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NO CATALYST ALTERNATING COPOLYMERIZATION OF CYCLIC IMINO ETHERS

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Abstract - This article presents first the general concept of "no catalyst alternating copolymerization", in which a nucleophilic monomer M_N is combined with an electrophilic monomer M_E preferably in aprotic polar solvents to produce a zwitterion $^+M_N\text{-}M_E^-$, the key intermediate of the copolymerization. Then it describes some aspects of the new copolymerization. Cyclic imino ethers are empolyed as M_N, which are combined with several electrophilic monomers such as β-propiolactone, acrylic acid, propanesultone, acrylamide, ethylenesulfonamide, hydroxyalkyl acrylate and cyclic acid anhydride. In all combinations except the last one with cyclic acid anhydride, 1:1 alternating copolymers were produced. In the last one, 2:1 alternating copolymers were formed. The scheme of each copolymerization is shown.

NO CATALYST COPOLYMERIZATION ——— THE GENERAL CONCEPT

Almost all polymerization reactions require initator, catalyst or high energy radiation. Recently we have developed a series of copolymerizations which occur without any added catalyst (Ref. 1). The fundamental idea of the "no catalyst copolymerization" is based on the fact that the reactions between nucleophiles and electrophiles in organic chemistry take place without any catalyst. In copolymerization, a polymerizable compound (M_N) having nucleophilic reactivity is combined with another polymerizable compound (M_E) having electrophilic reactivity. Interaction between M_N and M_E generates a zwitterion $^+M_N\text{-}M_E^-$ which is the key intermediate in the "no catalyst copolymerization" as shown in the following scheme of reactions.

$$^+M_N\text{-}M_E^- + {}^+M_N\text{-}M_E^- \longrightarrow \underset{\underline{1}}{{}^+M_N\text{-}M_E M_N\text{-}M_E^-} \qquad (1)$$

$$\underline{1} + {}^+M_N\text{-}M_E^- \longrightarrow \underset{\underline{2}}{{}^+M_N\text{-}(M_E M_N)_2\text{-}M_E^-} \qquad (2)$$

In general,

$$^+M_N\text{-}(M_E M_N)_m\text{-}M_E^- + n\,{}^+M_N\text{-}M_E^- \longrightarrow {}^+M_N\text{-}(M_E M_N)_{m+n+1}\text{-}M_E^- \qquad (3)$$

$(m \geq 1)$

First, two moles of the genetic zwitterion react with each other to produce the smallest propagating species $\underline{1}$ (Eq. (1)), which continues to grow by the successive reactions with the genetic zwitterions (Eqs. —— (2) and (3)). As the reaction proceeds, the concentration of the propagating zwitterions (macro zwitterion) is increased, and the reaction between two moles of macro zwitterion takes place by which the molecular weight is sharply increased (Eq. (4)).

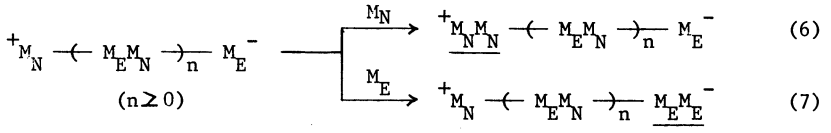
$$^+M_N\text{-}(M_E M_N)_p\text{-}M_E^- + {}^+M_N\text{-}(M_E M_N)_q\text{-}M_E^- \longrightarrow {}^+M_N\text{-}(M_E M_N)_{p+q+1}\text{-}M_E^- \qquad (4)$$

The intramolecular reaction between the cationic site and the anionic one in a single zwitterion (genetic and macro zwitterions) may occur to yield the corresponding cyclic

compound (Eq. (5)).

(5)

The above series of reactions (Eqs. (1) - (5)) give rise to the production of 1:1 alternating copolymers, $\cdots M_N M_E M_N M_E \cdots$. In addition to these reactions, the homo-propagations (ion-dipole reaction) are possible in which free monomers M_N and M_E react respectively with the cationic and anionic sites of zwitterions (Eqs. (6) and (7)).



