Preparation and Polymerization of 2-*p*-Styryl-2-oxazoline

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Introduction

In recent development of the research on functional polymers, much attention has been paid to the preparation of dual-functional monomers having two different types of polymerizable groups. Among such dual-functional monomers, glycidyl methacrylate is a well-known example. 2-Alkenyl-substituted cyclic imino ethers are a series of attractive dual-functional monomers, too, since cyclic imino ethers react under mild conditions with several kinds of electrophiles, such as carboxylic acids, acyl and alkyl halides, epoxides, and thiols. In addition, cyclic imino ether is easily converted to its onium salts by alkylation at the N atom, and the resulting salts react smoothly with various nucleophiles, such as amines and alcohols. It is also noteworthy that the polymerization of cyclic imino ethers proceeds without disturbance by chain-transfer and termination reactions under appropriate conditions of reaction.[1] 2-Vinyl-2-oxazoline (**1a**) is the simplest homologue among such 2-alkenyl-substituted cyclic imino ethers. However, **1a** is converted by an electrophilic initiator into an insoluble gel with unidentified structure probably due to the involvement of two types of functional groups.[2] The polymerization behavior of 2-isopropenyl-2-oxazoline (**1b**) with a cationic initiator is also complicated.[3]

The present paper describes the preparation and the polymerization of a new dual-functional monomer of 2-*p*-styryl-2-oxazoline (**2**). To clarify the reactivity of **2**, the radical and anionic vinyl polymerizations as well as the cationic ring-opening polymerization of **2** were examined.

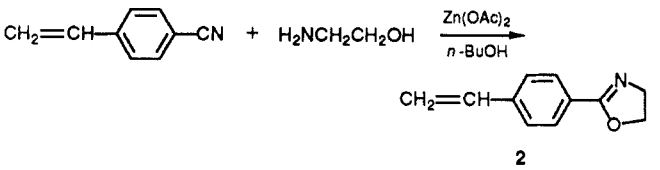
Experimental Section

Materials. *p*-Cyanostyrene was prepared as previously reported, and purified by repeated distillations under reduced pressure [bp 72–76 °C (2.8 mmHg)].[6] Other reagents and solvents were supplied commercially and purified by distillation under nitrogen.

Equipment. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-200 spectrometer at 60 MHz and on a Hitachi R-900 Fourier transform spectrometer operating at 22.6 MHz, respectively. An IR spectrum was recorded on a Hitachi 260-20 infrared spectrometer. GPC analysis was performed by using a TSK-Gel G2500H$_{XL}$ or G4000H$_{XL}$ column in DMF containing 0.4% of triethylamine at 50 °C.

Preparation of 2-*p*-Styryl-2-oxazoline (2). To a stirred solution of *p*-cyanostyrene (14.0 g, 0.11 mol), zinc acetate (1.21 g, 5.5 mmol), and a radical inhibitor of phenothiazine (4.38 g, 22 mmol) in 55 mL of *n*-butyl alcohol was added slowly 7.3 g of ethanolamine (0.12 mol) at room temperature. After the addition was over, the mixture was heated to reflux for 4.5 h. Then the mixture was poured into 600 mL of ether to remove a vinyl-propagated polymer of **2**. The supernatant ether layer was treated three times with 150 mL of cold 1 N aqueous HCl. By the addition of 40 g of NaOH to the combined aqueous layer, the crude product was separated as an oily material, which was extracted with ether. By evaporation of the solvent followed by distillation under reduced pressure, the product was obtained. The yield was 43%: mp 39.4–41.0 °C; bp 93–94 °C (0.4 mmHg); ^{13}C NMR ($CDCl_3$) δ 54.70 (N–CH_2), 67.28 (OCH_2), 115.33 (CH_2=CH), 125.19 and 128.19 (tertiary aromatic carbons), 126.8 (N=*C*C), 135.97 (CH_2=*C*H), 140.10 (CH_2=CH*C*), 164.2 (C=N); IR (KBr) 1645 ($\nu_{C=N}$), 1610 ($\nu_{C=C}$), 1362, 1263, 1070 (ν_{CO}), 945, 855, 670 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO\cdot0.2H_2O$ (hygroscopic): C, 74.72; H, 6.50; N, 7.92. Found: C, 74.80; H, 6.41; N, 7.94.

