Preparation of Block Copolymer of 2-Oxazoline and Butadiene

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ABSTRACT: A block copolymer of ABA type was prepared from 2-oxazoline (OXZ) (A) and polybutadiene (polyBD) (B). Polybutadiene having tosylate end groups (polybutadiene tosylate) was first prepared by the esterification of α,ω-poly(butadiene) glycol ($[\eta] = 0.13$) with tosyl chloride. The uv analysis of the tosylate end group indicated complete tosylation. Then, OXZ was polymerized by polybutadiene tosylate in a solvent mixture of toluene and dimethylformamide at 100°. Insoluble polymer precipitated from the OXZ polymerization mixture, which was shown to be an OXZ-BD block copolymer containing 61 mol % of OXZ unit. Alkaline hydrolysis of the block copolymer gave a rubbery material ($[\eta] = 0.33$) soluble in $CHCl_3$ which was shown to be a block copolymer consisting of ethylenimine and butadiene units.

The present paper describes the syntheses of two block copolymers of an ABA type. One consists of the poly(*N*-formylethylenimine) block (A block) and the polybutadiene block (B block). The other consists of the poly(ethylenimine) block (A block) and the polybutadiene block (B block). The syntheses are based on our recent findings of the isomerization polymerization of unsubstituted 2-oxazoline (OXZ)[2] by the alkyl tosylate initiator to produce poly(*N*-formylethylenimine) and the subsequent hydrolysis of the OXZ polymer into poly(ethylenimine) (polyEI) having a linear structure.[2] In the block polymer synthesis, α,ω-poly(butadiene) glycol was first esterified by tosyl chloride and, then, polybutadiene tosylate was used to initiate the OXZ polymerization. Before the present study, it had been reported that the polymerization of 2-substituted 2-oxazoline initiated by methyl tosylate proceeds *via* a living polymerization mechanism.[3,4] In addition, block copolymers of substituted oxazoline and substituted oxazine have been prepared by Litt.[5] The block copolymers of the present study are characterized by the combination of a nonpolar soft part of polybutadiene block and a crystalline hydrophilic part of polyOXZ (or poly(ethylenimine)) block.

Experimental Section

Reagents. OXZ was prepared and purified as reported previously.[2] Ethyl tosylate was purified by distillation: bp 134° (4 mm). Tosyl chloride (TsCl), diisopropyl ether (i-Pr_2O) and cyclohexane were commercial reagents and used without further purification. Toluene, 1-butanol, and dimethylformamide were purified by distillation and dried by molecular sieves 4A.

α,ω-Poly(butadiene) glycol was a commercial sample which was purified by reprecipitation (three times) from its benzene solution with methanol (nonsolvent), and dried *in vacuo* at 60°: mol wt 2840 (by vpo); $[\eta] = 0.13$.

Preparation of *n*-Butyl Tosylate. *n*-Butyl tosylate was prepared according to the method of Klamann:[6] bp 142° (0.9 mm). *Anal.* Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 6.88. Found: C, 58.10; H, 6.88.

Preparation of *p*-Toluenesulfonic Acid Ester of α,ω-Poly(butadiene) Glycol (Polybutadiene tosylate). Tosyl chloride (8.2 g, 43 mmol) was added to a stirred solution of α,ω-polybutadieneglycol (27.0 g, 7.64 mmol) in a pyridine (27 ml)-$CHCl_3$ (10 ml) mixture. The mixture was kept at 20° for 4 hr with stirring. Then, the product polymer was isolated by precipitation in cold methanol and purified by the precipitation (three times) from its $CHCl_3$ solution with cold methanol (nonsolvent). The isolated polymer was dried at 60° *in vacuo*: yield 26.8 g; $[\eta] = 0.13$.

