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Ring-Opening Polymerization of 5,6-Dihydro-4*H*-1,3-oxazin-6-ones, Six-Membered "Azlactones", to Poly(*N*-acyl-β-peptide)s

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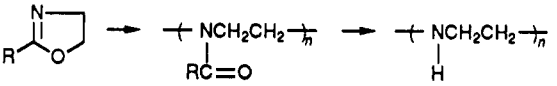
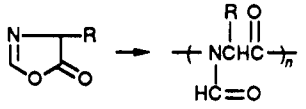
ABSTRACT: Five cyclic monomers, **1a–e**, having the ring structure of a six-membered azlactone, 5,6-dihydro-4*H*-1,3-oxazin-6-one (abbreviated as 6-oxazinone), have been prepared. 2-Ethyl- (**1b**), 2-isopropyl- (**1c**), and 4-phenyl-6-oxazinones (**1e**) were obtained in pure form. 2-Methyl-6-oxazinone (**1a**) and unsubstituted 6-oxazinone (**1d**) were not very stable and were obtained only as a nitrobenzene solution. Cationic polymerization of monomers **1a–c** gave polymers having clear-cut structures of poly(*N*-acyl-β-peptide)s **2a–c**, respectively. Polymers from **1d** and **1e**, however, have structures containing **2d** and **2e**, as well as other unit(s) due to side reaction(s). Thermal polymerization of **1a** and **1e** produced polymers consisting exclusively of structures **2a** and **2e**, respectively.

Introduction

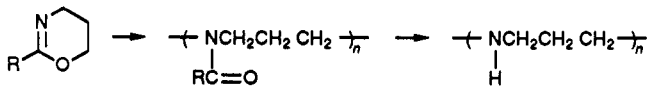
For more than a decade we have been studying extensively the ring-opening polymerizations of 2-oxazolines to produce poly(*N*-acylethylenimine)s or poly(*N*-formylethylenimine).[1] Hydrolysis of these polymers is a versatile method to prepare linear poly(ethylenimine).[2]



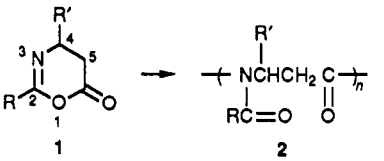
Very recently we have reported a new ring-opening polymerization of 2-unsubstituted 5-oxazolones (five-membered "azlactones"), an analogue of 2-oxazolines, giving rise to poly(*N*-formyl-α-peptide)s.[3]



A six-membered ring family of 2-oxazolines is 5,6-dihydro-4*H*-1,3-oxazines, whose ring-opening polymerizations have been accomplished[1,4] and product polymers gave linear poly(trimethylenimine) via hydrolysis.[2]



Studies on these reactions have been extended to examine the ring-opening polymerization of six-membered azlactones, 5,6-dihydro-4*H*-1,3-oxazin-6-ones (abbreviated as 6-oxazinones,[5] **1**), to give rise to poly(*N*-acyl-β-peptide)s and poly(*N*-formyl-β-peptide)s (**2**). We now report the polymerization results of **1**.

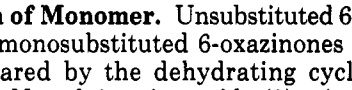


1 **2**

a: R = Me, R′ = H
b: R = Et, R′ = H
c: R = *i*-Pr, R′ = H
d: R = R′ = H
e: R = H, R′ = Ph

Results and Discussion

Preparation of Monomer. Unsubstituted 6-oxazinone (**1d**) and four monosubstituted 6-oxazinones (**1a–c** and **1e**) were prepared by the dehydrating cyclization of *N*-formyl- and *N*-acyl-β-amino acids (**3**). As the dehydration agent of **3**, *N*,*N*′-dicyclohexylcarbodiimide (DCC)[3] or ethyl chloroformate[5a] was employed. Monomers **1a** and **1d** were found to be less stable and obtained only as a nitrobenzene solution after vacuum codistillation using nitrobenzene as a carrier solvent. This codistillation technique was successfully applied previously for the isolation of 2-unsubstituted 5-oxazolones in solution.[3] 2-Ethyl- (**1b**), 2-isopropyl- (**1c**), and 4-phenyl-6-oxazinone (**1e**), on



