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Survey of Recent Progress in Polymerization Studies of Selected Heterocycles

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Survey of Recent Progress in Polymerization Studies of Selected Heterocycles

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INTRODUCTION

The last symposium exclusively on the polymerization of cyclic ethers and sulfides held at an ACS meeting took place in Atlantic City in September 1965 [1]. This survey is intended to give a general overview of the areas of active research since then and to summarize the progress that has been made in these areas. The polymerizations of cyclic ethers and cyclic sulfides are compared and contrasted. The influence of the size of the heterocyclic ring on the polymerization is described. In addition, the survey is intended to anticipate in a general way what the other participants in this symposium will discuss in detail so that the conference will seem more a single unit rather than a series of disconnected papers. As usual, limitations of time and space compel a certain selection process and no attempt has been made to be all-inclusive.

WHY HETEROCYCLES POLYMERIZE

Theoretical estimates [2] of the free energy of polymerization ΔF_p indicate that ΔF_p is negative for most members of the homologous series of cyclic ethers and cyclic sulfides. The calculations predict and experiments reveal that 3-, 4-, and unsubstituted 5-membered cyclic compounds are polymerizable. The theoretical prediction that ΔF_p will be positive for 6-membered ring members and substituted 5-membered rings also seems to be supported by experiment. Indeed tetrahydropyran has resisted efforts at direct polymerization by ring opening, and simple substituents in the 2-position on 5-membered rings do seem to inhibit their polymerization. However, in 1969 Chiang and Rhodes reported the polymerization of 3-methyl tetrahydrofuran to give a low molecular weight polymer [3]. In addition, it is well known that bicyclic, strained tetrahydrofurans do form polymers very readily [4, 5]. Two of the participants in this symposium discuss such polymerizations. Jørgen Kops and Hans Spanggaard report their studies on low temperature polymerization of endo- and exo-2-methyl-7-oxabicyclo-[2.2.1]-heptane, and J. Stejny discusses polymerization and crystallization of poly(1,4-epoxycyclohexane).

In agreement with the theoretical Eq. (1), derived by Dainton and Ivin [2], ring-opening polymerizations of cyclic ethers and of cyclic sulfides are very temperature (T) dependent.

$$\ln[M_e] = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} \tag{1}$$

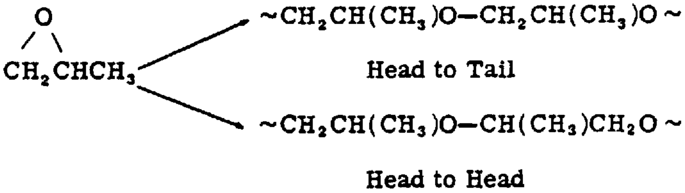
Tetrahydrofuran, for example, has a ceiling temperature of about 83°C [6], and no polymer forms above this temperature. The degree of conversion in bulk polymerizations increases rather rapidly as the temperature is lowered. Thus by 25°C, 75% conversion to polymer can already be obtained. The temperature dependence of the equilibrium monomer concentration $[M_e]$ illustrated by Eq. (1) also permits the determination of both the heat of polymerization ΔH_p and the entropy of polymerization ΔS_p from a simple plot of $\ln[M_e]$ vs 1/T. (In Eq. 1, R is the gas constant as usual.) The thermodynamic parameters determined in this way for polytetrahydrofuran using several different catalysts are in good agreement [6]. However, in recent years it has been observed that in the polymerization of dioxolane and some other monomers [7-9], $[M_e]$ is not unique, but varies with the polymer concentration as well as temperature. Since Eq. (1) assumes ideal behavior, and polymer solutions deviate from ideality, the theory has accordingly been modified to take this into account. J. Leonard and D. Maheux discuss the application of the modified theory to the polymerization of tetrahydrofuran in benzene.

As the temperature of polymerization is lowered, a change of phase occurs with some polyethers, and crystallization and polymerization continue simultaneously. How this effects the course of the polymerization of poly(1,4-epoxycyclohexane) and of polytetrahydrofuran is also discussed by J. Stejny.

