

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

No Catalyst Copolymerization by Spontaneous Initiation. A New Method of Preparation of Alternating Copolymers

Takeo Saegusa^a; Shiro Kobayashi^a; Yoshiharu Kimura^a; Hiroharu Ikeda^a

^a Department of Synthetic Chemistry Faculty of Engineering, Kyoto University, Kyoto, Japan

To cite this Article Saegusa, Takeo , Kobayashi, Shiro , Kimura, Yoshiharu and Ikeda, Hiroharu(1975) 'No Catalyst Copolymerization by Spontaneous Initiation. A New Method of Preparation of Alternating Copolymers', Journal of Macromolecular Science, Part A, 9: 5, 641 – 661

To link to this Article: DOI: 10.1080/00222337508065887

URL: <http://dx.doi.org/10.1080/00222337508065887>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

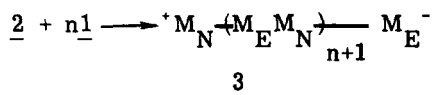
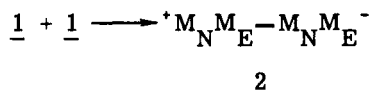
No Catalyst Copolymerization by Spontaneous Initiation. A New Method of Preparation of Alternating Copolymers

TAKEO SAEGUSA, SHIRO KOBAYASHI, YOSHIHARU KIMURA,
and HIROHARU IKEDA

Department of Synthetic Chemistry
Faculty of Engineering
Kyoto University
Kyoto, Japan 606

ABSTRACT

A new type of copolymerization is presented which proceeds without any added catalyst. A monomer of nucleophilic reactivity (M_N) is mixed with the second monomer having electrophilic reactivity (M_E) to produce a zwitterion $^+M_N-M_E^-$ (1), which is responsible for initiation as well as propagation. By the following scheme of reactions, alternating copolymer is formed.



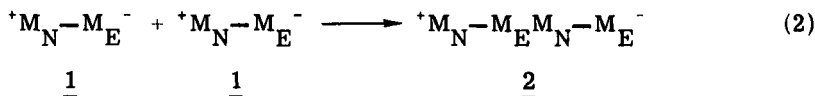
Sometimes the reactions between zwitterion species 1, 2, and 3 with free monomer occur, which give rise to the formation of copolymer having a biased composition. Cyclic imino ethers, exoimino cyclic ether, and azetidine have been explored as the M_N comonomers. β -Propiolactone, cyclic anhydride, sultone (sulfolactone), acrylic acid, acrylamide, and β -hydroxyethyl acrylate have successfully been adopted as the M_E comonomers. Copolymerization occurred without any catalyst with all combinations of M_N and M_E monomers, and various alternating copolymers were produced. Several important results which explicate the new concept are presented and discussed.

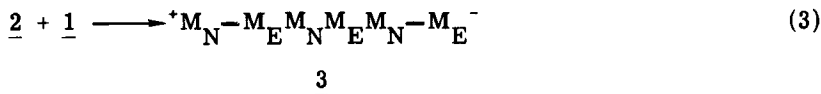
INTRODUCTION

Usually the initiation of polymerization requires a catalyst. This paper describes a new concept of copolymerization which proceeds without any added catalyst. An ionic initiating species is generated by the interaction of two comonomers. For this type of copolymerization, the combination of two comonomers is essential. One monomer (M_N) must have nucleophilic reactivity and the other (M_E) must possess electrophilic reactivity. From M_N and M_E , a zwitterion ${}^+M_N-M_E^-$ is generated, which functions as the initiator:

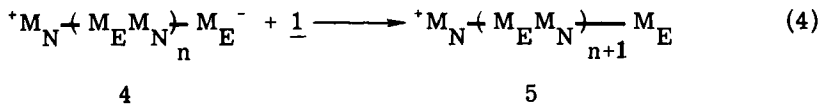


The genetic zwitterion 1 is responsible not only for initiation but also for propagation. The following series of reactions lead to the formation of alternating copolymer:



