Novel Covalent-Type Electrophilic Polymerization of 2-(Perfluoroalkyl)-2-oxazolines Initiated by Sulfonates

Masatoshi Miyamoto, Keigo Aoi, and Takeo Saegusa*

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

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ABSTRACT: Ring-opening polymerization of 2-(perfluoroalkyl)-2-oxazolines (1) with some sulfonate initiators was found to proceed via two different mechanisms of propagation according to the nature of the sulfonate initiators, i.e., the sulfonate counteranions derived from the initiators. With methyl *p*-nitrobenzenesulfonate or *p*-toluenesulfonate initiators, the propagating species of the polymerization of 1 was of covalent sulfonate ester. On the other hand, with methyl trifluoromethanesulfonate initiator, which gives more stable (less nucleophilic) triflate anion, the propagating species was of the structure of oxazolinium cation. Both of the above mechanisms were confirmed by the in situ ^1H and ^{19}F NMR spectroscopies of the polymerization systems as well as the isolation of the 1:1 adducts of 1 with each of the initiators. The results of kinetic studies on these polymerizations were to taken to support the above conclusion and gave quantitative evaluations of the reactivities of two different propagating species.

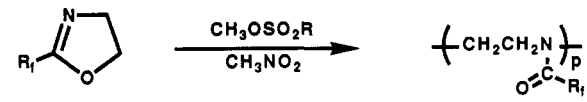
Introduction

In recent years, polymerization reactions in relation to the so-called "ionic polymerizations" have been reclassified from a mechanistic viewpoint.[1] Mechanisms of propagation via covalent (not ionic) electrophilic or nucleophilic species have recently been established in several polymerizations.[1] Therefore, it is not proper to categorize these polymerizations as "cationic" or "anionic" polymerization because they do not propagate through the respective ionic growing species. In the new classification, the scope of "ionic polymerization" has been extended to three categories depending on the reactivity characteristics of growing species, i.e., polymerizations via electrophilic, via nucleophilic, and via zwitterionic propagating species.[1]

Polymerization via electrophilic growing species includes the conventional cationic polymerizations as well as polymerizations proceeding covalent growing species. A typical example of the latter is seen in the ring-opening polymerization of 2-alkyl-2-oxazolines initiated by alkyl halides.[2-6] In these cases, an oxazolinium species is transiently generated by the reaction of 2-alkyl-2-oxazoline with the covalent electrophilic growing species of the type of alkyl halide, which is immediately opened by a nucleophilic attack of a halide anion to form a covalent alkyl halide species. Thus, the elementary step of propagation is a dipole–dipole reaction. In the polymerization of 2-alkyl-2-oxazolines with *p*-toluenesulfonate (tosylate) or trifluoromethanesulfonate (triflate) esters, on the other hand, the propagation reaction occurs between the growing oxazolinium species and the monomer. Therefore, it is an ion–dipole reaction. The difference between these two mechanisms has been rationalized by the difference of the nucleophilicity of counteranions in relation to that of the monomer.[1]

In a preceding paper, we briefly reported that the ring-opening polymerization of 2-(perfluoroalkyl)-2-oxazolines (1; Scheme I), with sulfonate esters proceeds by two different mechanisms of propagation depending upon the nature of initiators.[7] With methyl tosylate initiator, the propagating species of the polymerization of 1 is of covalent tosylate ester. With methyl triflate initiator, on the other hand, the propagating species is of the structure of oxazolinium cation. This interesting and significant phenomenon was due to the unusual reactivity of 1 due to a strong electron-withdrawing perfluoroalkyl group at the 2-position.

Scheme I



1a; $R_f=C_2F_5$ **2a**; $R=CF_3$ **3a**; $R_f=C_2F_5$
1b; $R_f=n\text{-}C_3F_7$ **2b**; $R=p\text{-}NO_2C_6H_4$ **3b**; $R_f=n\text{-}C_3F_7$
1c; $R_f=n\text{-}C_7F_{15}$ **2c**; $R=p\text{-}CH_3C_6H_4$ **3c**; $R_f=n\text{-}C_7F_{15}$

The present paper describes detailed and quantitative analysis of the mechanisms of the ring-opening polymerization of 2-(perfluoroalkyl)-2-oxazolines with some sulfonate initiators such as methyl *p*-nitrobenzenesulfonate (nosylate), tosylate, and triflate initiators.

Results and Discussion

Polymerization of 2-(Perfluoroalkyl)-2-oxazolines. Three 2-(perfluoroalkyl)-2-oxazolines (1), i.e., 2-(pentafluoroethyl)- (**1a**), 2-(*n*-heptafluoropropyl)- (**1b**), and 2-(*n*-pentadecafluoroheptyl)-2-oxazoline (**1c**), were prepared as previously reported.[8] Mechanistic studies were made on the ring-opening polymerization of these monomers **1** with methyl triflate (**2a**), methyl nosylate (**2b**), and methyl tosylate (**2c**) initiators.

The polymerization of **1** was carried out in a sealed tube under nitrogen. White powdery polymers were obtained by reprecipitation in a 50/50 mixture of diethyl ether with hexane.

