Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis of End-Reactive Polymers with Controlled Molecular Weight by Metalloporphyrin Catalyst

Tomokazu Yasuda[a]; Takuzo Aida[a]; Shohei Inoue[a]
[a] Department of Synthetic Chemistry Faculty of Engineering, University of Tokyo, Tokyo, Japan

To cite this Article Yasuda, Tomokazu , Aida, Takuzo and Inoue, Shohei(1984) 'Synthesis of End-Reactive Polymers with Controlled Molecular Weight by Metalloporphyrin Catalyst', Journal of Macromolecular Science, Part A, 21: 8, 1035 — 1047

To link to this Article: DOI: 10.1080/00222338408056590

URL: http://dx.doi.org/10.1080/00222338408056590

J. MACROMOL. SCI.—CHEM., A21(8&9), pp. 1035-1047 (1984)

Synthesis of End-Reactive Polymers with Controlled Molecular Weight by Metalloporphyrin Catalyst

Tomokazu Yasuda, Takuzo Aida and Shohei Inoue

Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT

α, β, γ, δ-Tetraphenylporphinatoaluminum carboxylate (TPPAlOCOR) and phenoxide (TPPAlOAr) bring about the polymerization of β-lactone and epoxide to give polymers with controlled chain length having a carboxylic ester or phenoxy group at the end of each polymer molecule. Acrylate (TPPAlOCOCH=CH_2) and p-vinylphenoxide (TPPAl-OC_6H_4CH=CH_2(p)) as initiator give polyester or polyether macromer with narrow molecular weight distribution.

INTRODUCTION

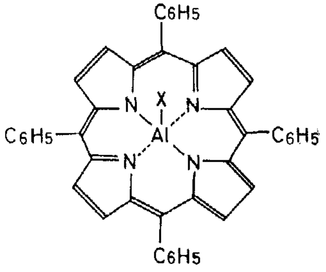
Synthesis of end-reactive polymers with controlled molecular weight is of particular importance and interest in the design of polymeric materials of well-defined structure.

Introduction of a reactive group to the terminal of a polymer molecule may be accomplished in principle either by the combination of the reactive group with the end of a polymer or by the initiation of polymerization of a monomer with initiator which carries the reactive group. Both procedures are very much dependent on the

0022-233X/84/2108-1035$3.50/0

efficiency of the reactions; the reaction involving polymer is usually difficult to proceed quantitatively for the former, and the efficiency of initiator is not quantitative, except for the limited cases, for the latter. In the latter procedure, the reactive group should not participate in termination and chain transfer reactions, in order to control the chain length of the polymer formed.

We have already reported that some aluminum porphyrins exhibit a quantitative efficiency as initiator for the ring opening polymerization of epoxide$^{1)}$ and β-lactone$^{2)}$, to give living polyether and polyester with narrow molecular weight distribution, respectively.



1

TPPAlX

The molecular weight of the polymers may be controlled, for example, by changing the molar ratio of monomer to initiator. Since α, β, γ, δ-tetraphenylporphinatoaluminum carboxylate (TPPAlOCOR, 1; X = OCOR) also shows high efficiency as initiator in the polymerization of β-lactone$^{3)}$ and epoxide$^{4)}$, we intended to produce polyester and polyether having reactive end group derived from the axial ligand of the catalyst (for example, eq. 1). Initiation by tetraphenylporphinatoaluminum phenoxide (TPPAlOAr, 1; X = OAr) was also examined.

(1)

MATERIALS

α, β, γ, δ-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform / methanol$^{5)}$. Dichloromethane, washed with concentrated sulfuric acid and neutralized with sodium bicarbonate, was dried over calcium hydride in a nitrogen atmosphere. Propylene oxide was purified by refluxing over a mixture of potassium hydroxide and calcium hydride, and then fractionally distilled twice in a nitrogen atmosphere. β-Propiolactone and β-butyrolactone were dried over calcium hydride, and then distilled under reduced pressure in a nitrogen atmosphere. p-Vinylphnol (supplied from Maruzen Oil Co., Ltd.) was purified by recrystallization from hexane and dried under reduced pressure in a nitrogen atmosphere at about 0°C. Other carboxylic acids and phenols were purified by usual procedures.