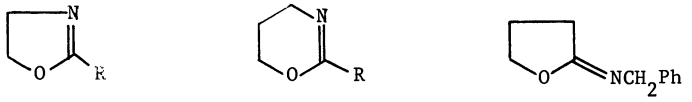
(6)

(7)

These homo-propagations are in competition with the monomer-monomer reaction between M_N and M_E producing the genetic zwitterion. Predominance of each process depends upon the reactivity characters of M_N and M_E. In case both M_N and M_E prefer the dipole-dipole reaction to produce the genetic zwitterion, alternating copolymer is formed. On the other hand, copolymer having a biased composition is formed when one or both of the ion-dipole reactions of homo-propagations (Eqs. (6) and (7)) occur concurrently with the dipole-dipole reaction.

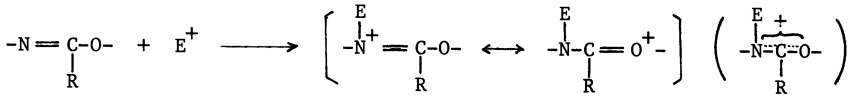
BEHAVIOR OF CYCLIC IMINO ETHERS AS NUCLEOPHILIC MONOMERS

The following three groups of imino ether monomers have been found to be reactive M_N monomers.

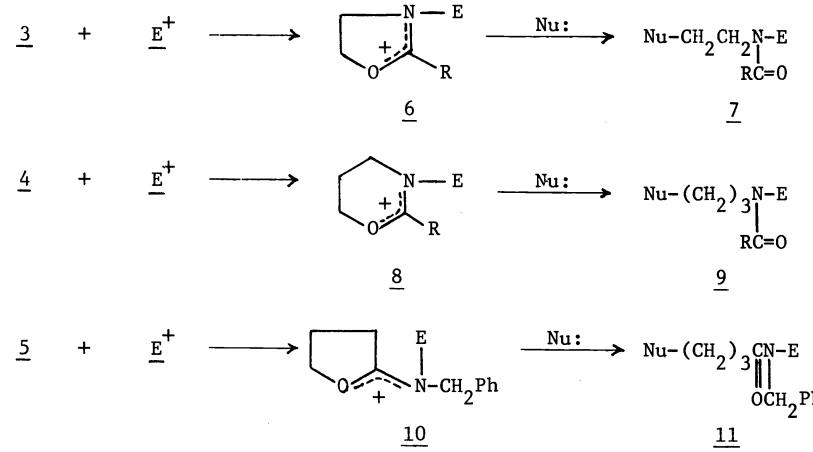


3 (Refs. 2-9) 4(Refs. 6,7,9&10) 5 (Ref. 11)

As will be discussed in the following sections, these monomers are copolymerized with eletrophilic monomers such as β-propiolactone (Refs. 2, 5, 10 & 11) ,propanesultone (Ref. 4), acrylic acid (Refs. 5 & 10), acrylamide (Ref. 6), β-(or γ-) hydroxyalkyl acrylate (Ref. 7), ethylenesulfonamide (Ref. 8) and cyclic acid anhydrides (Ref. 12). High reactivities of imino ether monomers are due to the stabilities of the products of the reactions with electrophiles, i.e., the products are being stabilized by the following resonance between ammonium and oxonium forms.



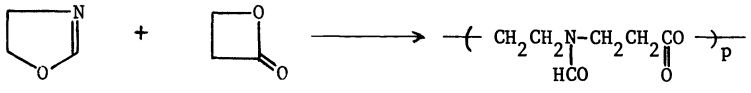
The following three structures, 6, 8 and 10, show respectively the resonance-stabilized cationic species derived from the above three monomers.



In each ring, the carbon atom, which is situated at the alpha position of the oxonium oxygen, is attached by a nucleophile, Nu: . The cationic onium rings are thus opened to produce 7, 9 and 11, respectively, which form the monomeric units in copolymers.