As shown in Table I, both the yield and the molecular weight distribution of the produced polymers with the initiator of **2a** were much affected by the solvent. It has already been clarified that polar solvents such as *N,N*-dimethylformamide (DMF) and acetonitrile are suitable for the polymerization of cyclic imino ethers.[9] In the present case, the polymerization of **1a** with **2a** to afford **3a** proceeded successfully in nitromethane, nitrobenzene, and acetonitrile as shown in Table I; however, no polymerization took place in DMF. Nevertheless, the dielectric constants of these solvents are of similar magnitude, i.e., in a range of 34–37. The yield of the polymer increases with decreasing nucleophilicity of the solvent (represented as DN, donor number, in Table I), and, hence, it can be concluded that relatively nucleophilic solvents, especially, DMF, react with the initiator or with a propagating species to form a stable complex, which is not electrophilic enough to induce the polymeri-

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Table I
Polymerization of 1

run no.	1	2 (mol %)	solvent	ϵ^a	DN[b]	temp, °C	time, h	polymer yield, %	3	$M_n/10^3$ [c]	M_w/M_n [c]	$[\eta]$,[d] dL/g
1	**1a**	**2a** (5)	CH_3NO_2	35.9	2.7	70	3	97	**3a**	3.2	1.1	
2	**1a**	**2a** (5)	$PhNO_2$	34.6	4.4	70	3	95	**3a**	2.8	1.1	
3	**1a**	**2a** (5)	CD_3CN	35.9	14.1	70	3	67	**3a**	3.4	1.5	
4	**1a**	**2a** (5)	DMF	36.7	26.6	70	3	0				
5	**1a**	**2a** (1)	CH_3NO_2			70	9	57	**3a**	>18		0.20
6	**1a**	**2b** (25)	CH_3NO_2			150	24	70	**3a**	0.49	1.4	
7	**1a**	**2c** (5)	CD_3NO_2			120	24	62	**3a**	2.0	1.3	
8	**1b**	**2a** (5)	CH_3NO_2			70	3	71	**3b**	*e*	*e*	0.040
9	**1b**	**2a** (1.5)	bulk			70	24	69	**3b**	*e*	*e*	0.10
10	**1c**	**2a** (25)	CH_3NO_2			40	12	91	**3c**	*e*	*e*	*f*

[a] Dielectric constant at 25 °C from ref 11. [b] Donor number from ref 12. [c] Determined by GPC in DMF at 50 °C. The values are estimated from poly(2-methyl-2-oxazoline) standards. [d] In CF_3CO_2H, at 30 °C. [e] Insoluble in DMF. [f] Insoluble in CF_3CO_2H.

Table II
Preparation of 1:1 Adducts of 1 with Sulfonate Initiators

1	2	feed ratio	solv	temp, °C	time, h	1:1 adduct structure	yield, %	mp, °C
1a	**2a**	2:1	CH_3NO_2	0	0.5	**4a**	76	50–52
1a	**2c**	2:1	neat	100	30	**6a**	52	56–57
1c	**2a**	2:1	CH_3NO_2	rt	24	**4c**	70	111–113
1c	**2c**	3:1	neat	110	72	**6c**	72	70–71

zation. In fact, the production of an N-alkylated salt by the reaction of DMF with a strong alkylating reagent, methyl fluorosulfate, has been reported.[10] Relatively wide molecular weight distribution of **3a** in the cases of run no. 3 may be ascribed to a termination reaction between the propagating end and the solvent. The least nucleophilic solvent, nitromethane, gave the polymer with a narrowest molecular weight distribution in an almost quantitative yield.

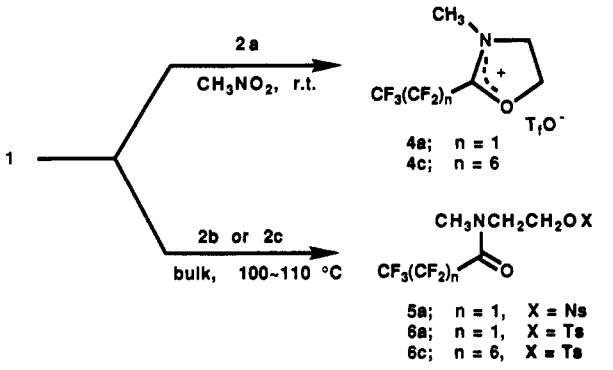
The number-average molecular weights of **3a** were estimated from their GPC data based on poly(2-methyl-2-oxazoline) calibration. (The estimation based on polystyrene calibration gave 4–5 times overestimated values.) The molecular weights of **3a** of run nos. 1 and 2 in Table I were also determined from vapor pressure osmometry (in acetonitrile, at 40 °C), which were 3300 and 2400, respectively. These two values were well agreed with those determined from the GPC measurement.

Conditions for suitable rate of polymerization were much dependent on the initiator. The polymerization of **1a** with **2a** proceeded smoothly at 70 °C, but with **2b** or **2c** it required a much higher temperature, e.g., 120 or 150 °C, respectively, even with a higher concentration of initiator.

A series of previous studies by us has clarified that the polymerizations of 2-oxazolines with initiators **2a** and **2c** proceed exclusively via cationic oxazolinium-type propagating species.[2] In these cases, the counteranion exerts no significant influence upon the value of propagation rate constant, the propagation rate constants with these two initiators being quite similar to each other. It is suggested that the difference in the required reaction conditions between the **1a**/**2a**, **1a**/**2b**, and **1a**/**2c** systems in the present study is due to the difference of propagation mechanism between these three systems.

Polymerization of **1a** in nitromethane proceeded smoothly in a homogeneous system throughout the whole polymerization. On the other hand, polymers of **3b** and **3c** showed poor solubility in common solvents. Oligomeric **3b** was soluble in DMF, but a higher molecular weight polymer of **3b** was soluble only in a ternary mixture of trifluoroacetic acid, chloroform, and diethyl ether (3:1:1, v/v). **3c** is quite insoluble even in concentrated sulfuric acid. Therefore, studies on the polymerization mechanism as well as kinetics were confined mostly to the monomer **1a**.