HOW HETEROCYCLES POLYMERIZE

The size of the ring has a marked effect on how the heterocycles polymerize. In particular, it is necessary to distinguish between 1,2-epoxides or episulfides and the higher heterocycles. The 3-membered ring heterocycles will polymerize by a variety of mechanisms: anionic, cationic, and coordinate. Examples of all three kinds of initiators are included in this symposium. The mechanism in the case of anionic initiators and anionic polymerization is reasonably straightforward. The negative charge seems to reside on the hetero atom. In this symposium there are three papers that describe polymers prepared from 3-membered rings after anionic initiation. They are presented by A. A. Oswald; by M. Morton and S. L. Mikesell; and by C. C. Price, Murali Krishna Akkapeddi, B. T. DeBona, and B. Furie. In these papers the emphasis is on the character of the polymers prepared rather than on the mechanism of their preparation. The synthesis of polymers from 1,2-epoxides using a coordinate covalent initiator is described by S. E. Cantor, T. J. Brett, and G. D. Brindell, In this case a complex initiator derived from an alkyl aluminum, acetyl acetone, and water was used. Although several mechanisms have been advanced to explain the course of such polymerizations, as far as the author knows agreement has not yet been reached [10]. The situation in the case of cationic polymerizations of 1,2-epoxides and episulfides is only a little better. In suspected cationic polymerizations of cyclic oxides it often cannot be stated unequivocally whether the polymerization proceeds through a carbenium ion or through an oxonium ion. The choice may be somewhat easier in the cationic polymerization of cyclic sulfides. E. J. Goethals discusses the cationic polymerization of cyclic sulfides in his paper and places the charge clearly on the sulfur atom. In summary, the mechanism of polymerization in the case of 1,2-heterocycles is not settled in all cases. It is even possible that with some initiators there is more than one initiating species and more than one mechanism of polymerization.

Nevertheless, by studying the polymerization of optically active epoxides such as ℓ-propylene oxide, which possesses an asymmetric carbon atom, Price and his collaborators [11, 12] and Vandenberg [13] have been able to clarify some features of the mechanism of their polymerization and to produce optically active polymers as well. Their studies indicate that in these special polymerizations at least, polymerizations occur predominantly by inversion at the asymmetric carbon atom and result in head to tail placement of the monomer. The polymer obtained is usually highly crystalline. Noncrystalline portions apparently are largely derived from units with head to head placement as shown in Eq. (2) rather than from any racemization during polymerization. It can be inferred that polymerizations with similar catalysts proceed by a similar mechanism.



$$\sim CH_2CH(CH_3)O{-}CH_2CH(CH_3)O\sim$$

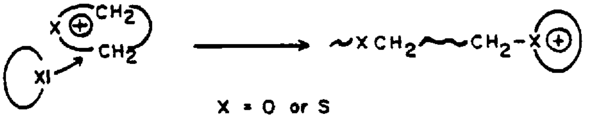
Head to Tail

$$\sim CH_2CH(CH_3)O{-}CH(CH_3)CH_2O\sim$$

Head to Head

(2)

In contrast, 4- and 5-membered cyclic ethers with a single hetero atom polymerize only by a cationic mechanism. At the Atlantic City symposium there was still some question about whether the charged species is a carbenium ion or an oxonium ion. It is now generally accepted that the charge resides on the hetero atom and that, as shown in Eq. (3), polymerization proceeds by nucleophilic attack of the free electrons of the monomer's hetero atom on the carbon alpha to the hetero atom of the polymerizing species [14-17]. Cyclic sulfides of the same ring size react similarly. A positively charged oxygen or sulfur ion does not seem able to react directly with a vinyl



monomer to produce a carbenium ion. Over the years there have been numerous claims to the contrary, but the polymers have eventually been shown to be mixtures of homopolymers or at best block polymers.

An interesting difference between oxygen and sulfur heterocycles has been observed by Morton, Kammereck, and Fetters [18-20]. Whereas the 4-membered cyclic ether, oxetane, can polymerize only by a cationic mechanism, the 4-membered cyclic sulfide, thietane, can polymerize by an anionic mechanism as well. However, when it does so, the propagating species is a carbanion rather than a thiolate ion. (This carbanion is capable of initiating polymerization of vinyl monomers.) This is an especially interesting observation since anionic polymerizations of the 3-membered ring sulfide, ethylene sulfide, proceed as expected and a negatively charged thiolate species is formed. Morton and Mikesell say more about these differences in their paper.

