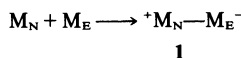


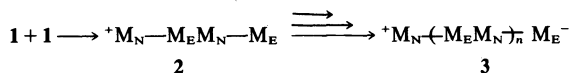
# NO CATALYST COPOLYMERIZATION BY SPONTANEOUS INITIATION MECHANISM

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**Abstract**—A new type of copolymerization is presented here, which requires no added initiator. A zwitterion **1** is generated by the interaction between two monomers; one monomer has nucleophilic reactivity ( $M_N$ ) and the other possesses electrophilic reactivity ( $M_E$ ).



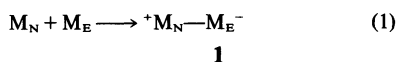
Two moles of the genetic zwitterion **1** react with each other to produce a dimeric zwitterion **2**.



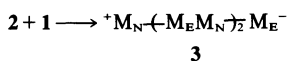
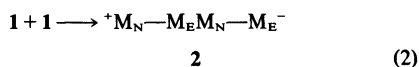
The dimeric zwitterion **2** grows by its reaction with **1** to polymeric zwitterion **3**. Intermolecular reaction of macro-zwitterions (dimeric **2** and polymeric **3**) also occurs, which brings about a sharp increase in molecular weight. In a series of studies, six  $M_N$  monomers and six  $M_E$  monomers have been investigated. As the  $M_N$  monomer, cyclic imino ether, exo-imino cyclic ether, azetidine, Schiff base and cyclic phosphonite have been selected. As the  $M_E$  monomer, lactone, cyclic anhydride, sultone (sulfolactone), acrylic acid, acrylamide and  $\beta$ -hydroxyethyl acrylate have been successfully used. Thus, thirty-six combinations (six times six) of copolymerization have now become conceivable. The present paper gives a survey of elemental reactions of selected combinations of copolymerization. The emphasis is laid on the discussions of recent results.

## 1. GENERAL SCHEME OF THE NEW CONCEPT

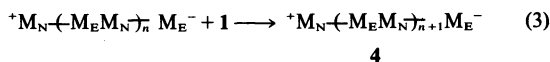
Usually polymerization and copolymerization require a so-called initiator. Recently we have explored a new type of copolymerization which does not require an initiator. In this new copolymerization, a zwitterion **1** is generated by the interaction between the two monomers; one monomer ( $M_N$ ) has nucleophilic reactivity and the other ( $M_E$ ) possesses electrophilic reactivity (eqn 1).



The genetic zwitterion **1** is responsible for initiation as well as for propagation. The following scheme shows the growth of the genetic zwitterion into the macro-zwitterions **2-4** having the structure of an alternating copolymer.

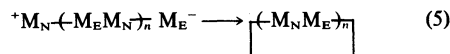
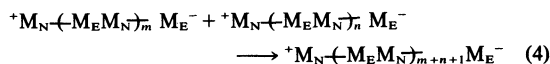


In general,



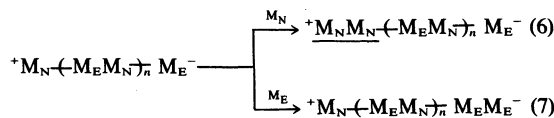
As to the site of the reaction between macro-zwitterions **2-4** and the genetic zwitterion **1**, there are two possibilities, i.e. the reaction between the cationic site of **2-4** and the anionic site of **1** and *vice versa*.

In addition to the above reactions, intermolecular (eqn 4) and intramolecular (eqn 5) reactions of the macro-zwitterion may possibly occur.



The intermolecular reaction gives rise to a sharp increase in the molecular weight. The intramolecular reaction leads to the production of cyclic molecules.

In some cases, the alternating arrangement of  $M_N$  and  $M_E$  units is disturbed by the following homo-propagation between the zwitterion and free monomer.



Reactions of eqns (6) and (7) are competitive with the alternating propagation (eqn 3). The relative contributions of these reactions are determined by the relative reactivities and concentrations of the respective species. In case where the propagation with the genetic zwitterion occurs exclusively, the alternating copolymer is produced.