COPOLYMERIZATIONS OF CYCLIC IMINO ETHERS WITH β-PROPIOLACTONES AND WITH ACRYLIC ACID

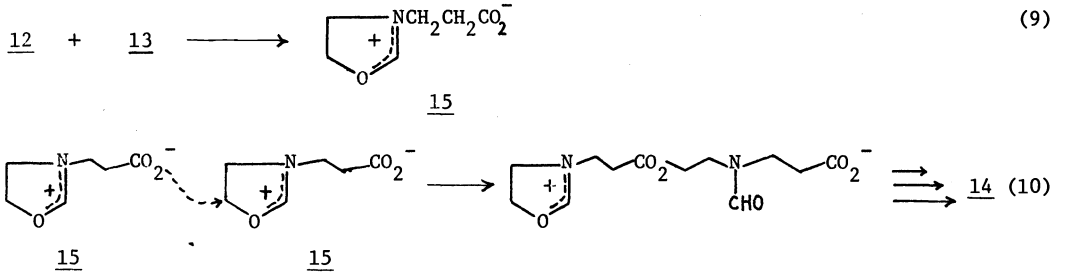
2-Oxazoline 12 is readily copolymerized with β-propiolactone 13 in an aprotic polar solvent at room temperature to produce an alternating copolymer 14 (Eq. (8)) (Ref. 2).



(8)

12 13 14

A zwitterion 15 is assumed to be the key intermediate of genetic zwitterion, which in turn is polymerized via the opening of cyclic onium group by the nucleophilic attack of the carboxylate group of other zwitterions.



(9)

(10)

15 15

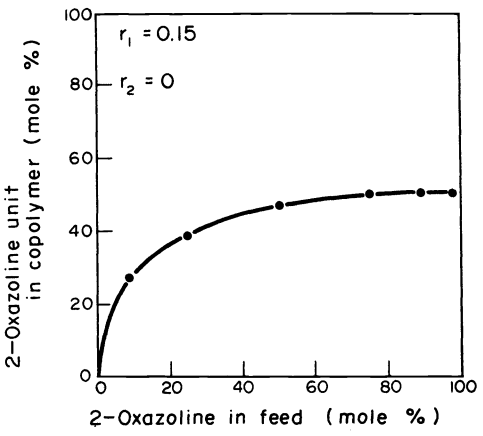


Figure 1. Copolymerization of 12 (M_2) with 13 (M_1). (40°C in DMF) (Ref. 2).

Fig. 1 shows a curve of copolymer composition with varying monomer feed ratios (Ref. 2). When the mole percent of 12 in the monomer mixture is below about 50 % (the mole percent of 13 is higher than 50 %), the monomeric unit of 13 in the copolymer exceeds 50 %. The production of copolymers containing an excess of unit 13 is due to the homo-propagation of 13 according to the general scheme of Eq. (7) which occurs concurrently with the alternating propagations (Eqs. (2) and (3) in the general scheme). The homo-propagation of 13 corresponds to the anionic homo-polymerization of 13, which has been known to be possible under the conditions of this copolymerization, i.e., in an aprotic polar solvent at room temperature. In the region where the mole fraction of 12 is higher than 0.5, however, the cationic homo-propagation of 12 has been known to be slow under these conditions (Refs. 13 & 14), and consequently 12 is consumed exclusively by its reaction with 13 to produce the alternating copolymer. The apparent values of monomer reactivity ratios were $r_1 = 0.15$ and $r_2 = 0$ at 40°C (M_1 = 13, M_2 = 12).

