Reaction of 2-Methyl-2-oxazoline with Trimethylsilyl Initiators. An Unusual Mode of Ring Opening

Jeffrey S. Hrkach and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: The initiation and early stages of propagation in the cationic ring-opening polymerization of 2-methyl-2-oxazoline by trimethylsilyl trifluoromethanesulfonate and trimethylsilyl iodide have been investigated by ^{1}H NMR. Our studies indicate that the formation of the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation is reversible due to a fast exchange process. As a result, the trimethylsilyl initiator is eventually attacked by the oxygen atom of 2-methyl-2-oxazoline, forming the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. Another monomer molecule reacts at C2 of the cation, leading to an unusual mode of ring opening that does not convert the imine moiety to an amide function. The resulting imine dimeric cation is very unreactive toward 2-methyl-2-oxazoline because of the distribution of positive charge away from the ring onto the exocyclic imine moiety. Eventually the imine dimeric cation reacts with excess monomer, leading to "normal" propagation. The presence of the imine dimeric cation was confirmed by ^{13}C NMR, ^{29}Si NMR, and mass spectrometry.

Introduction

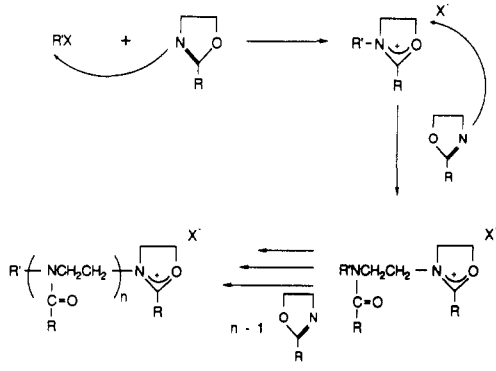
The cationic ring-opening polymerization of 2-oxazolines has been accomplished using a variety of initiators including Lewis acids, such as boron trifluoride, and alkyl esters and halides, such as methyl iodide, methyl triflate, and methyl tosylate.[1,2] Most five- and six-membered rings are not strained and do not undergo ring-opening polymerization. The five-membered rings of 2-oxazolines and the six-membered oxazines are not strained, but the polymerization of these cyclic imino ethers usually goes to completion. The main driving force of these polymerizations is not the relief of ring strain, as it is for many ring-opening polymerizations, but instead is the isomerization of the imino ether to the amide, which is more thermodynamically stable. Thus, the free energy change of isomerization compensates for the entropically unfavorable ring-opening polymerization of the strainless rings.[3]

The "normal" polymerization process for 2-oxazolines is presented in Scheme I. The initiator is attacked by the nucleophilic nitrogen atom producing the N-substituted 2-oxazolinium cation. Propagation takes place through subsequent attack by oxazoline at C5 (CH_2 adjacent to the oxygen) and the breaking of the C5–O bond, producing a poly(*N*-acylethylenimine).

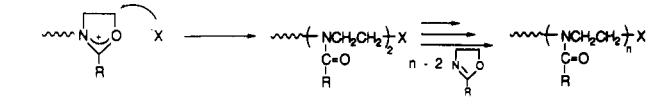
Scheme I shows an ionic propagating species. Under some conditions, e.g., in the polymerization of 2-oxazoline (R = H) with methyl iodide in acetonitrile at 70 °C, the counterion is more nucleophilic than the monomer. As a result, the oxazolinium cation is attacked by the counterion, creating a covalent species (see Scheme II). Propagation then takes place through attack by the monomer on the covalent active center.[1] The polymerization of 2-methyl-2-oxazoline (MeOXZ; R = CH_3) initiated by methyl iodide or methyl trifluoromethanesulfonate (triflate) proceeds via an ionic species, because MeOXZ is more nucleophilic than the iodide and triflate counterions.[2,4]

We are interested in preparing comblike graft copolymers with a polysilane backbone and poly(*N*-acetylethylenimine) side chains. Therefore, we have conducted model studies using trimethylsilyl triflate and trimethylsilyl iodide to initiate the polymerization of 2-methyl-2-oxazoline. In this paper we present an unusual mode of ring opening of 2-methyl-2-oxazoline. When trimethylsilyl initiators are used, they are eventually attacked by the oxygen atom of the oxazoline ring. The resulting *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation opens through cleavage of the O–C2 bond, instead of the typical O–C5 cleavage, to produce a stable imine dimeric cation. Later, polymerization proceeds in the "normal" manner as in Scheme I.

