with the cure time and then fell off. The ones at the maximum intensity increase were selected and presented as p.cured 1 on Figure 1A and Figure 2. The above observation tends to suggest that the extent of segregation depends on the initiator content.

The SANS results for sample C, which contains the most initiator among the three samples studied in this work, also reveal an extensive intensity increase in the low q region during the early stage of cure, followed by a decrease in the later stage (parts A and B of Figure 3). In the fully cured sample a rather pronounced maximum is visible. For this set of samples, the SANS result of the uncured sample is absent because the initiator was added to the "uncured" sample; during the course of SANS measurement the temperature was maintained at 50 °C, which resulted in partial curing. (For the other two sets of samples, no initiator was added to the uncured samples.)

At the present time we cannot rationalize all the findings,' and more work is apparently needed. Nevertheless, the SANS results covered in this note strongly suggest that cross-linking can induce segregation in bimodal networks. This result is consistent with earlier findings for the epoxy–amine system. In light of this new discovery, some of the earlier observations made on bimodal networks need to be reexamined.

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Wen-li Wu* and Laurence D. Coyne
Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Lei Jong, Aiko Hanyu, and Richard S. Stein
Polymer Research Institute, University of Massachusetts Amherst, Massachusetts 01002

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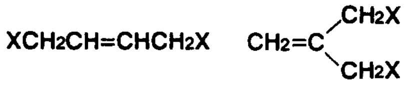
Novel Bifunctional Initiator for Polymerization of 2-Oxazolines via Fast Initiation

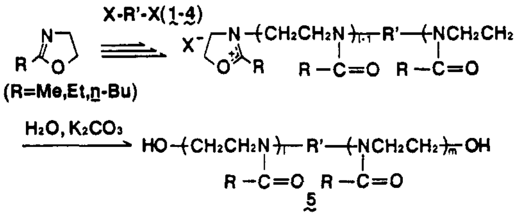
Electrophilic (cationic) ring-opening polymerization of cyclic imino ethers produces linear poly(N-acylalkylenimines), which become hydrophilic or hydrophobic depending on the nature of acyl group.[1] The polymerization is of highly living nature in using methyl iodide, methyl p-toluenesulfonate, and benzyl bromide as a monofunctional initiator, where the initiation rate is very close to or larger than that of propagation.[2] On the other hand, a bifunctional initiator is very important to prepare block copolymers[3] and telechelics.[4] Few examples of such initiators have been reported. α,ω-Dodecamethylene bis(p-toluenesulfonate) was first used as a bifunctional initiator for the polymerization of 2-oxazoline.[5] With the use of an alkylene bis(p-toluenesulfonate), the molecular weight distribution of the polymer was broad, which implies that the initiation rate was smaller than that of the propagation.[6] However, by using bis(oxazolinium salts) such as 3,3′-ethylene bis(2-oxazolinium trifluoromethanesulfonate)[7] and N,N'-dimethyl-2,2′-tetramethylene bis(oxazolinium tosylate)[3] as a bifunctional initiator, monodisperse poly(2-oxazolines) were obtained, indicating the relatively fast initiation with respect to the propagation. These salt-type initiators, however, are very elaborative to prepare and inconvenient to handle due to the easily hydrolyzable property. The present paper discloses a novel bifunctional initiator having an allylic dihalide structure 1–4 for the polymerization of 2-oxazolines giving rise to a "fast initiation system" of living nature.



$XCH_2CH{=}CHCH_2X$ $CH_2{=}C(CH_2X)_2$

1: X=Br **3**: X=I
2: X=Cl **4**: X=Cl

1,4-Dibromo-2-butene (trans) (**1**) and 3-iodo-2-(iodomethyl)-1-propene (**3**) have been used for the first time in this study as a bifunctional initiator for the polymerization of 2-alkyl-2-oxazolines (ROZOs). Initiator **1** is commercially available, and **3** is readily obtained from a commercially available chloro analogue, **4**. Telechelic poly(2-oxazolines) having a hydroxyl group at both ends, **5**, were synthesized by the polymerization of ROZO using these initiators followed by hydrolysis of a terminal oxazolinium group as previously reported.[4] The structure of **5** was confirmed by ^{1}H NMR and IR spectroscopy (Table I). In most cases the yield of polymer **5** was quantitative. The degree of polymerization (DP) of **5** determined by vapor pressure osmometry (VPO) is always very close to the monomer/initiator feed ratio. The M_w/M_n value obtained by gel permeation chromatography (GPC) is relatively small. These results are explained by the rapid initiation followed by the subsequent relatively slow propagation. With use of 1,4-dibromobutane (**6**) as a bifunctional initiator, the DP of **5** was larger than the feed ratio and the M_w/M_n value was large, indicating the slow rate of initiation compared with that of propagation.