The mechanism of polymerization of hetereocycles with more than one hetero atom is not as clearly established. At the IUPAC Meeting in Boston in 1971 there was still vigorous discussion about the exact description of the growing species itself and the mode of addition of monomer during the polymerization of dioxolane. The final resolution of the debate will have to come in future publications.

THE POLYMERS

Tacticity

The polymers produced by the ring-opening polymerization of heterocycles are generally linear. Branched polymers are sometimes formed as the result of side reactions; however, branched polymers seem to be relatively unimportant. In the discussion of how 1,2-epoxides polymerize it was already pointed out that optically active polymers can be prepared from optically active monomer. It is also possible to use stereoselective catalysts to induce optical activity in the polymers. Tsuruta and co-workers have used this technique to prepare optically active polyethers [21-23], and Spassky and Sigwald as well as Furukawa, Kawabata, and Kato [24] have applied it to prepare optically active polysulfides. The last two groups also prepared optically active polymer from resolved propylene sulfide. The proportion of optically active sequences is usually lower when stereoselective catalysts are used, but the resulting rotations are significant, and unreacted monomer is optically active. Changes in optical activity influence the properties of the polymers. Increased stereoregularity seems to produce polymers with considerably different transition temperatures and altered mechanical properties [25]. The changes in tacticity are also noticed in a different texture in the spherulities seen in thin films viewed in polarized light [26].

The presence of an asymmetric carbon atom in the monomer leads to the possibility of preparing optically active polymers. Similarly, the presence of the two different groups on the same carbon atom after the monomer is polymerized leads to the possibility of preparing polymers with different tacticity. Most of the polyethers and polysulfides studied from this point of view to date are either isotactic or atactic [27]. Perhaps this is not surprising. The preparation of atactic polymers requires a catalyst which exerts little or no steric control, and should be relatively easy to achieve. The preparation of isotactic polymers requires a catalysts that will produce either . . . ℓℓℓ . . . or . . . ddd . . . sequences. However, the preparation of syndiotactic polymers would require a catalyst that would lead to regular . . . dℓdℓdℓ . . . alternation throughout. In this symposium Price and co-workers report some new observations on stereoselection in base-catalyzed polymerization of epoxides in which crystalline polymers that are not isotactic are produced. Instead polymers with regularly alternating isotactic and syndiotactic sequences, . . . ddℓℓddℓℓ . . . , are formed.

An interesting difference in stereoselectivity in the polymerization of cyclic oxides and cyclic sulfides was recently reported by Vandenberg [28]. He examined the polymers prepared from cis- and trans-2-butene episulfides and epoxides using cationic catalysts such as Et_2Zn-H_2O, $i-Bu_3Al-H_2O$, and BF_3. The cis oxide gave amorphous, disyndiotactic polymer, presumably as a result of steric effects. The cis sulfide gave crystalline, presumably racemic diisotactic polymer. The difference is attributed to the larger size of the C—S bond and the participation of the counterion in the formation of a 5-membered transition state. In contrast, the trans oxide gave crystalline, meso-diisotactic polymer, again presumably as a result of the decreased steric hindrance in the formation of this steric structure compared to other possible ones. The trans sulfide gave only amorphous polymer. In this case Vandenberg suggests that the larger C—S bond leads to nonstereoselectivity.

Molecular Weight Control

The ease of molecular weight control is another area of difference between 1,2-epoxides and higher cyclic ethers. With 1,2-epoxides there are still many problems. Certain initiators always seem to lead to polymers of very low molecular weight, and others give only polymers of very high molecular weight. When a catalyst leads to polymer with a certain desired tacticity, it is not always possible to vary the molecular weight within wide limits.

In contrast, enough is now known so that molecular weight control of the higher epoxides is easily achieved. It is only necessary to choose reaction conditions and an initiator that produce a reaction mixture reasonably free of transfer and termination reactions. Alternately, the molecular weight can be controlled by the addition of an appropriate transfer agent, possibly at the sacrifice of end group control, however. Tetrahydrofuran is probably the monomer most extensively studied in this regard and will serve as an example of the control that has been achieved.