Preparation of OXZ-BD Block Copolymer. OXZ (2.12 g, 29.2 mmol) was added to polybutadiene tosylate (2.03 g, 0.49 mmol) in a mixture of toluene and dimethylformamide (each 6 ml), and the reaction mixture was heated at 100° for 16 hr. As the reaction proceeded, polymer precipitated as a white powder. After the reaction, the mixture was poured into a large amount of diethyl ether and the solid polymer was filtered, washed with ether, and dried *in vacuo*. The yield of powdery product was 1.85 g. *Anal.* Found: C, 61.3; H, 8.3; N, 13.3.

Alkaline Hydrolysis of OXZ-BD Block Copolymer into EI-BD Block Copolymer. NaOH (0.7 g, 17.5 mmol) was added to OXZ-BD block copolymer (0.72 g, OXZ unit 6.8 mmol) in water (7 ml). The mixture was stirred at 100° for 6 hr. Insoluble product was isolated by filtration and washed with water until the washings became neutral. The material was dried *in vacuo* at 60° to give 0.48 g of rubbery polymer: $[\eta] = 0.33$; gel content (chloroform insoluble part), 1.4%.

Nmr Spectra. Nmr spectra were taken on a JNM 4H-100 nmr spectrometer (Jeol) using Me_4Si as an internal standard.

Ir Spectra. A solution of α,ω-poly(butadiene) glycol in i-Pr_2O, after it had been diluted to a specified volume, was subjected to ir spectrum measurement, and the hydroxyl groups at polymer ends were analyzed. Ir spectra were taken with Jasco Model DS-402G infrared spectrophotometer (Japan Spectroscopic Co., Ltd., Japan).

Uv Spectra. A cyclohexane solution of polymer, which was diluted to a specified volume, was subjected to uv spectroscopic analysis, and the tosylate groups at the polymer ends were determined. Uv spectra were taken with Hitachi Model EPS-3T spectrophotometer (Hitachi Ltd., Japan).

Molecular Weight Determination. Osmotic molecular weights were determined in benzene by means of a Mechrolab Model 301A membrane osmometer. Intrinsic viscosity ($[\eta]$) of the polymer was measured in $CHCl_3$ at 30°.

Results and Discussion

Characterization of Poly(butadiene) Glycol. α,ω-Poly(butadiene) glycol was a liquid polymer (mol wt 2840) consisting mainly of 1,2 linkage as shown by ir spectrum, *i.e.*, two strong absorption bands at 910 and 1000 cm^{-1} (Figure 1a). The primary alcohol groups at polymer ends were qualitatively characterized by the C-O stretching band at 1055 cm^{-1}. The nmr spectrum of the polymer (Figure 2a) showed a triplet at τ 6.35 due to *O*-methylene protons. From these results the following structure is reasonably assigned to the end groups of poly(butadiene) glycol.

$$HOCH_2CH_2{\sim\sim}CH_2CH_2OH$$

The amount of OH groups at the polymer ends was determined by ir analysis. The extinction coefficient of the band at 3500 cm^{-1} was estimated from the coefficient of a model compound of 1-butanol in the same solvent, which showed the same shape of absorption as poly(butadiene)

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(1) Tokyo Research Laboratories, Japan Synthetic Rubber Co., Kawasaki, Japan.

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(3) T. G. Bassiri, A. Levy, and M. Litt, *J. Polym. Sci., Part B*, **5**, 871 (1967).

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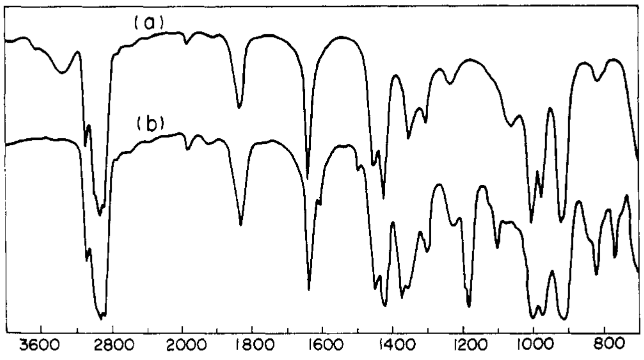


Figure 1. Ir Spectra of (a) poly(butadiene) glycol and (b) polybutadiene tosylate (neat).