1,4-Diiodo-2-butene is not stable enough to be isolated at room temperature. Therefore, sodium iodide was added to the mixture of 1,4-dichloro-2-butene (**2**) (trans:cis = 3:2) and 2-methyl-2-oxazoline (MeOZO) under stirring at 0 °C for 2 h to give an iodide counteranion in situ during the polymerization. The polymer yield was high, and the DP of the polymer was close to the feed ratio (Table II). The M_w/M_n value obtained by GPC is small (1.15). These results can be taken to support that the polymerization is of fast initiation and of slow propagation. Similarly, the polymerization of MeOZO was carried out using 3-chloro-2-(chloromethyl)-1-propene (**4**)/sodium iodide as a bifunctional initiator (entry 11). The DP of the polymer obtained was close to the feed ratio, and the molecular weight distribution evaluated by M_w/M_n was very narrow.

In order to evaluate the reaction rate quantitatively, a kinetic study of the polymerization of MeOZO initiated

Table I
Polymerization of ROZO Using 1 and 3 as a Bifunctional Initiator

	polymerization[a]				characterization of 5			
entry no.	ROZO	initiator	$[ROZO]_0/[initiator]_0$	time, h	yield, %	M_n[b]	DP[b]	M_w/M_n[c]
1	MeOZO	1	9.0	7	95	960	10.2	1.19
2	MeOZO	1	19.0	14	97	2110	23.8	1.26
3	MeOZO	3	9.4	7	94	1050	11.2	1.11
4	MeOZO	3	21.6	14	84	2010	22.6	1.30
5	EtOZO	1	20.8	18	70	2120	20.5	1.38
6	EtOZO	3	19.1	18	79	1760	16.8	1.33
7	*n*-BuOZO	1	19.1	26	96	2180	16.4	1.40
8	*n*-BuOZO	3	18.4	26	70	2130	16.1	1.29
9	MeOZO	6	9.6	8	79	1700	18.9	1.60

[a] [Initiator] = 1 mmol in 5 mL of acetonitrile at 80 °C under argon. [b] From VPO. [c] Obtained by GPC.

Table II
Polymerization of 2-Methyl-2-oxazolines Using Allylic Dichloride/Sodium Iodide as a Bifunctional Initiator

	polymerization[a]		characterization of 5			
entry no.	initiator	$[MeOZO]_0/[initiator]_0$	yield, %	M_n[b]	DP[b]	M_w/M_n[c]
10	2	10.1	85	1020	10.9	1.15
11	4	10.0	82	1040	11.2	1.19

[a] [Initiator] = 1 mmol, [NaI] = 2.2 mmol in 5 mL of acetonitrile at 80 °C for 7 h under argon. [b] From VPO. [c] Obtained by GPC.

Table III
Rate Constants of the MeOZO Polymerization in CD_3CN at 35 °C[a]

initiator	k_{i1}[b]	k_{i2}[b]	k_i[b]	k_p[b]
1	1.2	1.0		0.81[c]
3	1.5	2.1		0.76[d]
allyl bromide			0.38	0.81[c]
n-butyl bromide			0.015	0.81[c]
MeI			2.2	0.76[d]

[a] Polymerization conditions: [MeOZO] = 3.3 mol/L, [initiator] = 0.55 mol/L. [b] $\times 10^{-4}$ L/mol·s. [c] The value was obtained with benzyl bromide initiator.[2c] [d] The value is the calculated one at 35 °C from the data of methyl iodide initiator.[2b]

by 1 or 3 was carried out by ^1H NMR spectroscopy. Both initiators gave a living polymerization system. Table III lists the rate constants of initiation k_{i1} and k_{i2} for two reaction sites of initiator[8] and of propagation (k_p). The k_{i1} and k_{i2} values of 1 and 3 are not so much different and larger than the k_p value. It is to be noted that 1 showed a higher initiation reactivity than allylic bromide. The k_i value of *n*-butyl bromide was much smaller than k_{i1} and k_{i2} of 1. These data indicate that the polymerization using 1 or 3 as a bifunctional initiator is a "fast initiation–slow propagation system". More detailed studies on the related initiators including kinetic results will be reported in a forthcoming full paper.

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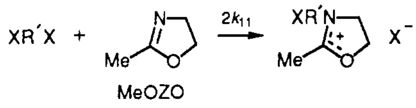

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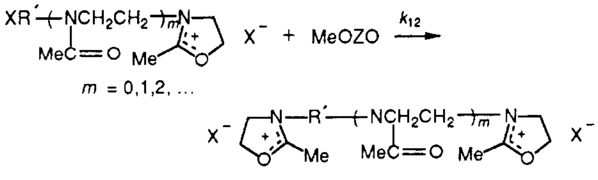

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Shiro Kobayashi,* Hiroshi Uyama, and Yutaka Narita

Department of Molecular Chemistry and Engineering
Faculty of Engineering, Tohoku University
Aoba, Sendai 980, Japan

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