Communications to the Editor

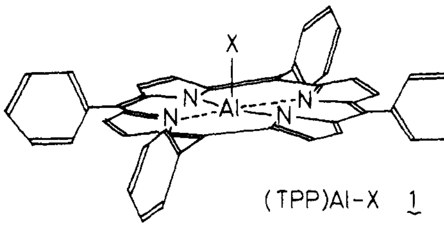
Sequential Addition-Ring-Opening Living Polymerizations by Aluminum Porphyrin. Synthesis of Alkyl Methacrylate-Epoxide and -Lactone Block Copolymers of Controlled Molecular Weight

Synthesis of block copolymers with well-defined structures is important for the design of polymeric materials with interesting properties and functions.

Living polymerization is very effective for the synthesis of block copolymers with well-defined block lengths but has been difficult to apply to block copolymers from monomers with very different structures and reactivities, such as vinyl compounds and cyclic compounds, since the reactivity of the growing species of a particular living polymer is usually suited to initiate the polymerization of a similar type of monomer.

Therefore, attempts have been made to synthesize block copolymers, for example, of methyl methacrylate and epoxide, via an additional step to convert the structure of the living chain end of the prepolymer into one displaying an appropriate reactivity to the second monomer.[1]

Recently, we have found that an aluminum porphyrin such as 1 is an excellent initiator for the living ring-opening and addition polymerizations of a wide variety of monomers such as epoxides,[2] lactones,[3] and methacrylic esters.[4] An application is the synthesis of various types of block copolymers such as polyether-polyether, polyester-polyester, polyether-polyester, and poly(methacrylate)-poly(methacrylate).



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In the present paper are described novel examples of the synthesis of block copolymers having polyvinyl-polyether and polyvinyl-polyester sequences with narrow molecular weight distributions, by the direct sequential addition-ring-opening living polymerizations initiated with aluminum porphyrin.

For example, to a flask containing methyl(5,10,15,20-tetraphenylporphinato)aluminum ((TPP)AlMe: 1, X = Me) (0.2 mmol as a 0.025 mol/L solution in CH_2Cl_2) was added methyl methacrylate (10 mmol, 1.08 cm^3; an amount 50 times that of initiator) through a syringe in a dry nitrogen atmosphere. The flask was illuminated at room temperature for 18 h by a 300-W xenon arc lamp through a glass filter to cut out the light of wavelength shorter than 420 nm, to give the living poly(methyl methacrylate) by 100% conversion, the gel permeation chromatogram (GPC) of which is shown in Figure 1a ($\bar{M}_n = 5500$ (M_n(calcd) = 5022), $\bar{M}_w/\bar{M}_n = 1.14$). To this living prepolymer (a (porphinato)aluminum enolate)[4] was added 1,2-epoxypropane (propylene oxide) (100-fold versus the amount of living chain end). The reaction mixture was kept for 18 h without irradiation of visible light, after the initial exothermic reaction subsided. The GPC chromatogram of the product (Figure 1b) clearly shifted toward the higher molecular weight region, while retaining the narrow distribution ($\bar{M}_n = 12\,800$, $\bar{M}_w/\bar{M}_n = 1.16$).

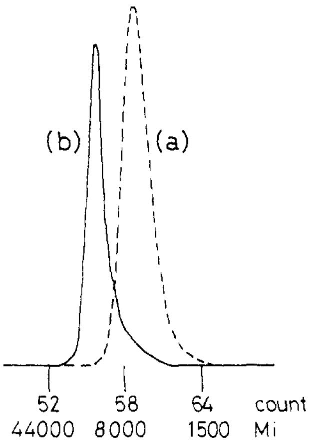

Figure 1. GPC profile of the block copolymerization of 1,2-epoxypropane (propylene oxide, PO) initiated by the living prepolymer of methyl methacrylate obtained with (TPP)AlMe; $[PO]_0/[prepolymer]_0 = 100$, in CH_2Cl_2 at room temperature, 18 h, conversion ≈100%: (a) starting prepolymer, $\bar{M}_n = 5500$, $\bar{M}_w/\bar{M}_n = 1.14$; (b) block copolymer, $\bar{M}_n = 12\,800$, $\bar{M}_w/\bar{M}_n = 1.16$.

