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Oxonium Ion Ring-Opening Polymerization

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Oxonium Ion Ring-Opening Polymerization

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ABSTRACT

Oxonium ion ring-opening polymerization is reviewed with emphasis on unsolved problems. New findings in cationic ECH polymerization and in cyclic oligomer formation are given. Participation of the Cl of ECH in the cationic center is suggested.

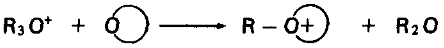
The vigorous activity in the area of oxonium ion ring-opening polymerization in the past few years is reflected in the number of recent symposia [1-3] and reviews [4, 5]. This activity has contributed greatly to our knowledge and understanding of these polymerizations. It is the purpose of this paper to survey this progress while particularly emphasizing the gaps that still exist in our knowledge. When possible, recent progress in our own laboratories will be used to show how some of these gaps are being filled.

As the title of this paper indicates, the nature of the propagating species in cyclic ether ring-opening polymerization is now well established and accepted. For this reason and because we must initiate before we can propagate, we will first consider initiation.

INITIATION

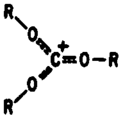
Meerwein [6] first described the basic requirements necessary to generate oxonium ions in 1937. Many different methods and systems to accomplish the same end have been described since that time. While some are novel and different from Meerwein's work, an impressive number reduce to the basic principles embodied in Meerwein's work of the 1930s.

Initiation by trialkyl oxonium salts, shown in Eq. (1), is perhaps the most straightforward initiation reaction, since it is most nearly like the propagation reaction itself and directly gives the desired propagating species. This has been quite clearly shown to be the case in four- and five-membered cyclic ethers [4, 5]. However, the situation is already more complex in the case of cyclic acetals where there is still considerable argument over the exact structure of the propagating species. Also, initiation by trialkyl oxonium salts may or may not be as straightforward as shown in Eq. (1) in the cases of the bridged cyclic ethers and especially of the 1,2-epoxides, where the occurrence of this alkylation reaction has yet to be demonstrated.

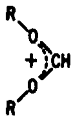


(1)

Related to the trialkyl oxonium salts are the carboxonium salts I and II. These salts behave as alkyl donors in a very analagous way.

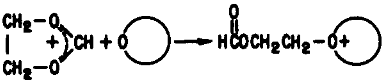


I



II

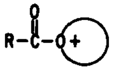
Initiation with dioxolenium ion shown in Eq. (2) is just a little different.



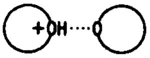
(2)

The two alkyl groups of the dialkyl carboxonium ion are joined and hence the formate ester residue is not lost, but remains attached as an often convenient end group. The formate ester is useful for NMR end group analyses and can be removed by hydrolysis to give the often desired hydroxyl end group.

The acylium salts and the free acids seem relatively straightforward at this point. But this may only be so because they have not been studied extensively. It is known that propagation beyond the first step, from species III and IV, is rather slow. Participation of the acyl oxygen in shielding the environment of the positive oxygen and the strong dietherate complexes that secondary oxonium ions form are probably the reasons for this slow reaction.



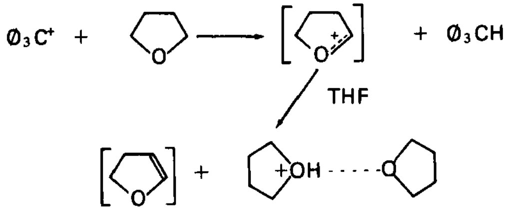
III



IV

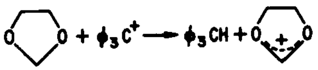
Initiation by the trityl carbenium ion—the triphenyl methyl carbenium ion—is now fairly well understood.

In all cases the first step is probably one of hydride ion abstraction to form triphenyl methane. What then? In the case of THF it appears to be the loss of a proton to complete a dehydrogenation, as shown in Eq. 3, and initiation is then by the proton dietherate.



(3)

In other cases, the loss of the hydride ion is followed by other reactions. For example, in the case of 1,3-dioxolane (Eq. 4),



(4)

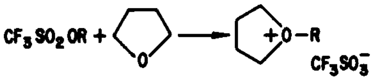
a dioxolenium ion is formed and the initiation reduces to the use of that species. The initiation chemistry using trityl ion initiation for the 1,2-epoxides and the oxetanes has not been very extensively studied. The loss of a proton to complete a dehydrogenation is not very likely on the basis of such evidence as exists, but hydride ion abstraction is probably still the important first step and has been so shown in some cases. The next step or steps still await study and definition.

