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Reactivity of cyclic imino ether salts having vinyl group

7. Preparation of *N*-methylated salt of 2-*p*-styryl-2-oxazoline and its related polymerizations

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SUMMARY

3-Methyl-2-*p*-styryl-2-oxazolinium trifluoromethanesulfonate (**2**) consisting of a polymerizable styryl group and a highly electrophilic oxazolinium ring was prepared by the *N*-alkylation of 2-*p*-styryl-2-oxazoline. The radical homo- and copolymerizations of **2** with styrene proceeded successfully. The copolymerization parameters (monomer reactivity ratio) were determined; 1.2 (for **2**) and 0.25 (for styrene). This salt functions also as an initiator for the oxazoline polymerization. Poly[(*N*-acetyl)iminoalkylene] macromonomers with quite narrow molecular weight distributions were easily prepared by the ring-opening polymerization of 2-methyl-2-oxazoline and of 2-methyl-5,6-dihydro-4*H*-1,3-oxazine by using **2** as the initiator.

INTRODUCTION

Polymers containing pendant chlorobenzyl groups have been widely used as the starting materials for the preparations of polymeric reagents and catalysts, in which the chlorobenzyl group is subjected to the reactions of various kinds of nucleophiles(1). But, the functional polymers thus produced usually possess some disadvantages. For example, the efficiency of functionalization is low because the nucleophilicity of chlorobenzyl group is not strong enough, and the produced chemical bond is often cleaved because of a relatively high stability of each of benzyl cation, anion, and radical.

Cyclic imino ether salts are strong electrophiles which react smoothly with almost all kinds of common nucleophiles, for example, amines, alcohols, carboxylic acids and their salts, and even water under mild conditions(2). Our previous work on the ring opening-polymerization of cyclic imino ethers has already revealed that an *N*-alkylated salts of cyclic imino ether shows about 100 times higher reactivity toward 2-methyl-2-oxazoline than benzyl chloride (3).

A previous paper of us described the polymerizations of a novel dual-functional monomer of 2-*p*-styryl-2-oxazoline (**1**). Each of vinyl and 2-oxazoline functionalities of **1** was polymerized selectively in radical (vinyl), anionic (vinyl) and cationic (ring-opening) mechanisms, respectively(4).

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In the present paper, an *N*-methylated salt of **1**, 3-methyl-2-*p*-styryl-2-oxazolinium trifluoromethanesulfonate (triflate) (**2**), was prepared by the alkylation of **1** with methyl triflate. The salt, **2**, consists of a polymerizable styryl group and a highly electrophilic oxazolinium moiety, which is applicable for various purposes in place of chloromethylstyrene. The reactivity of each of two functional groups of **2** was examined in the radical polymerization of **2** affording the vinyl propagated polymer (**3**) and in the cationic ring-opening polymerization of cyclic imino ether monomers with the initiator of **2** producing a macromonomer with the styryl terminal group (**4**).

EXPERIMENTALS

Materials: 2-*p*-Styryl-2-oxazoline were prepared and purified as previously reported(4). Other reagents and solvents were supplied commercially and purified by distillation under nitrogen.

3-Methyl-2-*p*-styryl-2-oxazolinium triflate (**2**). All procedures was carried out under nitrogen. To a vigorously stirred solution of 9.7 mmol of methyl triflate in 10 mL of diethyl ether was added dropwise 8.1 mmol of **1** dissolved in 5 mL of diethyl ether at 0 °C. On every drop of **1**, a white powdery product precipitated out. After the addition was over, the product was collected by filtration, washed thoroughly with diethyl ether, and dried *in vacuo*. The yield was 89 %. The salt was further purified by recrystallization from dichloromethane. White needles; mp. 77.8-79.9 °C; ^{1}H NMR (CD_3CN) δ 3.53 (s, 3H, CH_3), 4.1-4.6 (m, 2H, N-CH_2), 4.9-5.4 (m, 2H, O-CH_2), 5.53 (dd, 1H, C=CH trans), 6.04 (dd, 1H, C=CH cis), 6.85 (dd, 1H, C=CH gem), 7.6-8.1 (m, 4H, aromatic protons); ^{13}C NMR (CD_3CN) δ 36.23 (CH_3), 54.21 (N-CH_2), 71.47 (O-CH_2), 117.24 (N=C-**C**), 119.26 (**C**H_2=CH), 128.08 and 131.08 (tertiary aromatic carbons), 135.66 (CH_2=**C**H-), 144.93 (C=C-**C**), 172.01 (C=N); IR (Nujol) 1655 ($\nu_{C=N}$), 1603 ($\nu_{C=C}$), 1260, 1160, 1140, 1030, 912, 858 cm^{-1}. Anal., Calcd for $C_{13}H_{14}NO_4SF_3 \cdot 0.2H_2O$ (hygroscopic): C, 46.29; H, 4.18; N, 4.15; F, 16.90. Found: C, 46.18; H, 4.05; N, 4.23; F, 17.01.

