Macromolecules

Volume 18, Number 9 September 1985

“Spontaneous” Vinyl Polymerization of 2-Vinyl-2-oxazolines

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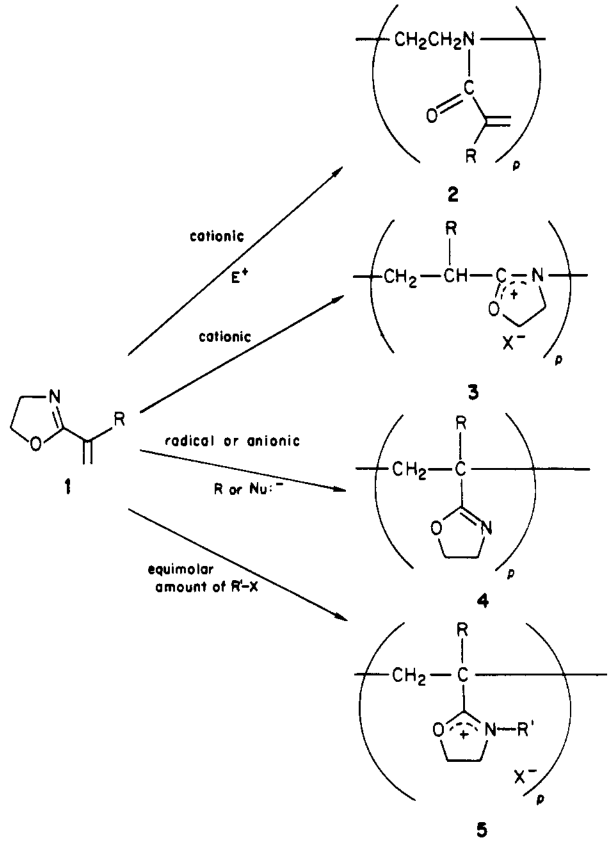
ABSTRACT: 2-Vinyl- and 4,4-dimethyl-2-vinyl-2-oxazolines were polymerized via the opening of the olefinic bond when they were alkylated with alkyloxonium salts or superacid esters. The polymers produced had a general structure of poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene]. Concerning the mechanism of this peculiar polymerization, it has been assumed that a 3-alkyl-2-vinyl-2-oxazolinium salt, which is produced by alkylation initiation, is so reactive that it enters into an anionic polymerization initiated by the nucleophilic attack of free monomer. The reaction of the oxazolinium ring of the product polymer with amine was also examined.

Introduction

Reactivities of various 2-substituted 2-oxazolines in cationic ring-opening polymerization have been studied quite extensively.[1] Among them, 2-vinyl- (R = H in 1) and 2-isopropenyl-2-oxazolines (R = Me in 1) are polymerized by three reaction modes: cationic ring-opening polymerization to poly[(*N*-acryloyl(or methacryloyl)imino)-ethylenes] **2**,[2-4] cationic polymerization to give ring-preserved polymers **3**,[5] and olefinic polymerization via a radical[2,4,6] or anionic[5] mechanism to produce poly[(2-oxazolin-2-yl)alkenes] **4** (Scheme I).

In this paper we describe a fourth mode of polymerization of 2-vinyl-2-oxazolines which occurs by the N-alkylation of the 2-oxazoline moiety with strong alkylating agents such as trialkyloxonium salts, alkyl sulfates, and alkyl sulfonates. The product polymers have a general structure of poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene] **5**, which cannot be produced in pure form by direct alkylation of the vinyl polymer of **4**. The new mode of polymerization is related to the “spontaneous” polymerization of 2- and 4-vinylpyridines.[7-11]

Scheme I



Results and Discussion

“Spontaneous” Polymerization. It is known that an equimolar reaction of 2-substituted-2-oxazoline with alkylating agents or strong Brønsted acids produces stable 3-alkyl-2-oxazolinium salts or 3-protio-2-oxazolinium salts in high yields.[4,12] The salts correspond to the propagating species of the cationic ring-opening polymerization of 2-oxazolines, and in fact they induce the cationic ring-opening polymerization of 2-oxazolines. In the present study, the alkylation of 2-vinyl- (**1a**) and 4,4-dimethyl-2-vinyl-2-oxazolines (**1b**) was tried by using four kinds of strong alkylating agents **6**, i.e., so-called Meerwein reagents **6a-1** and **6a-2** and superacid esters **6b-1** and **6b-2**. As soon as **1** was added to a solution of **6** in CH_2Cl_2 at 0 °C, a white

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Scheme II

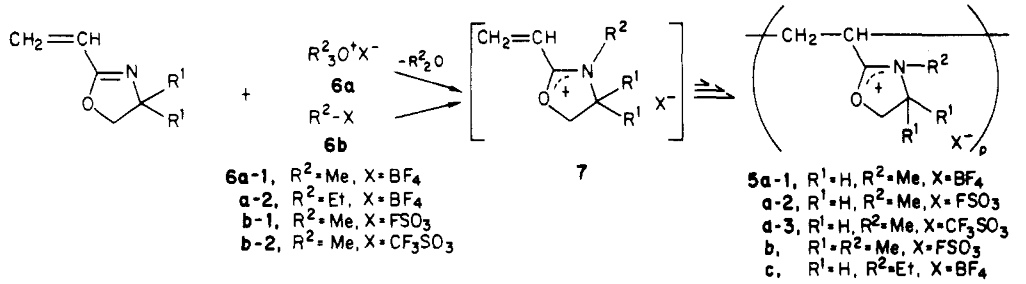


Table I
"Spontaneous" Polymerization of 1[a]

run no.	1	6	feed ratio [1]/[6]	solvent	temp, °C	time, h	product polymers structure	product polymers yield, %	η_{sp}/C,[b] dL/g
1	**1a**	**6a-1**	0.84	CH_2Cl_2	0	2	**5a-1**	100	0.038
2	**1a**	**6a-1**	2.00	CH_2Cl_2	0	2	**5a-1**	98	0.030
3	**1a**	**6a-1**	5.00	CH_2Cl_2	0	2	**5a-1**	91	0.035
4	**1a**	**6b-1**	0.84	CH_2Cl_2	0	1	**5a-2**	83	0.044
5	**1a**	**6b-1**	0.84	PhMe	0	1	**5a-2**	94	0.034
6	**1a**	**6b-1**	0.84	PhCl	0	1	**5a-2**	100	0.043
7	**1a**	**6b-1**	0.84	Et_2O	0	1	**5a-2**	88	0.043
8	**1a**	**6b-1**	0.84	CH_3CN	-30	4	**5a-2**	94	0.033
9	**1a**	**6b-2**	0.88	CH_2Cl_2	0	1	**5a-3**	74	0.020
10	**1b**	**6b-1**	1.00	CH_2Cl_2	0	1	**5b**	81	0.052
11	**1a**	**6a-2**	0.84	CH_2Cl_2	0	2	**5c**	96	0.030

[a] Typically, 5 mmol of **1** and 10 mL of solvent were used. [b] In 2% $NaBF_4$–DMF solution (C = 0.5 g/dL) at 30 °C.

or a slightly yellow material precipitated out. The product was obtained in a high yield, which was found to be a polymer of structure **5** instead of the monomeric salt, i.e., 3-alkyl-2-vinyl-2-oxazolinium salt **7** (Scheme II). Quite surprisingly, these products differ from the proton-initiated products obtained by Tomalia et al.[5] The results are summarized in Table I.