MEASUREMENT

Gel Permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-802A gel permeation chromatograph equipped with a differential refractometer detector using tetrahydrofuran as the eluent; the flow rate: 1,1 ml·min^{-1}; columns: 60 cm length with pore size 7000Å - 3000Å (two), 3000Å (one) and 2000Å (one). The molecular weight and the molecular weight distribution were calculated on the basis of the calibration curve obtained by using either standard polypropylene glycols (PPG) for the lower molecular weight region and standard poly (ethylene oxide)s (PEO) for the higher molecular weight region, or standard polystyrenes. Standard poly (ethylene oxide)s were obtained from 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 polypropylene glycols were obtained from Lion Fat & Oil Co., Ltd.; $\bar{M}n = 1000$ and 2000 ($\bar{M}w/\bar{M}n \simeq 1.0$). Standard polystyrenes were obtained from Toyo Soda Manufacturing Co., Ltd.; $\bar{M}n = 300$ ($\bar{M}w/\bar{M}n = 1.2$), $\bar{M}n = 2800$ ($\bar{M}w/\bar{M}n = 1.05$), $\bar{M}n = 6200$ ($\bar{M}w/\bar{M}n = 1.04$), $\bar{M}n = 16700$ ($\bar{M}w/\bar{M}n = 1.02$), $\bar{M}n = 107000$ ($\bar{M}w/\bar{M}n = 1.01$) and $\bar{M}n = 420000$ ($\bar{M}w/\bar{M}n = 1.05$).

The ^{1}H-NMR spectrum was measured in deuterated chloroform in a sealed tube in a nitrogen atmosphere, using a JEOL Type 4H-A spectrometer operating at 100 MHz. $^{13}C\{^{1}H\}$ - NMR measurement on the polymer was performed in deutrated chloroform in a capped tube using a JEOL PFT-100 spectrometer. The spectrum pattern was recorded in a JEOL data terminal, Model SILENT 700 ASR connected to a spectrometer at 25.03 MHz.

METHODS

The Equimolar Reaction between Tetraphenylporphinatoaluminum Ethyl and Carboxylic Acid or Phenol.

α, β, γ, δ-Tetraphenylporphinatroaluminum ethyl (TPPAlEt, 1 ; $X = C_2H_5$) was obtained by the reaction between $TPPH_2$ and triethylaluminum (Et_3Al) as described previously[6]. The tear drop type flask equipped with a three way cock containing $TPPH_2$ (0.6147 g, 1 mmol) was purged by dry nitrogen, CH_2Cl_2 (20 ml) was introduced in the flask using syringe, and then Et_3Al (0.14 ml, 1 mmol) was added to the solution at room temperature with syringe. After the reaction mixture was kept for about an hour, the volatile materials were removed off under reduced pressure, and CH_2Cl_2 (20 ml) was introduced into the flask to dissolve the product, TPPAlEt. To this solution, propionic acid (0.07 ml, 1 mmol), for example, was added at room temperature with magnetic stirring, where rapid reaction was observed by the dissapearance of ^1H-NMR signals due to ethyl group of TPPAlEt. The reaction mixture was allowed to stand overnight. After the completion of the reaction, the color of the solution turned to purple from green color of TPPAlEt. The volatile materials were removed under reduced pressure from the above reaction mixture to give a purple solid. Then 20 ml of CH_2Cl_2 was added to dissolve the product and this solution was used as the catalyst.

Polymerization

To the catalyst solution, β-propiolactone, for example, was introduced by syringe with a definite initial molar ratio of the monomer to the catalyst ($[Mon.]_o/[Cat.]_o$), and the mixture was kept at room temperature with magnetic stirring. After a definite time, a large excess of methanol was added to the reaction mixture to stop the polymerization, and then volatile materials (residual monomer, solvent and methanol) were removed under reduced pressure. The conversion was calculated either from the amount of the residue by subtracting the amount of the catalyst or from the signal intensity of ^1H-NMR spectrum of the reaction mixture. In order to determine the molecular weight and molecular weight distribution, a part of the obtained polymer was dissolved in tetrahydrofuran, insoluble part (the catalyst residue) was filtered off using a Teflon filter with pore size 0.45μm, and the solution was subjected to the GPC analysis.

RESULTS AND DISCUSSION

Reaction Product between Tetraphenylporphinatoaluminum Ethyl and Carboxylic Acid.