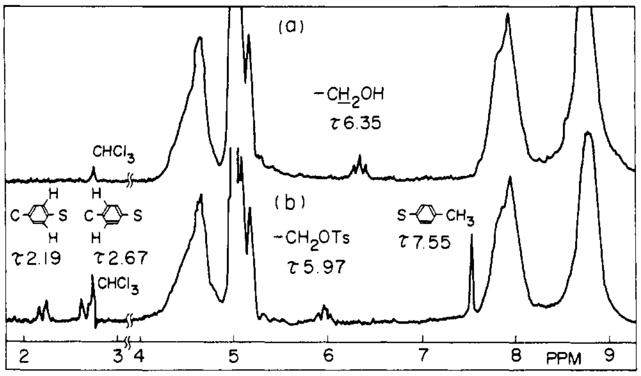


Figure 2. Nmr spectra of (a) poly(butadiene) glycol and (b) polybutadiene tosylate in $CDCl_3$.

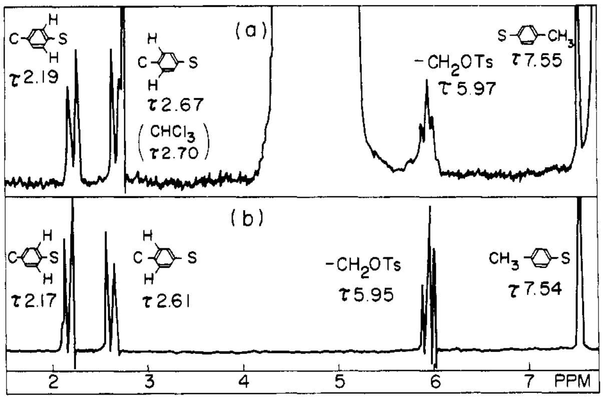


Figure 3. Nmr spectra of (a) polybutadiene tosylate and (b) *n*-butyl tosylate in $CDCl_3$.

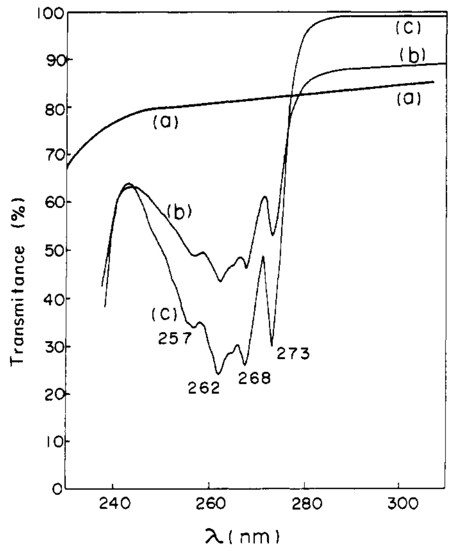


Figure 4. Uv spectra of poly(butadiene) glycol (a), polybutadiene tosylate (b), and ethyl tosylate (c) in cyclohexane.

glycol. The molar extinction coefficient of 1-butanol was determined from the slope of the linear relationship between the optical density at 3500 cm^{-1} and the concentration, ϵ_{max} at 3500 cm^{-1} was 129. From the amount of the terminal OH group and the molecular weight of the polymer (2840), the number of the OH functionality (the number of OH group per one polymer molecule) was calculated; $f = 1.65$. This value means that 82% of the polymer ends are of OH group.

