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Novel Initiators Having Acetylene Group for Polymerization of 2-Oxazolines

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Propagylic halide type compounds such as propagyl bromide, 1,4-dibromo-2-butyne, and 1,6-dibromo-2,4-hexadiyne, were used for the polymerization of 2-oxazolines. The polymerization initiated by these initiators gave polymers with narrow molecular weight distribution. From kinetic study, the polymerization using these initiators is found to be a relatively fast initiation system.

Cationic ring-opening polymerization of 2-oxazolines (ROZO) provides a convenient method to produce linear poly(*N*-acrylethylenimine)s (PROZO). The polymerization chemistry has been thoroughly investigated and product polymers have found various applications.1) Very recently we have shown that allylic dihalides, 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-1-propene, are very effective as a novel bifunctional initiator for 2-oxazoline monomers giving rise to a fast initiation and slow propagation system.2) Polymerization of ROZO using the latter two initiators followed by hydrolysis of the living terminal ends gave telechelic PROZOs having an olefinic group with narrow molecular weight distribution.

It is well known that propagylic halides as well as allylic halides are highly reactive electrophiles. The present paper describes the polymerization of ROZO using a propagylic halide as an initiator. The initiators used are propagyl bromide (**1**), 1,4-dibromo-2-butyne (**2**), and 1,6-dibromo-2,4-hexadiyne (**3**).3)

$$HC\equiv C-CH_2Br$$

1

$$BrCH_2-C\equiv C-CH_2Br$$

2

$$BrCH_2-C\equiv C-C\equiv C-CH_2Br$$

3

Polymerization of ROZO initiated by **1-3** was carried out in acetonitrile. Subsequent hydrolysis[6] of the polymer ends gave quantitatively PROZO possessing a hydroxyl group at the chain end (Table 1).[7] The structure of the resulting polymer was confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy. The degree of polymerization (*DP*) of the polymer obtained by vapor pressure osmometer (VPO) was close to the feed ratio of the monomer to initiator. The molecular weight distribution evaluated by M_w/M_n obtained by gel permeation chromatography (GPC) was relatively narrow. These results indicate that the polymerization initiated by these initiators is of a relatively fast initiation system.

Table 1. Polymerization of 2-oxazolines ROZO using **1-3** as an initiator

	Polymerization				Characterization			
Entry	ROZO	Initiator	$\frac{[\mathrm{ROZO}]_0}{[\mathrm{Initiator}]_0}$	Temp °C	Yield %	M_n [a]	*DP* [a]	M_w/M_n [b]
1	MeOZO	**1**	10.2	70	quant.	1000	11.1	1.21
2	MeOZO	**1**	19.9	70	quant.	1720	19.5	1.29
3	EtOZO	**1**	10.1	70	92	960	9.1	1.23
4	MeOZO	**2**	9.5	70	quant.	1110	12.0	1.19
5	MeOZO	**2**	8.8	35[c]	95	770[d]	8.1[d]	1.30
6	MeOZO	**2**	20.4	70	quant.	1830	20.5	1.24
7	EtOZO	**2**	9.9	70	quant.	1330	12.5	1.20
8	EtOZO	**2**	20.1	70	quant.	2100	20.3	1.27
9	MeOZO	**3**	10.0	70	quant.	1130	11.9	1.24
10	MeOZO	**3**	19.8	70	quant.	1620	17.8	1.38
11	EtOZO	**3**	9.9	70	quant.	1170	10.7	1.35

a) From VPO. b) Obtained by GPC. c) Reaction time; 48 h. d) Determined by ^{1}H NMR.

Table 2. Rate constants of the MeOZO polymerization in CD_3CN at 35 °C[a)]

Initiator	k_i[b)]	k_p[b)]
1	1.5	7.2 (8.1)[c)]
2	1.1	7.4
3	2.1	7.4
Allyl bromide	3.8	7.0
n-Butyl bromide	0.14	7.7

a) Polymerization conditions: $[\mathrm{MeOZO}]_0=3.3$ mol/L, $[\mathrm{initiator}]_0=0.55$ mol/L.

b) x 10^5 (mol · s).

c) The value in the parenthesis was obtained by benzyl bromide initiator at 35 °C in CD_3CN.[8a)]

In order to evaluate the reaction rate quantitatively, a kinetic study of the polymerization of MeOZO initiated by these initiators was carried out by ^{1}H NMR spectroscopy,[8)] where the instantaneous concentrations of monomer and initiator were determined. The rate constants of initiation k_i and propagation k_p are listed in Table 2. In the case of the bifunctional initiators **2** and **3**, the k_i values denote average ones of two reaction sites. The initiation rate constants of **1**-**3** are very close and slightly smaller than that of the propagation. It can be seen that the initiation by **1** proceeded a little smaller than that by allyl bromide. These results imply that the polymerization using **1**-**3** as an initiator is a relatively fast initiation system.

In this study, a propagylic halide compound was used for the first time for the polymerization initiator of ROZO, giving a relatively fast initiating system. The initiation reactivity of the present initiaors was slightly smaller than that of allylic halides, used in our previous study.[2)] The resulting polymer possesses an acetylene or a diacetylene group, which is well known to be a polymerizable group. Applications of the polymer as a macromonomer are currently under progress in our laboratory.

References

1) For recent papers on 2-oxazoline polymerizations, see: S. Kobayashi, *Prog. Polym. Sci.*, **15**, 751(1990); S. Kobayashi and H. Uyama, *Polym. News*, **16**, 70(1991); H. Uyama and S. Kobayashi, *Macromolecules*, **24**, 614(1991); M. Miyamoto, K. Aoi, and T. Saegusa, *ibid.*, **24**, 11(1991); G. Cai, M. H. Litt, and I. M. Krieger, *J. Polym. Sci., Polym. Phys. Ed.*, **29**, 773(1991).

2) S. Kobayashi, H. Uyama, and Y. Narita, *Macromolecules*, **23**, 353(1990).

3) Initiator **1** is commercially avairable, and **2** and **3** were obtained by the reaction of the corresponding diols and phosphorus tribromide.4,5)

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5) J. B. Armitage and W. C. Whiting, *J. Chem. Soc.*, **1952**, 2005.

6) Quantitative introduction of a hydroxyl group at the chain end was achieved according to the following literature: G H. Hsiue, A. X. Swamikannu, and M. H. Litt, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 3043(1988).

7) A typical run was as follows (entry 1). Under argon, 0.859 g (10.1 mmol) of MeOZO and 0.118 g (0.991 mmol) of propagyl bromide (**1**) were dissolved in 5 mL of dry acetonitrile. The reaction mixture was heated at 70 °C for 24 h. After cooling to room temperature, 1 mL of 1.0 mol/L NaOH methanol solution was added to the mixture. Then, the solvent was evaporated and the residue was extracted with 30 mL of chloroform. The chloroform layer was separated, concentrated, and poured into a large amount of diethyl ether to precipitate white powdery solids. The solid was collected and dried in vacuo to give 0.967 g of the polymer (yield 99%).

8) a) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 392(1972); b) T. Saegusa, S. Kobayashi, and A. Yamada, *Makromol. Chem.*, **177**, 2270(1976).

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