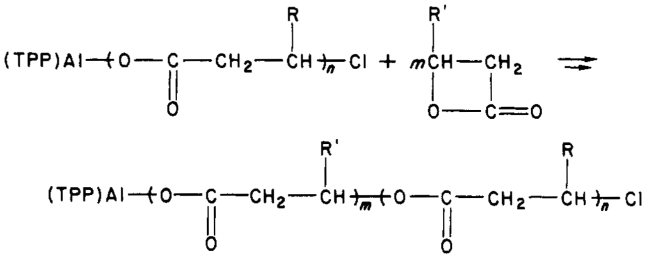


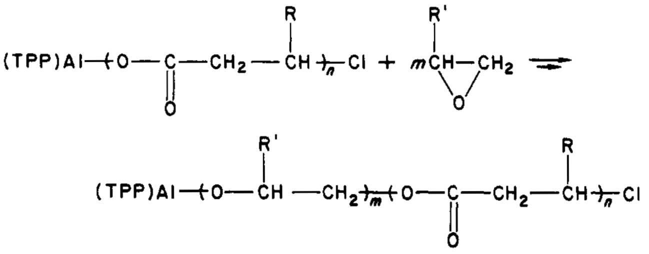
Figure 5. Polymerization of β-butyrolactone (BL) with (TPP)AlCl. Relationship between the ratio of number of polymer molecules (*N*) to number of aluminum atoms in catalyst (Al) and the initial mole ratio of BL to (TPP)AlCl.

Scheme II



$$(TPP)Al\!-\!\!\left(O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R}{|}}{C}H\right)_{\!n}\!-Cl + m\,\overset{\overset{R'}{|}}{C}H-CH_2\ (\text{ring } O-C{=}O) \rightleftharpoons (TPP)Al\!-\!\!\left(O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R'}{|}}{C}H\right)_{\!m}\!\!\left(O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R}{|}}{C}H\right)_{\!n}\!-Cl$$

Scheme III



$$(TPP)Al\!-\!\!\left(O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R}{|}}{C}H\right)_{\!n}\!-Cl + m\,\overset{\overset{R'}{|}}{C}H-CH_2\ (\text{ring } O) \rightleftharpoons (TPP)Al\!-\!\!\left(O-\overset{\overset{R'}{|}}{C}H-CH_2\right)_{\!m}\!\!\left(O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R}{|}}{C}H\right)_{\!n}\!-Cl$$

β-Butyrolactone–β-Propiolactone Block Copolymerization. By virtue of the living nature of the polymerization of β-lactones by (TPP)AlCl, block copolymerization of two different β-lactones was attempted. As the first step of the copolymerization, the living polymer of β-butyrolactone was prepared with (TPP)AlCl ($[BL]_0/[(TPP)AlCl]_0 = 100$, reaction time: 33 days, conversion = 60%, $\bar{M}_n = 4.4 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.05$ (GPC)). To this prepolymer, β-propiolactone was introduced with the initial mole ratio of the second monomer to the living prepolymer of 600. After 35 days β-propiolactone was found reacted to 100% conversion. As shown in GPC of the product thus obtained and of the prepolymer (Figure 6), the increase in molecular weight from that of the prepolymer, with a unimodal distribution, is confirmed, although a slight tailing in the lower molecular weight region is observed. The content of β-propiolactone unit in the block copolymer as determined by the ^{1}H NMR spectrum was found to be 88.8%, in good agreement with the calculated value from the conversion (90.0%). Thus, a polyester–polyester block copolymer with narrow molecular weight distribution can be prepared by the polymerization of β-propiolactone initiated from the living poly(β-butyrolactone) obtained with (TPP)AlCl (Scheme II).

Block Copolymerization of β-Lactone and Epoxide Catalyzed by (TPP)AlCl. (5,10,15,20-Tetraphenylporphinato)aluminum chloride ((TPP)AlCl) provides the living polyester from β-lactone[4] with a (tetraphenylporphinato)aluminum carboxylate as propagating end group.[5] If this carboxylate can react with epoxide, the