Tosylation of Poly(butadiene) Glycol. The reaction of poly(butadiene) glycol with excess tosyl chloride was carried out in a $CHCl_3$-pyridine mixture at 20°. As the reaction proceeded, pyridine-HCl salt precipitated. The conversions were determined by nmr, *i.e.*, the peak intensity ratio of *O*-methylene protons of poly(butadiene) glycol (τ 6.35) and of polybutadiene tosylate (τ 5.97) was measured. The reaction occurred smoothly and was found to be almost complete after 4 hr. The tosylated polymer was also a liquid having a molecular weight of 3450 ($[\eta] = 0.13$). In the ir spectrum of the polymer (Figure 1b), the absorptions at 767 and 821 cm^{-1} are ascribed to the benzene ring of tosylate and the absorptions at 1370, 1181, and 1100 cm^{-1} are assigned to the sulfonate ester group. The absorption at 3330 cm^{-1} in the starting poly(butadiene) glycol disappeared by tosylation. The bands due to the polybutadiene structure remained unchanged.

$$\underset{\text{I}}{HOCH_2CH_2\sim\sim CH_2CH_2OH} \xrightarrow{TsCl} \underset{\text{II}}{TsOCH_2CH_2\sim\sim CH_2CH_2OTs}$$

These results clearly indicate almost quantitative tosylation of the OH group of the poly(butadiene) glycol. In the nmr spectrum of the tosylated polymer (Figure 2b), the peak of *O*-methylene protons (τ 5.97) appeared at a lower field than that of *O*-methylene protons (τ 6.35) of the starting polymer (Figure 2a). The nmr peak assignment was made by comparison with the spectrum of a model compound; *n*-butyl tosylate (Figure 3). Two doublets at τ 2.19 and 2.67 were due to aromatic protons, and a singlet at τ 7.55 and a triplet at τ 5.97 were respectively, due to methyl protons and *O*-methylene protons of tosylate group. Also, the product polymer was shown to be free from methyl tosylate, which might have been formed by the reaction of excess of tosyl chloride with methanol.

Quantitative analysis of tosyl group at the polymer end was performed by means of uv spectroscopy. Figure 4 shows the uv spectra of poly(butadiene) glycol (a), of polybutadiene tosylate (b), and of ethyl tosylate (c) in cyclohexane. The two tosylates have the same characteristic absorption maxima at 257, 262, 268, and 273 nm, whereas the glycol has no characteristic absorption band in this region. A small correction was made for the absorption at $\lambda_{max} = 273$ nm due to the polybutadiene part, by extrapolating of the absorption curve of the tosylated polymer in the region of 290 ~ 310 nm.

The extinction coefficient (ϵ_{max}) of the absorption at 273 nm of the tosylate group in polymer was estimated from the coefficients of two alkyl tosylates, ethyl and butyl tosylates. In cyclohexane, the two alkyl tosylates showed the same absorption spectra and the same extinction coefficient at 273 nm; ϵ_{max} at 273 nm was 390 l./(mol cm). From these results, the ϵ_{max} value of ethyl tosylate was reasonably assigned also to the tosylate group at the

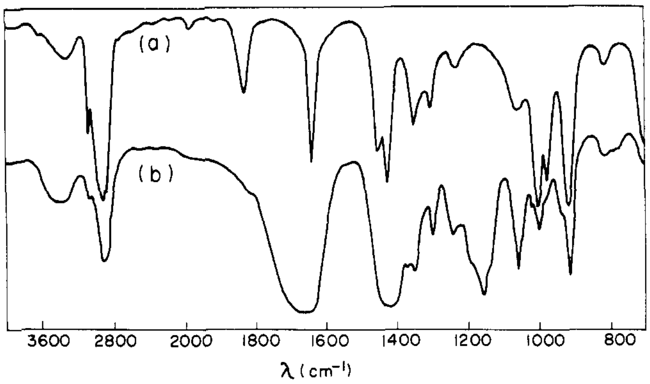


Figure 5. Ir spectra of poly(butadiene) glycol (neat) (a) and OXZ-BD block copolymer (b) (KBr).