The equimolar reaction between tetraphenylporphinatoaluminum ethyl (TPPAlEt) and carboxylic acid proceeds in several minutes at room temperature to give a porphinatoaluminum carboxylate (TPPAlOCOR **1**, X = OCOR) (eq. 2).

$$\text{Al–Et} + \text{H–O–}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{–R} \longrightarrow \text{Al–O–}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{–R} + \text{Et–H} \qquad (2)$$

In the ^{1}H-NMR spectrum of the reaction mixture from TPPAlEt and acetic acid, for example, a singlet signal due to TPPAlOCOC$\underline{H_3}$ group strongly influenced by the large magnetic effect of the porhyrin ring was observed at such a high magnetic field as -1.4ppm. The intensity ratio of the signal due to acetate methyl (-1.4ppm, 3.0H) to that due to pyrrole groups of the porphyrin (9.1ppm, 8.0H) was in good agreement with the calculated value. On the other hand, the signals due to methyl and methylene groups of TPPAl$\underline{\text{Et}}$ at -3.6ppm and -6.4ppm were not observed (Fig. 1.).

Reaction Product between Tetraphenylporphinatoaluminum Ethyl and Phenol.

The equimolar reaction between tetraphenylporphinatoaluminum ethyl (TPPAlEt) and phenol proceeds in several hours at room

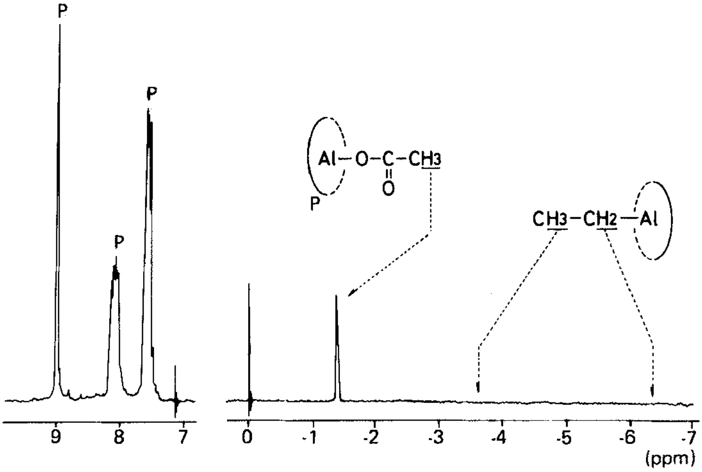


FIGURE 1. ^{1}H-NMR spectrum of the equimolar reaction mixture between TPPAlEt and CH_3COOH in $CDCl_3$.

temperature. In the ^{1}H-NMR spectrum of the reaction mixture, the signals due to ethyl group of TPPAlEt were found to disappear (Fig. 2.). Instead, new signals were observed at 2.7 ppm (a) and at 6.0 ppm (b), which are assigned to the protons of ortho position and of meta/para position, respectively, of phenoxy group attached to aluminum porphyrin, located at unusually high magnetic field. The intensity ratio of the signals (a) (2.7 ppm, 2.0H) and (b) (6.0 ppm, 3.0H) to that for pyrrole groups of the porphyrin (9.1 ppm, 8H) was in good agreement with the calculated value. Thus, the formation of tetraphenylporphinatoaluminum phenoxide (TPPAlOAr; 1, $X = OC_6H_5$) was confirmed.

Polymerization of β-Lactone Catalysed by Tetraphenylporphinatoaluminum Carboxylate.

Aluminum porphyrins having various carboxylate groups as axial ligand, prepared from the reaction between TPPAlEt and various

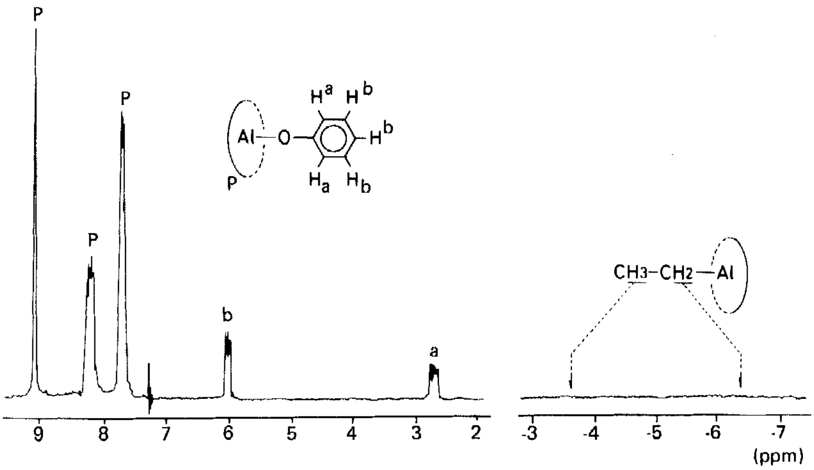
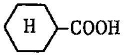
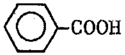
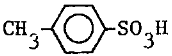