Scheme I



Scheme II



Experimental Section

2-Methyl-2-oxazoline was distilled and stored over 4-Å molecular sieves prior to use. Trimethylsilyl triflate was distilled on a high-vacuum line and stored in an ampule in a drybox under inert atmosphere (Model HE-493, Vacuum Atmospheres Co.). 2,6-Di-*tert*-butylpyridine was used as received. Deuterated acetonitrile and methylene chloride were dried over calcium hydride. NMR tubes were prepared in the drybox, capped with rubber septa, and sealed with Teflon tape. Those tubes used for dilutions in the low-temperature studies were flame-dried under argon and capped and sealed as the others, with additions made via syringe. NMR data was obtained from an IBM NR/300 300-MHz FT NMR spectrometer or a GE-300 300-MHz FT NMR spectrometer.

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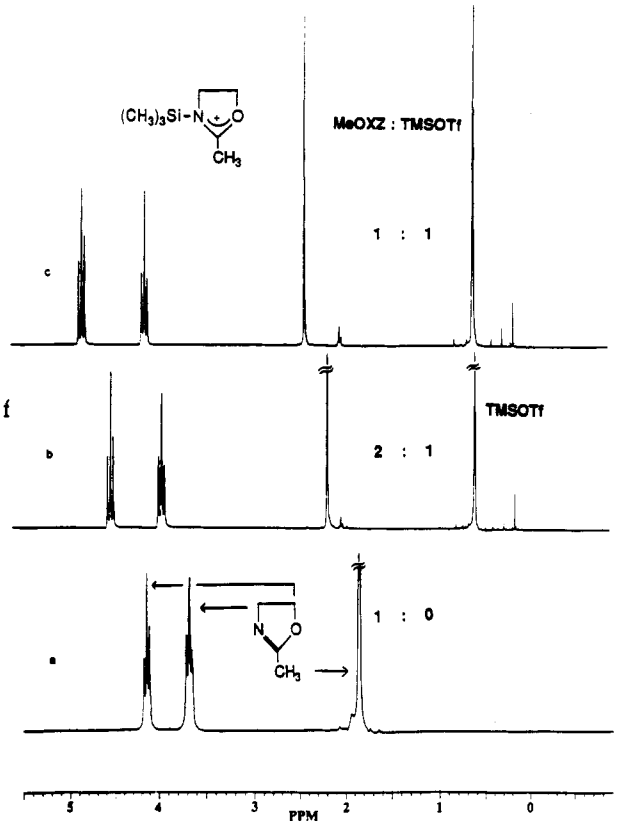


Figure 1. ^{1}H NMR spectra: (a) MeOXZ in CD_3CN; (b) 2:1 MeOXZ/TMSOTf ratio; (c) 1:1 MeOXZ/TMSOTf ratio. $[MeOXZ]_0 = 0.25$ M, $[TMSOTf]_0 = 0.25$ M in CD_3CN at 22 °C.

Results and Discussion

Exchange Reaction. Initial studies indicated the polymerization of 2-methyl-2-oxazoline (MeOXZ) with trimethylsilyl triflate (TMSOTf) or trimethylsilyl iodide (TMSI) was extremely slow, as observed earlier for the polymerization of THF with trimethylsilyl triflate.[5] This could be due to slow initiation caused by an unfavorable charge distribution in the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. Therefore, we conducted ^{1}H NMR studies at low MeOXZ/TMSX ratios (1:1, 2:1, 4:1, 10:1) to study the initiation and early stages of propagation.

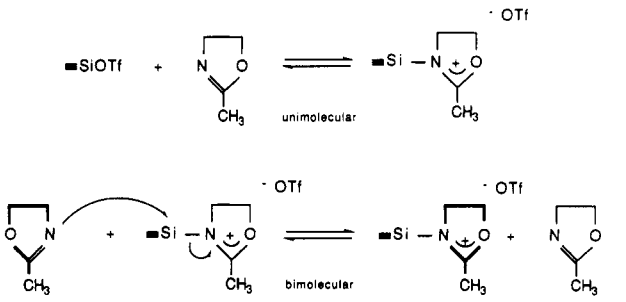
Figure 1a shows the ^{1}H NMR spectrum of MeOXZ in acetonitrile. The downfield triplet at 4.14 ppm represents the CH_2 adjacent to oxygen, while the other triplet at 3.68 ppm is attributed to the CH_2 adjacent to nitrogen. The singlet at 1.85 ppm is due to the exocyclic 2-methyl group. When equimolar amounts of MeOXZ and TMSOTf are reacted, nucleophilic attack by nitrogen on the silicon atom produces *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation (Figure 1c). The chemical shifts for this cation, 4.74 (t), 4.04 (t), and 2.31 ppm (s), resemble those of a "normal" oxazolinium cation. If MeOXZ is in excess of TMSOTf, a fast exchange reaction takes place between silylated and free MeOXZ. The spectrum representing this exchange reaction for a 2:1 MeOXZ/TMSOTf ratio is seen in Figure 1b. A single set of peaks, 4.44 (t), 3.86 (t), and 2.08 ppm, is seen representing the rapidly exchanging MeOXZ and *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. This exchange reaction between free and silylated MeOXZ is due to the distribution of the positive charge in the cation onto the exocyclic silyl group. MNDO calculations show that the charge located at C5 in the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation is not significantly different than that in MeOXZ or the *N*-methyl-2-methyl-2-oxazolinium cation which is produced when CH_3X-type initiators

