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Nucleophilic vinyl polymerization of 2-alkenyl-2-oxazolines activated by trimethylsilyl trifluoromethanesulfonate

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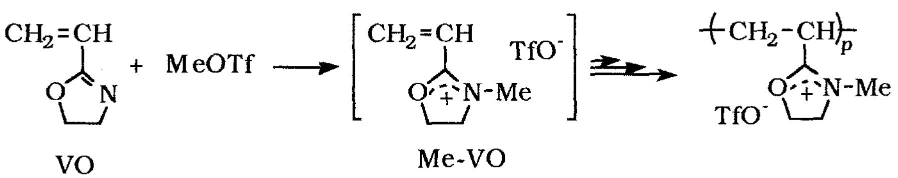
Summary

The present paper describes a novel nucleophilic vinyl polymerization of 2-alkenyl-2-oxazolines catalyzed by trimethylsilyl trifluoromethanesulfonate (TMSOTf) via an activated monomer mechanism. When 2-isopropenyl-2-oxazoline (IPO) was treated with 5 mol % of TMSOTf at 40 °C, a vinyl propagated polymer was obtained almost quantitatively. The yield of the polymer increased as the increase of the concentration of TMSOTf, while the molecular weight of poly(IPO) was independent of it. 4,4-Dimethyl-2-vinyl-2-oxazoline and 2-isopropenyl-4,4-dimethyl-2-oxazoline also produced vinyl propagated polymers in the presence of TMSOTf, whereas 2-vinyl-2-oxazoline gave an insoluble gel even at -78 °C.

Introduction

The family of 2-alkenyl-2-oxazolines has been known to polymerize via a variety of mechanisms to afford polymers of different structure (1-6). One of the polymerization mode reported by us is the "spontaneous polymerization" on alkylation of 2-vinyl-2-oxazoline (VO) (Scheme 1) (6-8).

Scheme 1



In this spontaneous polymerization, the polymer having 2-oxazolinium pendant groups is formed by mixing VO with an equimolar or excess amount of alkylating agent, e.g., methyl trifluoromethanesulfonate (MeOTf). In this polymerization, the once formed alkylated salt of VO (Me-VO), which is the true monomeric species, is so reactive toward nucleophiles that it is polymerized spontaneously by the attack of the unreacted VO. Therefore, the spontaneous polymerization of VO requires at least a stoichiometric amount of alkylating agent for the complete conversion of VO. "Spontaneous polymerization" has also been known in the family of vinylpyridines (9).

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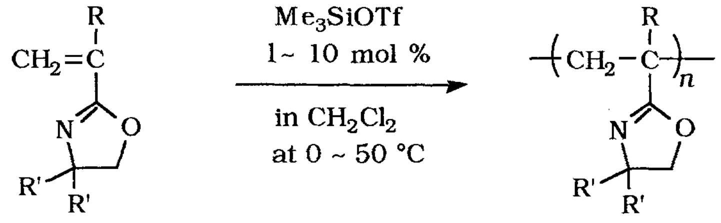
In the present paper the authors describe a novel nucleophilic polymerization of 2-alkenyl-2-oxazolines with trimethylsilyl trifluoromethanesulfonate (TMSOTf) to afford vinyl propagated polymers.

Scheme 2



VO; R=H, R'=H
IPO; R=Me, R'=H
DMVO; R=H, R'=Me
DMIPO;R=Me, R'=Me

In the present polymerization, a complex between 2-alkenyl-2-oxazoline and TMSOTf is considered to be the true monomeric species as in the case of the spontaneous polymerization of VO. However, a catalytic amount of TMSOTf is enough for the complete consumption of the monomer and the structure of the resulting polymer is not poly[(3-trimethylsilyl-2-oxazolinium-2-yl)ethylene], but poly[(2-oxazolin-2-yl)ethylene] (Scheme 2).

Experimental

Materials.
2-Vinyl-, 2-isopropenyl- (IPO), 4,4-dimethyl-2-vinyl- (DMVO), and 2-isopropenyl-4,4-dimethyl-2-oxazolines (DMIPO) were prepared and purified as previously reported (6,7,10). TMSOTf was dried on molecular sieves 4Å and stored under nitrogen. Zinc iodide was used as purchased. Other reagents and solvents were supplied commercially and purified by distillation under nitrogen.