Scheme II



Isolation of 1:1 Adducts of 1 with 2. In order to clarify the mechanisms of polymerization, the reactions of **1a** with an excess amount of **2** were carried out, where the 1:1 adducts, which correspond to the first propagating species of the polymerization, were isolated as shown in Scheme II. The results are summarized in Table II. The structures of adducts were determined by ^1H, ^{13}C, and ^{19}F NMR, IR, and mass spectra as well as elemental analyses (see the Experimental Section). The comparison between the ^1H NMR spectra of these adducts of **4a** and **6a** clearly shows that their structures are quite different from each other (Figure 1). The 1:1 adduct of **1a** with **2a** was an ionic species, 3-methyl-2-(perfluoroethyl)-2-oxazolinium trifluoromethanesulfonate (**4a**). The peaks due to oxazolinium ring protons of **4a** are observed at around δ 4.72 (NCH_2) and 5.47 (OCH_2) in the ^1H NMR spectrum (Figure 1a).

On the other hand, the 1:1 adducts of **1a** with **2b** and with **2c** were covalent sulfonate ester species, *N*-methyl-*N*-[2-[(*p*-nitrobenzenesulfonyl)oxy]ethyl]perfluoropropionamide (**5a**) and *N*-methyl-*N*-[2-[(*p*-toluenesulfonyl)oxy]ethyl]perfluoropropionamide (**6a**), respectively. **6a** was isolated as a white solid material, which had two isomeric forms, *syn*-**6a** and *anti*-**6a**, because of restriction of free rotation around the amide C–N bond linkage. The structure of the major isomer was identified as *syn*-**6a** from

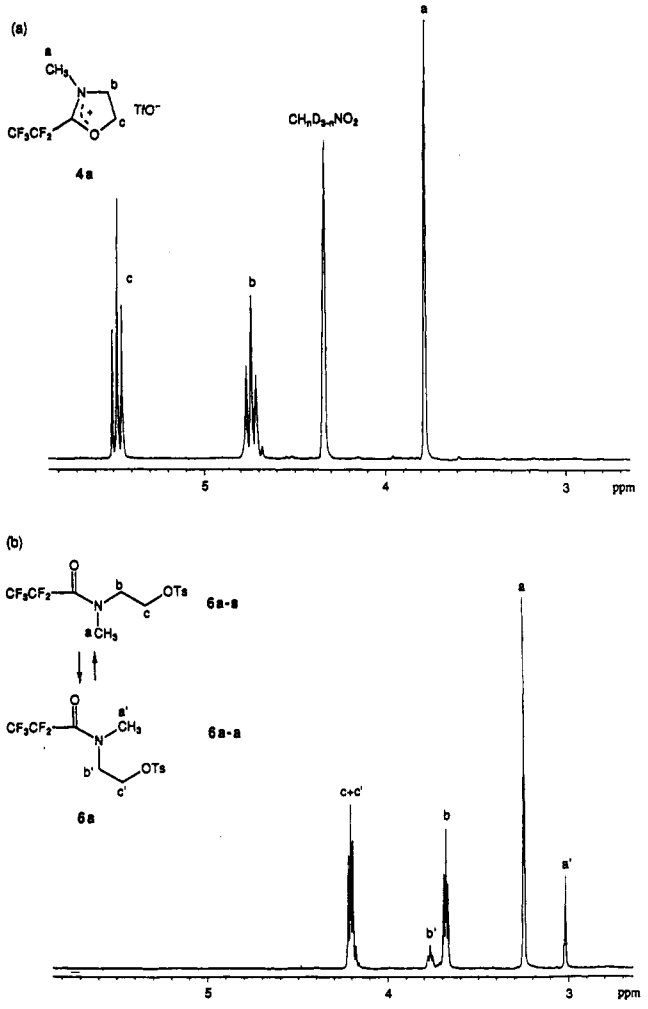


Figure 1. 400-MHz ^{1}H NMR spectra of (a) **4a** (in CD_3NO_2) and (b) **6a** (in $CDCl_3$).

its ^{13}C NMR spectrum.[13] The ratio of *syn*-**6a**/*anti*-**6a** was determined as 81/19 in $CDCl_3$ from its ^{1}H NMR spectrum. The peaks at around δ 3.68 (NCH_2 of *syn*-**6a**), 3.77 (NCH_2 of *anti*-**6a**), 4.19 (OCH_2 of *anti*-**6a**), and 4.21 (OCH_2 of *syn*-**6a**) in the ^{1}H NMR spectrum shown in Figure 1b are reasonably ascribed to ester-type ethylene protons.

The difference of structure between **4a** and **6a** is most clearly indicated in their ^{19}F NMR spectra. The chemical shifts of the peaks due to CF_2 fluorine atoms in ^{19}F NMR spectra of **4a** and **6a** are quite different from each other. The peak ascribed to CF_2 fluorine atoms of **4a** is observed at δ −40.2 while the peaks ascribed to those of **6a** appear at δ −38.6 (*syn*-**6a**) and −36.4 (*anti*-**6a**) (cf. Figure 2).