Table I
Charge Distributions for a Series of 2-Methyl-2-oxazolines Based on MNDO Calculations

	charge						
molecule	N	C4	C5	O	C2	2-CH_3	C exo
MeOXZ	-30.0	4.1	10.8	-27.0	14.6	9.4	
N-MeMeOXZ	-33.7	9.8	11.2	-18.2	38.1	3.9	19.8
imine-MeOXZ	-41.6	4.6	5.2	-25.2	44.9	-5.3	22.1
N-(TMS)MeOXZ	-45.5	7.1	11.3	-19.6	35.6	4.2	78.4[a]
O-(TMS)MeOXZ	-18.2	5.0	11.1	-32.3	14.9	7.1	81.5[a]

[a] Denotes Si exo.

Scheme III



(X = OTf, OTs, I) are used to initiate polymerization. On the other hand, 78.4% of the positive charge lies on the exocyclic silicon atom (see Table I). This value can be compared to 19.8% of the charge lying on the *N*-methyl carbon in the *N*-methyl-2-methyl-2-oxazolinium cation. As a result of the charge distribution, attack by another MeOXZ molecule at C5 does not take place, but instead the silicon atom of the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation is attacked (see Scheme III, bimolecular reaction). In addition to this bimolecular exchange reaction, the cation could simply dissociate into TMSOTf and MeOXZ (Scheme III, unimolecular reaction).

Low-temperature ^{1}H NMR was utilized to gain a better understanding of the exchange reaction between 2-methyl-2-oxazoline and trimethylsilyl triflate. We expected to see separation of the averaged signals observed at room temperature (see Figure 2a) into signals for unreacted MeOXZ and for the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. MeOXZ and TMSOTf were reacted at a 2:1 ratio in deuterated methylene chloride at -90 °C. At this temperature the peaks were broadened, but no separation of peaks was observed, indicating that the exchange reaction is very fast (see Figure 2b). The signals of 2,6-di-*tert*-butylpyridine (used as a proton trap and a standard for NMR) were also broadened, probably due to poor solubility upon initial cooling to -90 °C. The half-height line width of the average peak for the methyl group of MeOXZ and *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation (2.20 ppm) was 2.9 Hz broader than that of the *tert*-butyl peak (1.20 ppm) for 2,6-di-*tert*-butylpyridine. Figure 2c shows that a 10-fold dilution of the reactants does not produce separation of the signals. After dilution, however, the averaged signals of MeOXZ and *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation are considerably broader than the other peaks in the spectrum. The half-height line width of the average methyl group peak was 21.6 Hz broader than that of the *tert*-butyl peak for 2,6-di-*tert*-butylpyridine. A bimolecular exchange reaction is dependent on the concentration of the reactants, whereas a unimolecular exchange reaction is not. The greater broadening of the signals representing the exchanging species indicates the contribution of the bimolecular reaction. On the basis of these results, the rate constant