Instrumentations.
^1H NMR spectra were recorded on a 60 MHz Hitachi R-600 spectrometer. IR spectra were obtained on a Hitachi 260-50 infrared spectrometer. GPC analysis was performed by using a Shodex A803 column in chloroform at room temperature.

Polymerization.
A typical procedure was as follows: In a test tube equipped with a three-way stopcock and a stirrer bar chip were placed 4 mmol of IPO, 0.04 mmol of benzoquinone as radical inhibitor, and 3 mL of dichloromethane under nitrogen. To the mixture was added 0.4 mmol of TMSOTf at -78 °C. Then, the tube was sealed and the mixture was allowed to react at 40 °C with stirring. After 20 hr, the tube was opened, and the mixture was added dropwise into 40 mL of diethyl ether to precipitate the resulting polymer, which was isolated by centrifugation and the subsequent decantation. The polymer was washed thoroughly with diethyl ether and dried in vacuo. The spectroscopic data of the polymer coincided well with those prepared by the radical polymerization (10).

Results and discussion

Polymerization of 2-Isopropenyl-2-oxazoline (IPO).

The polymerization of IPO in the presence of TMSOTf was carried out in dichloromethane at below 40 °C to avoid the ring-opening reaction of the 2-oxazoline ring, which prefers more polar solvents and a higher temperature. The results are summarized in Table 1. The polymerization of IPO scarcely proceeded at room temperature with 1 mol % of TMSOTf. But, as the increase of the amount of TMSOTf, both the yield of poly(IPO) and, very interestingly, the number average molecular weight (M_n) of poly(IPO) increased (run Nos. 1-4). This phenomenon strongly suggests that TMSOTf is not a simple cationic initiator: the increment of the amount of initiator in a conventional polymerization system results in an apparent increase of the polymer yield at an early stage of polymerization, which accompanies a slight decrease of the molecular weight. This observation as well as the experimental results shown below suggest that TMSOTf acts as an activator for the monomer.

Table 1. Nucleophilic Polymerization of IPO with TMSOTf[a]

Run No	$\frac{[TMSOTf]}{[IPO]}$ (%)	Temp. (°C)	Time (hr)	Yield (%)	Mn[b] (GPC)	Mw/Mn[b] (GPC)
1	1	r.t.	20	1	---	---
2	2	r.t.	20	4	3,600	1.44
3	5	r.t.	20	28	6,300	1.27
4	10	r.t.	20	59	7,500	1.21
5	2	40	20	12	5,600	1.15
6	5	40	20	55	4,300	1.11
7	5	40	70	68	4,000	1.24
8	5	40	100	96	4,800	1.24
9	10	40	20	100	5,000	1.19
10	5[c]	40	100	17	3,100	2.00
11[d]	5	40	20	64	2,700	1.31

[a] In CH_2Cl_2. [b] With polystyrene calibration. [c] *t*-$BuMe_2SiOTf$ was used as the activator. [d] Containing zinc chloride, $[ZnCl_2]/[IPO]_0 = 0.2$.

Polymerization Mechanism.

Figure 1a shows the 60 MHz ^1H NMR spectrum of IPO. By the addition of twice molar amount of TMSOTf, the every peak of IPO moves toward a lower field due to the complexation with TMSOTf, and the original peaks due to the free IPO are completely disappeared (Figure 1b). For example, the peaks ascribed to the oxazoline ring protons are observed at δ 3.8 - 4.6 as an AA'BB'-type multiplet in Figure 1a, while the corresponding peaks move to δ 4.2 ($N-CH_2$) and 4.8 ($O-CH_2$) as two broad triplets. It means that a rapid equilibrium exists between IPO and TMSOTf and the complex of IPO with TMSOTf (TMS-IPO). The peaks due to the olefinic protons also move from δ 5.4 and 5.8 in Figure 1a to δ 5.7 and 5.9 in Figure 1b.