The properties of the products varied a little according to the substituents R^1 and R^2 as well as the gegenanion X^- (see Experimental Section). In general, the products are soluble in aprotic polar solvents such as CH_3CN, DMF, and Me_2SO, whereas they are insoluble in hydrocarbons, ethers, and halogenated hydrocarbons. They are decomposed in protic solvents such as EtOH, MeOH, and H_2O. The molecular weight of **4** could not easily be determined because of the salt structures. It was considered to be low, judging from the values of relative viscosity in DMF solution containing 2 wt % $NaBF_4$.

Figures 1, 2a, and 2c show respectively ^1H and ^{13}C NMR spectra of a polymer **5a-2** and 2-isopropyl-3-methyl-2-oxazolinium fluorosulfonate (**8**), a monomeric unit model for **5a-2**. In the ^1H NMR spectra of **5a-2** and **8** (Figure 1), the signals due to oxazolinium ring protons appear around δ 3.3–3.7 (NCH_3), 4.0–4.6 (NCH_2), and 4.8–5.3 (OCH_2). In the ^{13}C NMR spectra (Figure 2), the signals at approximately δ 33 (NCH_3), 51 (C_4), 71 (C_5), and 177 (C_2) are assigned to the onium ring. The peaks ascribed to the main chain of the polymer appear as broad peaks around δ 1.5–2.5 in Figure 1a and around δ 25–33 in Figure 2a. The broadening may be due to the lack of stereoregularity of the polymer, the sterically rigid structure of the polymer induced by the electrical repulsion between the pendant group, and the nuclear quadropole effect of the nitrogen atom.

In Figure 2a, neither the peaks ascribed to the acrylamide group (ca. δ 127 for both alkenyl carbons and ca. δ 166 for the carbonyl carbon) derived from the poly[(N-acryloylimino)ethylene] unit nor the peaks ascribed to the unalkylated oxazoline group (ca. δ 170 for the 2-position, ca. δ 55 for the 4-position, and ca. δ 68 for the 5-position) derived from the poly[(2-oxazolin-2-yl)ethylene] unit are observed.

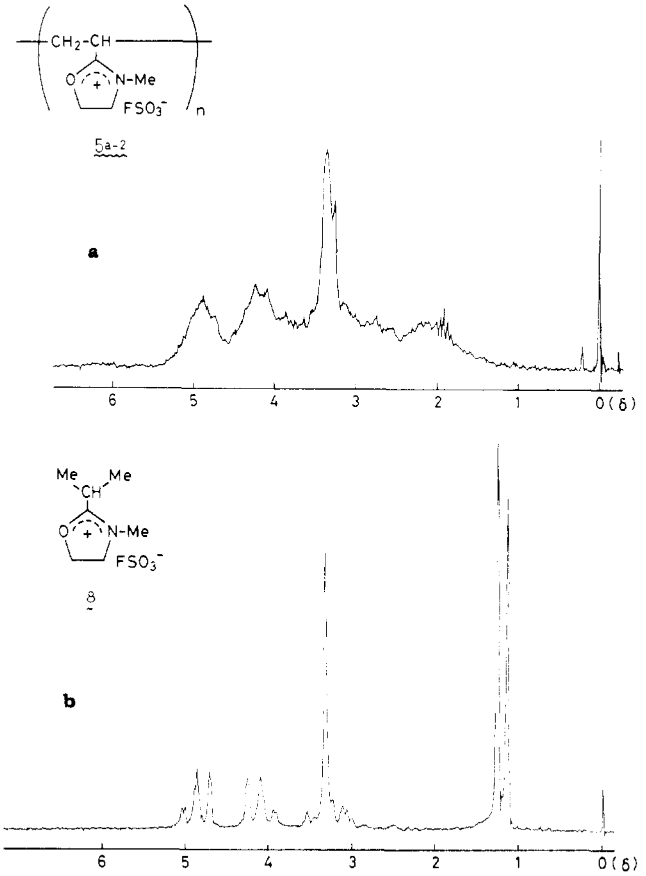


Figure 1. 60-MHz ^1H NMR spectra of (a) **5a-2** (20% CD_3CN solution) and (b) a model compound **8** (10% CD_3CN solution) (internal standard: Me_4Si).

The above NMR data are taken to show that the structure of the vinyl-polymerized chain has the 3-methyl-2-oxazolinium pendant group. IR spectra and

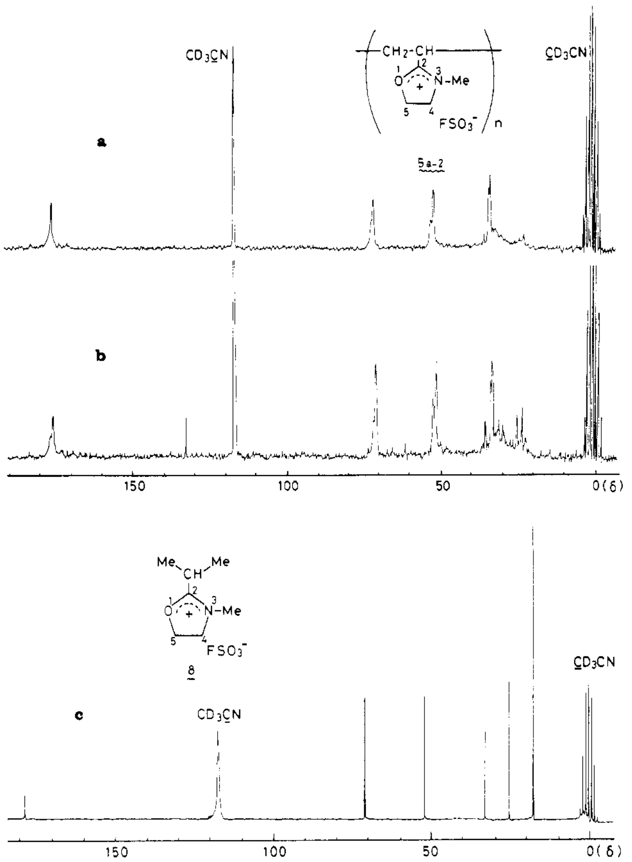


Figure 2. 22.6-MHz $^{13}C\{^1H\}$ NMR spectra of (a) **5a-2** (25% CD_3CN solution), (b) its fractionized oligomer (15% CD_3CN solution), and (c) **8** (20% CD_3CN solution) (internal standard: Me_4Si).