Figure 2 shows the variations of two parameters during the progress of the copolymerization; i.e., the solid line shows the relation between the molecular weight of the product copolymer and conversion percents and the broken line shows the change of the quotient of the amount of copolymer divided by its molecular weight (Ref. 1b). The quotient is taken to be a parameter which is proportional to the number of copolymer molecules. The number of macro-zwitterions, i.e., copolymer molecules, increases at the begining (points 1-3), then attains the maximum (point 4), and finally decreases as the conversion becomes higher (points 5-7). This variation is explained by the balance between the rate of the production of macro-zwitterion (Eq. (1) in the general scheme) and the rate of the decrease of the zwitterion molecule (Eq. (4) in the general scheme). Before point 4, the process of Eq. (1) is faster

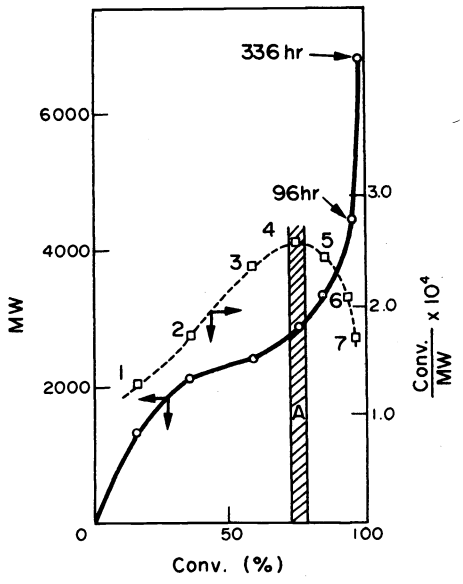
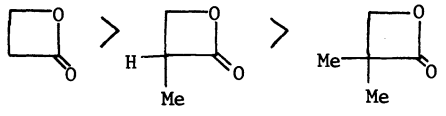


Figure 2. Alternating Copolymerization of 12 with 13 (25°C in Acetonitrile) (Ref. 1b).

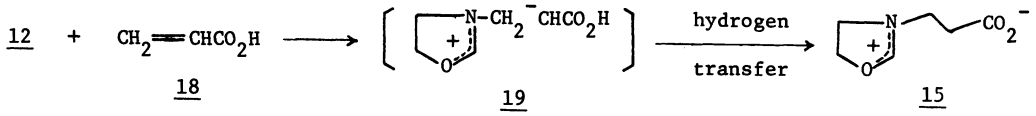
than that of Eq. (4) because the concentrations of both monomers are high (hence, the production of genetic zwitterion 15 is fast). This relationship becomes opposite after point 4 because the concentration of macro-zwitterion becomes higher and the monomer concentrations become lower. In the stage of transition (points 3-5), the change of the number of macro-zwitterion is small, where the polyaddition type processes of Eqs. (2) and (3) are predominant.

Copolymerizations of 12 with α-methyl-β-propiolactone 16 and with α,α-dimethyl-β-propiolactone 17 occurred in a similar way. The overall rates of copolymerization are in the following order (Ref. 3):



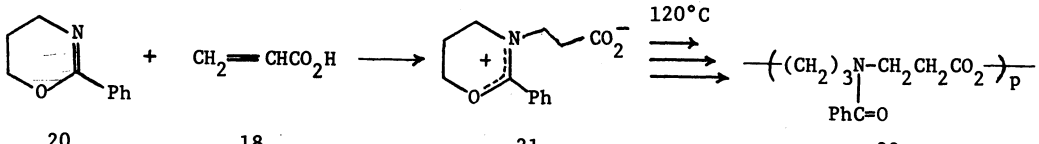
13 16 17

The above order agrees with the reactivity order of unsubstituted and substituted β-lactones towards nucleophiles (Ref. 15). This order is quite compatible with the results of kinetic studies showing that the rate-determining step of the copolymerization is the formation of genetic zwitterion such as 15 (Ref. 16). Copolymerization of 12 with acrylic acid 18 took place at 60°C in acetonitrile in the presence of a small amount of p-methoxyphenol as radical inhibitor (Ref. 5). The product was an 1:1 alternating copolymer 14 which was the same as that produced from 12 and 13. The formation of the same zwitterion 15 was assumed, which leads to the same alternating copolymer.