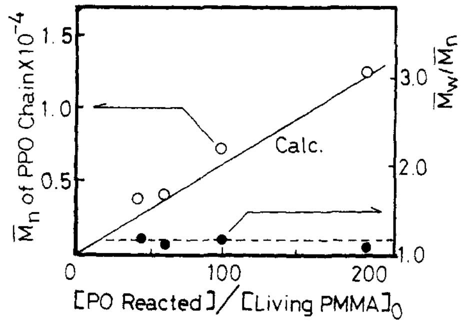

Figure 2. Relationship between the molecular weight of the poly[oxy(methylethylene)] (PPO) chains in methyl methacrylate (MMA)-1,2-epoxypropane (propylene oxide, PO) block copolymers and the amount of reacted 1,2-epoxypropane. Solid line represents theoretical molecular weight.

Furthermore, the peak corresponding to the prepolymer of methyl methacrylate was not observed anymore. The product was separated from the residual catalyst by dissolving the reaction mixture in acetone followed by filtration. The contents of methyl methacrylate[5] and oxy(methylethylene)[6] units of the product estimated by ^1H NMR analysis were 32% and 68%, respectively, compared to the 33/67 ratio theoretically expected.

Thus, the polymerization of 1,2-epoxypropane was initiated from the living end of poly(methyl methacrylate) to produce a methyl methacrylate-1,2-epoxypropane (addition-ring opening) block copolymer with quantitative efficiency.[7]

In order to control the length of the polyether chain, various amounts of 1,2-epoxypropane were added in the second stage of the polymerization. As illustrated in Figure 2, the molecular weight of the polyether chain, calculated by subtracting the molecular weight of the prepolymer from that of the block copolymer, increased linearly with the amount of 1,2-epoxypropane reacted, without broadening of the molecular weight distribution. The observed molecular weights of the block copolymers were in good agreement with the values calculated from monomer/in-

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itiator ratio. A proportional relation was observed between the composition of the polymer (^1H NMR) and the mole ratio of methyl methacrylate and 1,2-epoxypropane reacted. A similar result was obtained in the block copolymerization of methyl methacrylate and epoxyethane.

When δ-valerolactone was employed in the second stage of polymerization, the reaction proceeded rather sluggishly. For example, a living polymer of methyl methacrylate was prepared by polymerization initiated with (TPP)AlMe (0.025 mol/L solution in CH_2Cl_2) at 100% conversion, where the molar amount of the monomer was 40 times that of the initiator ($\bar{M}_n = 3700$, $\bar{M}_w/\bar{M}_n = 1.13$). To this living prepolymer was added δ-valerolactone with a mole ratio to the prepolymer of 100. After 10 days at 30 °C under irradiation with visible light, the GPC of the reaction mixture showed a sharp elution curve at an increased molecular weight ($\bar{M}_n = 5000$, $\bar{M}_w/\bar{M}_n = 1.11$), with disappearance of the peak due to the starting prepolymer of methyl methacrylate. The ^1H NMR analysis of the polymer obtained by the reprecipitation of the product from CH_2Cl_2/methanol also confirmed the formation of poly(methacrylate)-polyester block copolymer, the contents of methyl methacrylate and δ-valerolactone[8] units being 74% and 26%, respectively, exactly the same as calculated from the GPC results.

These results demonstrate unprecedented versatility in the application of aluminum porphyrin to the synthesis of various block copolymers.

Registry No. (TPP)AlMe, 108971-21-7; (methyl methacrylate)(propylene oxide) (block copolymer), 115678-83-6; (methyl methacrylate)(δ-valerolactone) (block copolymer), 115678-84-7.

References and Notes

(1) See, for example: (a) Suzuki, T.; Murakami, Y.; Tsuji, Y.; Takegami, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 675. (b) Gomes, A. S.; Coutinho, F. M. B.; Marinho, J. R. D. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 237.
(2) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162.
(3) (a) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792. (b) Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076. (c) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982. (d) Trofimoff, L. R.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991.
(4) Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4737.
(5) For poly(methyl methacrylate), ^1H NMR in $CDCl_3$ δ 3.6 (OCH_3), 2-1.8 (CH_2), 1.1-0.8 (CH_3).
(6) For poly[oxy(methylethylene)], ^1H NMR in $CDCl_3$ δ 3.5-3.4 (CH and CH_2) and 1.1 (CH_3).
(7) The attempted synthesis of the block copolymer by the polymerizations of propylene oxide initiated with (TPP)AlCl (1, X = Cl) followed by methyl methacrylate (upon irradiation or in the dark) under similar conditions was unsuccessful.
(8) For poly(δ-valerolactone), ^1H NMR in $CDCl_3$ δ 4.1 (OCH_2), 2.3 ($CH_2C(O)$), 1.7 ($CH_2(\text{-}CH_2)_2\text{-}CH_2$).