Scheme I



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Polymerizations of 2 were carried out in a sealed tube under nitrogen according to the conventional procedures.

Vinyl-propagated polymer (3): white powder; ^{13}C NMR ($CDCl_3$) δ 39.9–45.0 (carbons of main chain), 54.69 (NCH_2), 67.19 (OCH_2), 125.3 (N=*C*C), 125.6–128.5 (tertiary aromatic carbons), 147.3–148.5 (CH_2*C*H), 164.33 (C=N); IR (KBr) 2900 (ν_{CH}), 1640 ($\nu_{C=N}$), 1350, 1255, 1065 (ν_{CO}), 835 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO\cdot0.4H_2O$ (hygroscopic): C, 73.23; H, 6.59; N, 7.76. Found: C, 72.99; H, 6.25; N, 7.74.

Ring-opened homopolymer of 2 (4): white powder; ^{13}C NMR ($CDCl_3$) δ 38.0–52.1 (NCH_2CH_2), 113.9–116.7 (N=*C*C and *C*H_2=CH), 124.2–130.5 (tertiary aromatic carbons), 131.9–136.0 (CH_2=*C*H), 137.4–140.1 (CH_2=CH*C*), 171.5 (C=N); IR (KBr) 1626 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$), 1425, 1270, 917, 852, 752 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO\cdot0.09C_2H_3F_3O_3S\cdot0.2H_2O$ (Table II, no. 1; DP = 11): C, 74.72; H, 6.50; N, 7.92. Found: C, 74.80; H, 6.41; N, 7.94.

Results and Discussion

Preparation of 2. 2-*p*-Styryl-2-oxazoline (**2**) was prepared by the reaction of *p*-cyanostyrene with ethanolamine as shown in Scheme I.[7] The yield was not so high (43%) because of the loss of **2** due to its vinyl polymerization. **2** was a white waxy solid material with a melting point 39–41 °C. The structure of **2** was reasonably established by both spectroscopic and elemental analyses (see the Experimental Section and Figure 1a).

Vinyl Homopolymerization of 2. As shown in Table I, the radical polymerization of **2** occurred under conventional conditions by using AIBN or BPO as initiator. Poly[[4-(2-oxazolin-2-yl)phenyl]ethylene] (**3**; Scheme II) was successfully obtained as a white powder after reprecipitation from diethyl ether. The conversions of **2** were almost quantitative since no unreacted **2** was detected from the supernatant precipitant layer by GLC, but the isolated yield of the polymer was much decreased due to the loss of **3** of low molecular weight during the purification procedures since **3** is slightly soluble in the precipitant.[8] The structure of **3** was confirmed by ^{1}H and ^{13}C NMR spectra as well as IR measurement. In parts a and b of Figure 1 is compared the ^{1}H NMR spectrum of **3** (Figure 1a) to that of **2** (Figure 1b). The signals at around δ 3.7–4.7 in both spectra are ascribable to the protons of the oxazoline ring, which is preserved in the polymer in the pendant groups.

The similar vinyl-propagated polymer, **3′**, was also obtained by the anionic polymerization of **2** with *n*-butyllithium in THF at −78 °C. No substantial difference was observed between the structures of **3** and **3′** by the spectroscopic measurements.

Recently, Ishino et al. reported the preparation and the anionic polymerization of 4,4-dimethyl-2-*p*-styryl-2-oxazoline (**5**), and they found the anionic polymerization of **5** proceeded in a living mechanism.[9] They only mentioned use of the oxazolinyl group as a protecting group of carboxylic acid and did not examine the ring-opening polymerization of **5**. It is known that the ring-opening reactivity of such 4,4-disubstituted oxazolines is very low.[1] In the present case, the apparent molecular weights of **3′** determined by GPC increased with a decrease in the