The formation of **5a** by the reaction of **1a** with **2b** was also confirmed by the ^{1}H and ^{19}F NMR spectra of a crude product. The peaks ascribed to ester-type ethylene protons of *syn*-**5a** were observed at around δ 3.78 (NCH_2) and 4.34 (OCH_2) in the ^{1}H NMR spectrum, and the peaks ascribed to CF_2 fluorine atoms were observed at δ −38.2 (*syn*-**5a**) and −36.0 (*anti*-**5a**). These chemical shift values agree well with the corresponding values of **6a**. The purification of **5a** could not be performed, however, because the polymerization of **1a** accompanied simultaneously and the isolation of **5a** from oligomeric byproducts was not successful. Similar alkylation of **1c** with **2a** and with **2c** also produced an ionic-type adduct (**4c**) and an ester-type one (**6c**), respectively.

In general, **4** was very reactive toward nucleophiles and was highly sensitive to moisture, although it was stable in dry nitromethane even at 70 °C for 3 h. **6** was less sensitive toward moisture than **4**, which could be handled under the usual atmosphere without decomposing.

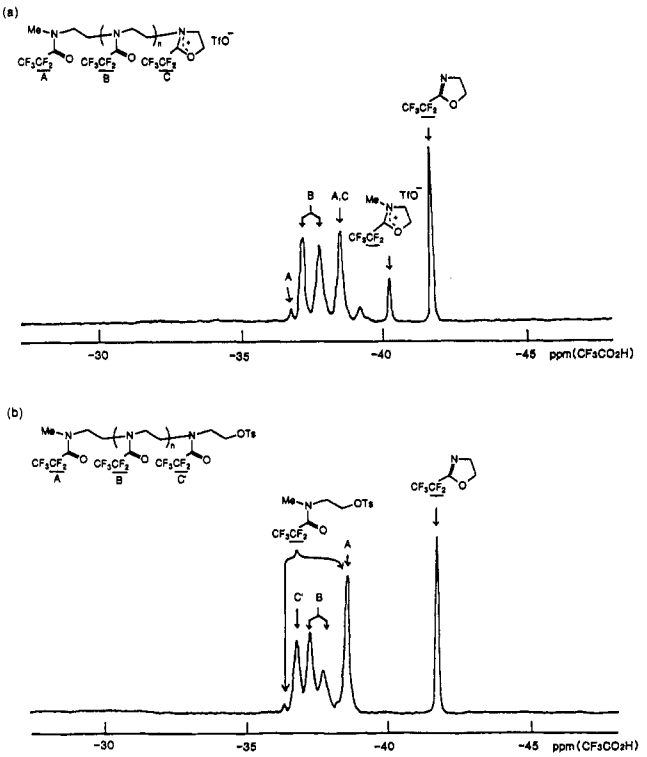


Figure 2. 84.7-MHz ^{19}F NMR spectra of the polymerization systems of (a) **1a**/**2a** ($[\mathbf{1a}]_0$ = 0.62 mol/L, $[\mathbf{2a}]_0$ = 0.20 mol/L, at 35 °C, after 400 min) and (b) **1a**/**2c** ($[\mathbf{1a}]_0$ = 1.61 mol/L, $[\mathbf{2c}]_0$ = 0.41 mol/L, at 150 °C, after 15 h) in CD_3NO_2 (external standard, CF_3CO_2H).

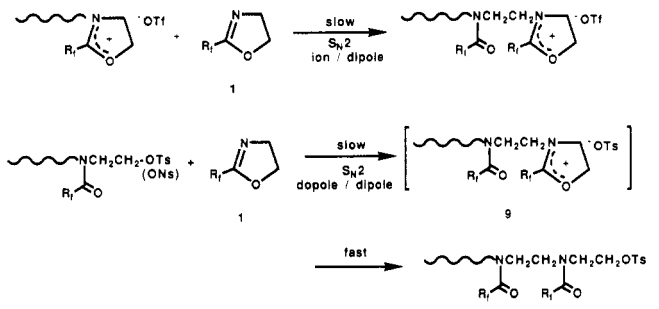
^{19}F NMR Measurements of the Polymerization Systems. Two different mechanisms of propagation in the polymerization of **1a** were established also by the direct ^{19}F NMR spectroscopy of the polymerization systems in CD_3NO_2. Parts a and b of Figure 2 show, respectively, the peaks of CF_2 fluorine atoms in ^{19}F NMR spectra of the **1a**/**2a** and **1a**/**2c** systems ([M]/[I] = 3–4). Although some peaks are commonly observed, these spectra are quite different from each other. The peaks at δ −37.2 and −37.8 in both spectra are assigned to the CF_2 fluorine atoms of the main unit (B). The peaks ascribable to the CF_2 fluorine atoms of perfluoropropionamide at the propagating ends (A) were also shown in the both spectra at δ −36.7 (anti) and −38.5 (syn).

The intermediacy of **4a** during the polymerization of **1a** with **2a** has been confirmed by the presence of the signal due to the species of **4a** in the **1a**/**2a** polymerization system (Figure 2a). The peak ascribed to the CF_2 fluorine atoms of the oxazolinium ring at the propagating ends (DP > 2) (C) appears at δ −38.5 in Figure 2a, which is overlapped with the peak due to A.

On the other hand, the two peaks due to the 1:1 covalent species, *syn*-**6a** and *anti*-**6a** are observed in the **1a**/**2c** polymerization system (Figure 2b). The peak due to the covalent propagating species (DP > 2) (C′) appears at δ −36.7, but no peak ascribed to ionic propagating species is observed. In the **1a**/**2b** polymerization system, the in situ ^{19}F NMR spectrum much resembled that of the **1a**/**2c** polymerization system, and the intermediacy of **5a** in the polymerization has also been confirmed.

