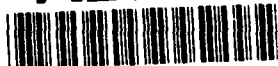


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by

Krzysztof Matyjaszewski, Jeffrey S. Hrkach

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**CATIONIC RING OPENING POLYMERIZATION OF
OXAZOLINES INITIATED BY TRIMETHYLSILYL
DERIVATIVES**

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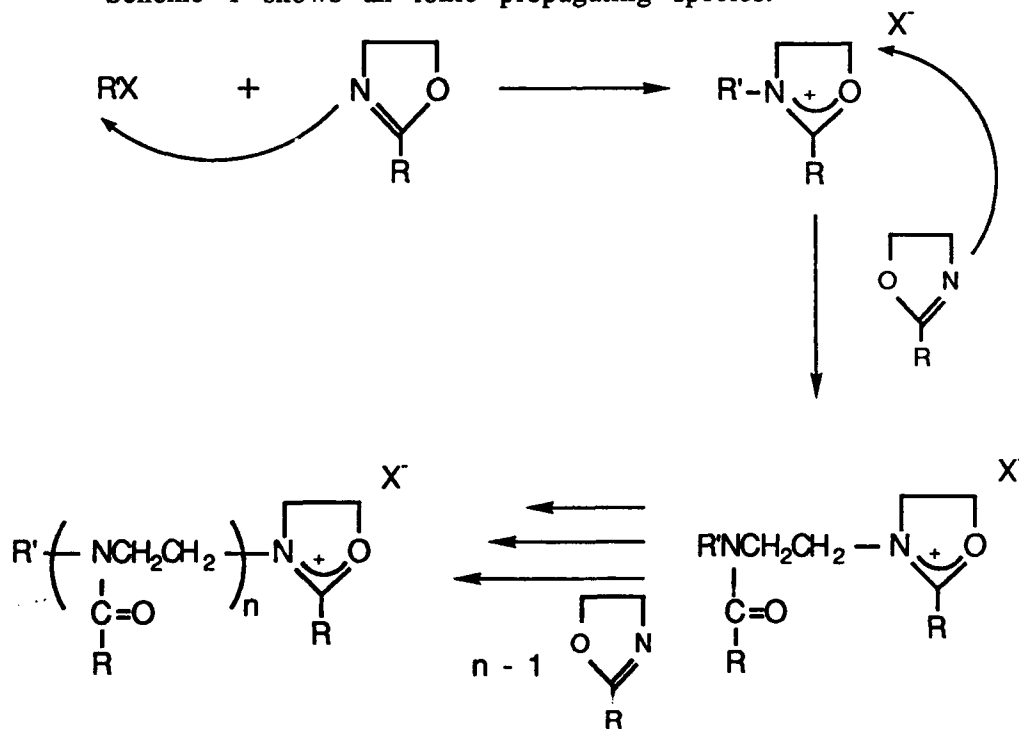
ABSTRACT: Cationic polymerization of oxazoles was initiated by trimethylsilyl triflate and trimethylsilyl iodide. Initiation is slow due to the formation of a imine dimeric cation which is very unreactive toward oxazoline. The presence of the imine dimeric cation was confirmed by NMR and FAB-MS.

Introduction

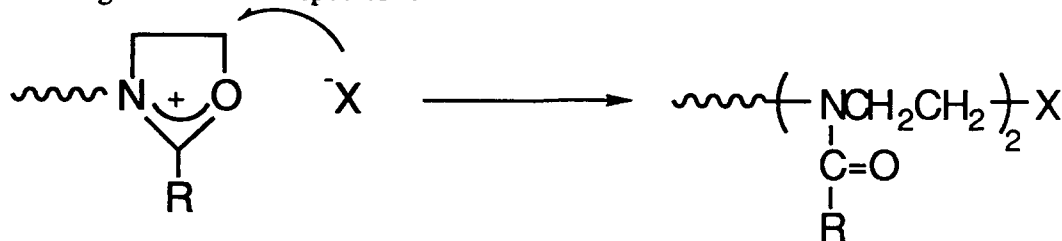
The cationic ring opening polymerization of oxazolines has been accomplished using a variety of initiators including Lewis acids such as boron trifluoride, aluminum trichloride, and antimony pentafluoride, and alkyl esters and halides such as methyl iodide, methyl triflate, and methyl tosylate. Most 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.