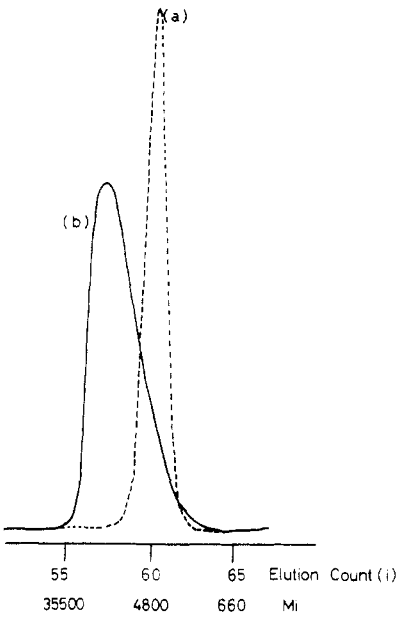


Figure 6. GPC of a β-butyrolactone–β-propiolactone block copolymer and the corresponding prepolymer of β-butyrolactone: (a) prepolymer, $\bar{M}_n$ = 4.4 × 10^3, $\bar{M}_w/\bar{M}_n$ = 1.05; (b) block copolymer, $\bar{M}_n$ = 1.02 × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.30, $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

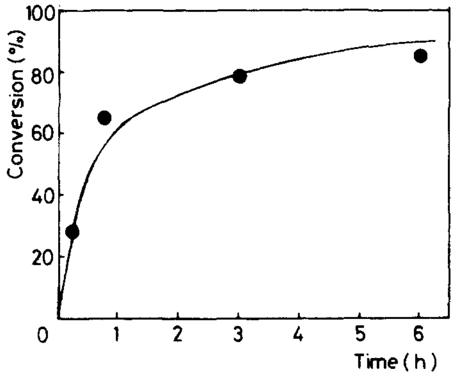


Figure 7. Time–conversion curve for the block copolymerization of ethylene oxide (EO) from prepolymer of β-butyrolactone (prepoly-BL) at room temperature in CH_2Cl_2. $[EO]_0/[prepoly\text{-}BL]_0$ = 200, $[prepoly\text{-}BL]_0$ = 26.9 mM.

product is a (porphinato)aluminum alkoxide which is known to be the propagating end group in the ring-opening polymerization of epoxide by aluminum porphyrin.[2] Such a transfer of the living nature of propagating end from carboxylate to alkoxide species will lead to the synthesis of polyester–polyether block copolymer with narrow molecular weight distribution (Scheme III).

β-Butyrolactone–Ethylene Oxide Block Copolymerization. When ethylene oxide was introduced into the living poly(β-butyrolactone) prepared by (TPP)AlCl ($\bar{M}_n$ = 2.0 × 10^3, $\bar{M}_w/\bar{M}_n$ = 1.09 (GPC)) with the initial mole ratio of ethylene oxide to the prepolymer of 200, ethylene oxide was rapidly consumed (Figure 7) and completely converted to the polymer. The GPC of the product obtained at 100% conversion (Figure 8) showed the absence of the prepolymer or homopoly(ethylene oxide) in the product. Thus, it is evident that β-butyrolactone–ethylene oxide block copolymer with narrow molecular weight distribution was produced with 100% efficiency. Between the number-average molecular weight of the block copolymer thus formed and the conversion of ethylene oxide, there was found a linear relationship as shown in Figure 9. Furthermore, the number-average molecular weight of the block copolymer obtained at 100% conver-

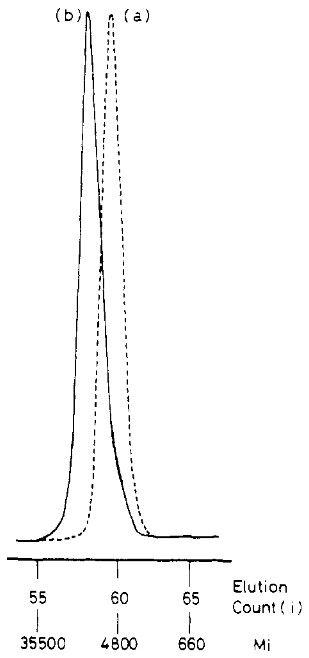


Figure 8. GPC of a β-butyrolactone–ethylene oxide block copolymer and the corresponding prepolymer of β-butyrolactone: (a) prepolymer, $\bar{M}_n$ = 2.0 × 10^3, $\bar{M}_w/\bar{M}_n$ = 1.09; (b) block copolymer, $\bar{M}_n$ = 7.7 × 10^3, $\bar{M}_w/\bar{M}_n$ = 1.14. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