From these observations it is concluded that the polymerization of **1a** with **2a** and that with **2b** or **2c** proceed in two quite different mechanisms, i.e., via ionic-type and covalent-type propagating species, respectively, as shown

Scheme III



in Scheme III. It is important to note here that the polymerizations of unsubstituted 2-oxazoline and 2-alkyl (unfluorinated alkyl) substituted 2-oxazolines with **2a** and with **2c** proceed exclusively via the oxazolinium (ionic) propagating species.[2,3] Thus, the finding of the present study disclosing the propagation through the covalent sulfonate ester constitutes a sharp contrast to the previous results with the conventional oxazoline monomers.

Equimolar Reaction of Adducts with 2-Oxazolines. Since the above 1:1 adducts of **1a** with **2a** and with **2c** are considered to be the models of propagating species in the polymerizations of **1** with the respective initiators, the equimolar reactions of these adducts with 2-oxazoline monomers were examined further to clarify the reactivities of the propagating species. The results are summarized in Table III. The reaction of an ionic adduct **4a** with **1a**, which corresponds to the propagation of the polymerization of **1** with the **2a** initiator, proceeded smoothly at 35 °C in nitromethane. After 30 min, the extents of conversion of **4a** and **1a** were 56 and 75%, respectively (run no. 1). On the other hand, the reaction of **6a** with **1a** did not occur (run no. 3), under the above reaction conditions, and a much higher reaction temperature of 150 °C and a longer reaction time of 40 min (run no. 4) were required to attain similar extents of conversion. A similar tendency of the reactivity difference was observed also when 2-methyl-2-oxazoline (**7**) was employed as monomer (run nos. 2 and 5). Thus, the lower reactivity of covalent species has clearly been demonstrated.

The decreased nucleophilic reactivity of **1a** in comparison with **7** was clearly indicated by the following results, i.e., the reaction of **4a** with **7** was complete within 1 min at 35 °C (run no. 2), whereas the reaction of **4a** with **1a** proceeded much more slowly as described above. Similarly, the reaction of **6a** with **7** proceeded smoothly at 60 °C (run no. 5), but no reaction between **6a** and **1a** took place under the same conditions (run no. 3). The lower nucleophilicity of **1a** is ascribed to the strong electron-withdrawing effect of the perfluoroalkyl substituent to decrease the electron density on the nitrogen atom.

On the other hand, the introduction of a perfluoroalkyl group into the cationic 2-oxazolinium ring enhances its ring-opening reactivity. Although **4a** reacted with **1a** easily at 35 °C, its 2-alkyl (unfluorinated alkyl) analogue, 2,3-dimethyl-2-oxazolinium trifluoromethanesulfonate (**8**), reacted with **1a** only above 100 °C (run nos. 1 and 7). In the latter case, a very low conversion of **8** is due to the fact that when a highly reactive perfluoroalkyl-substituted cationic species is once produced by the reaction of **8** with **1a**, it immediately causes the polymerization of **1a**, and, consequently, most of **8** remains unreacted.

Mechanisms of Propagation. As described above, the introduction of a perfluoroalkyl group at the 2-position of oxazoline greatly affects both the nucleophilicity of the monomer and the ring-opening reactivity of the corresponding onium ring. In the oxazoline polymerization, the nature of the propagating species, i.e., whether it is the ionic oxazolinium species or the ring-opened covalent electrophilic species, is controlled by the relative nucleophilicities of monomer and counteranion as shown in Scheme III. In the propagation reaction of the polymerization of **1a** with **2b** or **2c** as the initiator, the covalent sulfonate growing end reacts with the monomer **1a** to produce a transient species of oxazolinium, which is immediately opened by the nucleophilic attack of a sulfonate anion to form the covalent sulfonate ester. Thus, the S_N2 dipole–dipole reaction between a covalent sulfonate ester and the monomer **1** is the rate-determining step of propagation. On the contrary, in the polymerization initiated by **2a**, triflate anion is less nucleophilic than the monomer **1a**, and the oxazolinium species is opened with the nucleophilic attack of monomer. Therefore, the S_N2 cation–dipole reaction is the rate-determining step of propagation.

Kinetic Study on the Polymerization of 1a. Kinetic study was performed on the polymerizations of **1a** with each of two different initiators of **2a** and/or **2b**. The **1a**/**2c** system was not subjected to kinetic analysis because the polymerization rate of this system was too low at temperatures below 150 °C for getting reliable data.

The kinetic analysis on the above two polymerization systems was carried out on the basis of the direct determination of the instantaneous concentrations of propagating species, monomer, and initiator by means of ^1H and ^{19}F NMR spectroscopies. The rate constants of initiation (k_i) and propagation (k_p) were determined for each of the polymerization systems at various temperatures according to the procedure reported in the previous paper.[6] The results are given in Table IV. For the purpose of comparison with the values of k_i and k_p for the **1a**/**2a** system, the corresponding values for the **1a**/**2b** system were determined by the extrapolation of the linear Arrhenius plots, because these values for the **1a**/**2b** system were too small to obtain by direct analytical procedure of kinetics. The activation parameters for the propagation of the both systems are also listed in Table IV.

In the case of the **1a**/**2b** system, the k_i value is much smaller than that for the **1a**/**2a** system. The ratio of the k_i values between the **1a**/**2a** and **1a**/**2b** systems was 7000:1. This result is well explained by the well-established fact that triflate esters are more highly electrophilic than *p*-nitrobenzenesulfonate esters.