The polymerization of IPO was so rapid under the experimental condition ($[TMSOTf]_0/[IPO]_0 = 0.5$, at 35 °C) that a broad peak ascribed to the methyl protons of

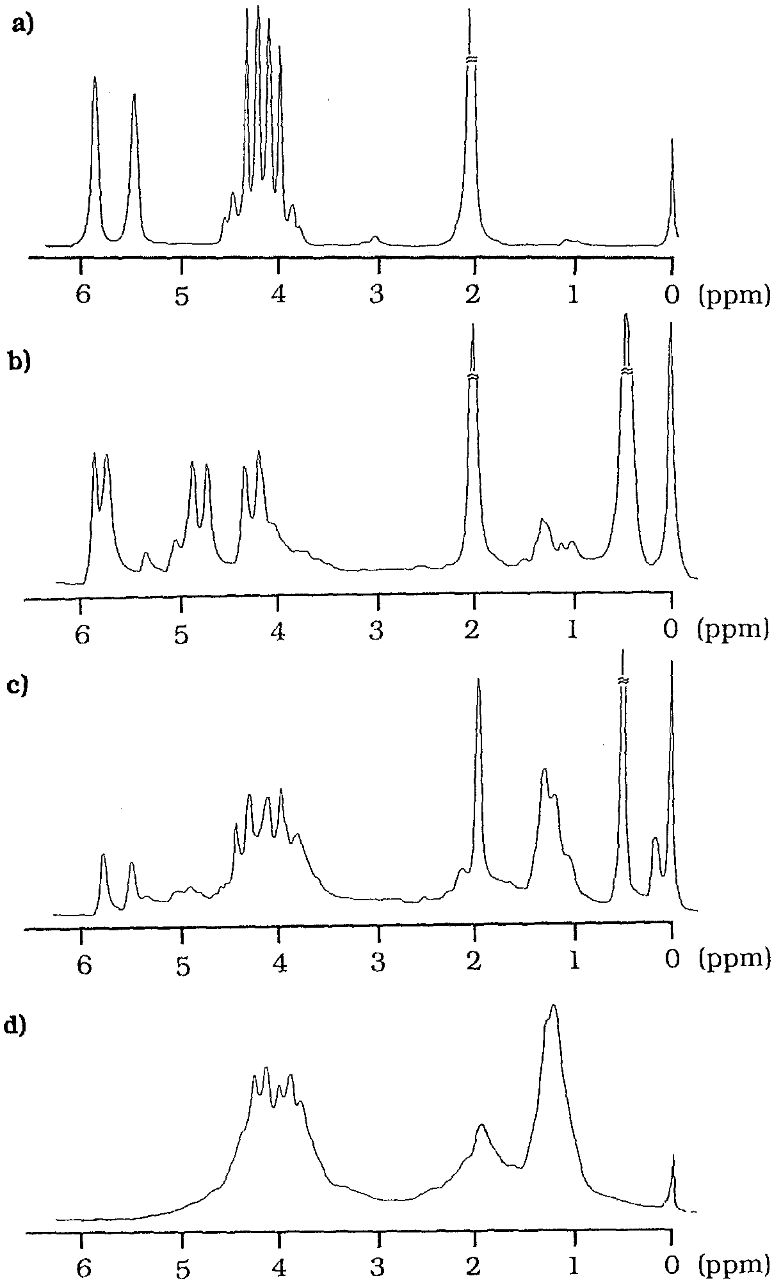


Figure 1. ^{1}H NMR spectra of IPO in $CDCl_3$ (a), a mixture of IPO with twice molar amounts of TMSOTf in CD_2Cl_2 (b (after 2 min.) and c (after 20 min.)), and poly(IPO) in $CDCl_3$ (d).

polymer appears at δ 1.0-1.4 even after 2 min in the *in situ* ^{1}H NMR spectrum of the polymerization mixture, *i.e.*, Figure 1b. Although the formation constant for TMS-IPO could not be obtained due to the rapid polymerization of IPO in the presence of TMSOTf, that for a similar adduct between 2-methyl-2-oxazoline, a model compound for IPO, and TMSOTf was determined as 7.6 in dichloromethane at 20 °C by IR spectroscopy.

Figure 1c shows the in situ ^{1}H NMR spectrum of the mixture after 20 min. Approximately 70% of IPO was consumed at this time, which was determined by the integral ratio of the peaks ascribed to the olefinic protons (δ 5.5 and 5.8) to those for the ring protons. But, no peak due to the oxazoline pendant group in the resulting polymer can be distinguished in this figure, which was also ascribed to the rapid TMS group transfer from the monomer to the polymer and vice versa. The in situ NMR measurement of a polymerization system often gives important information concerning its polymerization mechanism. However, in the present case the information we could obtain was so limited due to these equilibria. The only exception was the formation of an oxazolinium-type species that did not participate in these equilibria: the peaks at around δ 4.9 in Figure 1c were ascribed to the O-CH_2 protons of oxazolinium species.