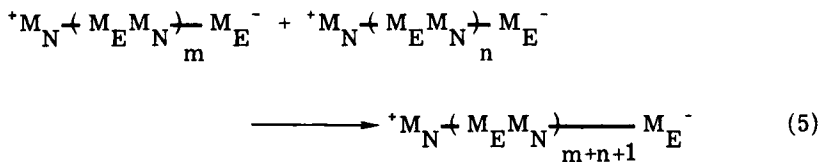


Generally,

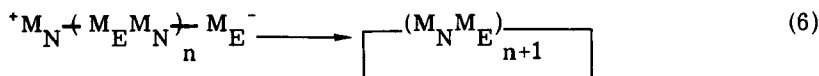


First, 2 moles of the genetic zwitterion 1 react with each other to produce an oligomeric zwitterion 2 (Eq. 2). Then the oligomeric zwitterion 2 grows to be polymeric (4 and 5) by its reaction with the genetic zwitterion 1 (Eqs. 3 and 4). Hereafter, the oligomeric zwitterions (2 and 3) and polymeric ones (4 and 5) are called "macrozwitterion" which are differentiated from the genetic zwitterion 1. As to the sites of the reaction between the macrozwitterion and the genetic zwitterion, there are two possibilities, i.e., the reaction between the cationic site of the macrozwitterion and the anionic site of the genetic one, and vice versa.

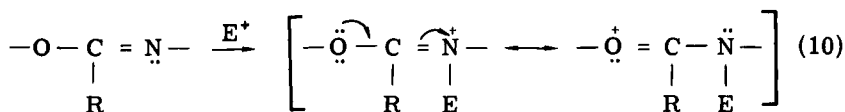
In addition to the propagation involving the genetic zwitterion, the intermolecular and intramolecular reactions of macrozwitterion may be considered to occur. The intermolecular reaction between macrozwitterions (Eq. 5) increases the molecular weight of alternating copolymer without consuming the monomer.



The possibility of an intramolecular reaction between the cationic and anionic sites in a single macrozwitterion may not be excluded, which leads to the formation of a macrocyclic molecule:

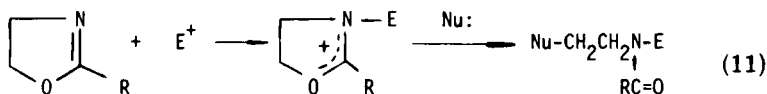


Three of four M_N monomers contain an imino ether (imidate) group as the functional group responsible for the reaction with M_E monomers. The high reactivity of imino ether may be ascribed to the stabilization of the product onium due to resonance between the oxonium and ammonium structures.



E = electrophile

The cyclic onium ring thus formed is opened by the attack of a nucleophile (:Nu) onto the carbon atom at the α -position of the oxonium oxygen, e.g.:



M_E monomers have a wider variety of functional groups. Some are cyclic compounds and some are electron-deficient olefins. By the nucleophilic attack of M_N , lactone and cyclic acid anhydride are opened to form the genetic zwitterion consisting of carboxylate anion, e.g.,

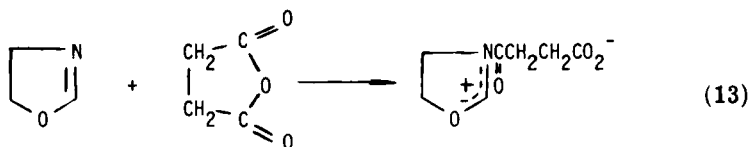
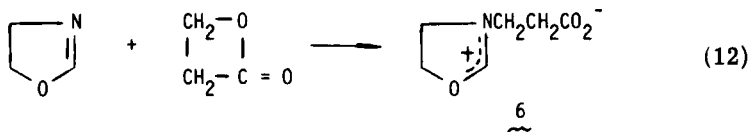
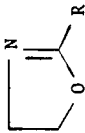
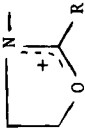
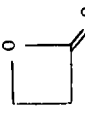
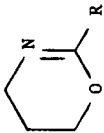
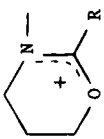

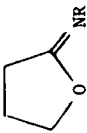
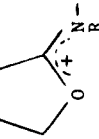
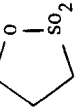
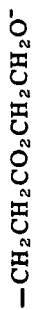
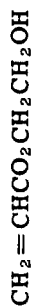
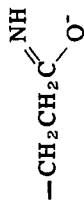
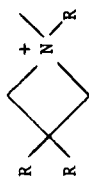
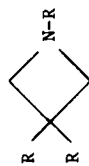
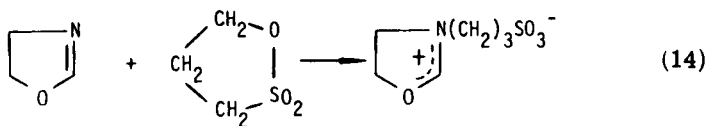