There have been many reports of the preparation of "living polymers" from polytetrahydrofuran [14-16]. The choice of counterion seems to be particularly important, especially if polymerizations are carried out at room temperature or above [29]. Polymerizations with PF_6^- and SbF_6^- counterions produced polymers for which the molecular weight could be calculated directly from the ratio of monomer charged to catalyst charged. Initially, the molecular weight distributions were narrow but in a short time they became broader. The time was too short to be accounted for by polymerization-depolymerization reactions alone, and Dreyfuss and Dreyfuss [29] have suggested that transfer reactions with the ether oxygens are responsible. When the $SbCl_6^-$ counterion was used, evidence for both termination and transfer reactions has been found not only in polymerizations with tetrahydrofuran but in polymerizations with other monomers as well [30]. With the popular BF_4^- counterion, termination often occurs before maximum conversion can be attained. Similar studies have not been carried out for the important aluminum alkyl-water initiators with or without additives. The counterion is generally generated in situ and calculated molecular weights are based on a number of active centers determined by some special means, so that a direct comparison is not possible.

Control of the molecular weight of polytetrahydrofuran with the aid of transfer agent is illustrated in Fig. 1 and in Table 1. The figure shows that with a constant level of diazonium initiator, the molecular weight of the polymer formed depends on the amount of trimethylorthoformate used [31]. The table shows the same effect in polymerizations initiated with a triethyloxonium salt. Trimethylorthoformate is a particularly efficient transfer agent that leads to ether end groups [32].

The discussion so far has been concerned with control of molecular

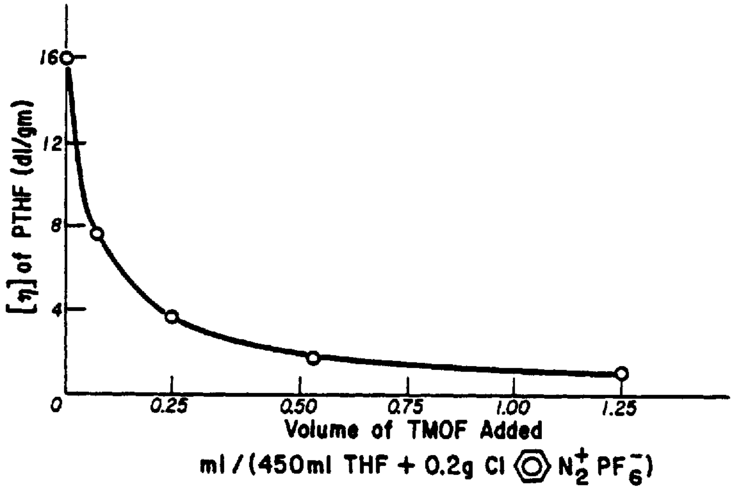


FIG. 1. Effect of adding transfer agent to a tetrahydrofuran polymerization.

TABLE 1. Effect of Trimethylorthoformate on Molecular Weight

mmole Et_3OPF_6 / mole THF	mmole TMOF / mole THF	~Mol wt calcd for THF	$[\eta]$
0.152	5.39	10,000	0.38
0.156	2.75	19,000	0.53
0.151	1.35	38,000	0.79

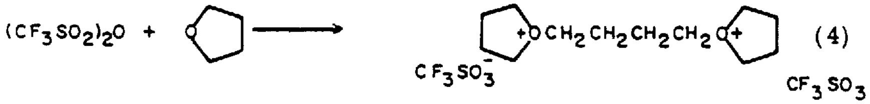
weight in cyclic ether polymerizations. Similar control in polymerizations of cyclic sulfides has not been as widely explored. The problem of termination by reaction of active end with polymer sulfur presents a new hurdle that has no direct analogy in the polyether polymerizations [33].

Amphicationic Polyethers

In 1965 it was not yet possible to prepare polyethers of definite molecular weight with cations on both ends. In recent years this has been accomplished in two ways. Smith and Hubin [34, 35] simply react trifluoromethane sulfonic anhydride with tetrahydrofuran to produce the dicationically active (amphicationic) initiator shown in Eq. (4). They discuss the details of this preparation and the interesting chemistry that accompanies it in their paper. They also point out the many uses of this species. Yamashita et al. prepared an amphicationic dioxolenium salt by the series of reactions shown in Eq. (5). This dication could then be used to initiate cyclic ether polymerization by bonding with tetrahydrofuran molecules [36].