## 2. VARIETY OF NUCLEOPHILIC AND ELECTROPHILIC MONOMERS

The new type of copolymerization has two novel features, i.e. the occurrence of the reaction without added initiator and the production of alternating copolymers. The

Table 1. Structures of  $M_N$  monomers, cationic species and monomeric units

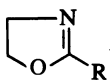
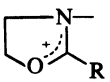
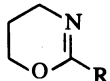
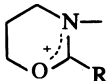
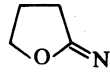
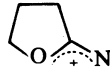


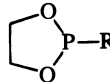
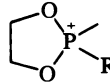
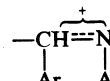



$M_N$ monomers	Cationic species	Monomeric units
		$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{N---} \\   \\ \text{RC=O} \end{array}$
		$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{CH}_2\text{N---} \\   \\ \text{RC=O} \end{array}$
		$\begin{array}{c} \text{---(CH}_2\text{)}_3\text{CN---} \\    \\ \text{OR} \end{array}$
		$\begin{array}{c} \text{---CH}_2\text{CR}_2\text{CH}_2\text{N---} \\   \\ \text{R} \end{array}$
		$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{OP---} \\    \\ \text{O} \end{array}$
$\text{Ar---CH=N---Ar}'$		$\begin{array}{c} \text{---CH---N---} \\   \quad   \\ \text{Ar} \quad \text{Ar}' \end{array}$

Table 2. Structures of  $M_E$  monomers, anionic species and monomeric units

$M_E$ monomers	Anionic species	Monomeric units
	$\text{---CH}_2\text{CH}_2\text{CO}_2^-$	$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{CO---} \\    \\ \text{O} \end{array}$
	$\text{---C(=O)CH}_2\text{CH}_2\text{CO}_2^-$	$\begin{array}{c} \text{---C(=O)CH}_2\text{CH}_2\text{CO---} \\    \quad \quad    \\ \text{O} \quad \quad \quad \text{O} \end{array}$
	$\text{---(CH}_2\text{)}_3\text{SO}_3^-$	$\text{---(CH}_2\text{)}_3\text{SO}_3\text{---}$
$\text{CH}_2=\text{CHCO}_2\text{H}$	$\text{---CH}_2\text{CH}_2\text{CO}_2^-$	$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{CO---} \\    \\ \text{O} \end{array}$
$\text{CH}_2=\text{CHC(=O)NH}_2$	$\text{---CH}_2\text{CH}_2\text{C(=O)NH}^-$	$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{CO---} \\   \\ \text{NH} \end{array}$ or $\text{---CH}_2\text{CH}_2\text{CNH---}$
$\text{CH}_2=\text{CHCOCH}_2\text{CH}_2\text{OH}$	$\text{---CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{O}^-$	$\text{---CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{O---}$

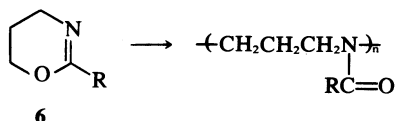
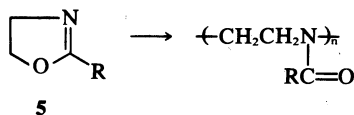
former character is always assumed, whereas the latter is not always realized. Research for the monomers is decisive to the progress of this new copolymerization. The following points are to be considered in the efforts of searching for the monomers. First, the monomers should have the required thermodynamic polymerizability as well as enough reactivity as nucleophile or electrophile to generate the zwitterion. Secondly, the alternating copolymerization is realized when the monomers are consumed only by the reaction between the two monomers to produce genetic zwitterion. The reactions of monomers with the ionic sites of the zwitterion should not occur. In other words, the dipole-dipole reaction of two monomers should predominate over the dipole-ion reaction of a monomer with a zwitterion. Some heterocyclic and unsaturated compounds having high polarizability may satisfy these conditions.

In a series of studies, six  $M_N$  monomers and six  $M_E$  monomers have been explored. Tables 1 and 2 show  $M_N$  and  $M_E$  monomers, respectively, and the structures of the ionic groups derived from them, as well as the structures of the monomeric units in copolymers. The derivation of some ionic groups and monomeric units are discussed in the subsequent parts of this paper.

