Notes

Synthesis of Poly(2-oxazoline) Macromonomers Having a Vinyl Ester Group

HIROSHI UYAMA AND SHIRO KOBAYASHI*

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

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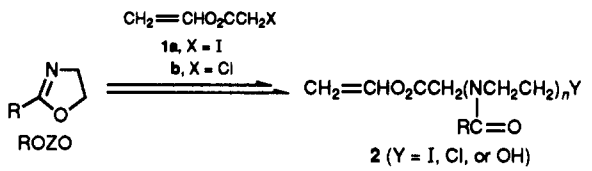
Introduction

Macromonomers are widely used for the convenient preparation of graft copolymers of well-defined structures.[1] Most of these macromonomers possess a styryl or (meth)acryl type polymerizable group. These macromonomers are usually copolymerized with comonomers having the same polymerizable group such as styrene or (meth)acryl ester wherein the radical reactivity ratios of the macromonomer are then almost the same as that of the comonomer. For this reason these macromonomers can rarely be copolymerized radically with less reactive monomers such as vinyl acetate or vinyl chloride.

Cationic ring-opening polymerization of 2-oxazolines (ROZO) provides a convenient method to prepare poly(*N*-acylethylenimines) (PROZO).[2] PROZO macromonomers having styryl, (meth)acryl, or glycol type polymerizable groups have been recently synthesized.[3-5] The present paper describes the first synthesis of PROZO macromonomers **2** possessing a polymerizable vinyl ester group. Relative to the present study, only one example of a macromonomer with a vinyl ester group at the chain end has been reported so far: a polystyrene macromonomer having a vinyl ester group was synthesized by termination of the living polystyrene end with vinyl chloroacetate.[6]



Results and Discussion

Synthesis of Macromonomer Having a Vinyl Ester. The polymerization of ROZO was carried out with vinyl iodoacetate (**1a**) as initiator at 60 °C in acetonitrile to give a vinyl ester type macromonomer **2**. The structure of **2** was confirmed by ^{1}H NMR spectroscopy.

Polymerization results are given in Table I. In all cases the polymer yields of **2** were almost quantitative (entries 1-4). The degrees of polymerization (DP) of **2** determined by vapor pressure osmometry (VPO) and ^{1}H NMR spectroscopy were always close to the feed ratio. The M_w/M_n values obtained by gel permeation chromatography (GPC) were relatively small. The functionality, i.e., the number of vinyl ester groups per molecule, is almost exactly 1.0. These data can be taken to support that the polymerization is of fast initiation with relatively slow propagation and proceeds through a highly living system.

Instead of choosing **1a** as the initiator, a mixture of vinyl chloroacetate (**1b**) and sodium iodide was used for the polymerization of ROZO;[7] a 10% molar excess of sodium iodide was added, under stirring to the mixture of **1b** and ROZO at 0 °C over 2 h, giving rise probably to an in situ iodide counteranion during the polymerization. The DP values of **2** thus obtained were close to the feed ratio, and the molecular weight distributions (M_w/M_n) were narrow (entries 5-7). Furthermore, the functionality of **2** was close to 1.0 in all runs, which indicates that the vinyl ester group was quantitatively introduced upon initiation.

Kinetics of Initiation Reaction. In order to evaluate the reaction rate quantitatively, a kinetic study of the polymerization of MeOZO initiated by **1a** was carried out by ^{1}H NMR spectroscopy.[8] Figure 1 shows the time-conversion curves for MeOZO monomer and for initiator **1a**. It can be seen that **1a** was consumed in the early stages of polymerization. Once **1a** was consumed, the ratio of the integrated area of the peak at δ 5.0 showing the vinyl protons from **1a** (CH_2=CHO, 2 H) and the peak at δ 2.5 ascribed to the methyl protons (3 H) of the terminal oxazolinium species was close to 2:3. These data are in favor of quantitative initiation and imply that the polymerization proceeds through a living mechanism.

The initiation rate constant k_i of **1a** is almost the same as that of propagation (Table II), indicative of fast initiation and relatively slow propagation. It should be noted that **1a** showed an initiation reactivity comparable with that of methyl iodide, a widely used and fast initiator for the ROZO polymerization.

Applications of macromonomer **2** including copolymerization with vinyl monomers for the preparation of a graft copolymer are now in progress.