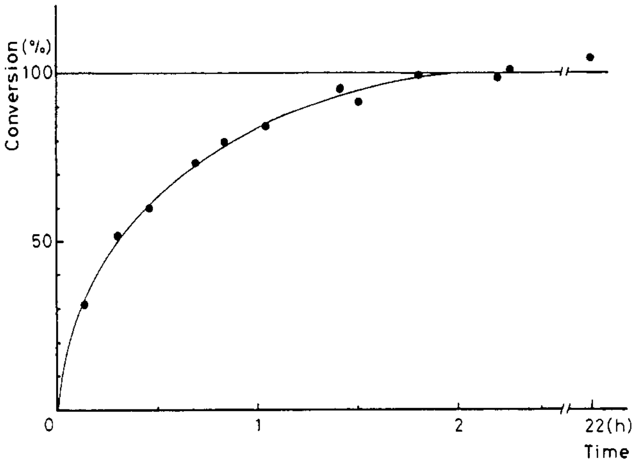
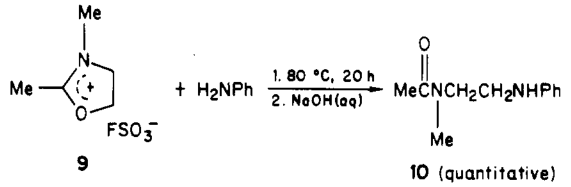


Figure 3. Time–conversion curve of "spontaneous" polymerization of **1a** with **6a-1**.

elemental analyses also support the polymer structure. Similar results leading to the same conclusion were obtained with other polymer products (Table I).

In the present reactions, the polymerization of the vinyl group was caused simultaneously with the N-alkylation of the oxazoline ring. This polymerization occurs with strong alkylating agents such as **6a-2**, **5a-2**, and **6b-2**. The rate of polymerization was very fast in CH_2Cl_2 at 0 °C; i.e., the conversion was instantaneously completed as soon as one drop of **1** was added to **6**. At temperatures below −30 °C, however, no reaction was observed. When the temperature of an equimolar mixture of monomer and a strong alkylating agent was raised to −30 °C, precipitation of polymer **5** suddenly started. Similar results were obtained in other solvents such as toluene, chlorobenzene, ether, and acetonitrile. Polymerization with trimethyloxonium tetrafluoroborate (**6a-1**), however, was much slower because it is less soluble in CH_2Cl_2. Figure 3 shows a time–conversion curve of the heterogeneous polymerization of **1a** with **6a-1** in CH_2Cl_2 at 0 °C where the feed mole ratio of **6a-1**/**1a** was 2.0. The extent of conversion of **1a** was determined by GLC analysis (internal standard, toluene) of the amount of unreacted **1a**, and that of **6a-1** was determined by dimethyl ether. After 2 h, the conversion reached 100% (Figure 3) and the unreacted **6a-1** remained without change even if the reaction mixture was further maintained under reaction conditions for 20 h. During the first 2 h, cationic ring-opening polymerization of the free monomer **1a** might possibly occur. However, no such polymerization was detected.

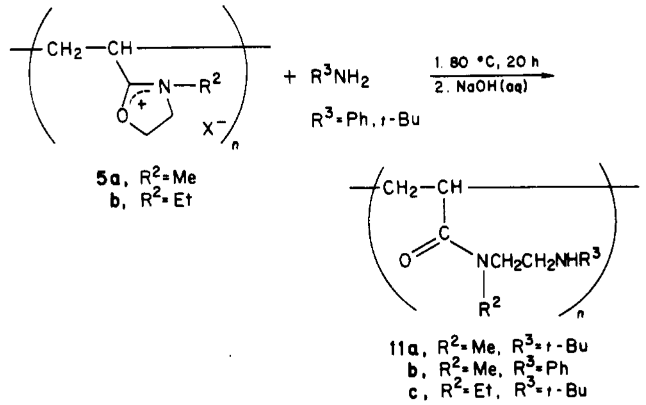
Scheme III



9

10 (quantitative)

Scheme IV



5a, R^2=Me
b, R^2=Et

11a, R^2=Me, R^3=t-Bu
b, R^2=Me, R^3=Ph
c, R^2=Et, R^3=t-Bu

When the alkylating agent was added to a solution of **1** at 0 °C, a vigorous exothermic reaction occurred, the temperature of the reaction mixture was raised to about 30 °C, and the ring-opening polymerization proceeded concurrently with the "spontaneous" polymerization of the onium salt. When weak alkylating agents such as methyl iodide and tosylate were used, pure alkylation/vinyl polymerization was not observed. Treatment of **1** with these agents at temperatures higher than 40 °C brings about the normal alkylation as well as the ring-opening polymerization of **1**, producing an insoluble gel.

Polymer Reaction of 4 with Amines. The oxazolinium salt readily reacts with amine to produce the ring-opening product with C–O bond scission.[4] For example, reaction of 2,3-dimethyl-2-oxazolinium fluorosulfonate (**9**) with aniline gave *N*-methyl-*N*-[2-(phenylamino)ethyl]acetamide (**10**) quantitatively, as shown in Scheme III.

Reaction of the polymeric oxazolinium salt **5** with amine (aniline and *t*-$BuNH_2$) (Scheme IV) was examined in CH_3CN at 80 °C. The results are shown in Table II. The low yields of the isolated polymeric products **11** are attributed to the loss of the low molecular weight parts of the product in the isolation process by reprecipitation (see Experimental Section). The conversion of the oxazolinium salt **5** to the amine–amide side chain of **11** was clean and complete. The structure of **11** is supported by ^1H and ^{13}C NMR and IR spectra which are analogous to those of the respective spectra of the model compound **10**. Figure 4

Table II
Reaction of Poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene] (5) with Amine[a]

			products			
run no.[b]	5	amine R^3	11	yield, %	$\bar{M}_n$[c]	$\bar{DP}$
1	**5a-1**	*t*-Bu	**11a**	83	2110	11.4
4	**5a-2**	*t*-Bu	**11a**	46	3800	18.6
4	**5a-2**	Ph	**11b**	65	3150	15.4
5	**5a-2**	Ph	**11b**	90	2390	11.6
6	**5a-2**	Ph	**11b**	60	4320	21.1
8	**5a-2**	*t*-Bu	**11a**	46	1300	7.0
8	**5a-2**	Ph	**11b**	55	1890	9.3
9	**5a-3**	Ph	**11b**	37	3390	16.6
11	**5c**	*t*-Bu	**11c**	77	2130	10.7

[a] In CH_3CN at 80 °C for 20 h. The molar ratio of **5**/amine was 1/5. [b] Run numbers are the same as those of Table I. [c] Determined by VPO in $CHCl_3$ at 40 °C.

Table III
UV Analysis of 10 and 11b[a]

sample	concn × 10^2, g/dL	abs band	λ_{max} (ϵ_{max}), nm	calcd concn of **11b**[b] × 10^2, g/dL
10		E_2	246 (10300[c])	
		B	295 (2090[c])	
11b[d]	2.555	E_2	247	2.451
		B	295	2.531

[a] In $CHCl_3$, at room temperature. [b] Calculated values by using ϵ_{max} of **10**. [c] Average value of the four values obtained at concentrations from 2.9 × 10^{-2} to 0.96 × 10^{-2} g/L. [d] The sample of run no. 4 in Table II was used.

shows typical ^{13}C NMR spectra of **11b** and **10**. Both spectra are complex because of the existence of two stereoisomers arising from rotational restriction around the amide bonds (see Experimental Section).