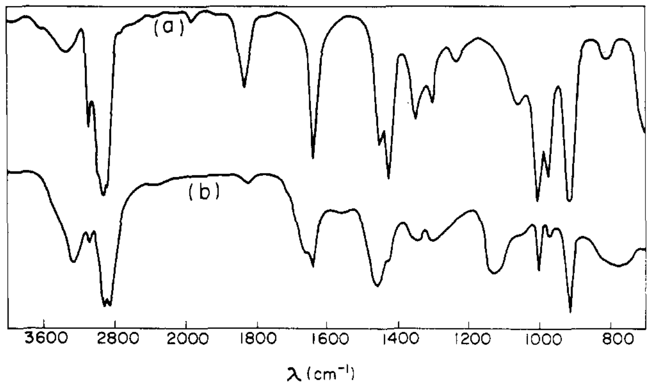


Figure 6. Ir spectra of (a) poly(butadiene) glycol and (b) EI-BD block copolymer (neat).

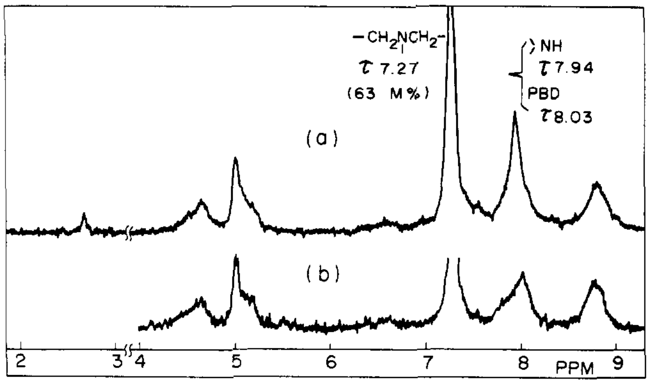
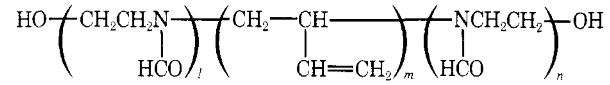


Figure 7. Nmr spectra of (a) EI-BD block copolymer and (b) EI-BD block copolymer treated with D$_2$O in CDCl$_3$.

polymer end. Then, the content of tosylate group in polymer was determined from the value of optical density at 273 nm. From the values of tosylate group content and the molecular weight (3450) of the polymer, the functionality of the tosylated polymer was calculated; f = 1.65. This value was in good agreement with that of the OH functionality. Thus, the complete tosylation of the polybutadieneglycol has also been demonstrated.

Preparation of OXZ-BD Block Copolymer. OXZ was added to a toluene-dimethylformamide solution of α,ω-polybutadiene tosylate and the mixture was stirred at 100°. As the reaction proceeded, the system became heterogeneous and the system soon solidified. The solid mass was pulverized in ether and washed with ether to remove the unreacted monomer and the starting polybutadiene. The product was a white powder and insoluble in ether, benzene, and CHCl$_3$ which dissolved polybutadiene tosylate. The block copolymer was insoluble also in methanol, dimethylformamide, and water. PolyOXZ is soluble in water. These solubility characteristics indicate that the polymer obtained is a OXZ-BD block copolymer. As will be described below, the results of the alkaline hydrolysis of the copolymer showed that the insoluble character of the copolymer was not due to a cross-linked structure.