Table I
Synthesis of Macromonomer Having a Vinyl Ester Group (2)

	polymerization				macromonomer 2				
entry	initiator	R of ROZO	$[ROZO]_0/[1]_0$	time, h	yield, %	M_n[a]	DP[b]	M_w/M_n[c]	functionality[b]
1	**1a**	Me	5.1	7	92	660	5.4	1.13	0.95
2	**1a**	Me	9.8	24	96	1000	9.3	1.10	0.98
3	**1a**	Me	30.6	31	93	2920	31.8	1.29	1.01
4	**1a**	Et	9.9	21	100	1270	10.4	1.10	1.01
5	**1b**/NaI[d]	Me	7.1	7	95	810	7.1	1.14	0.98
6	**1b**/NaI[d]	Me	15.7	20	96	1470	14.7	1.26	1.04
7	**1b**/NaI[d]	Et	8.7	24	91	1150	9.6	1.08	0.95

[a] By VPO. [b] By VPO and ^{1}H NMR. [c] By GPC. [d] [NaI]/[**1b**] = 1.1.

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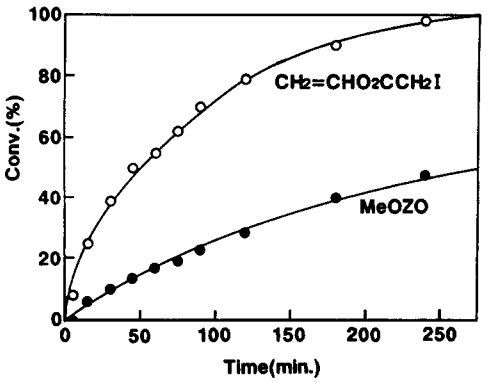

Figure 1. Time–conversion curves of the MeOZO polymerization initiated by **1a** in CD_3CN: $[MeOZO]_0$ = 3.3 M, $[1a]_0$ = 0.55 M.

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

initiator	k_i[b]	k_p[b]
1a	8.1	7.6[c]
MeI	22[d]	7.6[c]

[a] Polymerization conditions: [MeOZO] = 3.3 mol/L, [initiator] = 0.55 mol/L. [b] $\times 10^5$ L/(mol·s). [c] The value is calculated from the data obtained with methyl iodide as initiator at 35 °C.[8a] [d] The value at 35 °C from ref 7.

Experimental Section

Materials. The solvent, acetonitrile, was purified by distillation over calcium hydride. The monomers, MeOZO and EtOZO, were purified by distillation over potassium hydroxide. Vinyl iodoacetate (**1a**) was synthesized by halogen-exchange reaction between vinyl chloroacetate (**1b**) and sodium iodide.[9] All operations were performed under argon.

Synthesis of Macromonomer 2. A typical run was as follows (entry 2). A mixture of 1.018 g (12.0 mmol) of MeOZO and 0.258 g (1.22 mmol) of **1a** in 2 mL of acetonitrile was kept at 60 °C for 24 h under argon. The reaction mixture was poured into a large amount of diethyl ether to precipitate the polymeric material. After filtration the product was dried in vacuo to give 1.22 g of **2** (96% yield): ^1H NMR ($CDCl_3$) δ 2.1 (s, $CH_3C{=}O$), 2.5 (s, $CH_3CN(O)$), 3.4–4.6 (m, NCH_2, and OCH_2), 4.8 (m, $CH_2{=}CH$), 7.2 (m, $CH_2{=}CH$).

Kinetics of Initiation Reaction. Initiator **1a** (0.0583 g, 0.275 mmol) was added to 0.140 g (1.65 mmol) of MeOZO at 0 °C in an NMR tube under argon. Then CD_3CN was added to the mixture until the total volume was 0.5 mL. The polymerization was carried out at 35 °C and monitored by recording the ^1H NMR spectra.

Measurements. ^1H NMR spectra were recorded on a 60-MHz Hitachi R-24A spectrometer or a 250-MHz Bruker AC-250T spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a TOSOH SC 8010 with an RI detector under the following conditions: Gelpack GL-A130 column with chloroform as eluent at a flow rate of 1.0 mL/min. The molecular weight of the polymers was measured by means of a Corona 117 vapor pressure osmometer (VPO) in DMF at 70 °C.

References and Notes

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Registry No. **1a**, 52590-49-5; **1b**, 2549-51-1; **2** (Y = I, R = Me), 38796-76-8; **2** (Y = I, R = Et), 69488-61-5; MeOZO, 1120-64-5; NaI, 7681-82-5.