Product **11b** contains a phenyl group in the side chain, whose amount is determined by UV spectroscopy (Table III). The concentration of the repeat unit of **11b** was calculated for the two bands by using the molar absorption coefficients of monomeric **10**. The actual concentration and the calculated values are in substantial agreement with each other. Thus, the oxazolinium–amine reaction of the polymer is almost quantitative. The molecular weight of **11** was determined by VPO. The values were from 1300 to 4320, and the average degree of polymerization was calculated to be in the range 7–21. These results are taken to indicate that the degree of polymerization of the original "spontaneous" polymers is within this range.

Mechanism of the "Spontaneous" Polymerization. The mechanism of the present polymerization should be considered in connection with the so-called spontaneous polymerization of vinylpyridines.[7-11] In the polymerization of 2- and 4-vinylpyridines, the N-alkylation of the monomer causes the vinyl polymerization via an anionic mechanism. The free monomer functions as the initiator to add vinylpyridinium, producing an anionic propagating species (Scheme V).

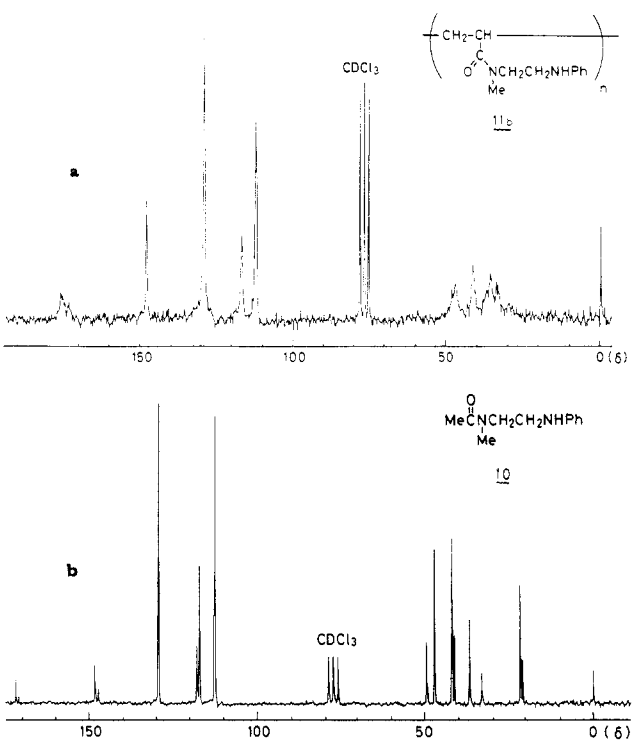
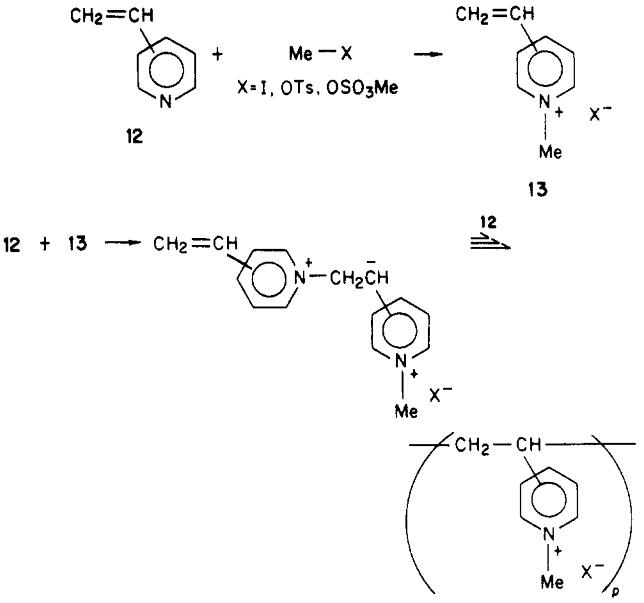


Figure 4. 22.6-MHz $^{13}C\{^1H\}$ NMR spectra of (a) poly(amine amide) **11b** (25% $CDCl_3$ solution) and (b) model compound **10** (20% $CDCl_3$ solution) (internal standard: Me_4Si).

Scheme V



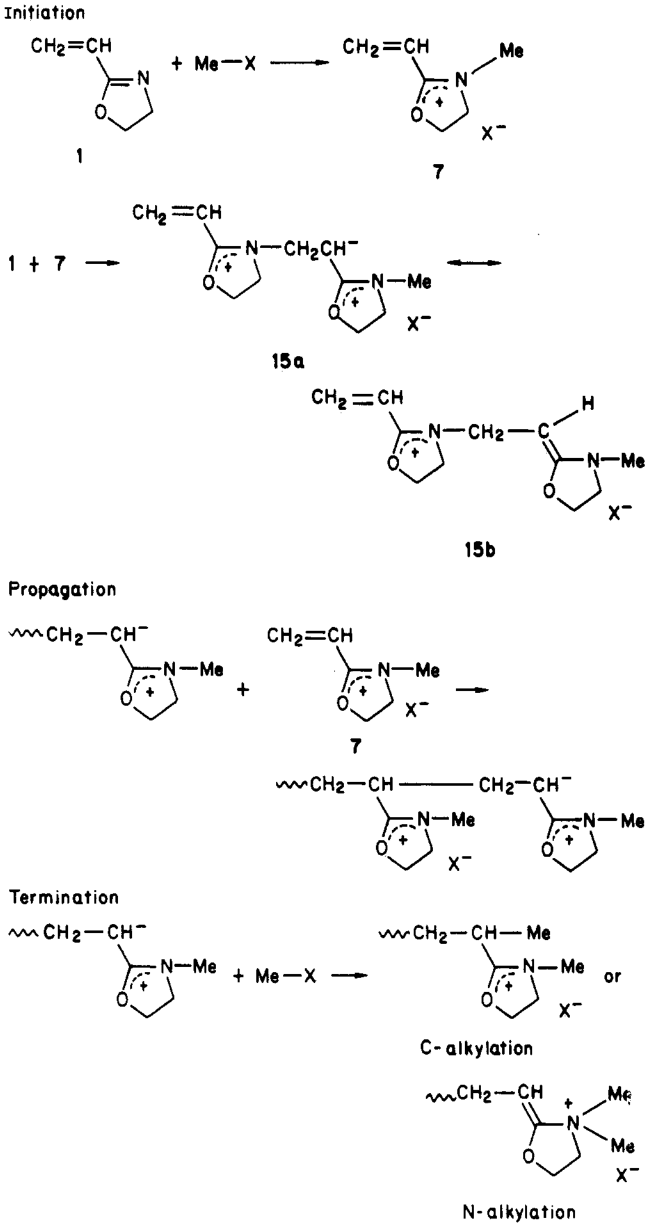
In order to clarify the reaction mechanism of the present "spontaneous" polymerization of **1a**, the reaction was carried out in the presence of various additives. The results are shown in Table IV. Benzoquinone did not inhibit

Table IV
"Spontaneous" Polymerization of 1a: Effect of Additives[a]

						product polymers	
run no.	6	feed ratio [**1a**]/[**6**]	additive	molar ratio to **1a**	5	yield, %	η_{sp}/C,[b] dL/g
1	**6a-1**	1.01			**5a-1**	100	0.038
2	**6a-1**	1.00	benzoquinone	0.51	**5a-1**	96	0.028
3	**6a-1**	1.06	styrene	0.96	**5a-1**	98	0.030
4	**6a-1**	1.00	methyl methacrylate	1.00	**5a-1**	97	0.032
5	**6b-1**	0.67	pyridine	0.34	**5a-2**	87	0.040

[a] In CH_2Cl_2 at 0 °C for 2 h. [b] In 2% $NaBF_4$-DMF solvent (C = 0.5 g/dL) at 30 °C.