TABLE 1. Variety of Monomers of Spontaneous Initiation Copolymerization

M_N	$^+M_N^-$	M_E	$-M_E^-$
			$-\text{CH}_2\text{CH}_2\text{CO}_2^-$
			$-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CO}_2^-$
			$-(\text{CH}_2)_3\text{SO}_3^-$

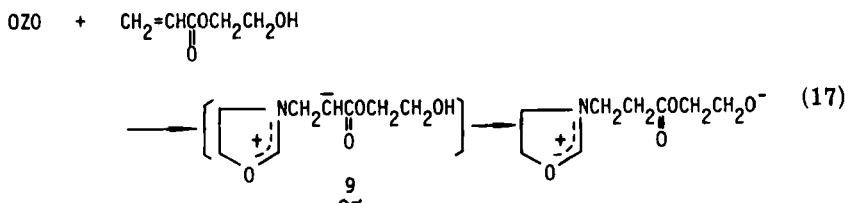
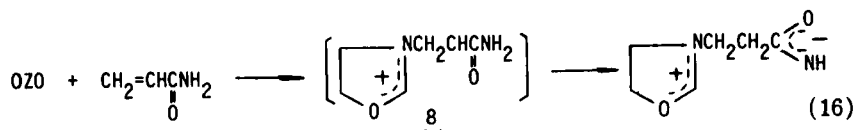
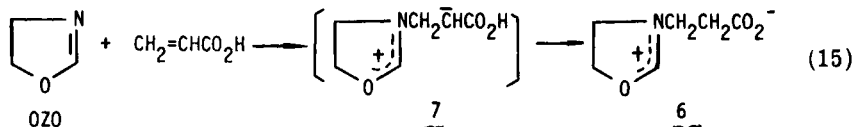


Sulfolactone (sultone) is opened to produce the sulfonate zwitterion:

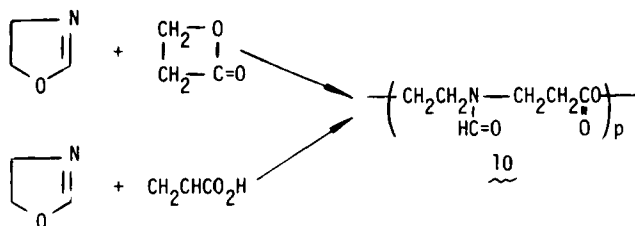


The nucleophilic reactivity of the sulfonate group, however, is not high. Alternating copolymerizations with sultone usually require higher reaction temperatures.

Acrylic acid, acrylamide, and β -hydroxyethyl acrylate behave as M_E monomer in an interesting way. M_N monomer adds to the α, β -unsaturated bond of these M_E monomers to produce the transient carbanionic zwitterion which, following proton transfer, leads to the more stable zwitterion, e.g.:



It is quite interesting to note that the key zwitterion 6 produced from 2-oxazoline (OZO) and acrylic acid is the same as that generated from 2-oxazoline and β -propiolactone (BPL). Accordingly, the structure of the alternating copolymer 10 from acrylic acid and OZO is the same as that produced from BPL and OZO:



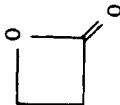
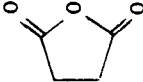
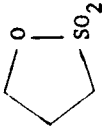
The detailed mechanism of proton transfer to the carbanion site in the transient zwitterion (7-9) has not been clarified. There are two possibilities: the direct rearrangement in the transient zwitterion and the indirect proton transfer which proceeds via the acidic hydrogen of the free monomer.

From four M_N monomers and six M_E monomers, 24 pairs of combinations can be constructed (Table 2). Fourteen of these pairs have been examined. In all combinations examined, no catalyst copolymerization occurred without an added catalyst. Alternating copolymers were not always obtained. As has been discussed before, the character of copolymerization, i.e., the arrangements of two kinds of monomeric unit in the copolymer, is dependent upon the natures of the monomers involved. In Table 2, A indicates the cases in which alternating copolymers are produced under a wide variety of reaction conditions, B means that alternating copolymers are obtained under suitable conditions of reaction, and C designates the combinations in which alternating copolymer has not been accomplished. The following part of this paper describes several experimental findings which are reasonably explained by the general principle proposed in the preceding section.