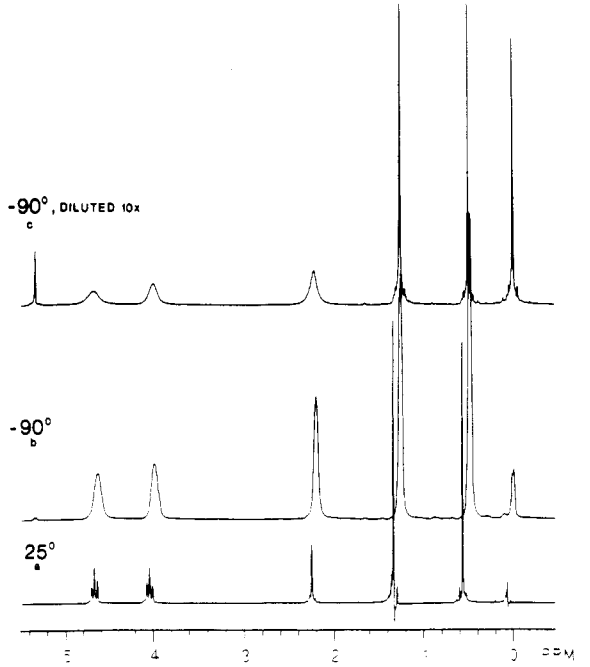


Figure 2. ^{1}H NMR spectra of a 2:1 MeOXZ/TMSOTf mixture: (a) at +25 °C, (b) at −90 °C, (c) at −90 °C after a 10-fold dilution. $[MeOXZ]_0 = 0.45$ M, $[TMSOTf]_0 = 0.22$ M, [2,6-di-*tert*-butylpyridine]$_0$ = 0.09 M in CD_2Cl_2.

Table II
Bond Lengths for a Series of 2-Methyl-2-oxazolines Based on MNDO Calculations

	bond length, Å						
molecule	N–C4	C4–C5	C5–O	O–C2	C2–CH_3	C2–N	N exo
MeOXZ	1.466	1.564	1.419	1.374	1.504	1.309	
N-MeMeOXZ	1.499	1.556	1.455	1.328	1.515	1.357	1.465
imine–MeOXZ	1.497	1.557	1.437	1.329	1.514	1.359	1.471
N-(TMS)MeOXZ	1.487	1.555	1.431	1.335	1.514	1.347	1.870
O-(TMS)MeOXZ	1.464	1.556	1.456	1.432	1.507	1.291	1.865[a]

[a] Denotes O exo.

for the bimolecular reaction is roughly estimated to be 10^5 M^{-1} s^{-1}.

Formation of the Imine Dimeric Cation. As stated earlier, attack by MeOXZ at C5 of the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation does not lead to ring opening. Instead, because of the exchange reaction, the trimethylsilyl initiator is eventually attacked by the oxygen atom of MeOXZ which is less nucleophilic than the nitrogen atom. This attack takes place because of the high affinity of silicon for oxygen. The resulting *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation is then attacked by the nitrogen atom of another MeOXZ molecule at C2, leading to a unique mode of ring opening in which isomerization to the amide does not occur, but instead an imine dimeric cation is produced. MNDO calculations (see Table II) indicate that the O–C2 bond is much longer in the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation (1.432 Å) than in the *N*-methyl-2-methyl-2-oxazolinium cation (1.328 Å). Thus, cleavage of this bond is much more likely in the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. The formation of the dimeric cation is outlined in Scheme IV. The ^{1}H NMR spectrum of a reaction with a 4:1 MeOXZ/TMSOTf ratio after 6 days at room temperature in acetonitrile is seen in Figure 3. One set of peaks (M) in the spectrum represents the average signals for free and N-silylated MeOXZ. The other peaks (●) correspond to the unusual imine dimeric cation. Also present are peaks for CD_3CN (1.93 ppm) and hexamethyldisiloxane, a product of the hydrolysis of TMSOTf. It

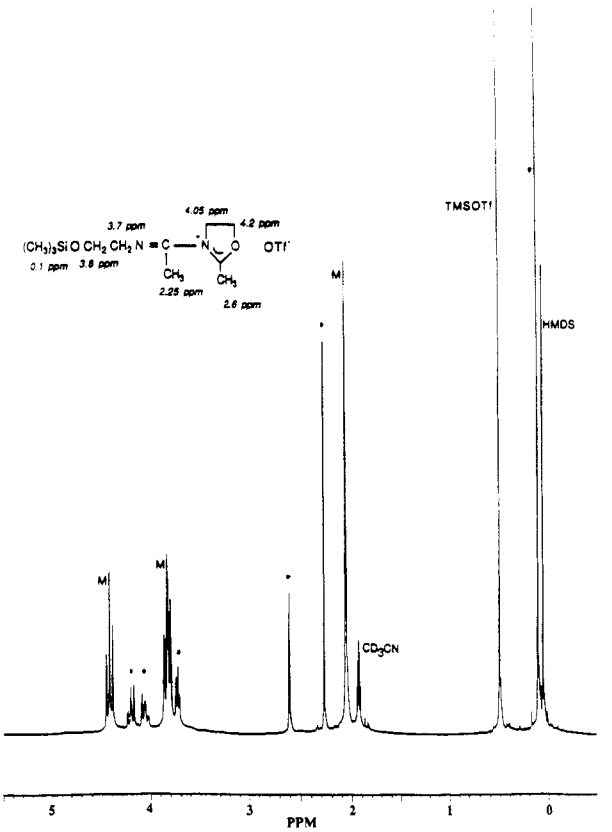
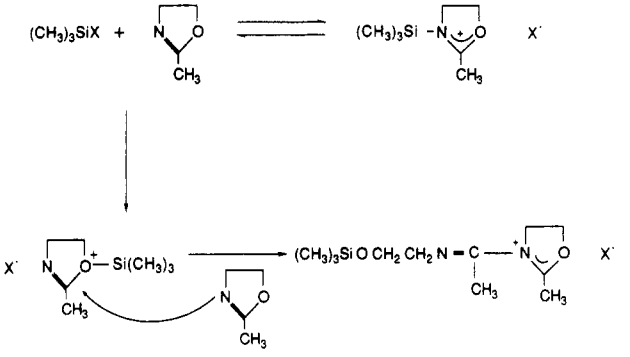