The trialkylaluminum-water-promoter system was discovered and extensively studied in Japan by Furukawa and Saegusa [7]. It was for this system that Saegusa [5, 8] developed the elegant end capping method for measuring the concentration of active ends—the number of oxonium ions formed. However, this catalyst system is still a complex system and little understood. The trialkyl-water reaction is understood in broad terms, but the exact mixture of products is not known. Since rather inefficient initiation based on trialkylaluminum has been shown, a minor reaction product may be responsible for initiation.

What is the initiation reaction? How are the oxonium ions formed? What is the exact function and fate of the promoter? What is the counterion? Is an aluminate ester involved? These are important questions also because it is a very similar catalyst indeed that constitutes the Vandenberg catalyst used to make high molecular weight polyepichlorohydrin rubber. It is worth noting that we use a trialkylaluminum-water catalyst with ECH promotion to initiate cationic THF polymerization, and the Hercules (Vandenberg) process for high molecular weight polyepichlorohydrin rubber also uses a trialkylaluminum-water catalyst. The latter is used under conditions which result in what is generally agreed to be a coordinate polymerization mechanism. A fruitful area of future research should be the sorting out of the relationships in this mystery and defining the chemistry of this system in a manner that Kennedy is doing in the trialkylaluminum-initiated cationic polymerization of olefins.

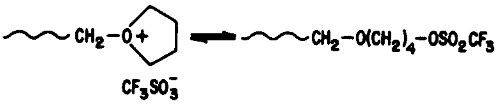
In regard to the effect of promoters, we might ask: Do we really understand the chemistry in the Lewis acid-promoter initiation? These initiating systems are frequently used, even extensively studied, but our understanding of the initiator chemistry has not really progressed since Meerwein first studied this chemistry some 40 years ago.

A relatively new class of initiators, the fluorosulfonates, was discovered at the 3M Company by Smith and Hubin [9] in the early 1960s. These initiators include the esters and anhydrides of trifluromethane sulfonic acid and fluorosulfonic acid. They have only recently been studied in any detail. Initiation with such an ester is shown by



(5)

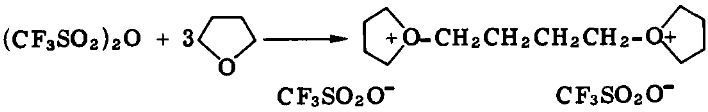
Both Saegusa [10] in Japan and Penczek [11] in Poland have gone a long way toward sorting out some interesting new chemistry. They are developing an understanding of the ion-ester equilibrium that is so important here:



(6)

The perchlorate counterion also appears to belong to this class of materials for which the formation of the corresponding ester must be considered to play an important role.

The use of the anhydrides presents an exciting new development since it allows the very simple preparation of dicationic systems. The direct interaction of, for example, trifluoromethane sulfonic anhydride with tetrahydrofuran yields a dicationically active polymer, as indicated by

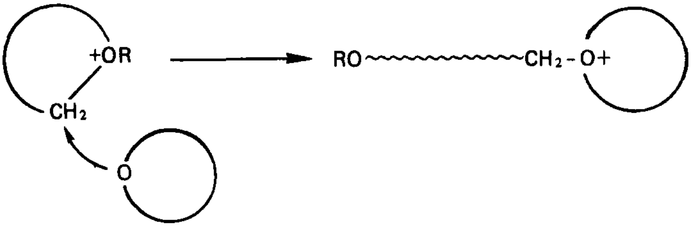


(7)

Polymers with active cations at both chain ends open up a host of possibilities for preparing block copolymers and polymers with functional end groups. Many of these possibilities had been recognized and were explored by Smith and Hubin [9], but some of the more elegant work in the area of multiblock copolymers, using quite different chemistry, has been carried out by Yamashita and co-workers [12]. This is certainly an area in which we can expect important new developments.