Alternating Copolymerization of 2-Oxazoline with β -Propiolactone

When OZO was mixed with an equimolar amount of BPL in an aprotic polar solvent at 40°C, the solution gradually became

TABLE 2. Copolymerizations between M_N and M_E Monomers^a

M_N	M_E						
			$\text{CH}_2=\text{CHCO}_2\text{H}$	$\text{CH}_2=\text{CHCNH}_2$	$\text{CH}^2=\text{CHCO}_2-$ $\text{CH}_2\text{CH}_2\text{OH}$		
1 (Refs. 1-3) R = H (B) Me (C) Ph (C)	5 (Ref. 8) R = H (A)	9 (Ref. 4) R = H (C) Me (B)	13 (Ref. 9) R = H (A) Me (A)	17 (Refs. 11, 12) R = H (A) Me (A)	21 (Ref. 13) R = H (B)		
2 (Refs. 4, 5) R = H (B) Me (C) Ph (C)	6	10	14 (Ref. 4) R = H (A) Me (A) Ph (A)	18 (Refs. 11, 12) R = H (A)	22 (Ref. 13) R = H (A)		
3 (Ref. 6) R = CH_2Ph (B)	7	11	15 (Ref. 6) R = CH_2Ph (A)	19	23		
4 (Ref. 7) R = Me (C)	8	12	16 (Ref. 10) R = Me (A)	20	24		

^a(A): Alternating copolymers are readily produced under a wide variety of conditions.

(B): Alternating copolymers are produced under suitable conditions.

(C): Copolymerizations occur without catalyst, but alternating copolymers have not been produced.

viscous and the 1:1 alternating copolymer 10 was produced [1]:



The structure of the alternating copolymer 10 has been established by its IR and NMR spectra as well as by alkaline (NaOH) hydrolysis experiment. The NMR spectrum of the alkaline hydrolysis product of the copolymer in D₂O was identical with that of an equimolar mixture of the authentic Na salts of formic acid and N-(β-hydroxyethyl)-β-alanine.

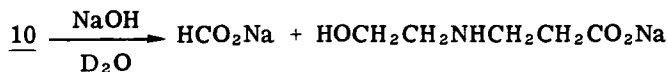


Figure 1 shows the composition curve of the OZO-BPL copolymerization in DMF at 40°C. The 1:1 alternating copolymer is obtained when the mole fraction of OZO in the feed monomers mixture is higher than about 0.5. At lower fractions of OZO in the monomer feed, copolymers consisting of more than 50 mole % BPL units are formed. This experimental finding is satisfactorily explained on the basis of two competitive propagations, i.e., the propagation at

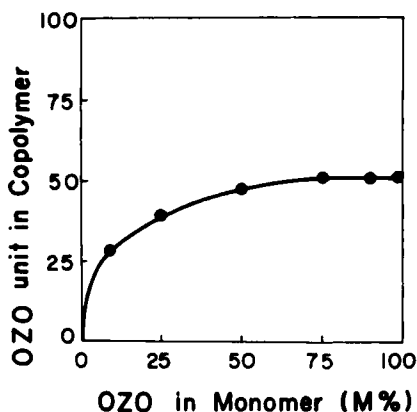
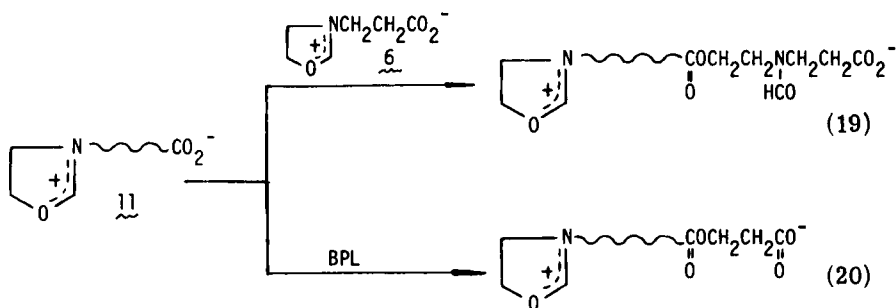


FIG. 1. OZO-BPL copolymerization in DMF at 40°C [1].

the carboxylate end of zwitterion **11** with the genetic zwitterion (Eq. 19) and the propagation with free BPL (Eq. 20).



At lower fractions of OZO in the monomer mixture, the concentration of the genetic zwitterion **6** is lower because its production rate is lower and the concentration of free BPL is higher. These two factors favor propagation with free BPL. Considering the reaction conditions of the anionic polymerization of BPL [14], the ring-opening process of BPL by carboxylate anion (Eq. 20) is deemed quite possible even under these mild conditions. On the other hand, the reaction between the oxazolinium ring and free OZO is assumed to be negligible [15].