Figure 3. ^{1}H NMR spectrum of the imine dimeric cation (●) and exchanging MeOXZ species (M). $[MeOXZ]_0$ = 0.5 M, $[TMSOTf]_0$ = 0.13 M in CD_3CN at 22 °C.

Scheme IV



should be noted that HOTf (or HI in the case of TMSI) is also produced by hydrolysis of TMSOTf. Therefore, most of the reactions studied later contain 2,6-di-*tert*-butylpyridine to trap the acid. Hindered pyridines of this type react with protons but do not react with the trimethylsilyl initiators or the cationic species of these reactions.[6]

The continuation of the exchange reaction and the existence of the dimeric cation at this stage explain why the polymerization of MeOXZ using trimethylsilyl initiators is extremely slow. After 6 days, propagation has yet to begin. The long lifetime of the dimeric cation indicates it is much less reactive than a "normal" N-substituted oxazolinium cation. The low reactivity can be explained by delocalization of the positive charge from the ring toward the exocyclic imine. The charge distribution of the dimeric cation can be compared to that of the *N*-methyl-2-methyl-2-oxazolinium cation. MNDO calculations (see Table I) show that only 5.21% of the positive charge is located at C5 in the dimeric cation compared to 11.2% in the *N*-methyl-2-methyl-2-oxazolinium cation.

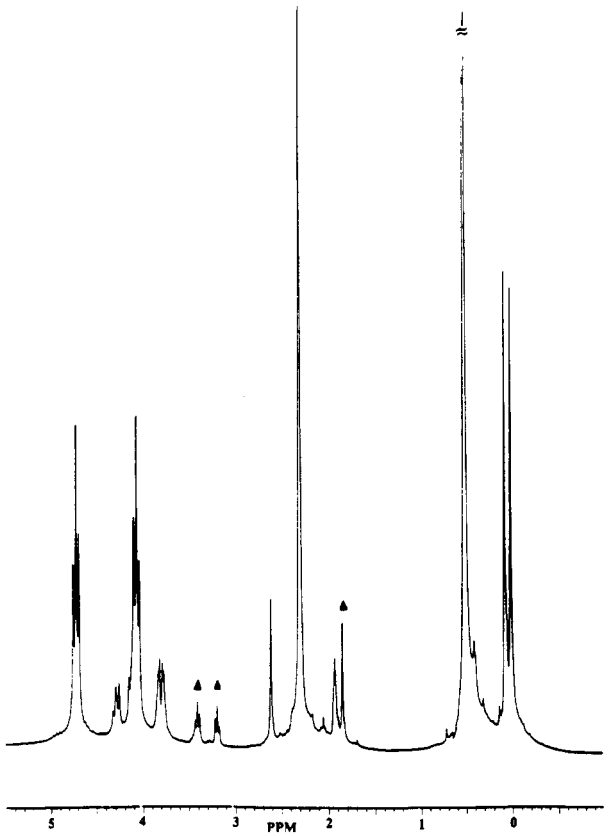
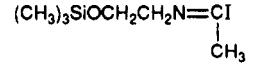


Figure 4. ^{1}H NMR spectrum of the covalent monomeric species (▲) in the reaction of MeOXZ with TMSI. $[MeOXZ]_0$ = 0.5 M, $[TMSI]_0$ = 0.5 M in CD_3CN at 22 °C.

Therefore, the reactivity of other MeOXZ molecules toward the imine dimeric cation is greatly reduced. However, in the presence of excess MeOXZ the dimeric cation very slowly reacts with the "normal" mode of ring opening. This will be addressed in the next section.