During the isolation and purification process the TMS groups were completely removed from the polymer. The ^{1}H NMR spectrum of the isolated TMS-free poly(IPO) is also shown in Figure 1d for reference: the broad peaks at δ 0.9-1.6 and δ 1.6-2.6 are respectively ascribed to the methyl and methylene protons of the main chain and the broad multiplet at δ 3.6-5.0 are ascribed to the TMS-free oxazoline rings.

Considering the above findings we tentatively explained the present polymerization mechanism in relation to that of the spontaneous polymerization as Scheme 3.

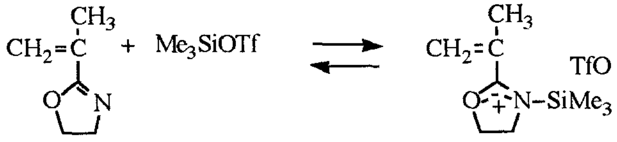
First, TMS-IPO is formed by the complexation of IPO with TMSOTf (Scheme 3A). It is attacked by the unreacted IPO to form a propagating species having a ketene silyl aminal end (Scheme 3B). The propagation exclusively occurs between this ketene silyl aminal end and TMS-IPO. During the propagation, the *N*-trimethylsilyl-2-oxazolinium ring regenerated at the penultimate position of the polymer (Scheme 3C). Then, the TMS group moves from the onium pendant to the unreacted IPO to regenerate TMS-IPO (Scheme 3D). Therefore, the concentration of TMSOTf is higher, that of the actual monomeric species (TMS-IPO) and the ratio of the real monomer to the real initiator ([TMS-IPO]/[IPO]) becomes higher, which results in the higher polymer yield and the higher polymer molecular weight in so far as the termination and the chain transfer are not so drastic as in the polymerization at 0 °C. The isopropenyl group of the initiating end is considered to be inactive for the propagation because 3-alkyl-2-isopropenyl-2-oxazolinium salt has a quite poor nucleophilic reactivity toward IPO due to the steric hindrance (10).

The steric bulkiness of Lewis acid strongly influenced on the polymerization. The polymerization of IPO with *t*-butyldimethylsilyl triflate yielded poly(IPO) of a relatively high polydispersity (2.0) in a low yield (run No. 10).

In the cationic polymerization of styrene in the presence of TMSOTf, it has been reported that the true initiating species is not TMSOTf, but trifluoromethanesulfonic acid (triflic acid), which is produced by the hydrolysis of TMSOTf(11). Therefore, it is possible to consider that the present polymerization catalyzed by triflic acid. However, it has been reported that the reaction of IPO with a strong acid forms a protonated stable adduct (H-IPO) (5,8) and the reaction between H-IPO and IPO yields linear or cyclic oligomers having oxazolinium ring(5).

Scheme 3

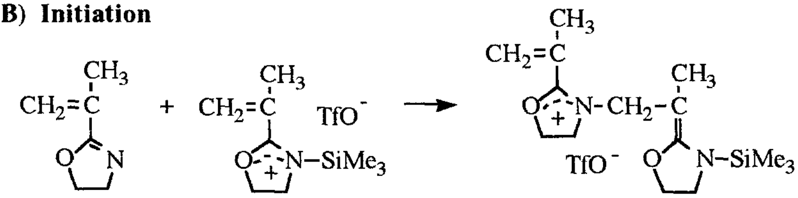
(A) Monomer Activation



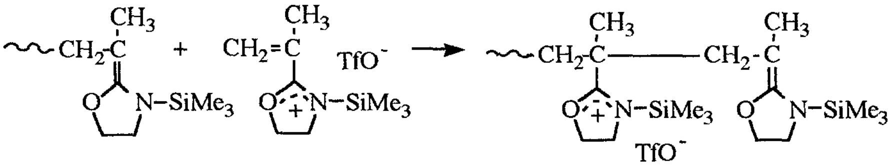
IPO

TMS-IPO

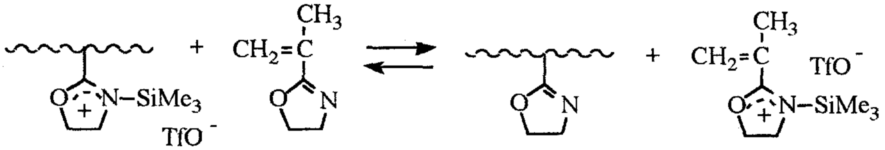
(B) Initiation



(C) Propagation



(D) Lewis Acid Transfer



Since the proposed propagation is the reaction between the ketene silyl aminal end and the Lewis acid activated monomer (TMS-IPO), the present polymerization mechanism is interestingly compared with that of the group-transfer polymerization (GTP) (12). It has already been reported that IPO caused the GTP by a ketene silyl acetal in the presence of tetrabutylammonium fluoride (13). At present we have no direct evidence that the TMS group did not transfer from the propagating end to the forthcoming monomer. However, the addition of tetrabutylammonium fluoride into the present polymerization system showed no apparent effect on the polymerization, which suggests that the mechanism for the present polymerization differs from that for the GTP.