Table 3 shows some results which illustrate the solvent effect upon the OZO-BPL alternating copolymerization with an equimolar feed. Qualitatively, the rate of copolymerization is higher in polar solvents than in nonpolar solvents. The results are compatible with the assumption that the rate of formation of the genetic zwitterion **6** is decisive in determining the overall rate. In general, the formation of ionic species from two neutral molecules is favored in polar solvents.

Figure 2, in which the average molecular weight and the quotient of the conversion percent divided by the molecular weight are plotted against the percent conversion, represents the growth of copolymer molecule during the course of copolymerization with 1:1 monomer feed. The quotient is an index which is proportional to the number of copolymer molecules. In these plots, a transient Region A is observed. The molecular weight, as well as the number of copolymer molecules, continues to increase up to Region A.

TABLE 3. Effect of Solvent on the Copolymerization of OZO with BPL^a [1]

Solvent	Copolymerization yield (%)	OZO in copolymer (mole %)
DMF	70	47
CH ₃ CN	39	52
CH ₂ ClCH ₂ Cl	26	50
n-Bu ₂ O	29	45
Toluene	9	46

^aOZO = BPL = 7.5 mmoles in 2 ml of solvent at 40°C for 3 hr.

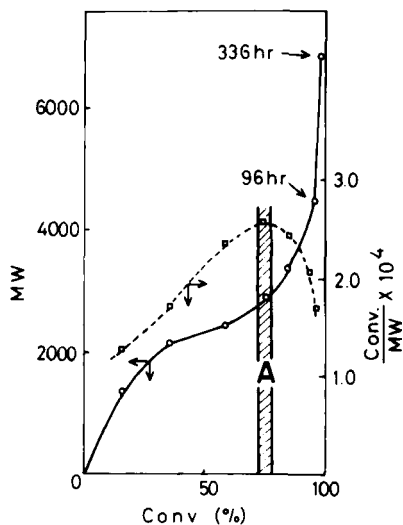
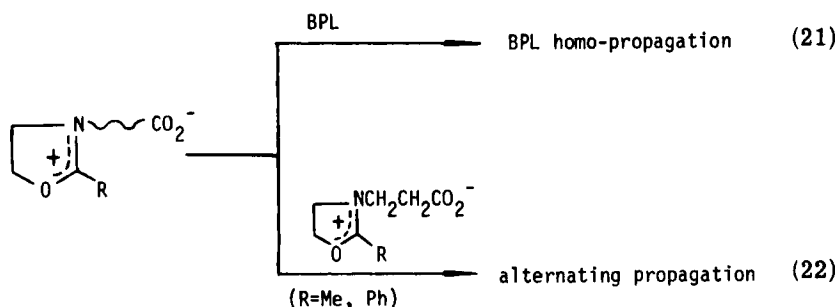


FIG. 2. OZO-BPL alternating copolymerization in acetonitrile at 25°C [11].

After Region A the increase of molecular weight becomes sharp, and the number of copolymer molecules begins to decrease. These plots are also compatible with the general scheme of Eqs. (1)-(5). As the reaction proceeds, the concentration of monomers continues to decrease and the concentration of macrozwitterions increases. Before Region A the rate of increase of macrozwitterions by the process of Eq. (2) prevails over the rate of decrease of macrozwitterions by the process of Eq. (5). After Region A the rate of the process of Eq. (5) exceeds that of the process of Eq. (2), and hence the number of copolymer molecules begins to decrease.

In Table 4 the OZO-BPL copolymerization is compared with the copolymerizations of BPL with 2-methyl-2-oxazoline (MeOZO) and with 2-phenyl-2-oxazoline (PhOZO). Even with an equimolar feed of monomers, copolymerizations with substituted 2-oxazolines produces copolymers containing more than 50 mole % BPL units. These results are also explained by the competitive processes of propagation in the general scheme (Eqs. 7-9).



The ring-opening reactivities of 2-methyl- and 2-phenyl-substituted oxazolinium rings have been found to be less than that of the unsubstituted one [15]. Thus the process of Eq. (21) predominates over the alternating propagation of Eq. (22). A similar tendency of substituent effects has been observed in the copolymerization of BPL with six-membered cyclic imino ethers of unsubstituted, 2-methyl-, and 2-phenyl-5,6-dihydro-4H-1,3-oxazines [4].