3 **1**

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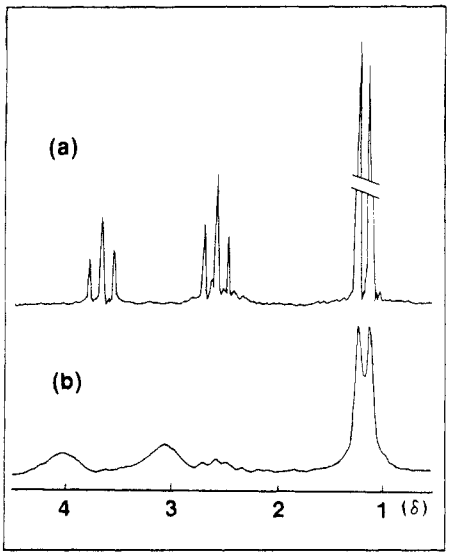
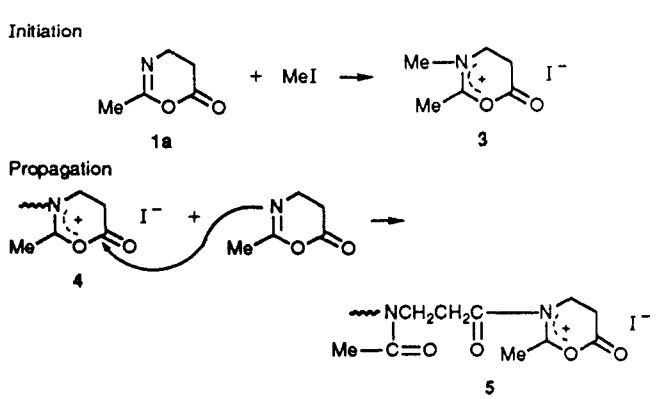


Figure 1. ^1H NMR spectra ($CDCl_3$) of 2-isopropyl-6-oxazinone (**1c**) (a) and poly(*N*-isobutyryl-β-alanine) (**2c**) (b) Signal assignments are given in the Experimental Section.

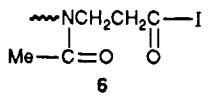
the other hand, proved stable enough to be isolated in pure form. Figure 1a shows the ^1H NMR spectrum of monomer **1c** as a typical example.

Cationic Ring-Opening Polymerization. The polymerization of monomers **1** is induced by a cationic initiator at room temperature (entries 1–6 in Table I). The reaction with MeI initiator proceeded cleanly. Product polymers are solids soluble in polar solvents such as chloroform and dimethylformamide (DMF). Structures of the polymers were determined by ^1H NMR, ^{13}C NMR, and IR spectroscopy. For example, spectral data used for the structural determination of poly(*N*-acetyl-β-alanine) (**2a**) are as follows: ^1H NMR ($CDCl_3$, with Me_4Si) δ 2.2 (br s, 3 H, CH_3), 2.8 (br, 2 H, $CH_2C(=O)$), 3.7 (br, 2 H, CH_2N), ^{13}C NMR ($CDCl_3$, with Me_4Si) δ 26 (CH_3), 37 ($CH_2C(=O)$), 41 (CH_2N), 173, 174 (both C=O); IR (KBr) 1720–1680 (vs) due to amide carbonyl groups. Similarly, the structures of other polymers from **1b** and **1c** were determined as **2b** and **2c**, respectively, which involve no other repeating units due to side reactions. However, the polymers from 2-unsubstituted monomers **1d** and **1e** showed a ^{13}C NMR signal around δ 91 and an IR absorption band at 1780 cm^{-1} in addition to major signals and bands ascribed to *N*-formyl-β-peptide units **2d** and **2e**, respectively. This suggests that the polymerizations of **1d** and **1e** involve side reaction(s) producing minor unit(s) having other structures than a β-peptide unit.

A mechanism of the cationic polymerization is proposed by taking that of monomer **1a** as a typical example.



The above mechanism represents an ion-dipole S_N2-type propagation. The carbon atom of the carbonyl in **4** is attacked by a monomer nucleophile to open the ring and produce the *N*-acetyl-β-alanine unit **5**. As previously considered about the nature of propagating species,[3] it is highly likely that ionic species **3**–**5** are rather unstable under the reaction conditions and convert quickly to covalent species as generally given by **6**. At present,



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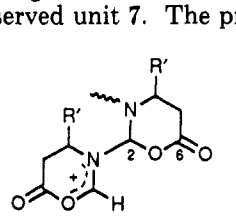
however, there has been no experimental finding for the identification of the nature of the propagating, i.e., ionic or covalent, species.