The k_p values also depend much upon the nature of the propagating species, i.e., ionic or covalent. The ratio of k_p values at 35 °C between **1a**/**2a** (ionic) and **1a**/**2b** (covalent) is 170:1, and it is concluded that the ionic-type propagating species is much more reactive toward the monomer (the common electrophile) in comparison with the covalent-type species.

The difference on the propagating mechanisms is well demonstrated by the difference of $\Delta S^{\ddagger}$ values, i.e., the reduced reactivity with the **2b** system (covalent) is due to the less favorable entropy term compared with that of the **2a** system (ionic). This may be explained in terms of solvation–desolvation phenomena. The rate-determining step of the system with **2a** is the S_N2 ion–dipole reaction between the oxazolinium salt at the growing end and the monomer **1a** to form an oxazolinium ion. In the course from the initial state to the transition state, the extent of solvation is decreased. On the other hand, in the **2b** system the rate-determining step is the S_N2 dipole–dipole reaction, which gives highly reactive oxazolinium intermediate, between the tosylate ester and the monomer **1a**. In this case the solvation at the transition state is, therefore, much increased in comparison with that of the initial state. The

Table III
Equimolar Reactions of 1:1 Adducts with Cyclic Imino Ethers[a]

run no	1:1 adduct	monomer	temp, °C	time, min	conv,[b] % monomer	conv,[b] % 1:1 adduct
1	**4a**	**1a**	35	30	75	56
2	**4a**	7[c]	35	<1	100	100
3	**6a**	**1a**	60	30	0	0
4	**6a**	**1a**	150	40	75	50
5	**6a**	7	60	30	85	57
6	8[d]	**1a**	35	250	0	0
7	8	**1a**	100	250	78	<1

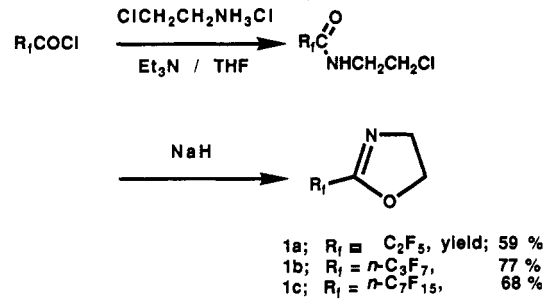
[a] In CD_3NO_2, [1:1 adduct]$_0$ = 1.20 mol/L. [b] Determined by the ^1H and ^{19}F NMR spectra. [c] 2-Methyl-2-oxazoline. [d] 2,3-Dimethyl-2-oxazolinium trifluoromethanesulfonate.

Table IV
Kinetics Results of the Polymerization of 1a[a]

initiator	temp, °C	$k_i \times 10^4$, L/mol·s	$k_p \times 10^4$, L/mol·s	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/K·mol
2a[b]	35	89	5.0	69	−85
2a[b]	45		11		
2a[b]	55		27		
2a[b]	65		56		
2b[c]	35	0.012[d]	0.029[d]	64	−144
2b[c]	110	3.6	4.6		
2b[c]	120	7.3	7.9		
2b[c]	131	11	14		

[a] In CD_3NO_2. [b] [**1a**]$_0$ = 1.00 mol/L and [**2a**]$_0$ = 0.201 mol/L. [c] [**1a**]$_0$ = 0.919 mol/L and [**2b**]$_0$ = 0.184 mol/L. [d] Data by extrapolation.

Scheme IV



entropy change from the less solvated initial state to the more solvated transition state with the **2b** system is less favorable (more negative) for the k_p value than that with the **2a** system.

Experimental Section

Materials. Commercially available methyl triflate (**2a**) and methyl tosylate (**2c**) were distilled under nitrogen. Methyl *p*-nitrobenzenesulfonate (**2b**) was prepared by the reaction of *p*-nitrobenzenesulfonyl chloride with sodium methoxide,[14] which was recrystallized from diethyl ether. Nitromethane, nitromethane-d_3, acetonitrile, and DMF were purified by distillation under nitrogen and stored over molecular sieves 3 Å.

Measurements. ^1H NMR spectra were recorded on a 60-MHz Hitachi R-600 or a 400-MHz JEOL-JNM-GX400 NMR spectrometer. ^{13}C and ^{19}F NMR spectra were recorded on a Hitachi R-900 NMR spectrometer (22.6 and 84.7 MHz, respectively). IR spectra were obtained on a Hitachi 260-20 infrared spectrometer. Mass spectra were measured with a JEOL-MS-DX 300. GPC analysis was performed by using a TSK-GEL G2500H_{XL} column in DMF containing 0.4% triethylamine at 50 °C. Molecular weight was measured by a vapor pressure osmometer (Hitachi Model 114) in acetonitrile at 40 °C.