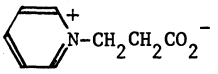
The addition of 12 to the electron-deficient double-bond of 18 forms a transient carbanion species 19 in which hydrogen transfer occurs to produce 15.

In the combination of 2-phenyl-5,6-dihydro-4H-1,3-oxazine 20 and acrylic acid 18, a zwitterion 21 was in fact isolated in the form of a crystalline solid from an equimolar mixture of 20 and 18 in acetonitrile at a lower temperature (e.g., 5°C) in comparison with the temperature range of copolymerization (above 100°C) (Ref. 9). When the isolated crystalline sample of 21 was heated at 120°C, it polymerized to produce 22 which corresponded to the 1:1 alternating copolymer between 20 and 18.



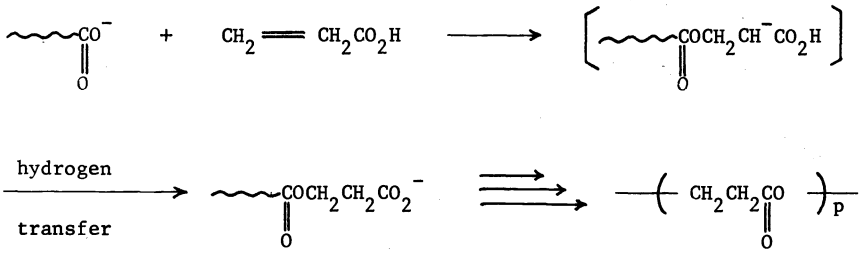
20 18 21 22

The above reaction pattern of acrylic acid, i.e., the addition of a nucleophile onto its electron deficient double bond followed by the hydrogen transfer, had not been known. Now, it has been found to be quite general. For example, a betaine 23, which used to be prepared by the reaction of pyridine with β-propiolactone, was prepared from pyridine and acrylic acid (Ref. 17).



23

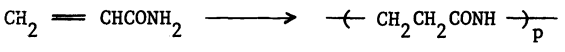
More interesting is the hydrogen-transfer polymerization of acrylic acid (Eq. (11)), which is initiated by phosphine, pyridine and other organic and inorganic bases (Ref. 18). The propagation consists of the addition of carboxylate to the double bond of the monomer followed by hydrogen transfer. The product 24 corresponds to the polymer of ring-opened β-propiolactone.



(11)

24

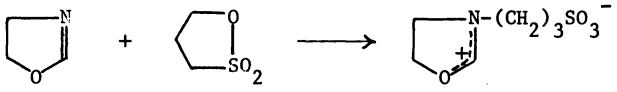
It is interesting to compare the hydrogen transfer polymerization of acrylic acid with a similar polymerization of acrylamide 25 producing poly-β-alanine (Ref. 19).



25

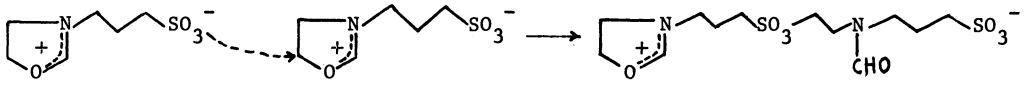
COPOLYMERIZATION OF CYCLIC IMINO ETHERS WITH PROPANESULTONE

Unsubstituted 2-oxazoline 12 was copolymerized with 3-hydroxy-1-propanesulfonic acid sultone (propanesultone) 26 at 10 - 40°C without any added catalyst. However, the copolymer formed from an equimolar feed of these two monomers contained the oxazoline unit (N-formylethylenimine) in excess, i.e., more than 66 molar percent (Ref. 4). In the following scheme involving a zwitterion 27 as the key intermediate, the homo-propagation of 12 (Eq. (14)) occurs concurrently with the alternating propagation.