The iodide anion is more nucleophilic than the triflate anion; therefore, it is possible that the iodide anion could compete with MeOXZ in the reaction with the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. Attack by iodide on the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation at C2, would produce the following compound:



The ^{1}H NMR spectrum in Figure 4 shows that the formation of a small amount of this open covalent species (▲) did take place. The triplets at 3.41 and 3.20 ppm can be assigned to the methylene units adjacent to oxygen and nitrogen, respectively, and the singlet at 1.85 ppm is due to the methyl group. The other peaks in the spectrum correspond to the dimeric cation and exchanging MeOXZ species. Two singlets are seen in the area of 0 ppm. The peak on the left corresponds to the trimethylsilyl group, and the other peak is due to hexamethyldisiloxane that formed from the hydrolysis of TMSI with trace amounts of water.

Chain Extension. Figure 5 shows ^{1}H NMR spectra from a study conducted at a 10:1 MeOXZ/TMSOTf ratio at room temperature in CD_3CN. After 72 h (Figure 5a) no propagation has taken place. The MeOXZ peaks are slightly downfield due to exchange with the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. They are not as far downfield as in Figure 1b, because the large excess of MeOXZ shifts the average signals toward the chemical

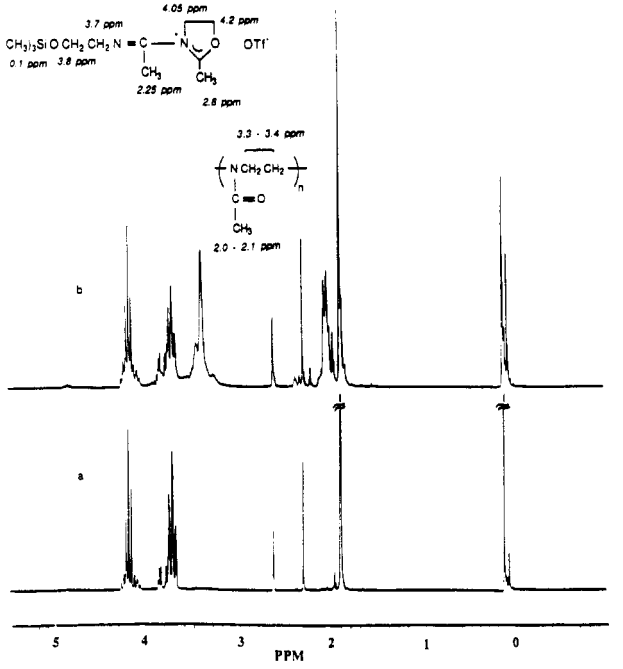
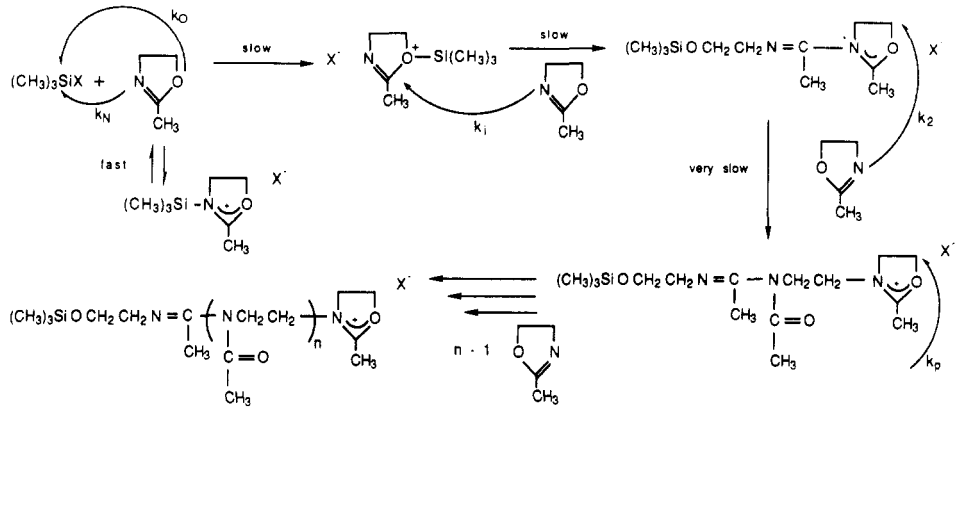


Figure 5. ^{1}H NMR spectra of a 10:1 MeOXZ/TMSOTf mixture: (a) after 72 h; (b) after 2 weeks. $[MeOXZ]_0$ = 0.7 M, $[TMSOTf]_0$ = 0.07 M in CD_3CN at 22 °C.

shifts for MeOXZ. The peaks corresponding to the dimeric cation are also evident. Figure 5b is the spectrum collected after 2 weeks. By this time some polymerization has taken place, as seen by the broad peaks around 3.4 and 2.1 ppm corresponding to the ethylene units within the chain and the acetylmethyl group of the amide, respectively. The peaks corresponding to the propagating cation can be seen, although they are very small. The triplet at 4.8 ppm and the singlet at 2.3 ppm correspond to the protons on C5 and the 2-methyl group of the propagating cation, respectively. The triplet at 4.2 ppm, corresponding to the C4 protons of the propagating cation, is buried under the larger peaks. An important aspect of this spectrum is the fairly substantial portion of dimeric cation that is still present at this time. This demonstrates the stability of the dimeric cation under these conditions and explains why polymerization is so slow.