PROPAGATION

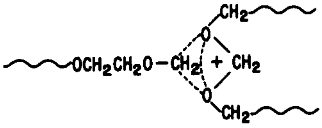
In many ways our knowledge about propagation is much better. We all seem to agree, at least with four- and five-membered cyclic ethers, that the growing species is an oxonium ion and propagation occurs, as shown in Eq. (8), by nucleophilic attack by an ether oxygen on an α-carbon atom:



(8)

Studies in recent years have focused on the details of the propagation step. There have been several studies [13, 14] which sought to define more closely the role of the ion pair, solvent separated ion pair, and free ion equilibria in these systems. The results of these studies show that there is relatively little difference in the rates of propagation of free ions over ion pairs, and that these differences vary with the dielectric constant of the solvent. This suggests the importance of solvent separated ion pairs in higher dielectric solvents. The question remaining is the importance of monomer itself in separating the ion pairs, a question to which it is believed some groups are currently addressing themselves. Closely related to this problem is the ion-ester equilibrium occurring during the propagation (Eq. 6) involving certain counter ions. This is now becoming understood, as mentioned above. Again, here we see a significant effect of solvent polarity. The highly polar solvents are clearly found to favor the ionic form, while nonpolar solvents favor the ester.

All cyclic ethers do not propagate by a pure oxonium ion mechanism as indicated in Eq. (8). The polymerization of cyclic formals is perhaps the best example. Although there are those who feel cyclic formals are no exception, others are equally certain Eq. (8) is not applicable. Penczek [15] has recently summarized these different points of view and presented his evidence supporting a carboxonium active end that is complexed with and stabilized by two polymer oxygen atoms. The resultant active end is Structure V.



V

Of course, the actual propagation step must then be modified. Thus, in the case of cyclic acetal polymerization, we may not have the trialkyl oxonium ions that we have come to accept and be comfortable with. Are there other cases?

We have no reason to doubt that trialkyl oxonium ion active centers are a reasonable representation of the situation with the larger single oxygen containing cyclic ethers. But the situation in the cationic polymerization of 1,2-epoxides is a little less clear. These materials can and do polymerize by cationic, anionic, and coordinate mechanisms. We feel that the propagating species in the cationic polymerizations of these epoxides is probably a tertiary oxonium ion, but we have to consider that the oxirane oxygen is one of the least basic, least nucleophilic, of the ether oxygens. Thus one has to question the validity of the typical S_N2 propagation mechanism in this case. (See discussion of epichlorohydrin polymerization below.)

Another aspect of propagation is the concurrent formation of cyclic oligomers in some cases. In the case of THF the monomer is the most favored oligomer; it and polymer are the only products. But the smaller ring systems do show cyclic oligomer formation under conditions of cationic polymerization. In the case of ethylene oxide, the formation of 1,4-dioxane is almost the predominant reaction. Kern [16] has shown that cyclic tetramer is the predominant oligomer formed from propylene oxide, 1,2-butylene oxide, and epichlorohydrin. Dimer and some higher cyclic oligomers were also observed in smaller amounts, but no trimer. In their studies of the cationic polymerization of oxiranes, Entelis and Korovina [17] conclude that cyclic tetramer formation is an important aspect of these polymerizations. Is cyclic oligomer formation a competing side reaction to linear polymer formation? Or is it a depolymerization reaction of linear polymer?

In his classic study of oxetane polymerization, Rose [18] showed that cyclic tetramer formation was important in oxetane and in 3,3-dimethyloxetane polymerizations. The amount of cyclic tetramer observed was markedly dependent on temperature. This aspect of oxetane polymerization was recently re-examined by Dreyfuss [19]. The study has produced some interesting and significant results. The disappearance of monomer was followed by gas chromatography. At the same time, the formation of two volatile products was observed. One corresponded to the cyclic tetramer described by Rose and the other was shown to be the cyclic trimer. There is no evidence as yet for cyclic dimer or for cyclic oligomers larger than tetramer. In agreement with Rose, polymerization temperature was found to be important. Under the conditions used, little cyclic oligomer was formed below about 25°C. As the temperature was raised, more oligomers were formed and the ratio of trimer to tetramer increased.

Counterion is very important. Dreyfuss finds that cyclic oligomer formation is really an important reaction only when the counterion is tetrafluoroborate. In his studies, Rose used BF_3 as initiator. Had he used another Lewis acid, he may never have observed cyclic tetramer formation. Other counterions (such as PF_6^-, SbF_6^-, $SbCl_6^-$) gave only very small amounts of cyclic oligomer, but always there was evidence for both trimer and tetramer.

The use of ethyl trifluoromethane sulfonate as initiator gave significantly different results. Relatively much more trimer was formed. The use of a nonpolar solvent such as benzene favored trimer over tetramer. The effect of increasing polymerization temperature in the benzene solvent case was to increase the amount of cyclic trimer formed while the amount of tetramer formed stayed more or less constant.