Polymerizations were carried out in a sealed tube under nitrogen according to the conventional procedure. The polymer was obtained by reprecipitation from acetonitrile (solvent) to diethyl ether (non-solvent).

Vinyl Propagated polymer (**3**): white solid; ^{1}H NMR (CD_3CN) δ 1.1-2.2 (3H, CH_2-CH), 3.2-3.5 (3H, CH_3), 4.0-4.6 (2H, N-CH_2), 4.8-5.3 (2H, O-CH_2), 6.3-8.0 (4H, aromatic protons); ^{13}C NMR (CD_3CN) δ 36.0 (CH_3), 40.1-44.3 (carbons of main chain), 54.0 (N-CH_2), 71.4 (O-CH_2), 114.2 (N=C-**C**), 128.8-130.4 (tertiary aromatic carbons), 151.4-154.5 (C-C-**C**), 171.7 (C=N); Anal., Calcd for $C_{13}H_{14}NO_4SF_3 \cdot 0.8H_2O$ (hygroscopic): C, 44.39; H, 4.47; N, 3.98. Found: C, 44.14; H, 4.21; N, 4.05.

Macromonomer derived from 2-methyl-2-oxazoline (**4a**): white solid; ^{1}H NMR ($CDCl_3$) δ 1.9-2.2 (CH_3-CO), 3.06 (s, 3H, NCH_3), 3.0-3.8 (N-CH_2),

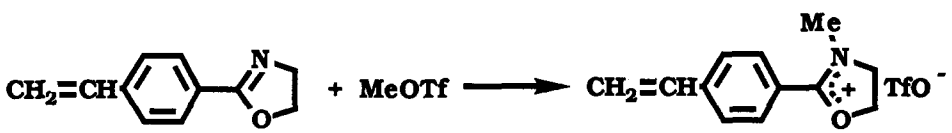
5.2-5.9 (m, 2H, CH_2=C-), 6.5-6.8 (m, 1H, C=CH-), 7.2-7.6 (m, 4H, aromatic protons).

Macromonomer derived from 2-methyl-5,6-dihydro-4*H*-1,3-oxazine (**4b**): white solid; ^{1}H NMR ($CDCl_3$) δ 1.5-2.7 (CH_3-CO and C-CH_2-C), 3.04 (s, 3H, NCH_3), 3.1-4.1 (N-CH_2), 5.2-5.9 (m, 2H, CH_2=C-), 6.5-6.9 (m, 1H, C=CH-), 7.2-7.6 (m, 4H, aromatic protons).

RESULTS AND DISCUSSION

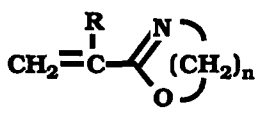
Preparation of monomer. 3-Methyl-2-*p*-styryl-2-oxazolinium triflate (**2**) was prepared in a high yield by the reaction of **1** with a small excess amount of methyl triflate in diethyl ether at 0 °C. The salt, **2**, is slightly hygroscopic, white needles, which is soluble in methylene chloride, acetonitrile, DMF, and other polar solvents. The structure of **2** was reasonably established by both spectroscopic and elemental analyses (see EXPERIMENTALS).

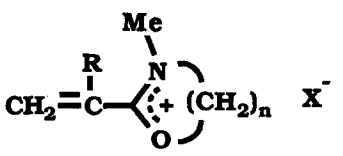
Scheme 1



1 **2** 89 % yield

The polymerizations of *N*-methylated salts of 2-alkenyl substituted cyclic imino ethers have already been reported by us (5-7). Concerning the vinyl homologue of **2**, i.e., 2-vinyl-2-oxazoline (**5a**), the corresponding *N*-methylated salt, 3-methyl-2-vinyl-2-oxazolinium salt (**6a**) could not be isolated because it was highly electrophilic, and spontaneously entered into a polymerization by a nucleophilic attack of the unreacted monomer(5). Comparing with **6a**, **2** is less reactive toward nucleophiles (*vide infra*), and hence, was successfully isolated .