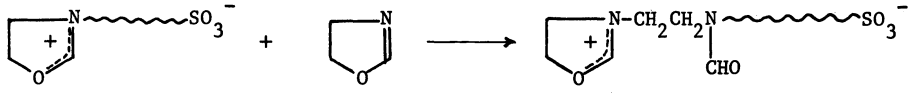
(12)

12 26 27



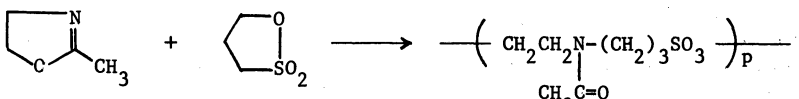
(13)

27 27



(14)

The copolymerization of 2-methyl-2-oxazoline 28 with 26 took place at 100°C in DMF. With monomer mixtures containing more than 40 molar percent of 28, 1:1 alternating copolymer 29 was produced (Ref. 4).

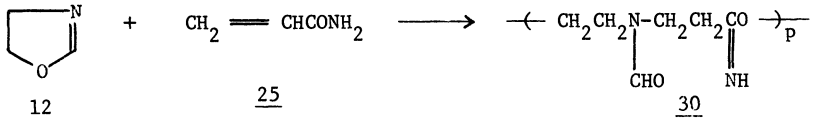


28 26 29

The nucleophilic reactivities of 12 and 28 as well as the ring-opening reactivities of the onium rings derived therefrom were compared in the respective polymerization reactions (Refs. 18 & 19). The difference in copolymer composition between the two copolymerizations 12 - 26 and 28 - 26 may be ascribed to the decreased reactivity of the onium ring derived from 28. Full elucidation of this problem requires further studies. An equimolar mixture of 20 and 26 also produced 1:1 alternating copolymer (Ref. 4).

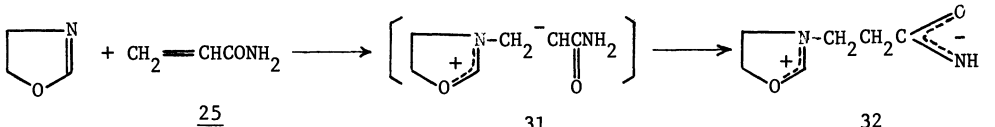
COPOLYMERIZATIONS OF CYCLIC IMINO ETHERS WITH ACRYLAMIDE AND WITH ETHYLENESULFONAMIDE

Copolymerization of 12 with acrylamide 25 occurred successfully to produce 1:1 alternating copolymer 30 (Ref. 6).

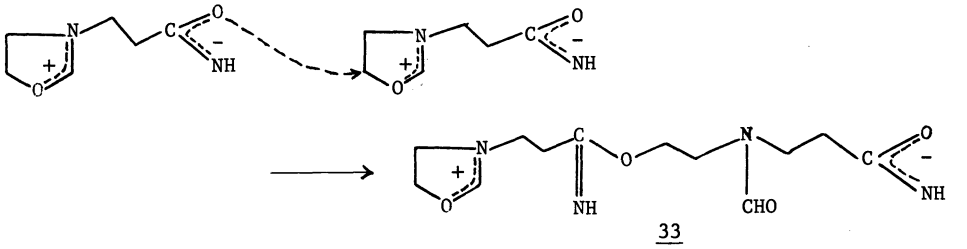


12 25 30

On the basis of the structural analysis of the product polymer 30, the following scheme of copolymerization was presented (Eqs. (15) & (16)).



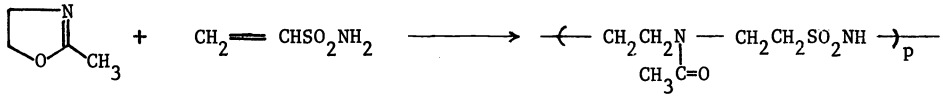
12 25 31 32 (15)



33 (16)