Typically, 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 α to oxygen) and the breaking of the C5-O bond producing a poly(N-acylethylenimine).

Scheme 1 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 :



Propagation then takes place through attack by monomer on the covalent active center. The polymerization of 2-methyl-2-oxazoline (MeOXZ; $R=\text{CH}_3$) initiated by methyl iodide or methyl trifluoromethanesulfonate (triflate) proceeds via an ionic species, because MeOXZ is more nucleophilic than the iodide and triflate counterions.

We are interested in preparing comb-like graft copolymers with a polysilane backbone and poly(N-acetylenimine) 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.

Results and Discussion

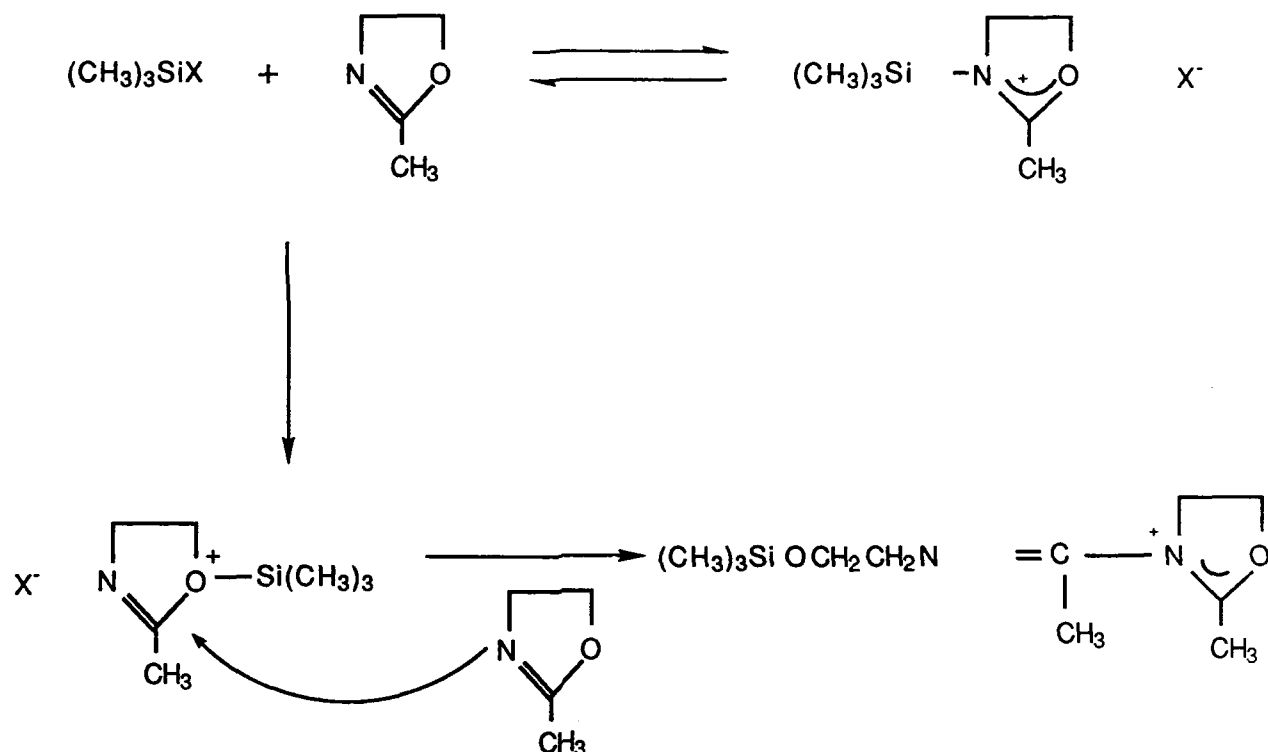
Exchange Reaction

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. 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 ^1H NMR studies at low MeOXZ:TMSX ratios (1:1, 2:1, 5:1, 10:1) to study the initiation and early stages of propagation.