Preparation of 2-(Perfluoroalkyl)-2-oxazolines (1). 2-(Pentafluoroethyl)- (**1a**), 2-(*n*-heptafluoropropyl)- (**1b**), and 2-(*n*-pentadecafluoroheptyl)-2-oxazoline (**1c**) were prepared from (β-chloroethyl)perfluoroalkanamide, which was prepared from perfluoroalkanoyl chloride according to Scheme IV.[15]

2-(*n*-Heptafluoropropyl)-2-oxazoline (1b). In a 100-mL flask equipped with a dropping funnel and a cold trap, 2.0 g of sodium hydride (in 60% oil suspension) (0.050 mol) was placed under nitrogen, to which 7.49 g of *N*-(β-chloroethyl)-*n*-heptafluorobutyramide (0.0272 mol) in 5 mL of *N*-methylpyrrolidone was added dropwise with vigorous stirring under reduced pressure (ca. 1 mmHg). The resulting crude product was collected in the trap, which was maintained at −78 °C during the reaction and then was purified by repeated distillation under reduced pressure [45 °C (27 mmHg)]. **1b**: colorless liquid (77% yield); ^1H NMR ($CDCl_3$) δ 3.8–4.3 (m, CH_2N, 2 H), 4.3–4.8 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 54.73 (CH_2N), 69.60 (CH_2O), 94.9–129.0 ((CF_2)$_2$-CF_3), 156.05 (N=CO); ^{19}F NMR ($CDCl_3$) δ −47.36 (s, CF_2CF_3, 2 F), −36.92 (q, CF_2C=N, 2 F), −1.25 (t, CF_3, 3 F); IR (neat) 2980 (ν_{CH}), 1680 ($\nu_{N=CO}$), 1280–1100 (ν_{CF}) cm^{-1}.

2-(Pentafluoroethyl)-2-oxazoline (1a) was similarly prepared from *N*-(β-chloroethyl)pentafluoropropionamide. **1a**: colorless liquid; ^1H NMR ($CDCl_3$) δ 3.8–4.3 (m, CH_2N, 2 H), 4.3–4.8 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 54.61 (CH_2N), 69.39 (CH_2O), 155.74 (N=CO); ^{19}F NMR ($CDCl_3$) δ 40.33 (s, CF_2, 2 F), −5.14 (s, CF_3, 3 F); IR (neat) 2950 (ν_{CH}), 1680 ($\nu_{N=CO}$), 1240–1130 (ν_{CF}) cm^{-1}.

2-(*n*-Pentadecafluoroheptyl)-2-oxazoline (1c) was also prepared from *N*-(β-chloroethyl)-*n*-pentadecafluorooctanamide. **1c**: colorless liquid [40 °C (0.2 mmHg)]; ^1H NMR ($CDCl_3$) δ 3.9–4.3 (m, CH_2N, 2 H), 4.3–4.8 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 54.70 (CH_2N), 69.54 (CH_2O), 98.3, 110.6, 123.0 (perfluoroalkyl carbon), 157.4 (N=CO); ^{19}F NMR ($CDCl_3$) δ −46.69 (m, CF_2CF_3, 2 F), −43.33, −42.50 (m, $(CF_2)_4CF_3$, 8 F), −36.67 (m, CF_2C=N, 2 F), −2.14 (m, CF_3, 3F); IR (neat) 2950 (ν_{CH}), 1685 ($\nu_{N=CO}$), 1250–1140 (ν_{CF}) cm^{-1}; MS *m/e* 439, 427, 414, 108, 70, 58. Exact mass. Calcd for $C_{10}H_4NOF_{15}$: *m/e* 439.005 32. Found: *m/e* 439.002 64.

General Procedure of Polymerization of 1. A typical run was as follows. To an ice-cooled NMR tube containing 0.0305 mmol of **2a** dissolved in 0.25 mL of nitromethane was added 0.635 mmol of **1a** under nitrogen. The tube was sealed and kept at 70 °C, and the progress of reaction was directly followed by ^{19}F NMR measurement. The white powdery polymer was obtained by reprecipitation from a 50/50 mixture of diethyl ether and hexane. **3a**: ^1H NMR (CD_3NO_2) δ 3.86 (br, CH_2N, 4 H); ^{19}F NMR (CH_3NO_2) δ −37.50, −37.00 (m, CF_2, 2 F), −5.06 (m, CF_3, 3 F); IR (cast film) 2950 (ν_{CH}), 1685 ($\nu_{C=O}$), 1450, 1240–1130 (ν_{CF}) cm^{-1}. **3b**: ^1H NMR (CD_3CN) δ 3.77 (br, CH_2N, 4 H); ^{19}F NMR (CH_3NO_2) δ −47.78 (m, CF_2CF_3, 2 F), −43.06 (m, CF_2C=O, 2 F), −2.78 (m, CF_3, 3 F). **3c**: IR (KBr) 2960 (ν_{CH}), 1680 ($\nu_{C=O}$), 1440, 1260–1120 (ν_{CF}) cm^{-1}.

Isolation of 3-Methyl-2-(pentafluoroethyl)-2-oxazolinium Trifluoromethanesulfonate (4). All operations were carried out under nitrogen. To an ice-cooled solution of **2a** (2.60 g, 15.9 mmol) in 2.0 mL of nitromethane was added **1a** (1.50 g, 7.9 mmol) dropwise with vigorous stirring. After mixing at 0 °C for 30 min, a large excess amount of diethyl ether was added to precipitate the crude onium salt, which was isolated by filtration and washed with diethyl ether. The crystalline salt was further purified by reprecipitation (a solvent was nitromethane and a nonsolvent was diethyl ether) to give 2.13 g (6.0 mmol, 76% yield) of **4**: white crystal; mp 50–52 °C; ^1H NMR (CD_3NO_2) δ 3.78 (s, CH_3N, 3 H), 4.74 (t, $|J|$ = 10.6 Hz, CH_2N, 2 H), 5.48 (t, $|J|$ = 10.5 Hz, CH_2O, 2 H); ^{13}C NMR (CD_3NO_2) δ 31.65 (CH_3N), 51.73 (CH_2N) 71.99 (CH_2O); ^{19}F NMR (CD_3NO_2) δ −40.2 (s, CF_2, 2 F), −5.3 (s, CF_3, 3 F), −1.75 (s, CF_3S, 3 F); IR (CD_3NO_2) 1695 (ν_{NCO})

cm^{-1}. Anal. Calcd for $C_7H_7NO_4SF_8 \cdot 0.3H_2O$ (hygroscopic): C, 23.45; H, 2.14; N, 3.96. Found: C, 23.53; H, 2.44; N, 3.99.