Scheme VI



the polymerization. Styrene and methyl methacrylate were not incorporated in the polymer product. The addition of pyridine gave rise to the production of polymer **5a** having a pyridinium end group. The effects of the above additives are taken to exclude radical and cationic mechanisms, and the anionic mechanism, which resembles that of 4-vinylpyridine, is the most probable, as shown in Scheme VI. In the polymerization shown in Scheme VI, 3-methyl-2-vinyl-2-oxazolinium salt **7**, which is produced by alkylation, is the key intermediate. It is reactive and rapidly enters into the anionic polymerization as soon as it is formed. The propagation is initiated by the attack of a small amount of free monomer.

Results of a reference experiment with *N*,*N*-dimethylacrylamide (**16**) may be used to support the above mechanism. With a strong alkylating agent of methyl fluorosulfonate **6b-1**, **16** is readily alkylated to produce the corresponding onium salt **17** without polymerization, as shown in Scheme VII. The salt **17**, which was found to polymerize almost explosively in the presence of a trace amount of pyridine at room temperature in CH_2Cl_2, may be regarded as an acyclic model of **7**. In the case of **17**, the precursor monomer **16** is not nucleophilic enough to cause the anionic polymerization of its salt, whereas the stronger nucleophile pyridine initiates the anionic polymerization of **17**.

In the vinyloxazolinium polymerization, the propagating zwitterionic species **15** can be stabilized by the resonance between the two structures **15a** and **15b** (see Scheme VIII). Concerning the propagation reactions, two possible ways are considered, i.e., the general anionic propagation via **15a**, and the conjugate 1,4-addition of an enamine form **15b** to the monomer. At present, the actual responsible form has not been assigned.

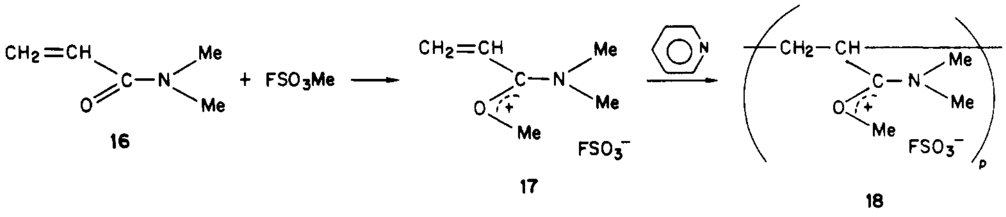
The termination reaction occurs at a considerable rate to produce the low molecular weight product. A possible pattern of the termination reaction is the alkylation of the propagating species in an enamine form.

This reaction mechanism was confirmed by the results of the fractional reprecipitation of the product polymer. By repeated addition of CH_2Cl_2 to a CH_3CN solution of **5a-2**, **5a-2** was fractionized into six portions, and then the last fraction was obtained by addition of Et_2O to the supernatant solution. Concerning these seven fractions, basically no difference was observed among their ^1H and ^{13}C NMR spectra except for the last fraction, whose ^{13}C spectrum is shown in Figure 2b. In this figure, peaks at δ 24.45, 26.12, 30.36, 31.82, 36.02, and 133.49, which can be ascribed to end groups of the polymer, are observed.

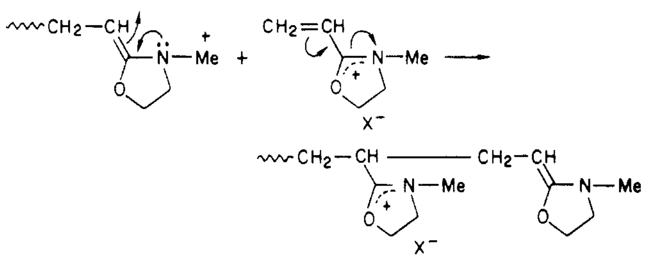
The peak at δ 133.49 can be ascribed to neither the acryloyl group derived from poly[(*N*-acryloylimino)ethylene] nor to the vinyl group derived from unreacted **1a** (δ 124.36 for the α-carbon and δ 125.09 for the β-carbon). Because the value δ 133.49 is quite similar to that for the β-carbon of **17** (δ 133.97), this peak is probably ascribed to the β-carbon of the vinyl group derived from the 2-vinyl-2-oxazolinium moiety at the initiating end of the polymer. The peak of the corresponding α-carbon of this vinyl group may be overlapped by the strong peak of the solvent. The peaks at δ 24.45 and 26.12 can be ascribed to the C–Me group of the C-terminated end of the polymer, although other peaks cannot be ascribed because of the lack of data for such compounds.

It is worthwhile to compare these polymerization mechanisms with those of the ring-preserved polymerization of 2-isopropenyl-2-oxazoline (**1c**) catalyzed by 2-isopropenyl-3-protio-2-oxazolinium bisulfate (**19**). In this ring-preserved polymerization, formation of an enamine-type intermediate **20** (see Scheme IX), which possesses a similar structure to **15b**, is postulated by an analogous initiation. Although, in this case, the more reactive enamine moiety of **20** was rapidly transformed into a stable

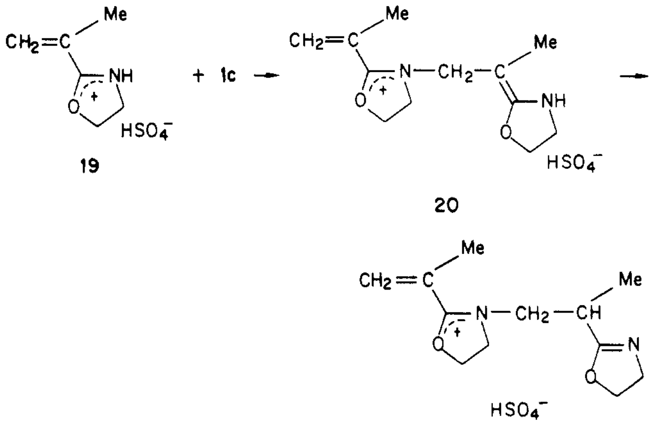
Scheme VII



Scheme VIII



Scheme IX



oxazoline form by a proton transfer, the propagation proceeded at the less reactive olefinic side through an attack of **1c**. Therefore the ring-preserved polymerization requires higher temperatures (25–35 °C) in CH_3CN than the spontaneous polymerization of the present study, which proceeds even at −30 °C in the same solvent.