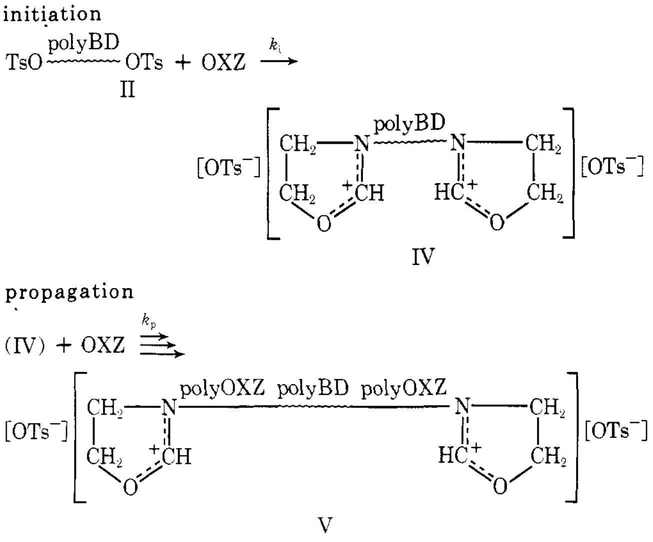
The ir spectrum of the block polymer (Figure 5b) showed absorption bands due to polybutadiene and a strong band at 1640 ~ 1670 cm^{-1} assignable to the amide ν_{CO}. DSC analysis of the block copolymer demonstrated the presence of an endothermic peak at 197° corresponding to the crystalline melting temperature of polyOXZ.[2] The content of the OXZ unit in the block copolymer was 61 mol %, which was calculated on the basis of the elemental analysis of the copolymer. These findings show that the product contains the ABA type of block copolymer composed of polyOXZ and polyBD blocks (III). The molecular weight of polyOXZ block was calculated to be 7100 ($l + n$ = 100 in III).



$$HO\left(CH_2CH_2\underset{HCO}{N}\right)_l\left(CH_2-\underset{CH=CH_2}{CH}\right)_m\left(\underset{HCO}{N}CH_2CH_2\right)_n OH$$

III

Polymerization of OXZ by polybutadiene tosylate is considered to proceed according to the reaction scheme which has been proposed for the OXZ polymerization initiated by alkyl tosylates.[7]



In the initiation reaction, a polymer oxazolinium salt (IV) is formed by bimolecular reaction of polybutadiene tosylate with OXZ monomer. Successive nucleophilic attack of OXZ on (IV) (propagation reaction) gives living block copolymer with oxazolinium ions at the polymer ends (V). The amount of the block copolymer product was small (see Experimental Section). It was even smaller than the amount of the starting polybutadiene prepolymer. This may be ascribed mainly to the following two reasons: (i) the presence of the prepolymer having no tosylate end group; (ii) smaller k_i value in comparison with the k_p value in the OXZ polymerization by polymer tosylate.[7]

Alkaline Hydrolysis of OXZ-BD Block Copolymer into Ethylenimine (EI)-BD Block Copolymer. The OXZ-BD block copolymer was subjected to alkaline hydrolysis, in which the block of poly(*N*-formylethylenimine) was converted into poly(ethylenimine) block. The alkaline hydrolysis was also important for the structure

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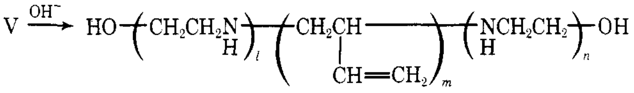
(7) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, in press.

analysis, because the OXZ-BD block copolymer was quite insoluble and could not be well analyzed. The OXZ-BD block copolymer was hydrolyzed in aqueous alkaline solution at 100° for 4 hr. A swollen product was washed by water and dried *in vacuo* at room temperature to give a powdery material. This became a rubbery polymer by treating at 90° *in vacuo*. The rubbery product was soluble in $CHCl_3$ having $[\eta]$ of 0.33 which is larger than that of polybutadiene tosylate ($[\eta] = 0.13$).

As shown in Figure 6b, the ir spectrum of the product has no absorption of amide group, but it has bands characteristic of the polybutadiene structure, as well as the bands at 3260 cm^{-1} (NH), 1122 cm^{-1} (C-N) and 784 cm^{-1}, which are attributable to the polyethylenimine structure.[8] The nmr spectrum of the polymer taken in $CDCl_3$ (Figure 7a) shows peaks at τ 4.65, 5.03, and 8.03 due to the protons of polybutadiene and peaks at τ 7.27 and 7.94, which are assignable to N-methylene protons ($(-CH_2)_2N-$) and amine proton (>NH), respectively. D_2O treatment of the nmr sample solution decreased the combined areas of the peaks at τ 7.8–8.2. The decrease corresponded to the number of the secondary amine proton. This observation is taken to confirm the structure of the block copolymer (Figure 7b). The peak intensity ratio of N-methylene protons to amine proton is 4:1. No peak due to amide structure ($-CH_2N(HCO)CH_2-$) was observed in the spectrum, which shows complete hydrolysis. These results indicate that the product of the alkaline hydrolysis is an ABA-type block copolymer (VI) with El block (A) and