Table 5 illustrates the effect of methyl substitution at the α -carbon of BPL on the overall rate of the OZO-BPL copolymerization. The qualitative order of the relative rates of 1:1 alternating copolymerization of OZO with BPL, with α -methyl- β -propiolactone (MeBPL),

TABLE 4. Copolymerization of BPL with 2-Oxazolines^a [1]

2-Oxazoline	Copolymer yield (%)	2-Oxazoline in copolymer (mole %)
OZO	70	47
MeOZO	52	11
PhOZO	23	4

^a2-Oxazoline = BPL = 3.8 mmoles in DMF at 40°C for 3 hr.

TABLE 5. Copolymerization of OZO with β -Lactones^a [2]

β -Lactone	Time (hr)	Yield (%)	Mol wt	β -Lactone in copolymer (mole %)
BPL	25	61	3500	50
MeBPL	27	42	4000	50
Me ₂ BPL	45	21	3610	56

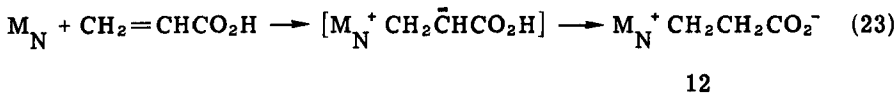
^a β -Lactone = OZO = 7.5 mmoles in 2.0 ml of acetonitrile at 10 to 20°C.

and with α,α -dimethyl- β -propiolactone (Me₂BPL) is BPL > MeBPL > Me₂BPL. The unfavorable effect of the methyl substituent has been reported in the anionic polymerization of substituted and unsubstituted propiolactones, in which the ring opening of lactone by the nucleophilic attack of carboxylate controls the rate [14]. The overall rate of the alternating copolymerizations of lactones with OZO is controlled by the rate of the zwitterion formation, which is also the ring-opening process of lactone by a nucleophile of OZO [2].

Alternating Copolymerizations of Acrylic Acid with M_N Monomers

Acrylic acid is copolymerized successfully with four M_N monomers to produce the respective alternating copolymers. This is an

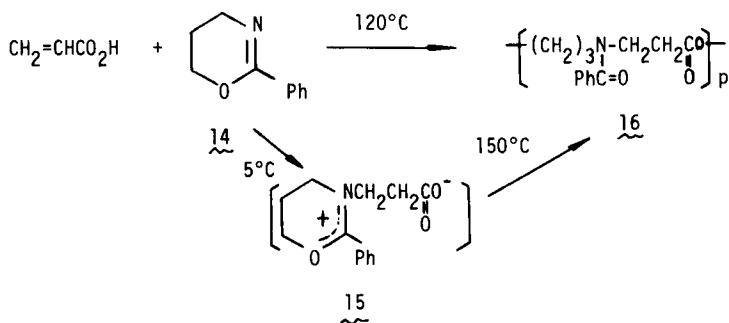
interesting example of copolymerization between heterocyclic monomers and olefinic monomers. As the key intermediates of this alternating copolymerization, zwitterions of the onium-carboxylate structures (12) are assumed, which are generated according to the following general process:



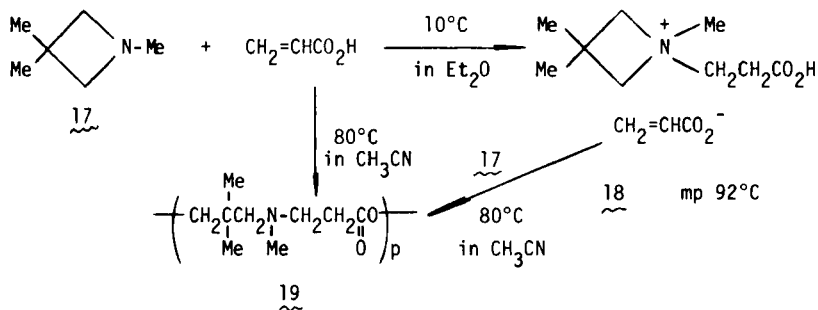
This mechanism has been supported by several experimental findings. First, betaine (13) was isolated as a crystalline material (mp 131 to 132°C) from pyridine and acrylic acid (Eq. 24), which used to be prepared from pyridine and BPL [9]:



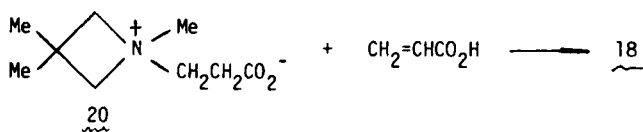
From a mixture of acrylic acid and 2-phenyl-5,6-dihydro-4H-1,3-oxazine (14) in acetonitrile at lower temperatures, e.g., 5°C, a zwitterion of 15 was isolated in a monohydrated form, mp 145 to 146°C. When 15 was heated at 150°C, 15 was converted quantitatively into the alternating copolymer 16, which was also produced by the direct alternating copolymerization of acrylic acid with 14 at 120°C.