Similar molecules have been known for a long time in anionic systems. Their use is one way to produce interesting multiblock copolymers from polyolefins [37, 38]. The availability of amphicationic polyethers opens the way for the preparation of block copolymers with well-defined cationic blocks and of polymers in which the cationic block is terminated on both ends with an anionic block after a cross termination reaction.

Block copolymers from polysulfides can also be prepared by an anionic mechanism. Morton and Mikesell discuss their ingenious techniques for the preparation of ABA block copolymers of dienes and cyclic sulfides and describe some properties of the polymers produced.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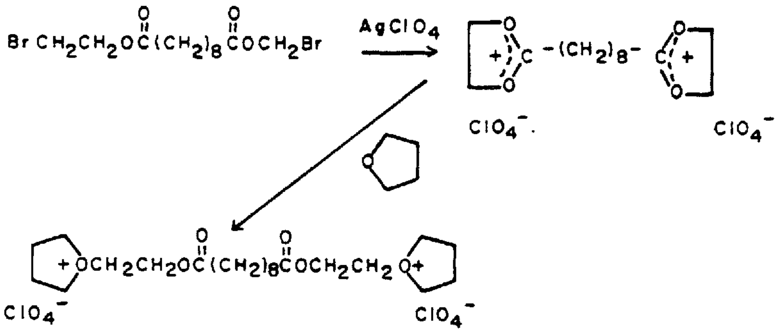
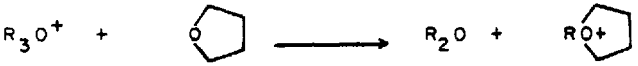

(5)

KINETICS

The kinetics of polymerization of cyclic ethers and cyclic sulfides has been reviewed many times before and indeed over the years has been the subject of many symposia [39]. In fact, kinetics of polymerization has probably been the area of most active research and is discussed by others in this symposium.* Hence remarks here will be restricted to a few illustrative highlights. For the most part, tetrahydrofuran will be used as an example. The exact form of the relevant equations obviously differs somewhat from monomer to monomer. Ring size and the size of the hetero atom can lead to large differences, as we have seen in the previous sections.

Mechanisms

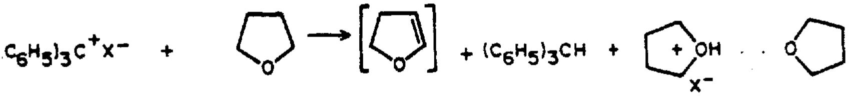
In the case of triethyloxonium ion initiators, the initiation mechanism has not been the subject of much controversy. A simple alkyl exchange from the triethyloxonium ion to the monomer results in the propagating species. Equation (6) shows the reaction. With


(6)

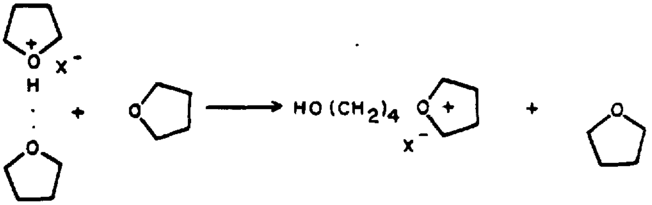
one of the more stable counterions, initiation is fast and efficient and leads to the expected molecular weights, at least initially.

Propagation then proceeds as discussed before by an S_N2 reaction between the monomer and the growing end of the propagating chain.

The initiation mechanism with carbenium ion initiators like trityl and diazonium salts is not quite as straightforward. Initially it was hoped that the mechanism would be the addition of the carbenium ion to the monomer to form a growing cation. But studies by Bawn et al. [40] and by Kuntz [41] soon showed that the carbenium ion abstracts a hydride ion from tetrahydrofuran to form, in the case of trityl cation, triphenylmethane. For a number of years there was a question about how the reaction proceeded afterwards. The evidence to date indicates that the reaction follows the course shown by Eqs. (7) and (8) [42]. The first step is dehydrogenation of tetrahydrofuran to form either furan or dihydrofuran and the free acid of the counterion, which is stabilized by complexing with the monomer. The free acid complex then reacts, probably quite slowly, with additional monomer to form the propagating cation. The acid is thus the true initiator.



(7)



(8)

When the cyclic compound has two hetero atoms as in dioxolane, the initiation mechanism seems to follow an even more complicated route [43].