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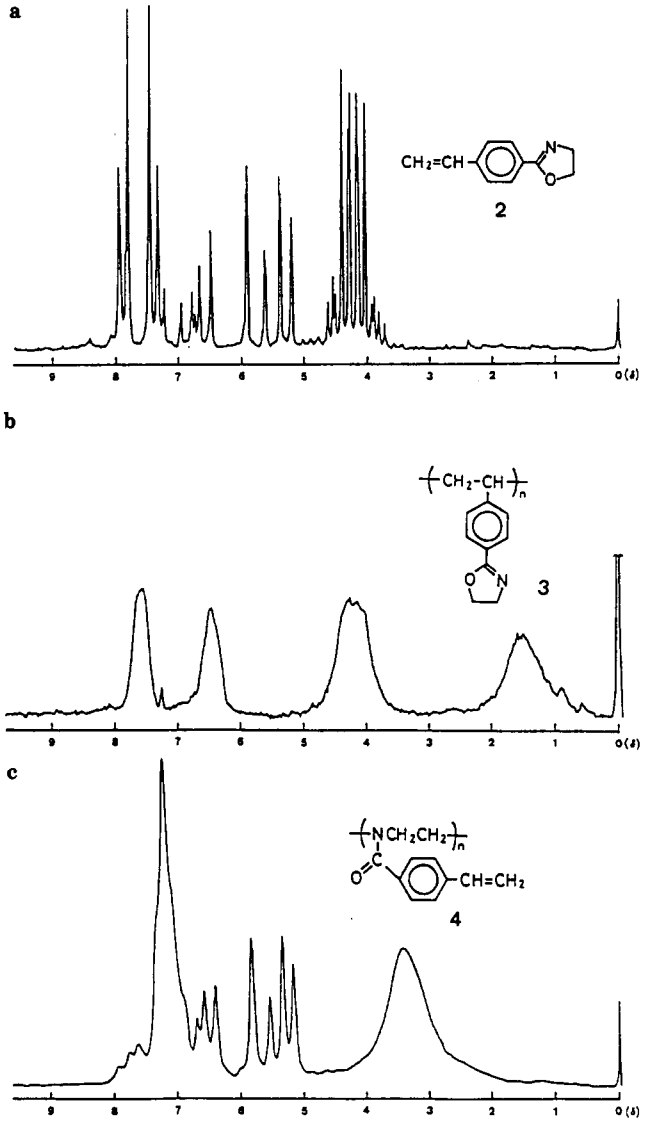

Figure 1. ^{1}H NMR spectra of **2** (a), **3** (b), and **4** (c) (in $CDCl_3$, 1% TMS).

Table I
Vinyl Homopolymerization of 2

initiator (mol %)	solvent	temp, °C	time, h	polymer yield, %	polymer $M_n/10^4$ [a]	polymer M_w/M_n [a]
AIBN (1.0)	benzene	70	20	60	2.0	1.7
AIBN (0.55)	benzene	70	20	55	5.1	2.0
BPO (1.0)	benzene	70	20	53	3.1	2.8
BPO (0.55)	benzene	70	20	52	7.4	1.8
n-BuLi (4.6)	THF	−78	4	60	0.57	1.03
n-BuLi (10.5)	THF	−78	4	84	0.28	1.27

[a] Determined by GPC with polystyrene calibration.

initiator concentration. This fact, as well as the narrow molecular weight distribution of **3′**, is taken to assume that the anionic polymerization of **2** also proceeds in a living mechanism. Although, the molecular weights of **3** and **3′** could not be determined by another method, such as VPO, because these polymers were readily gellified during its drying process for further measurements, probably due to the cross-linking reaction between the oxazoline moieties.

Radical Copolymerization of 2. The introduction of oxazoline groups to common polymers was achieved by the radical copolymerization of **2** with vinyl monomers. The monomer **2** was smoothly copolymerized with styrene (St), *n*-butyl vinyl ether, or methyl methacrylate. To quantify the radical copolymerization reactivity of **2**, the monomer reactivity ratios were determined for the copolymerization of **2** with St. The Kelen–Tüdös method was applied to the determination of the values of reactivity ratios, r_1 (for **2**) and r_2 (for St),[10] which were 1.4 and 0.29, respectively. Clearly, the radical polymerizability of **2** is higher than St. The Q and e values for **2** calculated from the reactivity ratios are 1.6 and 0.14, respectively. Obviously, the electron-withdrawing oxazolinyl group decreases the electron density of the vinyl group but enhances the radical reactivity of the monomer.