5a; R=H, n=2
5b; R=Me, n=2
5c; R=H, n=3

6a; R=H, n=2, X=TfO, BF_4
6b; R=Me, n=2, X=BF_4
6c; R=H, n=3, X=TfO

Homopolymerization of **2.** Under mild conditions using AIBN or BPO as radical initiator, the vinyl-propagated polymer, poly{[4-(3-methyl-2-oxazolinium-2-yl)phenyl]ethylene} (**3**) was successfully obtained in high yields (Table 1). The structure of the polymer was confirmed as **3** from ^{1}H and ^{13}C NMR measurements.

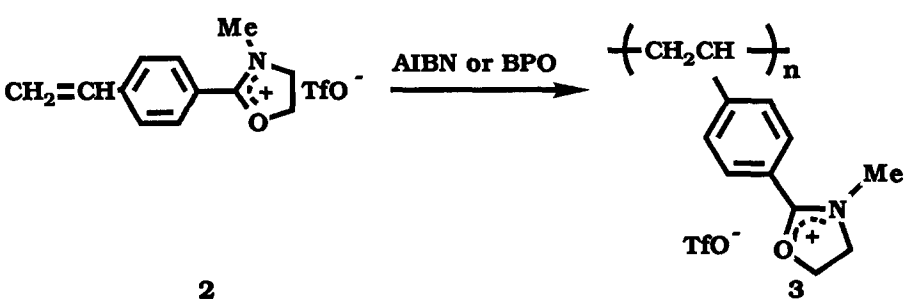
Table 1. Homo- and Copolymerization of **2**

Initiator (mol %)	Comonomer (mol %)	Conditions (°C, hr)	Product Polymer Yield (wt %)	**2** Content (mol %)	$[\eta]^a$ (dL/g)
AIBN (0.5)	— —	70, 20	92	100	0.16
BPO (0.5)	— —	70, 20	95	100	0.19
Et_3N (5)	— —	100, 3	0	—	—
MeONa(5)	— —	r.t., 30	0	—	—
AIBN (0.5)	MMA (50.0)	70, 5	67	72	0.12
AIBN (0.5)	St (9.9)	70, 5	14	21	0.14
AIBN (0.5)	St (24.9)	70, 5	28	42	b
AIBN (0.5)	St (34.9)	70, 5	43	51	b
AIBN (0.5)	St (45.0)	70, 5	50	60	b
AIBN (0.5)	St (50.0)	70, 5	58	62	0.10
AIBN (0.5)	St (69.9)	70, 5	55	72	0.10

[a] In DMF containing 2 wt % of $NaBF_4$ at 30 °C. [b] Not measured.

In Figure 1 is compared the ^{1}H NMR spectrum of **3** with that of **2**. From the peak assignments as described in EXPERIMENTALS, it is obvious that the polymer **3** contains pendant oxazolinium groups.