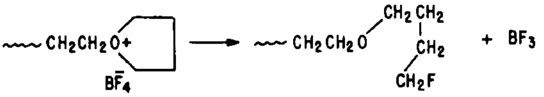
This appears to be an interesting approach to studying the effect of the various counterions on the polymerization reaction. Oligomer formation may be a more sensitive and more convenient way of studying some of these differences.

As was just pointed out, counterions can have a very important effect on the polymerization of cyclic ethers. All too often studies are undertaken with little regard to counterions. Initiators (and hence, counterions) are apparently chosen because of their availability or ease of preparation, rather than from any careful consideration of the properties of the counterion.

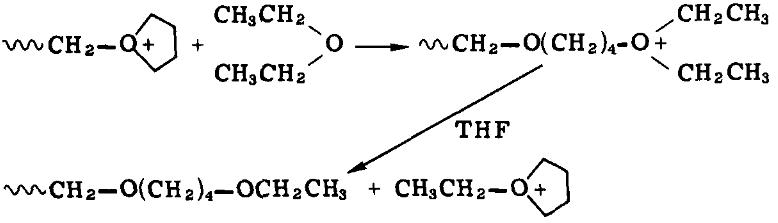
In general, the rates of oxonium ion polymerizations have been found to be quite independent of counterion. In recent years, great strides have been made, notably by Saegusa and co-workers [5], in the determination of the absolute rate constants and the thermodynamic parameters for a number of these systems. The ion-ester equilibrium mentioned above (Eq. 6) does have a marked influence on rate. The ester form is very much less reactive than the ionic form. Thus the amount of ester present greatly effects the overall rate of polymerization observed. The type of counterion used for a polymerization has a big influence on the transfer and termination reactions observed. Consequently, the counterion has an important influence on the molecular weight and molecular weight distribution of the polymers produced. These effects of counterions are really self-evident from oxonium ion chemistry. After all, the discovery and isolation of oxonium ion salts depended on the discovery and development of anions of very low nucleophilicity.

TRANSFER AND TERMINATION

The termination reaction that can occur with a counterion is well known:

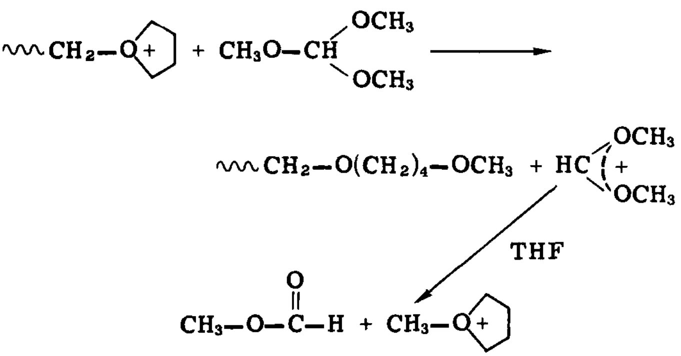

(9)

It is a termination reaction because generally BF_3 is not able to initiate a new chain by itself. On the other hand, in a case such as $SbCl_6^-$ the same reaction is also a transfer reaction. The $SbCl_5$ formed can initiate a new chain. But it probably takes two molecules of $SbCl_5$ to initiate a new chain. Thus since half a chain, that is, an active center, is lost by each such reaction, it is a combination of transfer and termination in this case. Transfer can and does occur with acyclic ethers:



(10)

Thus, obviously the polymer ether oxygens can and do also interact with the growing oxonium ion centers. Water and alcohols at low levels have also been reported to function as transfer agents. Long ago we reported that trimethylorthoformate is particularly effective as a transfer agent:

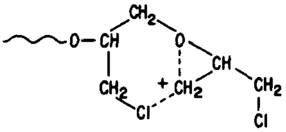


(11)

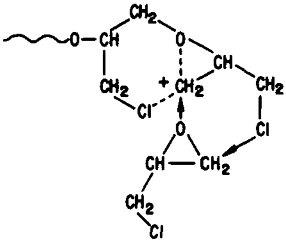
In THF polymerization it can be used to reliably control molecular weight [4]. The problem is that one only gets the inert methoxy ether end groups. A material which would be as effective a transfer agent as trimethylorthoformate and which would give functional end groups would be most desirable indeed.

The discussion on transfer so far has dealt mostly with THF polymerization. Transfer and termination reactions seem to be much more important in the case of the bicyclic ethers and the 1,2-epoxides. But the reactions in these cases are little, if at all, understood. It seems clear that these monomers react differently than the apparently straightforward THF case. But how? And why?