Concerning the side reaction in the polymerization of 2-unsubstituted monomers **1d** and **1e**, it is reasonably assumed that the C-2 carbon atom of the propagating species corresponding to **4** is attacked by the monomer to give a ring-preserved unit **7**. The production of unit



7

7 explains the ^{13}C NMR signal and the IR absorption band, i.e., the ^{13}C NMR signal due to a specific carbon atom at C-2 in **7** is expected to appear around δ 90 and the $\nu_{C=O}$ of C-6 in **7** should be at 1780 cm^{-1}.[3] The latter band is at almost the same position as that of the corresponding monomer. In 2-unsubstituted monomers like **1d** and **1e** the reaction of the C=N group is probably much favored due to the least steric hindrance at the C-2 carbon. A similar tendency has been observed not only in 2-unsubstituted 5-oxazolones[3] but also in 2-unsubstituted 2-oxazoline and 5,6-dihydro-4*H*-1,3-oxazine in the reaction with carboxylic anhydrides.[6] Actually, 2-isopropyl-6-oxazinone (**1c**) gave polymer **2c** exclusively of the β-peptide unit of higher molecular weight by MeI initiator. It is to be noted that monomer **1c** produced polymer **2c** with a clean structure also by MeO_3SCF_3 initiator, which induced the polymerization of 5-oxazolones accompanied always by side reactions.[3] The presence of a bulkier isopropyl group at C-2 prevents the occurrence of side reactions, leading to a higher molecular weight polymer. The ^1H NMR spectrum of polymer **2c** is given in Figure 1b.

Thermal Polymerization. Some of monomers **1**, i.e., **1a** and **1e**, were found to polymerize in the absence of initiator at a higher temperature, e.g., 120 or 110 °C (entries 7 and 8 in Table I). Both polymers obtained thermally from **1a** and **1e** showed structures **2a** and **2e**, respectively. They exhibit neither the signal at around δ 90 in their ^{13}C NMR spectra nor an absorption band at 1780 cm^{-1} in their IR spectra, indicating the absence of a side reaction in the thermal polymerization. Polymers **2a** and **2e** thus prepared consist of only the β-peptide unit.

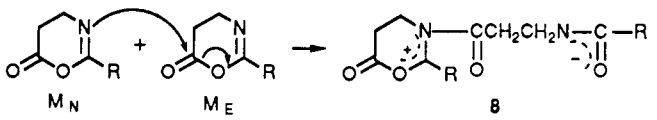
The mechanism of the thermal polymerization may be explained in a similar manner as that of 5-oxazolones.[3] Azlactone monomers **1** have a nucleophilic site of the imino ether group as well as an electrophilic site of the ester group in the same molecule. Therefore, **1** is regarded as an amphiphilic monomer, i.e., it acts as a nucleophilic monomer (M_N) as well as an electrophilic monomer (M_E),

Table I
Ring-Opening Polymerization of 6-Oxazinones (1)

	polymerization					polymers		
entry	6-oxazinones	initiators (mol %)	solvents	temp, °C	time, h	yield, %	struct	mol wt[a]
1	**1a**	MeI (5)	$C_6H_5NO_2$	rt	336	57	**2a**	1500
2	**1b**	MeI (3)	$CHCl_3$	rt	16	59	**2b**	
3	**1c**	MeI (3)	$CHCl_3$	rt	72	82	**2c**	5400
4	**1c**	MeO_3SCF_3 (3)	$CHCl_3$	rt	6	65	**2c**	1700
5	**1d**	MeI (10)	$C_6H_5NO_2$	rt	118	50	**2d**	800
6	**1e**	MeI (3)	$CHCl_3$	rt	11	79	**2e**	2600
7	**1a**	none	$C_6H_5NO_2$	120	120	68	**2a**	1600
8	**1e**	none	MeCN	110	45	31	**2e**	1100

[a] Determined by vapor pressure osmometry in chloroform at 35 °C.

giving rise to a genetic zwitterion 8. Subsequent reac-



tions between molecules 8 or the cationic polymerization of monomer from the cationic site in 8 will lead to the formation of polymer **2**.