^1H NMR spectrum of MeOXZ in acetonitrile shows the downfield triplet at 4.14 ppm represents the CH_2 α to oxygen, while the other triplet at 3.68 ppm is attributed to the CH_2 α to nitrogen. The singlet at 1.85 ppm is due to the exocyclic 2-methyl group. When an equimolar amount of MeOXZ and TMSOTf are reacted, nucleophilic attack by nitrogen on the silicon atom produces N-trimethylsilyl-2-methyl-2-oxazolinium cation. The chemical shifts for this cation, 4.74 ppm (t), 4.04 ppm (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 NMR spectrum representing this exchange reaction for a 2:1 MeOXZ:TMSOTf ratio shows a single set of peaks, 4.44 ppm (t), 3.86 ppm (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 78.4% of the positive charge lies on the exocyclic silicon atom. This value can be compared to 19.8% of the charge lying on the N-methyl carbon in N-methyl-2-methyl-2-oxazolinium cation which is produced when CH_3X type initiators ($\text{X} = \text{OTf}, \text{OTs}, \text{I}$) are used to initiate polymerization. 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.

Formation of the Imine Dimeric Cation

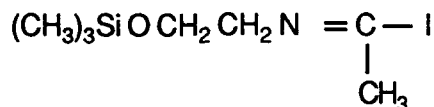
As stated earlier, attack by MeOXZ at C5 of the N-trimethylsilyl-2-methyl-2-oxazolinium cation does not lead to ring opening. Instead, because of the exchange reaction, the trimethylsilyl initiator is eventually attacked by the oxygen atom of MeOXZ which is less nucleophilic than the nitrogen atom. This 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 an imine dimeric cation is produced instead. The formation of the dimeric cation is outlined in Scheme 3. One set of peaks (M) in the ^1H NMR spectrum of a reaction with a 4:1 MeOXZ:TMSOTf ratio after 6 days at room temperature in acetonitrile represents the average signals for free and N-silylated MeOXZ. The other peaks correspond to the unusual imine dimeric cation.



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 six 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 N-methyl-2-methyl-2-oxazolinium cation, which is produced with MeX initiators (X=OTf, OTs, I). MNDO calculations 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. 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 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 ^1H NMR spectrum shows the formation of a small amount of this open covalent species did take place. The triplets at 3.41 ppm 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. It should be noted that HI (or HOTf in the case of TMSOTf) is also produced by hydrolysis of TMSI. Some of the reactions studied later contain 2,6-di-*tert*-butyl pyridine 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.

Chain Extension

^1H NMR spectra from a study conducted at a 10:1 MeOXZ:TMSOTf ratio at room temperature in CD_3CN shows that after 72 hours no propagation has taken place. The MeOXZ peaks are shifted slightly downfield due to the exchange with the N-trimethylsilyl-2-methyl-2-oxazolinium cation. They are not as far as usually downfield, because the large excess of MeOXZ shifts the average signals toward the chemical shifts for MeOXZ. The peaks corresponding to the dimeric cation are also evident. After two weeks some polymerization has taken place, as seen by the broad peaks around 3.4 ppm and 2.1 ppm corresponding to the ethylene units within the chain and the acetyl methyl 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 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. The peaks at 118 ppm and 1.3 ppm are due to acetonitrile. Based on 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. The peaks for the $\text{CH}_2\text{-O}$ and $\text{CH}_2\text{-N}$ of the ring are seen at 59 ppm and 52 ppm, respectively. The peaks at 51 ppm and 47 ppm correspond to the open $\text{CH}_2\text{-O}$ and $\text{CH}_2\text{-N}$ 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 α to nitrogen, whereas no peak is seen for the CH_2 α 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. It could also 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 non-volatile 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*-butyl pyridine, and acetonitrile.

The largest peaks in the spectrum were found at m/e 243 and m/e 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 m/e 185, although the peak at 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. 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 N-trimethylsilyl-2-methyl-2-oxazolinium cation.