In anionic polymerizations the equilibrium between ions and ion pairs involving the propagating species has an important effect on the rate of polymerization [44]. Free ions propagate about 1000 times faster than the ion pairs. Two of our symposium participants report studies of the effects of ions and ion pairs in cyclic oxide and cyclic sulfide polymerizations. Sangster and Worsfold discuss ion and ion pair contributions to the polymerization of tetrahydrofuran, and Goethals discusses similar effects in cyclic sulfides.

Rate Equations

Not all initiators are equally efficient for tetrahydrofuran polymerizations. Those initiators that react practically instantaneously to produce a constant number of growing centers fit the rate equation shown in Eq. (9). Here k_p is the rate of polymerization, $[I_0]$ is the initiator concentration, t is time, $[M_0]$ is the initial monomer concentration, and $[M]$ is the monomer concentration at time t. Polymerizations initiated by triethyloxonium salts are an example of the type of polymerizations that fit this equation.

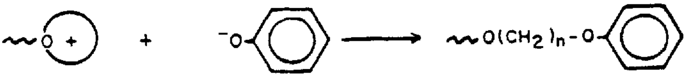
$$k_p[I_0]t = \ln \frac{[M_0] - [M_e]}{[M] - [M_e]} \qquad (9)$$

Many other initiators do not produce a constant number of active centers. Instead the number of active sites changes with time. Then the rate equation takes the form

$$k_p \int_{t_1}^{t_2} [P^*]\, dt = \ln \frac{[M]_{t_1} - [M_e]}{[M]_{t_2} - [M_e]} \qquad (10)$$

The symbols have the same meaning as in Eq. (9) with the additions that $[P^*]$ is the concentration of active sites at time t, and $[M]_t$ is the monomer concentration at time t. This equation fits, for example, polymerizations initiated with the aluminum catalysts. The equation is only useful if a method of determining the number of active centers is available.

Saegusa and co-workers recently developed a very useful phenoxy-endcapping method for studying the number of active sites in these polymerizations [45]. The method is sensitive and can be used with most initiators. It involves the reaction of the phenoxy group with the growing center to form a phenyl ether group that can be recognized in the ultraviolet. Very small concentrations of active centers can be detected. The reaction, shown in Eq. (11), is quantitative and apparently there are no significant side reactions. At the time of the last ACS sponsored symposium it seemed that the



(11)

relative reactivity of the cyclic ethers could be explained almost entirely by basicity. The work of Saegusa and co-workers with their phenoxy-endcapping procedures now suggests that ring strain and the kinetic frequency factor also need to be considered. They have further found that although the rate of propagation is not affected by changes in counterion, the rates of initiation and of termination are.

COPOLYMERS AND TERPOLYMERS

Another area that deserves some mention because of the progress in recent years is that of copolymers and terpolymers. Progress in making block copolymers from heterocycles has been discussed above. Kubisa and Penczek discuss the effects on polymerization kinetics of the copolymerization of tetrahydrofuran with oxetanes such as 3,3-dimethyloxetane, 3,3-bis(fluoromethyl)oxetane, and 3,3-bis(chloromethyl)oxetane. The novel feature of this work is that the polymerizations are carried out above the ceiling temperature of tetrahydrofuran. Yamashita reports the copolymerization of tetrahydrofuran with a cyclic ester; namely, the lactone ϵ-caprolactone. He describes some unexpected properties of the copolymers which suggest an unusual copolymerization mechanism in this system.

Novel, regularly alternating terpolymerizations of two cyclic ethers, such as tetrahydrofuran and ethylene oxide, with a cyclic anhydride, such as phthalic anhydride, are described by Hsieh. The conditions under which they form are discussed.

CONCLUSION

Progress in understanding and controlling the polymerization of cyclic ethers and cyclic sulfides has been very significant in the past 7 years. It has been clearly demonstrated that ring size has a marked influence on the mechanism of polymerization of cyclic ethers. The nature of the hetero atom also can have some surprising effects. Ways to prepare amphicationic polyethers have been discovered. New methods to assist in analyzing kinetics of polymerization have been described and have led to new knowledge about the factors that influence the polymerization of heterocycles. The new ability to control polymerizations and to analyze products has led to polymers with new and varied properties.

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