Experimental Section

Materials. The solvents chloroform, dichloromethane, nitrobenzene, acetonitrile, and diethyl ether were purified by distillation under nitrogen. Commercial *N,N'*-dicyclohexylcarbodiimide (DCC) and ethyl chloroformate were used as received. Formic acid, sodium formate, acetyl chloride, acetic anhydride, propionic anhydride, and isobutyric anhydride were commercial reagents and were employed without further purification. MeI and MeOTf prepared from TfOH and Me_2SO_4 were purified by distillation under nitrogen. β-Alanine was a commercial reagent. DL-2-Amino-2-phenylpropionic acid was obtained according to the reported procedure[7] in 16% yield: ^{1}H NMR (D_2O with DSS (sodium 3-(trimethylsilyl)propanesulfonate)) δ 2.59 (d, J = 7.5 Hz, 2 H, CH_2CO), 4.29 (t, J = 7.5 Hz, 1 H, CH), 7.48 (s, 5 H, C_6H_5); IR (KBr) 1625, 1590, 1515 cm^{-1}.

N-Acetyl-β-alanine was prepared by the reaction of β-alanine with acetic anhydride according to similar procedures as described[8] (57% yield): ^{1}H NMR (D_2O with DSS) δ 2.0 (s, 3 H, CH_3), 2.60 (t, J = 6.3 Hz, 2 H, CH_2CO_2), 3.45 (t, J = 6.3 Hz, 2 H, CH_2N); IR (KBr) 1705, 1610, 1560 cm^{-1}. Analogously,[8] the reaction of β-alanine with propionic anhydride gave *N*-propionyl-β-alanine (45% yield): ^{1}H NMR (D_2O with DSS) δ 1.10 (t, J = 7.5 Hz, 3 H, CH_3), 2.28 (q, J = 7.5 Hz, 2 H, $MeCH_2CO$), 2.40 (t, J = 7.2 Hz, 2 H, CH_2CO_2), 3.38 (t, J = 7.2 Hz, 2 H, CH_2N); IR (KBr) 1710, 1610, 1550 cm^{-1}. Similarly,[8] the reaction of β-alanine with isobutyric anhydride produced *N*-isobutyryl-β-alanine (80% yield): ^{1}H NMR (D_2O with DSS) δ 1.10 (d, J = 7.1 Hz, 6 H, 2 CH_3), 2.50 (m, J = 7.1 Hz, 1 H, Me_2CH), 2.60 (t, J = 6.3 Hz, 2 H, CH_2CO_2), 3.45 (t, J = 6.3 Hz, 2 H, CH_2N); IR (KBr) 1710, 1620, 1540 cm^{-1}. *N*-formyl-β-alanine was obtained by the reaction of β-alanine with acetic formic anhydride according to Muramatsu et al.:[9] ^{1}H NMR (D_2O with DSS) δ 2.65 (t, J = 6.5 Hz, 2 H, CH_2CO_2), 3.50 (t, J = 6.5 Hz, 2 H, CH_2N), 8.05 (s, 1 H, CHO). Similarly,[9] DL-2-formamido-2-phenylpropionic acid was prepared by the reaction of DL-2-amino-2-phenylpropionic acid with acetic formic anhydride (71% yield): ^{1}H NMR (D_2O + NaOH with DSS) δ 2.75 (d, J = 7.5 Hz, 2 H, CH_2CO_2), 5.38 (t, J = 7.5 Hz, 1 H, CH), 7.45 (s, 5 H, C_6H_5), 8.12 (s, 1 H, CHO); IR (KBr) 1710, 1620, 1525 cm^{-1}.

Monomers. 2-Methyl-6-oxazinone (**1a**) was prepared as follows. Into a 200-mL round-bottomed flask containing 3.0 g (22.9 mmol) of *N*-acetyl-β-alanine in dichloromethane (45 mL) and nitrobenzene (25 mL), a dichloromethane solution (20 mL) of DCC (4.86 g) was slowly added under nitrogen. The mixture was stirred for 90 h at room temperature. During the reaction *N,N'*-dicyclohexylurea precipitated, which was separated by filtration. The urea was washed three times with 10 mL of diethyl ether. The filtrate and washings were combined, concentrated, and distilled in vacuo. The distillate (bp 44–47 °C at 1.5 mmHg) was a nitrobenzene solution of **1a** (20 mL). The concentration of **1a** was 0.35–0.51 mol/L, determined by ^{1}H NMR with cyclohexane as an internal standard (yield of **1a** = 38%): ^{1}H NMR (nitrobenzene with cyclohexane as δ 1.43) δ 2.06 (t, J = 1.5 Hz, 3 H, CH_3), 2.66 (t, J = 7.1 Hz, 2 H, CH_2CO_2), 3.66 (t, J = 7.1 Hz, 2 H, CH_2N); IR (nitrobenzene solution) 1780, 1710 cm^{-1}.