Further Characterization. ^{13}C NMR spectroscopy was also used to study the reaction of MeOXZ with trimethylsilyl initiators. Figure 6 contains the ^{13}C spectrum of the reaction of MeOXZ with TMSI in acetonitrile at room temperature after 9 days. The peaks at 118 and 1.3 ppm are due to acetonitrile. On the basis of a literature value of 165 ppm for C2 of MeOXZ, the downfield peak at 170 ppm is assigned to the endocyclic, quaternary carbon, C2, of the dimeric cation.[7] The peaks for the CH_2–O and CH_2–N of the ring are seen at 59 and 52 ppm, respectively. The peaks at 51 and 47 ppm correspond to the open CH_2–O and CH_2–N methylene units, respectively. The peak for the methyl group of the imine is seen at 16 ppm, whereas that of the 2-methyl group is at 25 ppm. The large peak at 0 ppm corresponds to the trimethylsilyl group of the dimeric cation. The smaller peaks in the spectrum can be assigned to the covalent monomeric species described earlier. The peak at 22 ppm is attributed to the methyl group. The trimethylsilyl carbons are seen at 4 ppm. The peak at 42 ppm corresponds to the CH_2 adjacent to nitrogen, whereas no peak is seen for the CH_2 adjacent to oxygen. This peak may be hidden by the larger peaks in this region. The small peak at 92 ppm may be due to the quaternary imine carbon of the dimeric cation

Scheme V



$k_N >> k_p\ (\approx k_O \approx k_i) >> k_2$

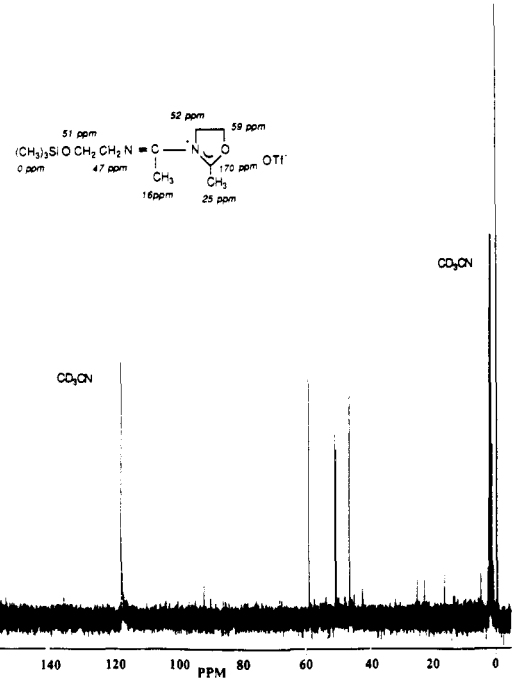


Figure 6. ^{13}C NMR spectrum of the imine dimeric cation. $[MeOXZ]_0$ = 0.5 M, $[TMSI]_0$ = 0.5 M in CD_3CN at 22 °C.

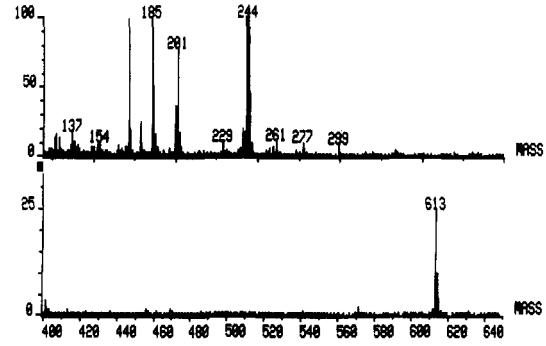


Figure 7. FAB (fast atom bombardment) mass spectrum of a 1:1 MeOXZ/TMSI reaction mixture. $[MeOXZ]_0$ = 0.2 M, $[TMSI]_0$ = 0.2 M, [2,6-di-*tert*-butylpyridine]$_0$ = 0.05 M in CD_3CN.

or could be attributed to the quaternary carbon of the open monomeric covalent iodide.