Noncoordinate cationic polymerizations of 1,2-epoxides have not been reported to give high molecular weight polymers. In fact, molecular weights of 1000 or less seem to be the rule. Transfer reactions and reactions leading to cyclic oligomers appear to predominate. Our own work has made some significant progress in controlling and perhaps even understanding these factors. Although we have not yet been able to exercise complete control over molecular weight, we have been able to polymerize epichlorohydrin cationically under certain conditions to considerably higher molecular weights. Our data to date suggest that ECH may be a somewhat unique monomer in this regard. This has led me to suggest an involvement of the chlorine atom in stabilizing the propagating end. This stabilization is thought to favor propagation at the expense of transfer and termination reactions and of reactions leading to cyclic oligomers. The chlorine atom that is invoked is the one on the penultimate monomer unit and the result is the cyclic intermediate VI. A modified oxonium ion is suggested. This ion is a six-membered ring active end in which the positive charge is spread out. This is not a true oxonium ion propagating species, but perhaps this is necessary for a successful cationic polymerization of an oxirane. A concerted growth step which directly forms the next such species can be readily visualized and is depicted in Structure VII. The two partial bonds break and a new active end just like the original one is formed. The process, of course, can readily and rapidly continue. It is this process, then, that favors

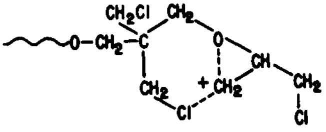


VI

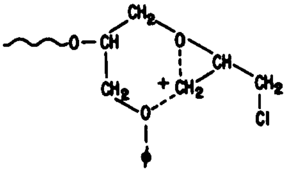


VII

propagation over transfer reactions and cyclic oligomer formation. This picture was developed because under the same conditions other epoxides do not polymerize as well nor lead to the same molecular weight as does epichlorohydrin. Additional evidence for this picture came from copolymerization studies. Copolymerization of other cyclic ethers with ECH under the present conditions were found to be generally very unsatisfactory, especially as compared to the results of ECH homopolymerization. Evidently the propagation pattern shown cannot be interrupted, even briefly. However, certain epoxides do copolymerize very satisfactorily. Since these epoxides were chosen on the basis of the scheme shown above, it has given us greater confidence that there may be some validity to this suggestion. For example, a smooth and satisfactory copolymerization was obtained with bischloromethyl oxetane and with phenyl glycidyl ether. The comonomers were incorporated into the polymers. The polymerizations did not suffer from premature termination, and the molecular weights of the copolymers were in the same range as observed for ECH homopolymerization. Both monomers can easily form analogous stabilized active ends as shown in Structures VIII and IX. It is interesting to note that alkyl glycidyl ethers were unsatisfactory as comonomers. Apparently the nucleophilicity or basicity of the atom on the pendent methylene of the epoxide must be in a specific narrow range and be very much like a chlorine atom.



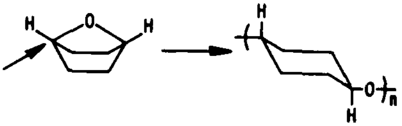
VIII



IX

THE POLYMERS

Monomers such as THF, BCMO, and oxetane give polymers of varying properties depending on the molecular weight. But they all give linear and readily crystallizable polymers. The bicyclic ethers tend to give highly crystalline polymers having a trans structure [20, 21]. Apparently the S_N2 propagation mechanism operates exclusively here to result in this trans product:



(12)

What about the corresponding cis isomer? Does the polymerization mechanism prevent our achieving this interesting isomer of the polymer shown in Eq. (12)? Or can we think of a way around this problem? Ionic polymerizations generally do not allow the preparation of isotactic and syndiotactic polymers. But it is interesting to point out here that isotactic polypropylene oxide is known, while the corresponding syndiotactic polymer is as yet unknown.

Copolymers can and are made by oxonium ion polymerizations. Mostly these are random copolymers. Some block copolymers have been made by some clever work of Saegusa [22] and by cotermination with anionic polymers [9, 12, 23]. But there has been relatively little work done on graft polymers using oxonium ion polymerization techniques. Alternating copolymers are another group that probably does not lend itself to a purely ionic polymerization process. Or can we find a way?

CONCLUSION

I have tried to point out and illustrate that we have many questions yet to be answered on all aspects of oxonium ion ring-opening polymerizations. I have indicated the type of progress we are making in some areas, notably on cyclic oligomer formation, which is very closely tied in with counterion effects. Also, in the area of 1,2-epoxide or oxirane polymerizations we may be making a small dent in understanding how to make higher molecular weights using a cationic mechanism.

ACKNOWLEDGMENTS

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