2-Ethyl-6-oxazinone (**1b**) was prepared in a similar manner as reported.[5a] In a 200-mL round-bottomed flask containing *N*-propionyl-β-alanine (1.57 g, 10.8 mmol), 50 mL of dichloromethane and 1.3 mL (11.7 mmol) of *N*-methylmorpholine were introduced with a syringe under nitrogen. A dichloromethane solution (20 mL) of ethyl chloroformate (1.11 mL, 11.6 mmol) was added in three portions to the mixture cooled at −15 °C. Then the reaction mixture was stirred at −13 °C for 20 min and at 0 °C for 40 min. The solvents were distilled out in vacuo and the residue was extracted three times with *n*-hexane (30-mL each). Evaporation of *n*-hexane in vacuo gave a transparent, viscous liquid of **1b** (0.197 g, 14% yield): ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 1.08 (t, J = 7.5 Hz, 3 H, CH_3), 2.29 (q, J = 7.5 Hz, 2 H, $MeCH_2$), 2.50 (t, J = 7.1 Hz, 2 H, CH_2CO_2), 3.58 (t, J = 7.1 Hz, 2 H, NCH_2); IR (chloroform solution) 1775, 1705 cm^{-1}.

By a procedure similar to that of **1a**, unsubstituted 6-oxazinone (**1d**) was obtained from *N*-formyl-β-alanine as a nitrobenzene solution, whose concentration was determined by ^{1}H NMR as 0.084 mol/L. ^{1}H NMR (nitrobenzene with cyclohexane as δ 1.43) δ 2.80 (t, J = 7.2 Hz, 2 H, CH_2CO_2), 3.80 (t, J = 7.2 Hz, 2 H, CH_2N); IR (nitrobenzene solution) 1780, 1660 cm^{-1}.

In a similar manner as monomer **1b**, 2-isopropyl-6-oxazinone (**1c**) (70% yield) and 4-phenyl-6-oxazinone (**1e**) (37% yield) were synthesized from *N*-isobutyryl-β-alanine and DL-2-formamido-2-phenylpropionic acid, respectively. **1c**: ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 1.20 (d, J = 6.8 Hz, 6 H, $(CH_3)_2$), 2.65 (m, J = 6.8 Hz, 1 H, CH), 2.59 (t, J = 7.0 Hz, 2 H, CH_2CO_2), 3.68 (t, J = 7.0 Hz, 2 H, CH_2N); IR (chloroform solution) 1780, 1700 cm^{-1}. **1e**: ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 2.55 (dd, J = 16.5, 10.8 Hz, 1 H, CH_2CO_2), 2.97 (dd, J = 16.5, 5.7 Hz, 1 H, CH_2CO_2), 4.75 (m, J = 10.8, 5.7, 2.7 Hz, 1 H, CHN), 7.23 (d, J = 2.7 Hz, 1 H, CH=N), 7.33 (s, 5 H, C_6H_5); IR (chloroform solution) 1790, 1665 cm^{-1}.

Cationic Polymerization. The polymerization of monomer **1a** (entry 1) is taken as a typical example. To a nitrobenzene solution of monomer **1a** (0.35 mol/L × 5 mL = 1.75 mmol) in a 10-mL reaction tube under nitrogen, 5.5 μL of MeI (5 mol % for **1a**) was added. The tube was sealed and kept for 336 h at room temperature. The tube was opened, and 0.5 mL of methanol and 1.0 mL of dimethylformamide were added to the reaction mixture. Then the mixture was poured into 150 mL of diethyl ether to precipitate polymeric materials, which were separated by filtration, washed two times with 5 mL of diethyl ether, and finally dried in vacuo to give 0.113 g of pale yellow powdery materials (57% yield). Spectroscopic data for the structural determination of poly(*N*-acetyl-β-alanine) (**2a**) are given in the text. The molecular weight determined by vapor pressure osmometry (VPO) in chloroform was 1500.