Scheme 2



2 **3**

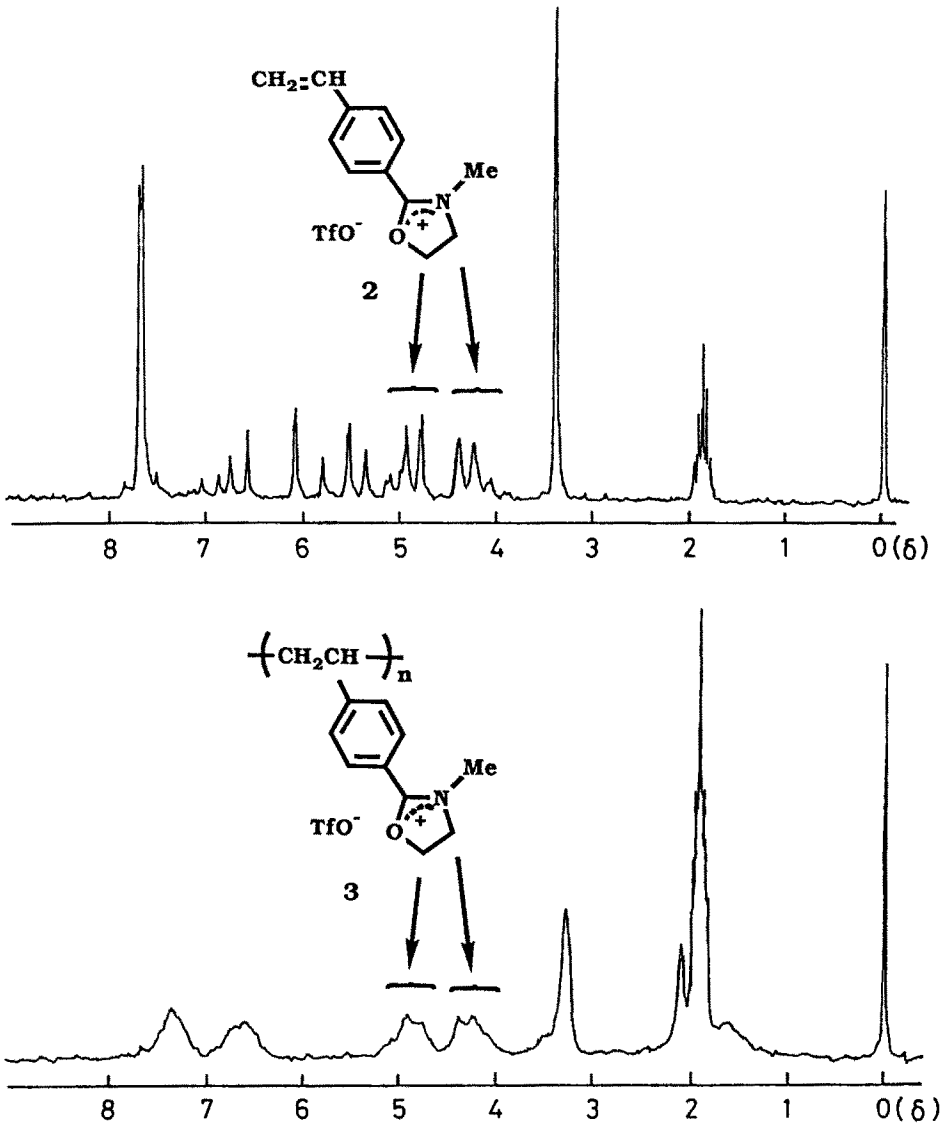


Figure 1 60 MHz ^{1}H NMR spectra of **2** (a) and **3** (b) (in CD_3CN).

We had already reported that **6a** was too reactive to be isolate (5) and **6b** and **6c** were also highly electrophilic, *i.e.*, they were vinyl-polymerized easily in the presence of a weak nucleophile such as an amine even at 0 °C (6,7). In the present case, however, **2** is less electrophilic than **6a**. Neither of triethylamine nor sodium methoxide could initiate the vinyl-polymerization of **2**. Obviously, the presence of phenyl group between the two functional groups would have weakened the electron withdrawing effect of oxazolinium group on vinyl group.

Copolymerization of **2**. The salt, **2**, is smoothly radical copolymerized with styrene (St) and with methyl methacrylate (MMA) (Table 1). The monomer reactivity ratios of **2** were determined in its copolymerization with St (Table 2). The conversions of both monomers were directly determined by the *in situ* ^{1}H NMR measurement.

Table 2. Copolymerization Parameters and *Q*,*e*-Values.[a]

M_1	M_2	r_1	r_2	Q_1	e_1	reference
1	St	1.4	0.29	1.6	0.14	this work
2	St	1.2	0.25	1.7	0.30	this work
5b	MA[b]			1.2	0.91	(6)
5c	MMA			1.1	1.6	(7)
6b	MA[b]			2.0	2.0	(6)
6c	MMA			3.8	1.9	(7)

[a] The values are calculated according to the Kelen-Tüdös method (8).
[b] Methyl acrylate.

In the copolymerization system of **2** with St, the homo-propagation of **2** is preferred. The monomer reactivity ratios of r_1 (for **2**) and r_2 (for St) were calculated according to the Kelen-Tüdös method (9), from which the *Q*,*e*-values of **2** were also calculated (Table 2). The corresponding values of **1** as well as the related monomers, **5b**, **5c**, **6b**, and **6c** are shown for comparison in Table 2. Comparing **2** with **1**, a slight increase in both *Q* and *e*-values was noted. A similar phenomenon was observed previously by us in the differences of these values in the **5b**/**6b** and **5c**/**6c** systems (6,7). Thus, the π-electron of vinyl group of **2** is more easily delocalized than that of **1**. The *e* values of **6b** and **6c** are one of the highest values among vinyl monomers, and they are consistent with their high anionic polymerizability by weak base initiator (5-7). On the contrary, in the present case, the electronic influence of oxazolinium group on vinyl group is quite weak as far as judging from the *Q*,*e*-values of **2**. In fact, **2** was not polymerized by a weak base.