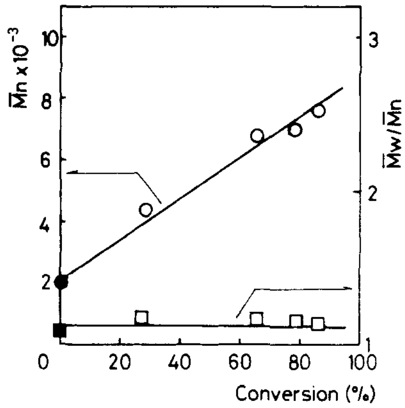


Figure 9. Block copolymerization of ethylene oxide (EO) from prepolymer of β-butyrolactone (prepoly-BL). Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (□) of the block copolymer and conversion. Prepolymer, $\bar{M}_n$ (●) = 2.0 × 10^3, $\bar{M}_w/\bar{M}_n$ (■) = 1.09. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

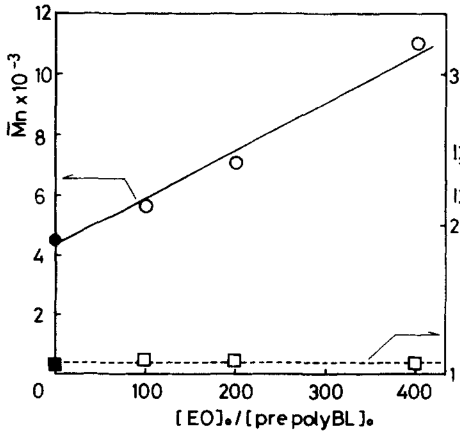


Figure 10. Block copolymerization of ethylene oxide (EO) from prepolymer of β-butyrolactone (prepoly-BL). Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (□) of the block copolymer and the initial mole ratio of EO to prepoly BL. Conversion ≃ 100%. Prepolymer, $\bar{M}_n$ (●) = 4.4 × 10^3, $\bar{M}_w/\bar{M}_n$ (■) = 1.05. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

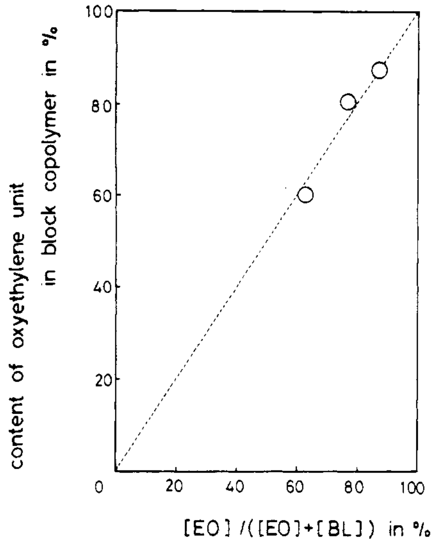


Figure 11. Block copolymerization of ethylene oxide (EO) from prepolymer of β-butyrolactone (prepoly-BL). Relationship between the mole fraction of reacted EO and the composition of the block copolymers. [BL], amount of prepoly-BL used, in moles with respect to repeating units; $[EO]_0$, amount of EO reacted in moles.

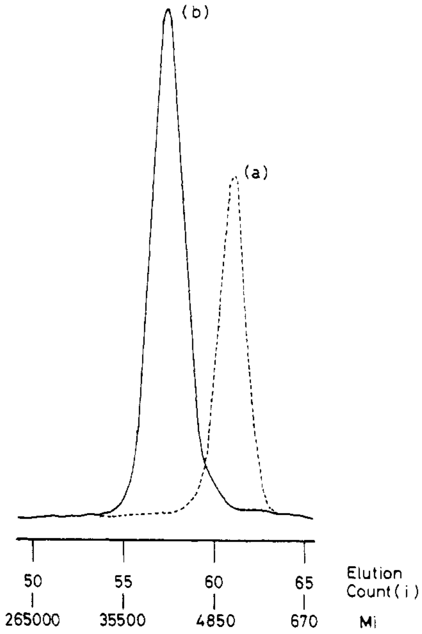


Figure 12. GPC of a β-butyrolactone–propylene oxide (PO) block copolymer and the corresponding prepolymer of β-butyrolactone (prepoly-BL). $[PO]_0/[\text{prepoly-BL}]_0 = 400$; conversion = 50.0%, (a) prepolymer, $\bar{M}_n = 3.2 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.09$; (b) block copolymer, $\bar{M}_n = 1.21 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.17$. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

sion of ethylene oxide increased linearly with the initial mole ratio of ethylene oxide to the living poly(β-butyrolactone) (Figure 10). A linear relationship was observed between the composition of the copolymer and the mole ratio of the β-lactone used as the prepolymer to the epoxide as the second monomer (Figure 11).