Comparison between "Spontaneous" Polymerization of 1 and 12. Both **1** and **12** have similarities in that their vinyl groups conjugated with an sp^2-hybridized amine moiety and that their amine basicity is in the same order.[13] However, two significant differences are noted between them. (1) In the case of **12**, the monomeric salts **13** can be isolated with active alkylating agents such as methyl sulfate[8b] and *p*-toluenesulfonate[8a] because the polymerization of the salt is slower in comparison with the alkylation reaction itself. In the case of **1**, however, the monomeric salts **7** could not be isolated at all. (2) The polymer **14**[8] produced from **12** is of relatively high molecular weight ($[\eta] = 2\text{–}12$), whereas the one produced from **5** is oligomeric ($\overline{DP} = 7\text{–}21$, η_{sp}/C = ca. 0.05). These differences may be explained by the difference of reactivity between the propagating species of the two polymerizations; i.e., vinyloxazolinium is more reactive (less stable) than vinylpyridinium and the propagating species of vinyloxazolinium is alkylated (terminated) more easily than that of vinylpyridinium.

As in the case of **12**, **1** is polymerized by superacids such as fluorosulfonic and trifluoromethanesulfonic acids. However, the polymerization is not clean, probably due to the proton transfer from the ammonium nitrogen to the carbanionic center of the propagating species.

Poly[1-(2-oxazolinium-2-yl)ethylene] **5** is very reactive toward many nucleophiles. Extension of studies on this versatile polymeric reagent is now under way.

Experimental Section

Materials. 2-Vinyl- (**1a**),[14] 4,4-dimethyl-2-vinyl- (**1b**),[14] 2-isopropenyl- (**1c**),[14] and 2-isopropyl-2-oxazoline[15] were prepared by the methods previously reported, purified by repeated distillations under reduced pressure, and dried over molecular sieves 4A. Trimethyl- and triethyloxonium tetrafluoroborate were prepared according to the procedure of Meerwein.[16] Methyl fluorosulfonate and methyl trifluoromethanesulfonate were prepared by transesterification reactions of their corresponding sulfonic acids with dimethyl sulfate as previously reported and were purified by distillation under nitrogen.[17,18] Aniline, *tert*-butylamine, *N*,*N*-dimethylacrylamide, and all the solvents were purified by distillation under nitrogen.

Preparation of Various Derivatives of 2-Oxazolinium Salts. These salts were prepared by an equimolar reaction of 2-oxazoline with an alkylating agent in CH_2Cl_2 at 0 °C.[13] These salts and polymer **5** were so hygroscopic that measurement of their NMR and IR spectra required anhydrous conditions, and elemental analyses were corrected with due regard to absorption of moisture.

2-Isopropyl-3-methyl-2-oxazolinium fluorosulfonate (8) was prepared by reaction of 2-isopropyl-2-oxazoline with **6b-1**: white needles (60% yield); ^1H NMR (CD_3CN) δ 1.24 (d, 6 H, $(CH_3)_2C$), 3.27 (m, 1 H, CH), 3.37 (s, 3 H, CH_3N), 3.90–4.35 (m, 2 H, CH_2N), 4.72–5.13 (m, 2 H, CH_2O); ^{13}C NMR (CD_3CN) δ 17.61 ($(CH_3)_2C$), 25.66 (CH), 33.52 (CH_3N), 52.27 (C_4), 71.34 (C_5), 179.98 (C_2); IR (in CH_3CN) 1668 ($\nu_{C=N}$), 1280, 1083, 1062, 713, 566 cm^{-1}. Anal. Calcd for $C_7H_{14}NO_4FS{\cdot}0.5H_2O$ (hygroscopic): C, 35.59; H, 6.40; N, 5.93. Found: C, 35.37; H, 6.85; N, 5.97.

2,3-Dimethyl-2-oxazolinium fluorosulfonate (9) was prepared by reaction of 2-methyl-2-oxazoline with **6b-1**: white solid (90% yield); ^1H NMR (CD_3CN) δ 2.39 (s, 3 H, CH_3C), 3.29 (s, 3 H, CH_3N), 3.95–4.04 (m, 2 H, CH_2N), 4.72–5.08 (m, 2 H, CH_2O); ^{13}C NMR (CD_3CN) δ 12.22 (CH_3-C_4), 33.95 (CH_3N), 52.07 (C_4), 71.39 (C_5), 176.41 (C_2); IR (in CH_3CN) 1680 ($\nu_{C=N}$), 1277 ($\nu_{S=O}$), 973, 710, 568 cm^{-1}. Anal. Calcd for $C_5H_{10}NO_4FS{\cdot}0.2H_2O$ (hygroscopic): C, 29.61; H, 5.17; N, 6.91. Found: C, 29.34; H, 5.29; N, 7.00.

Instrumentation. ^1H NMR spectra were recorded on a Hitachi R-20B spectrometer at 60 MHz. ^{13}C NMR spectra were recorded on a Hitachi R-900 Fourier transform spectrometer operating at 22.6 MHz. IR and UV spectra were recorded on a Hitachi 260-20 infrared spectrometer and on a Hitachi 200-20 spectrophotometer, respectively. GLC was performed on a Si column (2 m) at 100 °C by using a Shimadzu GC-4A gas chromatograph. Molecular weight determination was carried out by a vapor pressure osmometer (Hitachi Model 117) in $CHCl_3$ at 40 °C. Melting points were measured by DSC endotherms (Rigaku Thermoflex DSC) under a nitrogen atmosphere.

General Procedure for "Spontaneous" Polymerization of 1a. All procedures were carried out under a nitrogen atmosphere. A solution of methyl fluorosulfonate (6.2 mmol) in 10 mL of CH_2Cl_2 was vigorously stirred at 0 °C, to which **1a** (5.2 mmol) was slowly added. At the very beginning of the addition of **1a**, i.e., at the first drop of the solution, precipitation of a white solid product started. After the addition was complete, the mixture was stirred at 0 °C for 1 h to complete the reaction. The product was filtered, washed with CH_2Cl_2, dried in vacuo. A pale yellow powdery polymer was obtained, 1.09 g (100% yield).

5a-2: softening point 150–160 °C; ^1H NMR (CD_3CN) δ 1.9–2.6 (2 H, CH_2CH) 2.7–3.2 (1 H, CH_2CH), 3.3–3.7 (3 H, CH_3N), 4.0–4.6 (2 H, CH_2N), 4.8–5.3 (2 H, CH_2O); ^{13}C NMR (CD_3CN) δ 20.5–26.7 (CH_2CH), 27.7–35.4 (CH_2CH and CH_3N), 50.5–52.6 (C_4), 70.5–72.7 (C_5), 175.0–177.1 (C_2); IR (in CH_3CN) 1677 ($\nu_{C=N}$), 1280, 1068, 720, 573 cm^{-1}. Anal. Calcd for $C_6H_{10}NO_4FS{\cdot}0.2H_2O$ (hygroscopic): C, 33.55; H, 4.88; N, 6.52. Found: C, 33.55; H, 5.09; N, 6.62.

5a-1[19] was prepared by reaction of **1a** with **6a-1**: white powder; softening point 150–164 °C; IR (in CH_3CN) 1678 ($\nu_{C=N}$), 1285, 1091 cm^{-1}. Anal. Calcd for $C_6H_{10}NOBF_4$: C, 36.22; H, 5.23; N, 7.04. Found: C, 36.65; H, 5.23; N, 7.47.