Macromonomer Syntheses. In many cases of the cationic ring-opening polymerizations of cyclic imino ethers *N*-alkylated salts are

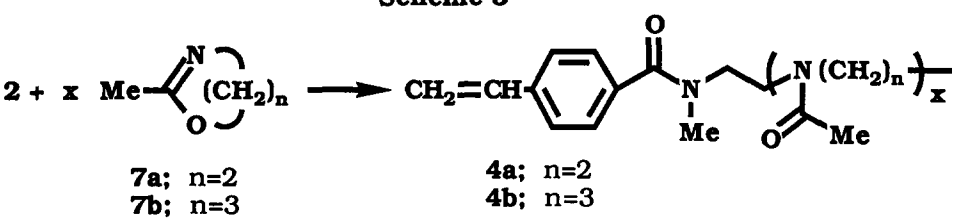
known as the propagating species (2). They are generally formed by the reaction of a monomer with an initiator in the first step of the polymerization. In the propagation step these salts reacted with monomers to make the extension of (*N*-acylimino)alkylene chain. In the present study, this principle has been applied to macromonomer synthesis. Two kinds of poly[(*N*-acetylimino)alkylene] macromonomers (**4**) were prepared by the polymerization of 2-methyl-2-oxazoline (**7a**) or 2-methyl-5,6-dihydro-4*H*-1,3-oxazine (**7b**) with the initiator of **2** (Scheme 3). The molecular weight of the produced macromonomer **7** was well controlled by changing the feed ratio of monomer to initiator. The molecular weight distributions were quite narrow (Table 3).

Table 3. Preparation of Poly[(*N*-acylimino)alkylene] Macromonomers.

Monomer **7**	[M]/[I]	Temp. (°C)	Time (hr)	Product Polymer **4**	Yield (wt %)	$\overline{DP}$ (NMR)	$\overline{DP}$ (VPO)	$\overline{DP}$ (GPC)[a]	$\overline{M}_w/\overline{M}_n$
7a	5.0	80	20	**4a**	85	4.0	6.4	4.7	1.11
7a	10.1	90	20	**4a**	95	8.1	7.5	8.4	1.11
7a	20.0	80	20	**4a**	95	23.9	23.0	24.6	1.16
7b	5.3	90	15	**4b**	97	5.4	5.1	—	1.18
7b	20.1	100	20	**4b**	96	22.1	21.3	—	1.08

[a] Determined from GPC in DMF by using the standards sample of the same polymer.

Scheme 3



7a; n=2
7b; n=3

4a; n=2
4b; n=3

In our previous study, the poly(2-oxazoline) type macromonomer synthesis had been achieved by the ring-opening polymerization of oxazolines with vinylbenzyl halide(9). But, **2** seems to be a more suitable initiator for the polymerization of oxazolines because of its high reactivity (the faster initiation reaction) which results in the narrow molecular weight distribution.

Recently poly(2-oxazoline)s have been shown to be quite effective polymeric modifier for enzymes and the resulting polymer/enzyme hybrid showed an excellent catalytic activity in organic media (10). The

present macromonomer is taken to be a potent material for such the purpose.

REFERENCES

(1) N. K. Mathur, C. K. Narang, and R. E. Williams, "Polymers as Aids in Organic Chemistry", Academic Press, New York, N. Y., 1980.
(2) S. Kobayashi and T. Saegusa, "Ring-Opening Polymerization", Vol. 2, Elsevier Applied Science Publishers, New York, N. Y.m 1985, Chapter 11.
(3) T. Saegusa, S. Kobayashi, and A. Yamada, *Makromol. Chem.*, **177**, 2271 (1976).
(4) M. Miyamoto, K. Hayashizaki, M. Tokumizu, and T. Saegusa, submitted to *Macromolecules*.
(5) M. Miyamoto, Y. Sano, Y. Kimura, and T. Saegusa, *Macromolecules*, **19**, 1641 (1985).
(6) M. Miyamoto, Y. Sano, and T. Saegusa, *Makromol. Chem.*, **187**, 1807 (1986).
(7) M. Miyamoto and T. Saegusa, *J. Macromol. Sci.-Chem.*, **25**, 627 (1988).
(8) T. Kelen and F. Tüdös, *J. Macromol. Sci.-Chem.*, **A9**, 1 (1975).
(9) S. Kobayashi, M. Kaku, S. , and T. Saegusa, *Polymer Bull.* **13**, 447 (1985).
(10) M. Miyamoto, K. Naka, M. Shiozaki, Y. Chujo, and T. Saegusa, Unpublished results.

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