Isolation of *N*-Methyl-*N*-[2-[(*p*-toluenesulfonyl)oxy]ethyl]-perfluoropropionamide (6a). All operations were carried out under nitrogen. **1a** (0.144 g, 0.762 mmol) was added to **2c** (0.273 g, 1.47 mmol) in an NMR tube. The tube was sealed and kept at 100 °C for 30 h. After the reaction was completed, the reaction mixture was dried at 130 °C in vacuo. The resulting crude produce was recrystallized from chloroform/hexane solution to give 0.150 g of **6a** (0.400 mmol, 52% yield). **6a** has two isomeric forms *syn*-**6a** and *anti*-**6a**, which are interconvertible. Since *syn*-**6a** is more stable than *anti*-**6a**, the *syn*-**6a**/*anti*-**6a** ratio was 81/19. **6a**: ^{1}H NMR ($CDCl_3$) δ 2.45 (s, CH_3Ph), 3.02 (s, CH_3N of *anti*-**6a**), 3.25 (t, $|J| = 2.3$ Hz, CH_3N of *syn*-**6a**), 3.68 (t, $|J| = 4.9$ Hz, CH_2N of *syn*-**6a**), 3.77 (m, CH_2N of *anti*-**6a**), 4.20 (m, CH_2O of *anti*-**6a**), 4.21 (t, $|J| = 5.0$ Hz, CH_2O of *syn*-**6a**), 7.56 (m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 21.06 (CH_3Ph), 35.13 (CH_3N of *anti*-**6a**), 36.32 (CH_3N of *syn*-**6a**), 47.49 (CH_2N of *anti*-**6a**), 48.96 (CH_2N of *syn*-**6a**), 66.72 (CH_2O), 89.5–124.2 (CF_2CF_3), 127.51, 129.82 (2- and 3-positions of the phenyl group), 132.05 (4-position of the phenyl group), 145.23 (1-position of the phenyl group), 157.64 (C=O); ^{19}F NMR (CD_3NO_2) δ −38.61 (s, CF_2 of *syn*-**6a**), −36.42 (s, CF_2 of *anti*-**6a**), −5.28 (s, CF_3); IR (KBr) 3040 (ν_{CH}), 2950 (ν_{CH}), 1685 ($\nu_{C=O}$), 1350 ($\nu_{S=O}$), 1210–1130 (ν_{CF}) cm^{-1}; MS *m/e* 375, 203, 190, 155. Exact mass. Calcd for $C_{13}H_{14}NO_4SF_5$: *m/e* 375.056 42. Found: *m/e* 375.052 96. Anal. Calcd for $C_{13}H_{14}NO_4SF_5$: C, 41.60; H, 3.76; N, 3.73; F, 25.31. Found: C, 41.78; H, 4.06; N, 3.80; F, 25.31.

Equimolar Reactions of Monomers with 1:1 Adducts. The whole operation was carried out in an NMR tube under nitrogen. Monomer was added to the 1:1 adduct solution in CD_3NO_2 at −78 °C. Concentrations of both monomers and 1:1 adducts were 1.20 mol/L. After the reaction at a desired temperature, the reaction mixture was directly subjected to NMR measurements.

Kinetics. A general procedure is as follows. To a test tube equipped with a three-way stopcock containing 0.0604 g of **2b** (0.278 mmol) dissolved in 1.2 mL of nitromethane-d_3 was added 7.5 μL of cyclohexane and 16.7 μL of chloroform (internal standards for ^{1}H NMR), 10.7 μL of hexafluorobenzene (an internal standard for ^{19}F NMR), and 0.262 g of **1a** (1.396 mmol) under nitrogen. Then, the mixture was divided into three NMR tubes. The progress of reaction was monitored directly by ^{1}H and ^{19}F NMR spectroscopies, and the kinetic analysis was performed by determining the instantaneous concentrations of the monomer, propagating ends, and polymer. The concentrations of the respective species were obtained directly from the integral intensity of the spectrum. The reaction system was homogeneous throughout the kinetic run.

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Registry No. **1a**, 7024-92-2; **1b**, 2499-91-4; **1c**, 7024-90-0; **2a**, 1493-13-6; **2b**, 138-42-1; **2c**, 104-15-4; **3a** (homopolymer), 114505-58-7; **3a** (SRU), 130380-07-3; **3b** (homopolymer), 114505-59-8; **3b** (SRU), 70468-29-0; **3c** (homopolymer), 130380-08-4; **3c** (SRU), 70468-30-3; **4a**, 114532-36-4; **4c**, 130380-05-1; **6a**, 114505-29-2; **6c**, 130380-06-2; **7**, 1120-64-5; **8**, 87020-08-4; *N*-(β-chloroethyl)-*n*-heptafluorobutyramide, 4314-29-8; *N*-(β-chloroethyl)pentafluoropropionamide, 7024-91-1; *N*-(β-chloroethyl)-*n*-pentadecafluorooctanamide, 335-89-7.