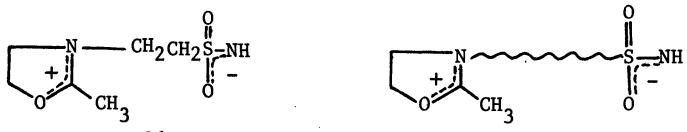
The addition of nitrogen atom of 12 onto the double-bond of acrylamide produces a transient species 31 in which hydrogen is transferred from amino group to the enolate anion center to form a zwitterion 32, the key intermediate. The anionic part of 32 is of ambident nature, i.e., the reaction of the acid amide anion with an electrophile may take place either at nitrogen or oxygen, or both of them. In the above copolymerization, the acid amide anion reacts almost exclusively at oxygen. As cyclic imino ether monomers, 2-methyl-2-oxazoline 27 and 5,6-dihydro-4H-1,3-oxazine 4 (R=H) were also copolymerized with acrylamide to produce the corresponding 1:1 alternating copolymers. The regio-specificity of the reaction of the proposed acid amide anion was similar.

On the basis of the resemblance of the reactivity between acrylamide 25 and ethylenesulfonamide 34, compound 34 was subjected to copolymerization with 2-methyl-2-oxazoline 28 (Ref. 8). As expected, an 1:1 alternating copolymer (co-oligomer) 35 was produced. The molecular weight of the product, however, was low, i.e., 300-810.



28 34 35

The structure of the sulfonamide unit of the copolymer indicates that the sulfonamide anion having ambident character in zwitterions (genetic 36 and macro 37) reacts exclusively at nitrogen.

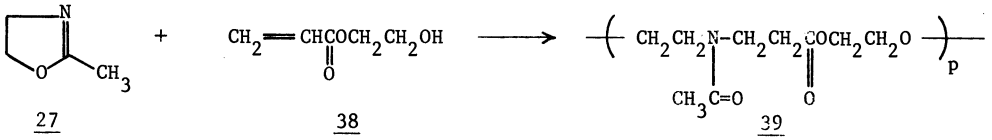


36 37

The reaction sites of acid amide anion and sulfonamide anion are opposite to each other, although the regio-specificity is very high in both cases. Understanding of this problem requires further studies.

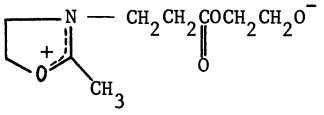
COPOLYMERIZATIONS OF CYCLIC IMINO ETHERS WITH HYDROXYALKYL ACRYLATES

The principle of the addition of a nucleophilic monomer to an electron-deficient olefin followed by hydrogen transfer from carboxyl or from amino group to the carbanion site was extended to the copolymerization of cyclic imino ether with hydroxyalkyl acrylate (Ref. 7). For example, an 1:1 alternating copolymerization occurred between 2-methyl-2-oxazoline 27 and β-hydroxyethyl acrylate 38.



27 38 39

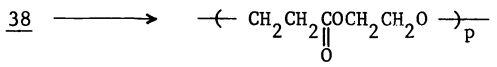
The structure of the 1:1 alternating copolymer 39 turned out as had been expected. Accordingly a zwitterion 40 was assumed to be the key intermediate.



40

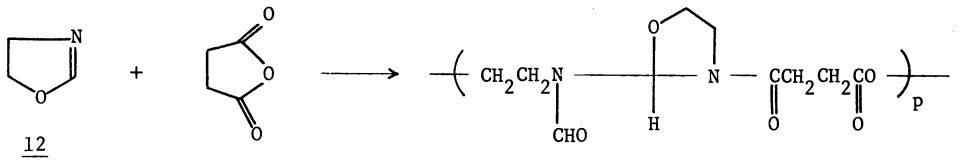
In general, the molecular weights of the product copolymers were low (i.e., 850-2390). This is attributed to chain transfer due to the abstraction of α-hydrogen of the ester group in the polymer by the alkoxide anion of zwitterion.

In relation to the copolymerization of 38, the base-catalyzed homo-polymerization of 38 was found (Ref. 20).