Scheme II

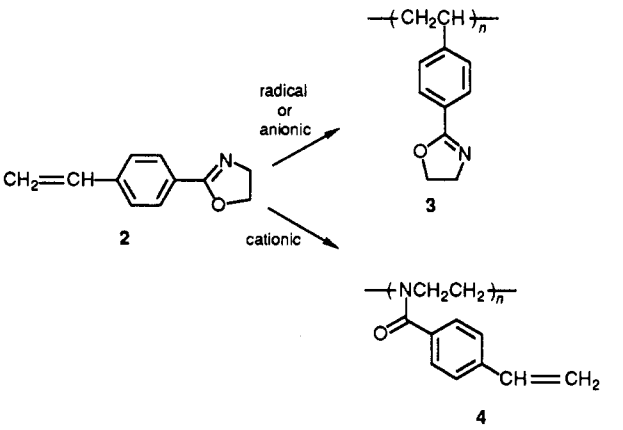

Table II
Ring-Opening Polymerization of 2[a]

run	initiator (mol %)	polymer yield, %	polymer M_n[b]	polymer M_w/M_n[b]
1	MeOTf (2)	73	7700	1.10
2	MeOTf (5)	65	3400	1.07
3	MeOTs (2)	65	6300	1.07
4	MeOTs (5)	95	4900	1.10
5	BF_3·Et_2O (5)	55	4500	1.16

[a] In DMF, at 100 °C, for 20 h. [b] Determined by GPC with polystyrene standards in DMF containing 0.4% of triethylamine.

Ring-Opening Polymerization of 2. The ring-opening polymerization of **2** was carried out by using sulfonate ester or boron trifluoride etherate as initiator at 100 °C in DMF, in the presence of a small amount of phenothiazine as radical inhibitor. The polymeric products were obtained in high yields, and their structures were determined as poly[*N*-(4-vinylbenzoyl)iminoethylene] (**4**) from NMR and IR measurements. The ^{1}H NMR spectrum of **4** is shown in Figure 1c. It is obvious that **4** possesses a structure quite different from that of **3**. The peaks ascribable to oxazoline ring protons at around δ 3.7–4.7 completely disappeared, and in their place, the peaks for the protons of iminoethylene units are observed at around δ 2.8–4.0. The vinyl groups are preserved unchanged in the polymer.

It has been established that polymerization of oxazolines proceeds without disturbance by chain transfer and chain termination. In Table II, the low polydispersity of the resulting polymer is shown, which suggests the absence of chain-transfer and -termination reactions. In run no. 4, in Table II where the polymer was obtained almost quantitatively, the observed number-average molecular weight of **4** determined by VPO, 3300, was in good agreement with the corresponding calculated one from the molar ratio of monomer to initiator, 3650.

References and Notes

(1) Kobayashi, S.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier Applied Science Publishers: New York, 1985; Vol. 2, Chapter 11.

(2) Miyamoto, M.; Sano, Y.; Kimura, Y.; Saegusa, T. *Macromolecules* **1985**, *18*, 1641.
(3) Although it was reported that **1b** could be selectively polymerized to give a ring-opened polymer with either Brønsted or Lewis acids,[4] Tomalia et al. reported that the polymerization of **1a** with Brønsted acids afforded gels, cyclic oligomers, or ring-preserved oligomers.[5]
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(5) Tomalia, D. A.; Thill, B. P.; Fazio, M. J. *Polym. J.* **1980**, *12*, 661.
(6) Iwai, K.; Furue, M.; Nozakura, S.; Shirota, Y.; Mikawa, H. *Polym. J.* **1980**, *12*, 97.
(7) Witte, H.; Seeliger, W. *Liebigs Ann. Chem.* **1974**, 996.
(8) In the case of run no. 1 in Table I, the lower molecular weight fraction of **3** was isolated from the supernatant ether layer, and the combined total yield of **3** reached 93%.
(9) Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1986**, *19*, 2307.
(10) Tüdös, F.; Kelen, T.; Foldes-Berezsnich, T.; Turcsanyi, B. *J. Macromol. Sci., Chem.* **1976**, *A10*, 1513.

Registry No. **2**, 125274-17-1; **2** (homopolymer), 129064-31-9; **4** (SRU), 129064-33-1; *p*-cyanostyrene, 3435-51-6; ethanolamine, 141-43-5; styrene, 100-42-5.