FIGURE 2. ^{1}H-NMR spectrum of the equimolar reaction mixture between TPPAlEt and phenol in $CDCl_3$.

carboxylic acids, were examined as the catalyst for the polymerization of β-propiolactone and β-butyrolactone. Obtained polymer was characterized by the narrow molecular weight distribution (Table 1). Thus, various end groups originating from the carboxylate group in the catalyst could be introduced to polyester with well-controlled chain length. In the case of using acrylic acid, synthesis of polyester macromer with well-controlled molecular weight having a vinyl group at the end of the polymer chain is expected. In order to prove the exsistence of vinyl group, obtained polymer was subjected to ^{13}C-NMR spectroscopy (Fig. 3) after reprecipitation from chloroform/n-hexane to remove residual acrylic acid, if any. Signals A (168.8 ppm), F (67.2 ppm), G (40.2 ppm) and H (19.3 ppm) are assigned to carbonyl, methine, methylene and methyl groups of poly (β-butyrolactone) unit[3)], while signal C (164.7 ppm) is

TABLE 1

Polymerization of β-Lactone with TPPAlEt-Acid System[a].

Run	Acid	Monomer[b]	$\frac{[\mathrm{Mon.}]_0}{[\mathrm{Cat.}]_0}$	Reaction Time(day)	Conversion (%)	$\bar{M}n$[c]	$\bar{M}w/\bar{M}n$[c]
1	CH_3CH_2-COOH	PL	100	25	93	3.4×10^3	1.10
2		BL	100	19	75	2.3×10^3	1.12
3		BL	100	19	73	4.1×10^3	1.13
4	CH_3-COSH	PL	120	19	100	5.1×10^3	1.09
5	CH_2=CH-COOH	BL	50	18	54	8.8×10^2	1.12
6		PL	100	30	100	3.4×10^4	1.24

a) In CH_2Cl_2 at room temperature.

b) PL, β-propiolactone; BL, β-butyrolactone.

c) $\bar{M}n$ and $\bar{M}w$ were estimated by GPC calibrated with standard poly(ethylene oxide) and polypropylene glycols.

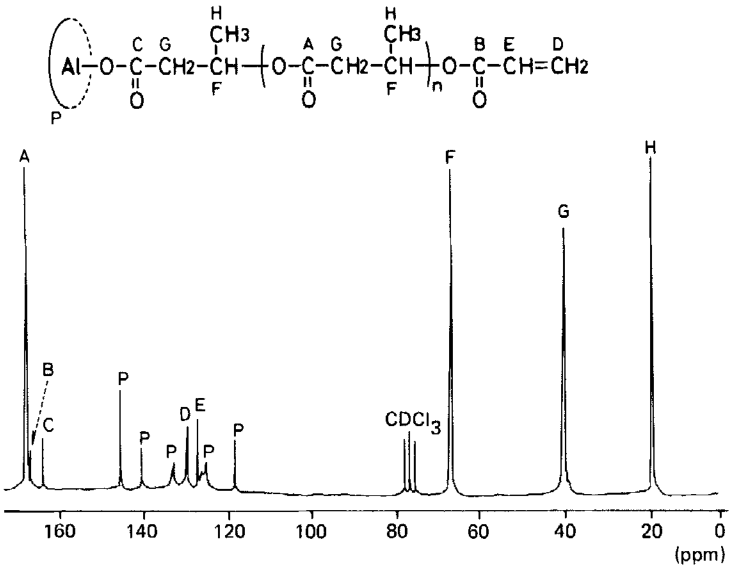


FIGURE 3. ^{13}C-NMR spectrum of poly (β-butyrolactone) macromer obtained with TPPAlOCOCH=CH_2 in $CDCl_3$.

assigned to the carboxylate group attached to aluminum porphyrin[3]. Signals D (130.4 ppm) and E (128.1 ppm) are considered due to methylene and methine group of acrylate group, respectively[7], confirming the formation of polyester macromer with narrow molecular weight distribution (Fig. 4).

The equimolar reaction product between TPPAlEt and p-toluenesulfonic acid was also effective as the catalyst for the polymerization of β-propiolactone to give the polymer with narrow molecular weight distribution.

Polymerization of Epoxide and β-Lactone Catalysed by Tetraphenylporphinatoaluminum Phenoxide.