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Diad Sequence Distribution in Copolyesters of 4-Hydroxybenzoic Acid and 6-Hydroxy-2-naphthoic Acid

Liquid-crystalline aromatic copolyesters based on 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) have been the subject of numerous physical and mechanical property investigations.[1,2] Important to the interpretation and understanding of these measurements is knowledge of the composition and the monomer sequence distribution in this copolyester system. This is made apparent by the recent ^{13}C NMR results[3,4] on the (60/40) copolyester of 4-hydroxybenzoic acid and poly(ethylene terephthalate) (PET) which demonstrate this copolyester to be compositionally heterogeneous with certain fractions displaying a nonrandom sequence distribution. These results correct initial reports of a homogeneous structure with a random sequence distribution[5] and aid in explaining many of the indirect observations of a nonrandom sequence distribution in the commercial copoly(HBA/PET).[6,7] The sequence distribution in copoly(HBA/HNA) is inferred to be random on the basis of X-ray fiber patterns.[8] However, the X-ray data provide only indirect information on the sequence distribution and only for crystalline regions of the sample. Furthermore, such X-ray data on the 2/1 copolyester of HBA and biphenol terephthalate (BPT)[9] suggest a random sequence of monomers while ^{13}C solid-state NMR has suggested some blockiness in this copolyester.[10] In light of the confusion manifest in the literature on the HBA/PET copolyester system and the different observations of the (HBA/BPT) microstructure, it is critical to have a direct measurement of the sequence distribution in the copolyesters of HBA and HNA.

Table I
Characterization of Copolyesters A1-A4

copolyester	polycondensn conditns[a]	DSC,[b] T, °C (ΔH, J/g)	solubil,[c] %	X[d]	$\overline{M}_n$[e]
A1	c = 4.5%, 18 h, 340 °C	-	0.4	0.48	>30K
A2	melt, 10 min-1 h, 280-340 °C, vacuum	285 (2.6)	2.0	0.73	10.3K
A3	c = 18%, 24 h, 245 °C	260 (1.2)	3.7	0.48	21K
A4	c = 4.5%, 18 h, 340 °C	-	0.2	0.47	>30K

[a] c, concentration (wt %) in therminol-66 (high-boiling inert aromatic hydrocarbon from Monsanto Co., St. Louis, MO). [b] Crystal-nematic transition temperature and enthalpy; -, no endotherm observed (however, see text for annealing results). [c] Weight percent in PFP at 100 °C. [d] Composition: number fraction of HBA units in the copolyester, determined by ^1H NMR analysis, see footnote *e* below. Note: The fraction of HBA units can also be determined from the ^{13}C NMR spectrum by using the relative intensities of other carbon signals, e.g., a and b in Figure 1b,c. [e] Determined by ^1H NMR end-group analysis of copolyester samples, hydrolyzed in $CD_3OD/D_2O/NaOD$ (12:3:1): Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475. Accurate determination of end-group signal intensity limits the technique to $M_n \lesssim 30K$.

In this paper, we report the first direct measurement (via ^{13}C NMR spectroscopy) of the diad sequence distribution of commercially available as well as synthesized copolyesters of HBA and HNA.

Four copolyesters have been examined in this study: the commercially available Vectra from Hoechst-Celanese Co., Summit, NJ (designated **A2**), and three copolyesters synthesized in-house (designated **A1**, **A3**, **A4**). Table I lists the polycondensation conditions, crystal-nematic transition temperatures and enthalpies, solubilities in pentafluorophenol, compositions, and number-average molecular weights of these copolyesters. The copolyester **A1** was synthesized from 4-acetoxy-[α-^{13}C]benzoic acid (50% ^{13}C) and 6-acetoxy-2-naphthoic acid; copolyester **A4** from 4-acetoxybenzoic acid and 6-acetoxy-[α-^{13}C)-2-naphthoic acid (50% ^{13}C). The copolyester **A3** was synthesized from

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