β-Butyrolactone–Propylene Oxide Block Copolymerization. β-Butyrolactone–propylene oxide copolymer was obtained similarly by reacting propylene oxide with living prepolymer of β-butyrolactone prepared by using (TPP)AlCl as catalyst. Figure 12 shows the typical GPC curve of the product thus obtained and that of prepoly(β-butyrolactone). The GPC curve of the product clearly shifted toward the higher molecular weight region from that of the prepolymer, with no peak of prepolymer, and the molecular weight distribution was quite narrow. Thus, β-butyrolactone–propylene oxide block copolymer with narrow molecular weight distribution was obtained in 100% efficiency. There was found a linear relationship between the number-average molecular weight of the block copolymer and the amount of propylene oxide reacted (Figure 13), where the molecular weight distribution was retained narrow. A proportional relation was observed between the composition of the copolymer and mole ratio of β-butyrolactone to the epoxide reacted, as shown in Figure 14.

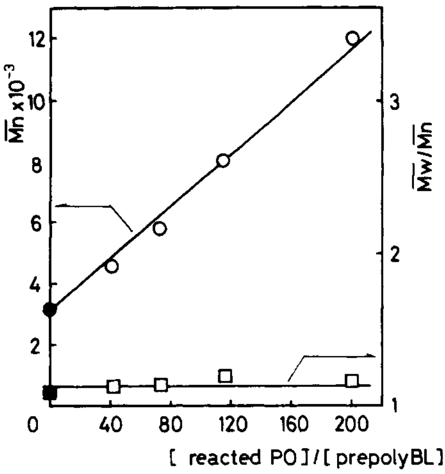


Figure 13. Polymerization of propylene oxide (PO) initiated by living poly(β-butyrolactone). Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (□) of the block copolymer and the amount of PO reacted. Prepolymer, $\bar{M}_n$ (●) = 3.2×10^3, $\bar{M}_w/\bar{M}_n$ (■) = 1.09. $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

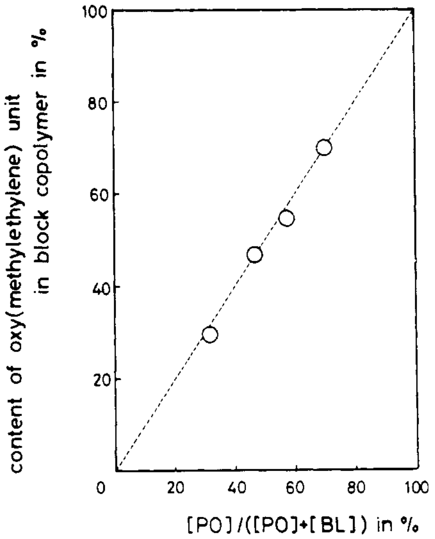


Figure 14. Polymerization of propylene oxide (PO) initiated by living poly(β-butyrolactone). Relationship between the composition of the block copolymers and the mole fraction of reacted PO. [BL], amount of β-butyrolactone prepolymer (prepoly-BL) used, in moles with respect to repeating units; [PO], amount of PO reacted, in moles.

Conclusion

The polymerization of β-propiolactone and β-butyrolactone catalyzed by (5,10,15,20-tetraphenylporphinato)aluminum chloride was confirmed to proceed with a living nature. It is of much interest that the same catalyst brings about the living polymerization of two different types of monomers, β-lactone and epoxide. This makes it possible to obtain polyester–polyether block copolymer with narrow molecular weight distribution and with well-controlled chain lengths, by the initiation of polymerization of epoxide from the propagating end of living poly(β-lactone).[9]

The attempted synthesis of polyether–polyester block copolymer by the polymerization of β-lactone from the living propagating end of poly(epoxide) initiated by (5,10,15,20-tetraphenylporphinato)aluminum chloride was not successful. This fact indicates that (porphinato)aluminum alkoxide is not a good initiator for the polymerization of β-lactone[10] and corresponds to the fact that the structure of the living propagating end in the polymerization of β-lactone catalyzed by (5,10,15,20-tetraphenylporphinato)aluminum chloride is a (porphinato)aluminum carboxylate but not an alkoxide.[5]