Tetraphenylporphinatoaluminum phenoxide was found to bring about the polymerization of epoxide and β-lactone to form porphi-

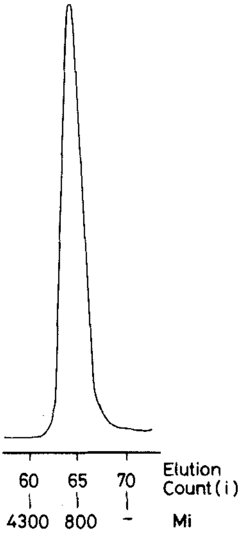


FIGURE 4. GPC curve of poly (β-butyrolactone) macromer obtained with $TPPAlOCOCH=CH_2$.

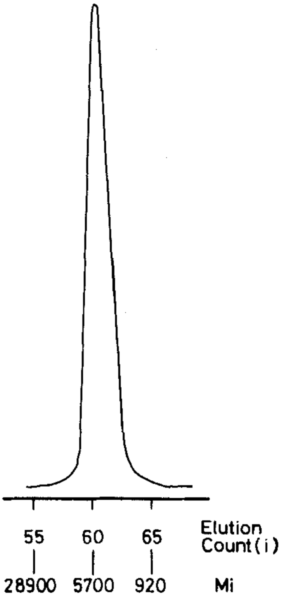
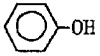
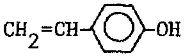
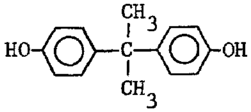


FIGURE 5. GPC curve of poly (β-butyrolactone) obtained with TPPAl-OPh.

TABLE 2

Polymerization of Epoxide and β-Lactone with TPPAlEt-Phenol System[a).]

Run	Phenol	Monomer[b)]	$\frac{[\mathrm{Mon.}]_0}{[\mathrm{Cat.}]_0}$	Reaction Time(day)	Conversion (%)	$\overline{M}n$[c)]	$\overline{M}w/\overline{M}n$[c)]
1		PO	100	11	78	4.0×10^3	1.06
		PL	200	2	100	2.4×10^3	1.07
2		PO[d)]	300	2	100	1.9×10^4	1.22
		PL[d)]	100	4	100	2.9×10^3	1.15
3		PO	100	6	94	5.6×10^3	1.04
4		PO	200	16	100	1.9×10^4	1.24

a) In CH_2Cl_2 at room temperature.

b) PO, propylene oxide; PL, β-propiolactone.

c) $\overline{M}n$ and $\overline{M}w$ were estimated by GPC calibrated with standard polystyrene.

d) Polymerization was carried out at -78°C.

natoaluminum alkoxide and carboxylate as the living propagating end, respectively. The structure was confirmed by ^1H-NMR spectrum; for the living polyether from propylene oxide prepared with TPPAlOPh, a signal at -2.0 ppm was observed$^{8)}$ and for the living polyester from β-propiolactone prepared with TPPAlOPh, signal at -0.7 ppm was observed$^{3)}$. The polymer thus obtained was characterized by the narrow molecular weight distribution as examplified for the polymer of β-butyrolactone (Fig. 5). The polymerization of epoxide or β-lactone catalysed by various substituted phenoxides also resulted in the formation of polyether or polyester with narrow molecular weight distribution (Table 2). The use of tetraphenylporphinatoaluminum p-vinylphenoxide as the catalyst gave polyether or polyester macromer having well-controlled molecular weight. TPPAlEt-bisphenol A system is also of interest in view of the synthesis of bifunctional polymer with narrow molecular weight distribution.

REFERENCES

[1] T. Aida and S. Inoue, Macromolecules, 14, 1162 (1981).
[2] T. Yasuda, T. Aida and S. Inoue, Makromol. Chem., Rapid Commun., 3, 585 (1982).
[3] T. Yasuda, T. Aida and S. Inoue, Macromolecules, in press.
[4] T. Yasuda, T. Aida and S. Inoue, 46th Ann. Meeting Chem. Soc. Japan (1982, Niigata) Abstracts, p.803.
[5] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, J. Org. Chem., 32, 476 (1967).
[6] S. Inoue and N. Takeda, Bull. Chem. Soc. Jpn., 50, 948 (1980).
[7] E. Breitmaier, G. Haas and W. Voelter, ATLAS OF CARBON-13 NMR DATA, Heyden & Son Ltd., London 1975, 1976.
[8] T. Aida and S. Inoue, Macromolecules, 14, 1166 (1981).