Mass spectrometry was also utilized to confirm the presence of the dimeric cation. A reaction solution in a glycerol matrix was analyzed using fast atom bombardment (FAB). This technique provides the opportunity to study nonvolatile materials such as salts and polymers. Because of several possible interactions between the sample and the matrix, FAB should be used only as a confirmational tool. This is especially true for our case, since the reaction mixture contains the dimeric cation, free and silylated MeOXZ, 2,6-di-*tert*-butylpyridine, and acetonitrile.

The largest peaks in the spectrum (see Figure 7) were found at *m/e* 243 and 244. These peaks correspond to the dimeric cation and the dimeric cation after it has picked up a proton, respectively. The large peak at *m/e* 171 results from the loss of the trimethylsilyl group. Glycerol is responsible for the peaks at *m/e* 277 and 185, although the peak at *m/e* 185 may also be due to the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation. The fairly large peak at *m/e* 613 corresponds to the complex of two dimeric cations with one iodide counterion. The peak at *m/e* 201 may be due to a trimeric species that has fragmented to the dimer and lost the acetyl group.

A reaction with an equimolar ratio of MeOXZ and TMSI was analyzed by ^{29}Si NMR. The spectrum contained two peaks (see Figure 8). The upfield peak at 13 ppm is attributed to the trimethylsilyl group of the dimeric cation. The downfield peak at 26 ppm is an average signal of TMSI and the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation.

Conclusions

Scheme V shows all of the steps involved in the reaction of MeOXZ with TMSOTf or TMSI. "Normal" attack on the initiator by the nitrogen atom does take place, but, due to the distribution of the positive charge onto the silicon atom in the *N*-(trimethylsilyl)-2-methyl-2-oxazolinium cation, subsequent attack by MeOXZ is on the silicon atom, leading to a fast exchange reaction. Eventually O-silylation occurs due to the high affinity of silicon for oxygen. Attack of another MeOXZ molecule on the *O*-(trimethylsilyl)-2-methyl-2-oxazolinium cation at C2 causes cleavage of the C2–O bond, creating an unusual mode of ring opening in which the imine is not isomerized to the amide. Recall that the driving force for the ring-opening polymerization of oxazolines is the isomerization of the imino ether to the amide and not the relief of ring strain because they are virtually strainless. The dimeric cation that is formed from this process is unreactive due to the delocalization of the positive charge away from the ring, particularly away from C5, the carbon atom attacked

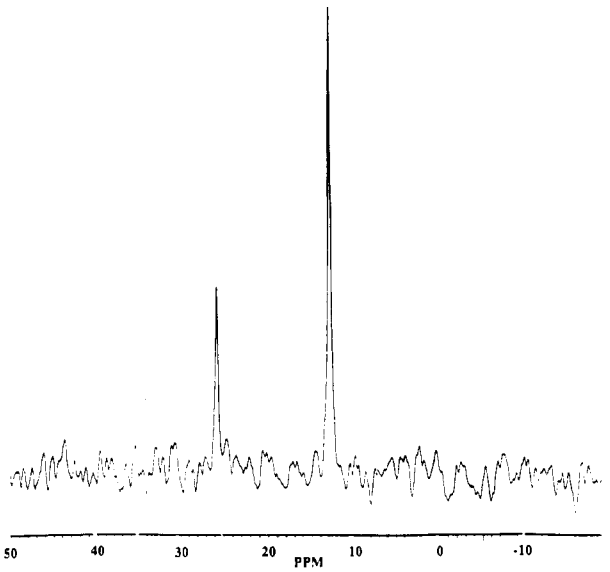


Figure 8. ^{29}Si NMR spectrum of a 1:1 MeOXZ/TMSI mixture. $[MeOXZ]_0$ = 0.2 M, $[TMSI]_0$ = 0.2 M, [2,6-di-*tert*-butylpyridine]$_0$ = 0.05 M in CD_3CN at 22 °C.

in the "normal" polymerization of MeOXZ. In the presence of excess MeOXZ the dimeric cation eventually is attacked at C5, resulting in normal ring opening, the production of the "normal" N-substituted oxazolinium cation, and propagation. The dimeric cation was detected by ^1H NMR and its structure confirmed by ^{13}C NMR, ^{29}Si NMR, and mass spectrometry.

Our goal is to graft poly(*N*-acetylethylenimine) from a polysilane backbone. A requirement for the production of well-defined graft copolymers by this method is fast, efficient initiation. As a result, we are currently investigating the use of promoters to increase the efficiency of initiation in the polymerization of MeOXZ with TMSOTf and TMSI initiators.

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References and Notes

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Registry No. TMSI, 16029-98-4; 2-methyl-2-oxazoline, 1120-64-5; trimethylsilyl triflate, 27607-77-8.