Registry No. (TPP)H_2, 917-23-7; Et_2AlCl, 96-10-6; (TPP)AlCl, 71102-37-9; β-propiolactone (homopolymer), 25037-58-5; β-propiolactone (SRU), 24938-43-0; β-butyrolactone (homopolymer), 36486-76-7; β-butyrolactone (SRU), 26744-04-7; (β-butyrolactone)·(β-propiolactone) (copolymer), 92078-52-9; (β-butyrolactone)·(ethylene oxide) (copolymer), 92078-53-0; (β-butyrolactone)·(propylene oxide) (copolymer), 52237-89-5.

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(9) (Tetraphenylporphinato)aluminum carboxylate ((TPP)-AlO_2CR), prepared by the equimolar reaction between (tetraphenylporphinato)aluminum ethyl and carboxylic acid, was found to initiate the living polymerization of epoxide and β-lactone to give the corresponding polymer with narrow molecular weight distribution carrying a RCO_2 end group.[5,11]

(10) The ring-opening reaction of β-lactone by (tetraphenylporphinato)aluminum alkoxide, prepared by the reaction between (TPP)AlCl and epoxide,[3] was found to proceed slowly, while ϵ-lactone reacts much faster to form an aluminum alkoxide. The polymerization of ϵ-caprolactone initiated by the living prepolymer of propylene oxide, a (porphinato)aluminum alkoxide, proceeds to give the corresponding block copolymer (unpublished data). The polymerization of ϵ-caprolactone initiated by bimetallic (μ-oxo)alkoxide as the catalyst proceeding with alkoxide as the propagating end was reported: Hamitou, A.; Jerome, R.; Hubert, A. J.; Teyssie, Ph. *Macromolecules* **1973**, *6*, 651.

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Polyurethane Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 3. Morphology and T_g Behavior of Polyurethane–Polystyrene Semi-IPN's and Linear Blends

Doo Sung Lee[†] **and Sung Chul Kim***

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Chongyangni, Seoul 131, Republic of Korea. *Received November 9, 1983*

ABSTRACT: Semiinterpenetrating polymer networks (semi-IPN's) and linear blends of polyurethane and polystyrene were prepared under high pressure to compare with full IPN's and to evaluate the effect of interpenetration in IPN synthesis. The morphology, dynamic mechanical properties, and density behavior were analyzed to determine the effect of synthesis pressure and the effect of interlocking on the degree of intermixing of the component polymers. The degree of intermixing increased with increasing synthesis pressure, and the relative degree of intermixing among IPN, semi-IPN, and linear blend was in the following order: IPN > semi-I IPN (PU cross-linked/PS linear) > semi-II IPN (PU linear/PS cross-linked) = linear blend. The morphology also showed a similar trend in the electron microscopy study. The relative degree of intermixing depended on the mobility of the polymer component having linear structure. Thus when PU component was made linear, the resulting semi-II IPN showed a higher degree of phase separation compared to semi-I IPN in which the relatively immobile PS component was linear.

Introduction

In previous papers,[1,2] the phase separation mechanism of the interpenetrating polymer network (IPN) synthesized under high pressure was illustrated with relation to the Gibb's free energy of mixing,[3,4] ΔG_m, conversion (molecular weight), mobility of polymer segment (polymer diffusion rate), and cross-link density[5] (gelation point and molecular weight between cross-links, $\bar{M}_c$). Particularly important factors in determining the morphology were the onset point of phase separation, the rate of phase separation, and the time of physical interlocking. The onset point of phase separation was the time when the molecular weight of the component polymers exceeded a certain critical value so that the ΔG_m of the mixture became positive as the polymerization proceeded. The rate of phase separation was related to the mobility of the polymer chain and thus was indirectly related to the synthesis temperature and pressure. The time of physical interlocking was the time when both component polymers reached the gel point and thus the phase domain size could not increase much further beyond this point.

The existence of the physical interlocking (interlocked macrocycles of the two component networks) had been the major factor in determining the characteristic properties

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[†] Present address: Department of Textile Engineering, Sung Kyun Kwan University, Suwon, Kyungki 170, Republic of Korea.

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