Concerning the alternating copolymerization of acrylic acid with 1,3,3-trimethylazetidinium (17), a cyclic ammonium salt (18) was isolated from a reaction mixture in Et₂O at a lower temperature, e.g., 10°C.

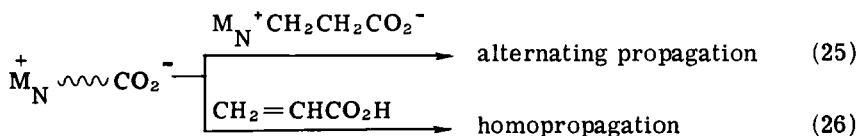


Isolation of 18 is taken as support to the intermediacy of the zwitterion 20, from which 18 is readily derived by the proton transfer between 20 and free acrylic acid. Heating of an equimolar mixture of a salt (18)



and another mole of 17 afforded alternating copolymer 19 [10].

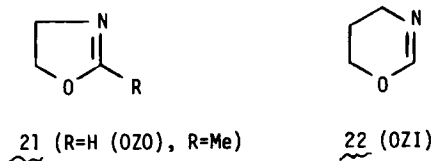
Unlike β -propiolactone, acrylic acid is reluctant to react with carboxylate anion under moderate reaction conditions. The homopropagation of acrylic acid (Eq. 26) scarcely occurs, and the alternating propagation (Eq. 25) is strongly favored in the following competitive processes:



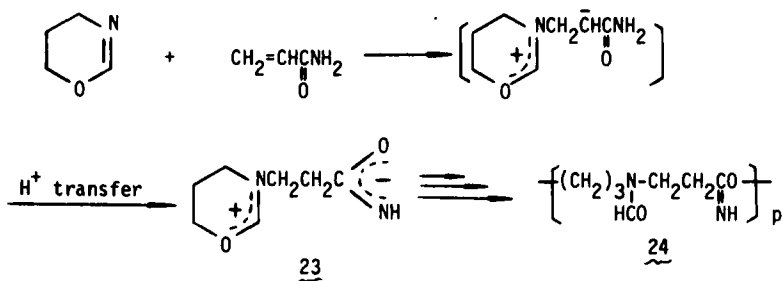
A strong indication of support of this consideration has been obtained, e.g., in the copolymerization of 2-benzyliminotetrahydrofuran (BIT) with acrylic acid (AA) and with BPL in acetonitrile, apparent copolymerization parameters of $\gamma_{\text{BIT}} = \gamma_{\text{AA}} = 0.00$ at 100°C and $\gamma_{\text{BIT}} = 0.00$ and $\gamma_{\text{BPL}} = 0.65$ at 50°C were determined [6].

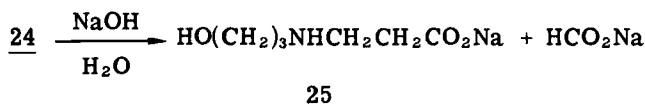
Alternating Copolymerizations of Acrylamide with Cyclic Imino Ethers

Copolymerization of acrylamide with cyclic imino ethers (21 and 22) presents another interesting example of alternating copolymerizations between heterocyclic monomers and olefinic monomers.

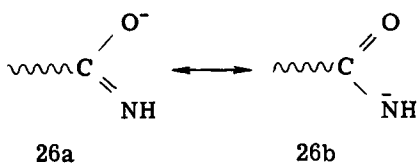


In the alternating copolymers, the acrylamide unit is incorporated as a structure of imidate group. The structures of alternating copolymers were established by IR and NMR spectra as well as the NMR identification of the alkaline hydrolysis mixture of copolymers. For example, the NMR spectrum of alkaline hydrolysis products of the alternating copolymer from acrylamide and 22 was identical with that of an equimolar mixture of the authentic salts of N-(γ -hydroxypropyl)- β -alanine (25) and formic acid. Thus the following scheme of alternating copolymerization is constructed:

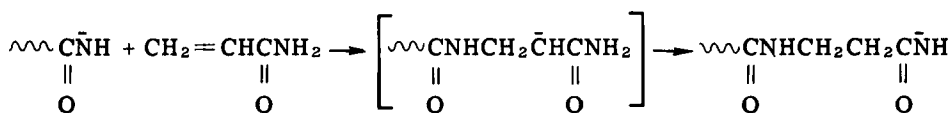




The amide anion part of zwitterion is of an ambient nature, having the two canonical forms of 26a and 26b which reacts in the form of 26a in the above copolymerization.