5a-3[20] was prepared by reaction of **1a** with **6b-2**: yellow solid; ^{13}C NMR (CD_3CN) δ 22.5–25.3 (CH_2CH), 29.1–34.4 (CH_2CH and CH_3N), 52.0–54.1 (C_4), 71.6–72.8 (C_5), 121.0 (q, CF_3, $|J_{C\text{-}F}| = 320$ Hz), 174.6–177.5 (C_2); IR (in CH_3CN) 1678 ($\nu_{C=N}$), 1270, 1160, 635 cm^{-1}.

5b was prepared by reaction of **1b** with **6b-1**: white powder; softening point 139–145 °C; ^1H NMR (CD_3CN) δ 1.1–1.6 (6 H, CH_3C), 1.8–2.3 (2 H, CH_2CH), 2.4–2.9 (1 H, CH_2CH), 3.0–3.5 (3 H, CH_2N), 4.5–4.9 (2 H, CH_3O); ^{13}C NMR (CD_3CN) δ 19.3–23.8 (CH_3-C_4 and CH_2CH), 26.5–33.6 (CH_3N and CH_2CH), 67.1–69.1 (C_4), 82.1–82.4 (C_5), 174.6–175.7 (C_2); IR (in CH_3CN) 1659 ($\nu_{C=N}$), 1284, 718, 573 cm^{-1}. Anal. Calcd for $C_8H_{14}NFSO_4{\cdot}0.3H_2O$ (hygroscopic): C, 39.27; H, 6.01; N, 5.73. Found: C, 39.17; H, 6.12; N, 5.90.

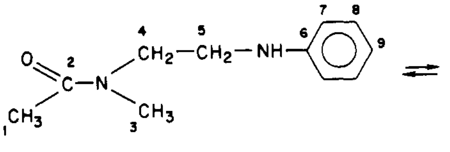
5c was prepared by reaction of **1a** with **6a-2**: pale yellow powder; softening point 140–145 °C; ^{1}H NMR δ 0.9–1.4 (3 H, CH$_3$), 1.5–2.3 (2 H, *CH*$_2$CH), 2.4–2.9 (1 H, CH$_2$*CH*), 3.0–4.3 (4 H, CH$_2$N), 4.5–5.1 (2 H, CH$_2$O); IR (in CH$_3$CN) 1660 ($\nu_{C=N}$), 1283, 1102 cm^{-1}. Anal. Calcd for $C_7H_{12}NOBF_4{\cdot}0.3H_2O$ (hygroscopic): C, 38.50; H, 5.82; N, 6.41. Found: C, 38.58; H, 5.48; N, 6.82.

Reaction of Poly[1-(2,3-dimethyl-2-oxazolinium-2-yl)ethylene] (4) with Amine. A typical run is as follows. In a tube under a nitrogen atmosphere 1.73 g (8.20 mmol based on the oxazolinium unit) of **5a-2** and 3.7 mL of aniline (5 molar equiv) were allowed to dissolve in 7 mL of CH$_3$CN. The tube was sealed and heated at 80 °C for 20 h. After complete evaporation of the solvent and excess aniline, the crude product polymer, having pendant ammonium ions, was obtained quantitatively. This ammonium-type polymer was dissolved in water and the mixture was poured into 50 mL of a 10% aqueous NaOH solution and extracted thoroughly with CH$_2$Cl$_2$. This extract was washed with brine and dried over MgSO$_4$. By evaporation of CH$_2$Cl$_2$ at reduced pressure, a crude product was obtained. It was then purified by repeated precipitation from CHCl$_3$ (solvent) to Et$_2$O (precipitant) and was finally dried in vacuo. The final yield of the product was 1.51 g (90% yield; $\bar{M}_n$ = 2390 (VPO (in CHCl$_3$) at 40 °C)). After evaporation of the combined supernatant Et$_2$O layer, 0.10 g more of the amine–amide type polymer, having a low molecular weight, was obtained (6% yield; $\bar{M}_n$ = 690).

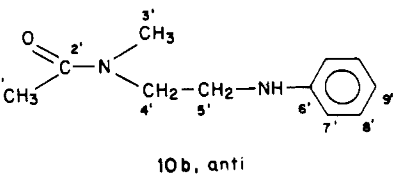
11b: brown solid; ^{1}H NMR (CD$_3$CN) δ 1.1–2.4 (3 H, CH$_2$CH), 2.5–4.0 (7 H, CH$_3$N and NCH$_2$CH$_2$N), 4.2–4.6 (1 H, NH), 6.3–7.4 (5 H, aromatic protons); ^{13}C NMR (CDCl$_3$) δ 25.3–38.7 (CH$_2$CH and CH$_3$N), 41.4–43.4 (N(CO)CH$_2$), 46.4–49.8 (PhNCH$_2$), 111.9–112.8 (2- and 6-positions of phenyl group), 116.4–117.6 (4-position of phenyl group), 128.6–129.9 (3- and 5-positions of phenyl group), 147.2–148.1 (1-position of phenyl group), 171.9–176.1 (C=O); IR (KBr) 3350 (ν_{NH}), 3020, 2920, 1625 ($\nu_{C=O}$), 1600, 1495, 1320, 1258, 748, 697, 680 cm^{-1}.

Reaction of 9 with Aniline. To a stirred solution of **9** in 5 mL of CH$_3$CN was added 25.2 mmol (5 equiv) of aniline dropwise at 0 °C. The mixture was stirred at room temperature overnight. It was then poured into 50 mL of a 10% aqueous NaOH solution, and the mixture was thoroughly extracted with CH$_2$Cl$_2$, washed with brine, and dried over MgSO$_4$. After the solvent was evaporated, a pale brownish liquid product **10** was quantitatively obtained, which was essentially pure. It was further purified by column chromatography (Wakogel C-200; eluent, ethyl acetate), by which the yield was decreased to 73%. The structure determination for this product is shown below.

As shown in the ^{13}C NMR spectrum (Figure 4), every signal indicates a pair of peaks with the intensity ratio of 1/0.42. The assignments were made on the basis of the literature.[21] From these data, it is reasonable to consider that product **10** has two isomeric forms, **10a** (syn) and **10b** (anti), which are interconvertible. Because **10a** is more stable than **10b**, the relative population of the former is larger, and the signal with the larger intensity is ascribed to **10a**. This fact was also supported by ^{1}H NMR spectroscopy. All these data are summarized as follows.