$$\mathrm{V} \xrightarrow{OH^-} HO\!\left(CH_2CH_2\underset{H}{N}\right)_l\!\left(CH_2\underset{CH=CH_2}{CH}\right)_m\!\left(\underset{H}{N}CH_2CH_2\right)_n\!OH$$

VI

BD block (B). The EI unit content in the block copolymer (VI) was found to be 63 mol % by nmr. This value was in good agreement with that of OXZ-BD block copolymer (61 mol %). The molecular weight of polyEI block was calculated to be 4700 ($l + n \sim 109$ in VI). The degree of polymerization of polyEI block agreed fairly well with that of polyOXZ block before hydrolysis.

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(8) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 108 (1972).

Isomerization Polymerization of 2-Oxazoline. VI. Kinetic Study on the Polymerization of 2-Methyl-2-oxazoline Initiated by Methyl Iodide

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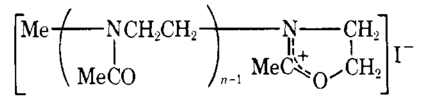
ABSTRACT: A kinetic study of the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) initiated by methyl iodide (MeI) was made on the basis of the determination of the instantaneous concentrations of MeI, MeOXZ, and the propagating species of oxazolinium salt by means of nmr spectroscopy. The rate was expressed by the equation $-d[M]/dt = k_i[MeI][M] + k_{p1}[P_1^*][M] + k_{pn}[M]\Sigma_{n=2}[P_n^*]$, where k_i, k_{p1}, and k_{pn} are the rate constants for the initiation, the first propagation step and the subsequent propagation steps, respectively. $[P_1^*]$ and $[P_n^*]$ ($n \geq 2$) are the instantaneous concentrations of the propagating species of two types having $n = 1$ and $n \geq 2$, respectively, of the formula



The values of k_{p1} and k_{pn} were in good agreement with the respective values of the MeOXZ polymerization initiated by the isolated species of $[P_1^*]$. The activation parameters were obtained from the Arrhenius plots of rate constants at different temperatures. The difference in the polymerization mechanism between the unsubstituted 2-oxazoline (OXZ) and MeOXZ by a common MeI initiator was discussed.

This paper deals with a kinetic study on the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) initiated by methyl iodide (MeI). As to the kinetics of the polymerization of 2-substituted 2-oxazolines, two studies have already been made by Tomalia *et al.*,[2] and by Kagiya *et al.*[3] In our previous kinetic studies on the polymerizations of substituted and unsubstituted oxazolines[4,5] a convenient method has been established in which each of the instantaneous concentrations of monomer, initiator, and propagating species is directly determined by means of nmr spectroscopy. In the MeI-initiated polymerization of unsubstituted 2-oxazoline (OXZ), the propagating species was shown to be a covalent-bonded alkyl iodide species.[5] In the present study, the MeOXZ polymerization by MeI has been shown to proceed through a different mechanism.

Experimental Section

Reagents. MeOXZ was prepared and purified as before.[4] MeI, a commercial reagent, was purified by distillation under nitrogen. Trideuterioacetonitrile (CD_3CN) was a commercial reagent which was dried by molecular sieves 4A (Union Carbide) and distilled under nitrogen.

Preparation of N-Methyl-2-methyl-2-oxazolinium Iodide (2). To a stirred solution of MeI (8.52 g, 60 mmol) in ether (10 ml) was slowly added MeOXZ (1.28 g, 15 mmol) at 5°. The solution

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