Similarly, polymers **1b–e** were obtained with MeI or $MeOSO_2CF_3$ initiator (entries 2–6). Spectral data for the determination of polymer structures are as follows. **2b** (white powdery materials): IR (KBr) 1710, 1680 cm^{-1}. **2c** (white powdery materials): ^{1}H NMR ($CDCl_3$ with Me_4Si, broad signals) δ 1.2

(6 H, $(CH_3)_2$), 2.6 (1 H, CH), 3.1 (2 H, CH_2CO), 4.0 (2 H, CH_2N); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 19.5 (CH_3), 34.5 (CH), 38 (CH_2CO), 41 (CH_2N), 174, 181 (C=O); IR (KBr) 1720–1680 cm^{-1}. **2d** (pale yellow powder materials): ^1H NMR ($CDCl_3$ with Me_4Si) δ 2.4–3.1 (2 H, CH_2CO), 3.2–3.9 (2 H, CH_2N), 7.0, 8.0, 8.4, 9.2 (four signals, total 1 H); IR (KBr) 1660, 1780 cm^{-1}. **2e** (pale yellow powdery materials): ^1H NMR ($CDCl_3$ with Me_4Si) broad signals δ 3.3 (2 H, CH_2), 6.1 (1 H, CHN), 7.5 (5 H, C_6H_5), 8.9 (1 H, CHO); IR (KBr) 1780, 1690–1660 cm^{-1}.

Thermal Polymerization. A nitrobenzene solution of monomer **1a** (0.35 mol/L × 7 mL = 2.45 mmol) was heated at 120 °C for 120 h in a sealed tube under nitrogen. The tube was opened and 0.1 mL of methanol and 0.4 mL of dimethylformamide were added to the solution. Then the mixture was poured into a mixed solvent of diethyl ether/*n*-hexane (110 mL/40 mL). The precipitated polymer materials were collected by filtration, washed three times with 10 mL of diethyl ether, and dried in vacuo to give 0.188 g of pale brown powder polymers (68% yield). Spectroscopic data were almost identical with those of polymer **2a** obtained by the cationic polymerization. The molecular weight was 1600.

Similarly, the thermal polymerization of monomer **1e** was carried out in acetonitrile at 110 °C for 45 h. After workup procedures, pale gray powdery polymers were obtained in low yield (31%). Spectral data were almost identical with those of polymer **2e** obtained by the cationic polymerization except for the lack of an IR band at 1780 cm^{-1}. This shows that the polymer obtained by the thermal polymerization has a regular structure given by **2e**.

Measurements. ^1H NMR and ^{13}C NMR spectra were taken respectively by a Hitachi 60-MHz R-20B NMR spectrometer and a Hitachi 22.6-MHz R-900 Fourier-transform NMR spectrometer. IR spectra were recorded on a Hitachi 260-50 infrared spectrophotometer. The molecular weights of polymers were determined by vapor pressure osmometry with a Corona 117 instrument in chloroform at 35 °C.

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Visible-Light-Mediated Living and Immortal Polymerizations of Epoxides Initiated with Zinc Complexes of N-Substituted Porphyrins

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ABSTRACT: The novel, visible-light-mediated *living* polymerization of epoxides was developed by using as initiators zinc N-methylated tetraphenylporphyrin complexes ((NMTPP)ZnX; X = $SCH_2CH_2CH_3$ (**1b**), $OCH(CH_3)_2$ (**1c**)) in benzene at room temperature. The NMR studies demonstrated that the polymerization is initiated by the attack of the axial group of the initiator onto the monomer, affording a (*N*-methyltetraphenylporphinato)zinc alkoxide as the growing species. The polymerization of 1,2-epoxypropane with **1b** proceeded with immortal character in the presence of a protic compound such as 1-propanethiol or methanol to give the polymer of narrow molecular weight distribution with the number of the molecules corresponding to the sum of those of **1b** and the protic compound. The polymerization of an episulfide, followed by an epoxide under visible light irradiation, afforded a block copolymer consisting of polythioether and polyether blocks of uniform block lengths.

Introduction

Photoinduced polymerization is a matter of fundamental interest as well as practical importance. For the ring-opening polymerization of epoxides, some photoinitiating systems have been developed, most of which serve as cationic initiators upon photodecomposition to generate protons or carbonium species.[1] In a preliminary communication, we have reported a different type of photoinduced polymerization, developed in the addition polymerization of methacrylic esters with methylaluminum porphyrin, which is initiated upon irradiation with visible light by the nucleophilic attack of the Al–CH_3 bond of the initiator to the monomer and proceeds without any side reactions (*living* character) via a (porphinato)aluminum enolate as the growing species.[2] Detailed stud-

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