10a, syn



10b, anti

10: ^{1}H NMR (CDCl$_3$) δ 2.02 (s, CH$_3$CO of **10b**), 2.08 (s, CH$_3$CO of **10a**), 2.95 (s, CH$_3$N of **10b**), 3.00 (s, CH$_3$N of **10a**), 3.13–3.75 (m, CH$_2$ of **10a** and **10b**), 6.50–7.31 (m, aromatic protons of **10a** and **10b**); ^{13}C NMR (CDCl$_3$) δ 21.22 (C$'_1$), 21.80 (C$_1$), 33.24 (C$'_3$), 36.82 (C$_3$), 41.48 (C$'$,4) 42.18 (C$_4$), 47.30 (C$_5$), 49.54 (C$'$,5), 112.45 (C$_7$), 112.68 (C$'_7$), 117.11 (C$_9$), 117.84 (C$'_9$), 129.28 (C$_8$), 129.51 (C$'_8$), 147.39 (C$'_6$), 148.28 (C$_6$), 171.00 (C$'_2$), 171.89 (C$_2$); IR (neat) 3320 (ν_{NH}), 3020, 2930, 2860, 1625 ($\nu_{C=O}$), 1600, 1500, 1405, 1325, 1263, 1020, 750, 698, 680 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.61; H, 8.52; N, 14.44.

Preparation of *N,N*-Dimethyl-*O*-methylacrylimidatonium Fluorosulfonate (17). **17** was prepared by the reaction of *N,N*-dimethylacrylamide with **6b-1** by following the procedure similar to the preparation of oxazolinium salts (93% yield): white needles; mp 84 °C; ^{1}H NMR (CD$_3$CN) δ 3.30 (s, 3 H, CH$_3$N), 3.38 (s, 3 H, CH$_3$N), 4.15 (s, 3 H, CH$_3$O), 5.94–6.81 (3 H, m, CH$_2$=CH); ^{13}C NMR (CD$_3$CN) δ 38.40 (CH$_3$N), 41.96 (CH$_3$N), 61.64 (CH$_3$O), 121.65 (*C*H$_2$=CH), 133.97 (CH$_2$=*C*H), 172.72 (C=N); IR (in CH$_3$CN) 1663 ($\nu_{C=N}$), 1286, 1068, 716, 570 cm^{-1}. Anal. Calcd for $C_6H_{12}NO_4FS{\cdot}0.2H_2O$ (hygroscopic): C, 32.69; H, 5.85; N, 6.35. Found: C, 32.52; H, 6.07; N, 6.44.

Registry No. **1a**, 13670-33-2; **1b**, 60824-09-1; **5a-1**, 97592-45-5; **5a-2**, 97592-47-7; **5a-3**, 97592-48-8; **5b**, 97592-50-2; **5c**, 97592-52-4; **6a-1**, 420-37-1; **6a-2**, 368-39-8; **6b-1**, 97592-56-8; **6b-2**, 97592-57-9; **8**, 97592-58-0; **9**, 97592-59-1; **10**, 97592-53-5; 2-isopropyl-2-oxazoline, 10431-99-9; *N,N*-dimethyl-*O*-methylacrylimidatonium fluorosulfonate, 97592-55-7; 2-methyl-2-oxazoline, 1120-64-5; aniline, 62-53-3; dimethylacrylamide, 2680-03-7; benzoquinone, 106-51-4; styrene, 100-42-5; methyl methacrylate, 80-62-6; pyridine, 110-86-1.

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Polymerization of Tetrahydrofuran Initiated by Isomeric 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts. Mechanism of the Initiation

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ABSTRACT: The course of tetrahydrofuran (THF) polymerization carried out in the presence of isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts was investigated. A polymerization initiation mechanism was proposed for that system on the basis of results of end-group and ^1H NMR analyses. It was shown that the initiation reaction proceeds with the formation of two products (reaction Scheme III), a polymer having ester end groups being obtained. The influence of the dioxolenium cation structure on the polymerization reaction was also discussed.

Introduction

Stable carbenium and oxonium salts have recently found widespread use as cationic polymerization initiators.[1,2] Owing to the specific properties of these salts, their application has eliminated a number of difficulties encountered when using such conventional initiators as protonic acids, Lewis acids, aluminium alkyl compounds, etc.

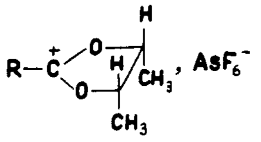
The 1,3-dioxolan-2-ylium salts also belong to the group of carbenium salt type initiators. The stable salts, derivatives of the trisubstituted dioxolane, have been recently used for initiating the polymerization of such heterocyclic monomers as 1,3-dioxolane[3] and trioxane.[4-6] Unsubstituted or monosubstituted dioxolenium salts have been also used to initiate the polymerization of tetrahydrofuran (THF).[7-11] The aim of the present paper is to discuss the effect of the structure of the isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts on the course of THF polymerization as well as to elucidate the mechanism of this reaction, especially its initiation step.

Experimental Section

Monomer and Solvents. THF and THF-d_8 were purified by hours of long boiling over Na/K alloy in an atmosphere of dry nitrogen. The THF used in the polymerization was distilled over Na/K alloy directly before use.

Methylene chloride, CD_2Cl_2, and *n*-heptane were purified by conventional techniques used in cationic polymerization.

Initiators. The following trisubstituted isomeric 1,3-dioxolan-2-ylium salts were used as THF polymerization initiators.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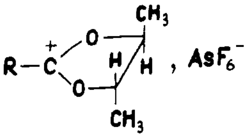
trans

$$R = \begin{cases} -CH_3 & \underline{1} \\ -CH_2CH_3 & \underline{2} \\ -CH(CH_3)_2 & \underline{3} \\ -C_6H_5 & \underline{4} \\ -CH{=}CH-C_6H_5 & \underline{5} \end{cases}$$

Table I
Viscosity-Average Molecular Weights of Polymers Obtained after 7 Days[a] from the Start of the Polymerization Reaction[b]

init	$\bar{M}_\eta$	init	$\bar{M}_\eta$
trans-1	18600	*cis*-4	20000
trans-2	18700	*trans*-4	21200
trans-3	19100	*cis*-5	26100
		trans-5	28000

[a] The time required for equilibrium conversion in the polymerization initiated by *trans*-5 initiator. [b] $[M]_0 = 7.9$ mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L, CH_2Cl_2 at 20 °C.

Table II
Theoretical and Experimental $\overline{DP}_n$ Values Obtained for Various Polymerization Times[a]

			$\overline{DP}_n$		
init	time, h	% conv	theor	UV	IR
trans-4	5	28	145	1702	
	10	35	181	1190	
	15	39	202	964	
	23	42	217	772	
	48	48	248	489	
cis-5	5	16	83	1560	1577
	10	26	134	1244	1250
	15	32	165	1140	1128
	23	37	191	956	953
	48	45	233	589	576

[a] $[M]_0 = 9.3$ mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L, CH_2Cl_2 at 20 °C.

These salts were obtained by reacting a corresponding acetal with a triphenylmethylium salt, according to the method described previously.[12]

Polymerization. The THF polymerization process was conducted in methylene chloride solution at 20 °C in the presence of the above-listed 1,3-dioxolan-2-ylium salts. The polymerization was terminated by adding to the system a methylene chloride solution of diethylamine. The polymer was precipitated with cold water, filtered off, and dried in vacuo to constant weight in order to determine the degree of conversion of the monomer.

Determination of Average Molecular Weights. The viscosity-average molecular weights were calculated from the Mark–Houwink relation:[13]

$$[\eta] = 2.98 \times 10^{-4} \bar{M}_\eta^{0.79}$$

0024-9297/85/2218-1648$01.50/0