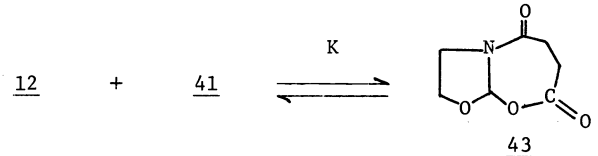
2:1 ALTERNATING COPOLYMRRIZATIONS OF 2-OXAZOLINE WITH CYCLIC ACID ANHYDRIDES

2-Oxazoline 12 was readily copolymerized with succinic anhydride 41 in acetonitrile at 35°C (Ref. 12). Interestingly the product copolymer had a 2:1 composition of (unit from 12)/(unit from 41). The copolymer structure was established by NMR and IR spectra, elemental analysis, and NMR spectroscopic identification of the products of alkaline hydrolysis.



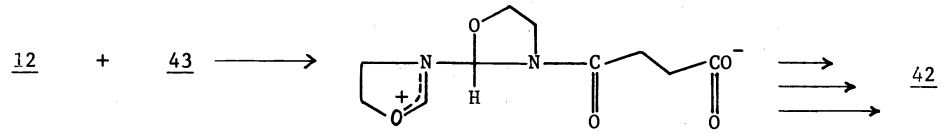
12 41 42

The 2:1 alternating copolymer was formed with monomer mixtures of feed ratios (12):(41) from 1:3 to 4:1. The following scheme of copolymerization is compatible with observations on the NMR spectrum of the reaction mixture of 12 and 41.



(17)

43



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The first step is the formation of an equimolar adduct, i.e. of the bicyclic intermediate 43 which has been found to be in equilibrium with a mixture of the two monomers (Eq. (17)).

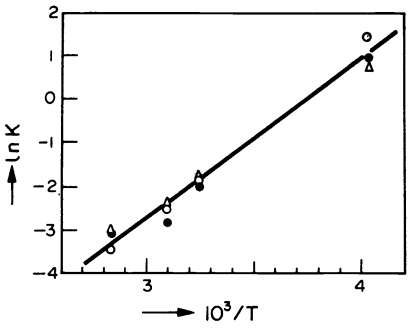
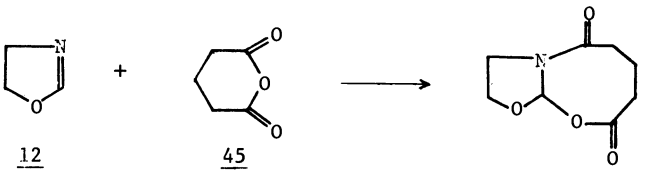


Figure 3. Temperature Dependency of K of Eq. 17 (Total monomer 2 mmol in 0.4 ml of CD_3CN). Feed ratio of 12/41: 2.0 (o), 1.0 (Δ), 0.5 (•).

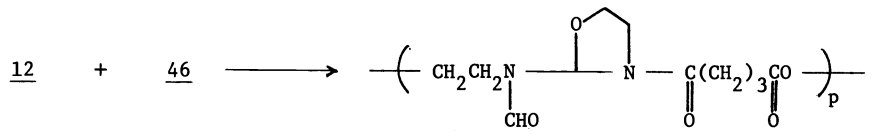
Figure 3 shows the temperature dependence of the equilibrium constant K (Ref. 12). From the straight line of the relationship of ln K vs 1/T, two thermodynamic parameters were determined, $\Delta H = -7.3$ kcal/mol, $\Delta S = -27$ cal/ deg. mol.

Then, an alternating copolymerization occurs between the second mole of 12 (as M_N) and 43 (as M_E) to produce 42. Thus, the first mole of 12 is incorporated into copolymer via ring opening and the second mole of it via the bond opening of the carbon-nitrogen double bond.

In the combination of 12 and glutaric anhydride 45 at 0°C in acetonitrile, a bicyclic intermediate 46 was isolated in quantitative yield, which was copolymerized with 12 at 80°C to produce the 2:1 alternating copolymer 47.



12 45 46



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