The addition of zinc iodide, which has been known to catalyze the GTP of acrylic monomers, did not accelerate the present polymerization (run No. 11 in Table 1). However, it influenced on the polymer molecular weight. The GPC curve for the polymer of run No. 11, which is compared with the chart for run No. 6 in Figure 2, is bimodal. This may suggest that two different types of propagating species exist in the present system and they propagate independently: one is based on the mechanism proposed in Scheme 3 and the other is the GTP type propagating species catalyzed by zinc iodide.

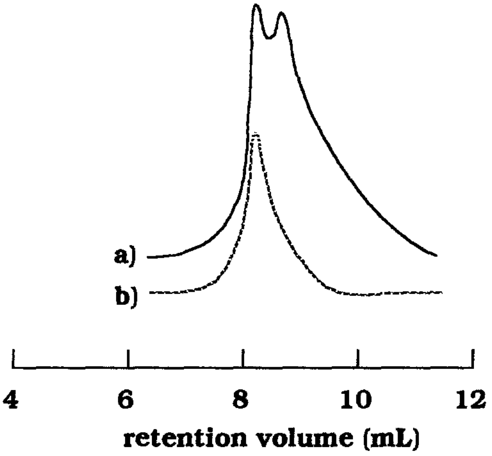


Figure 2. GPC charts of poly(IPO) prepared in the presence (**a**, run No. 11 in Table 1) and in the absence of zinc iodide (**b**, run No. 6 in Table 1).

Polymerization of Other 2-Alkenyl-2-oxazolines.

The polymerization of three other oxazoline monomers, i.e., 2-vinyl- (VO), 4,4-dimethyl-2-vinyl- (DMVO), and 2-isopropenyl-4,4-dimethyl-2-oxazolines (DMIPO), were examined to investigate the effect of substituent on their polymerizability. The results are summarized in Table 2.

The polymerization of VO proceeded very quickly even at -78 °C and afforded a gel. The IR measurement of the gel showed it had the vinyl-propagated main structure. Perhaps, a highly reactive vinyloxazolinium group at the initiating end concerned the crosslinking reaction.

The presence of 4,4-dimethyl substituents on the oxazoline ring significantly decreased the monomer polymerizability. The polymerization of DMVO with 5 mol % of TMSOTf gave a linear vinyl-propagated polymer in the quantitative yield at 40° C. On the other hand, the yields of poly(DMIPO) were generally poor and decreased as raising the polymerization temperature. The difference between the polymerizability of these monomers can be ascribed to the steric bulkiness around the nitrogen atom, which disturbs the formation of the adduct or suppresses the propagation.

Table 2. Nucleophilic Polymerization of 2-Alkenyl-2-oxazolines Activated by TMSOTf[a]

Monomer	[TMSOTf]/[M] (%)	Temp. (°C)	Time (hr)	Yield (%)	M_n[b] (GPC)	M_w/M_n[b] (GPC)
VO	5	-78	1	100	gelation	
DMVO	1	40	20	40	3,200	1.50
DMVO	2	40	20	70	7,600	1.20
DMVO	5	40	20	100	4,200	1.22
DMVO	10	40	20	100	2,500	1.18
DMIPO	2	40	20	4	3,300	1.22
DMIPO	5	40	20	9	3,600	1.14
DMIPO	10	40	20	11	3,100	1.25
DMIPO	10	50	20	7	3,000	1.35
DMIPO	10	60	20	4	3,000	1.37
DMIPO	10	40	20	11	3,100	1.34

[a] In CH_2Cl_2. [b] With polystyrene calibration.

The nucleophilic polymerization of Lewis acid-activated-monomer occurs not only among the family of 2-alkenyl-2-oxazolines, but also in the group of other monomers bearing a nucleophilic substituent. The polymerization of vinylpyridines and vinylketones with TMSOTf are now under way.

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