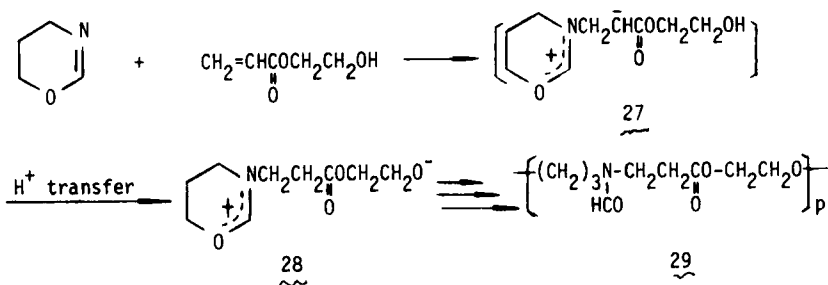


The above behavior of amide anion has been interestingly compared with the homopolymerization of acrylamide by strong base catalysts, in which the propagating species of amide anion reacts at the nitrogen site [12].



Alternating Copolymerizations of β -Hydroxyethyl Acrylate with Cyclic Imino Ethers

β -Hydroxyethyl acrylate (BHEA) is a reactive M_E monomer which is copolymerized readily with OZO and with OZI to give the corresponding alternating copolymers. The alternating copolymerization of BHEA with OZI is explained by the following reaction scheme in which the key intermediate of a zwitterion (28) is derived by the hydrogen transfer from the hydroxyl group to the carbanion center of the transient zwitterion 27. The structure of copolymer 29 corresponds to the 1:1:1 terpolymer of OZI-BPL-ethylene oxide.



In the present paper, no catalyst copolymerization by spontaneous initiation mechanism has been discussed, for the emphasis has been on the synthesis of alternating copolymers. On the basis of the general principle, there may be further possibilities of exploring other M_N and M_E monomers to develop new combinations of copolymerizations.

REFERENCES

- [1] T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, **5**, 354 (1972).
- [2] T. Saegusa, S. Kobayashi, and Y. Kimura, Ibid., **7**, 1 (1974).
- [3] T. Saegusa, Y. Kimura, and S. Kobayashi, Presented at 30th Annual Meeting of the Chemical Society of Japan, Osaka, April 1974.
- [4] T. Saegusa, Y. Kimura, H. Ikeda, S. Hirayanagi, and S. Kobayashi, Macromolecules, **8** (May/June 1975).
- [5] T. Saegusa, Y. Kimura, and S. Kobayashi, Presented at 29th Annual Meeting of the Chemical Society of Japan, Hiroshima, October 1973.
- [6] T. Saegusa, Y. Kimura, K. Sano, and S. Kobayashi, Macromolecules, **7**, 546 (1974).
- [7] T. Saegusa, Y. Kimura, and S. Kobayashi, Unpublished Results.
- [8] T. Saegusa, Y. Kimura, and S. Kobayashi, Presented at 28th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1973.
- [9] T. Saegusa, S. Kobayashi, and Y. Kimura, Macromolecules, **7**, 139 (1974).

- [10] T. Saegusa, Y. Kimura, S. Sawada, and S. Kobayashi, Ibid., 7, 956 (1974).
- [11] T. Saegusa, Y. Kimura, and S. Kobayashi, Presented at 23rd Annual Meeting of the Society of Polymer Science, Japan, June 1974.
- [12] T. Saegusa, S. Kobayashi, and Y. Kimura, Macromolecules, 8 (May/June 1975).
- [13] T. Saegusa, S. Kobayashi, and Y. Kimura, Unpublished Results.
- [14] Y. Yamashita, Y. Ishikawa, and T. Tsuda, Kogyo Kagaku Zasshi, 67, 252 (1964).
- [15] T. Saegusa, H. Ikeda, and H. Fujii, Polym. J., 4, 87 (1973).