From six  $M_N$  monomers and six  $M_E$  monomers, 36 varieties of combinations of copolymerization are possible. Among 36 combinations 20 essential ones have been investigated.<sup>15</sup> The results are summarized in Table 3. In all 20 combinations which we have examined, copolymerization occurred without any added initiator. The pairs of 16 boxes without note have not been examined yet. The character of copolymerization, i.e. whether it is alternating or not, depends upon the nature of monomers concerned as well as reaction conditions. In Table 3, letter A in parentheses in several boxes designates the cases in which alternating copolymerization occurred under a wide variety of reaction conditions, letter B means that an alternating copolymer was obtained under suitable conditions of reaction, and letter C designates the cases in which alternating copolymerization has not been realized. In the subsequent part of this paper, several important findings are presented, which are well explained by the general principle of the new copolymerization.

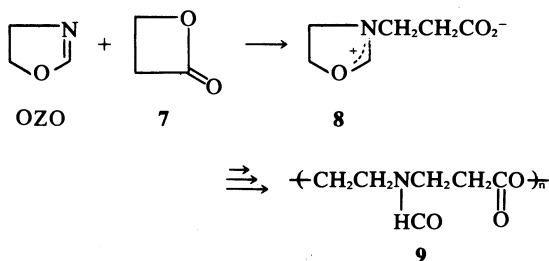
### 3. COPOLYMERIZATION OF CYCLIC IMINO ETHERS WITH $M_E$ MONOMERS (Boxes Nos. 1-12)

2-Oxazoline (OZO) 5 (R = H) and 5,6-dihydro-4H-1,3-oxazine (OZI) 6 (R = H), and their substituted derivatives at the 2-positions are reactive nucleophilic monomers, whose ring-opening propagation involves rearrangement and produces the corresponding poly(*N*-acylalkylenimines).<sup>16</sup>

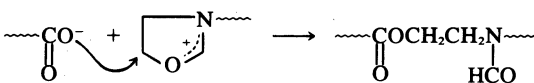


When OZO was mixed with an equimolar amount of  $\beta$ -propiolactone (BPL) 7 in an aprotic polar solvent such as

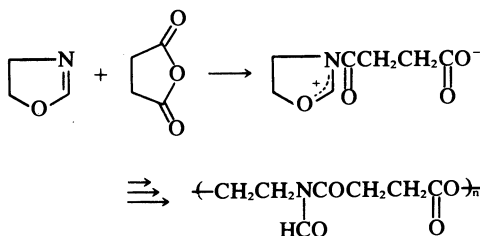
DMF at ambient temperature, the solution gradually became viscous and the 1:1 alternating copolymer 9 was produced.<sup>1</sup> On the basis of various experimental findings,<sup>1-3</sup> a reaction scheme involving a zwitterion 8 as the key intermediate was proposed.



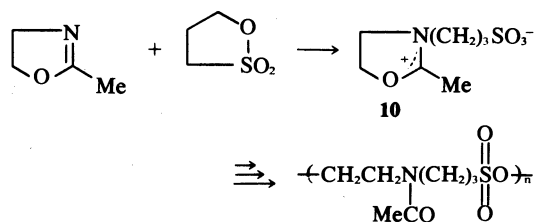
In the reaction between zwitterions (both genetic and polymeric zwitterions), the oxazolinium ring is opened to an *N*-formylethylenimine unit by the nucleophilic attack of carboxylate anion of another zwitterion.



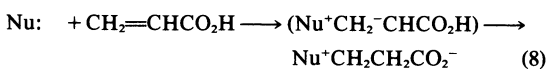
For the combination of OZO and succinic anhydride (Box No. 2), the following scheme was presented.<sup>4</sup>



Similarly, the alternating copolymerization of 2-methyl-2-oxazoline (MeOZO) 5 (R = Me) with 3-hydroxy-1-propanesulfonic acid lactone (Box No. 3) is well explained by the following scheme in which an oxazolinium sulfonate zwitterion 10 is the key intermediate.<sup>5</sup>

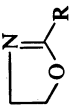



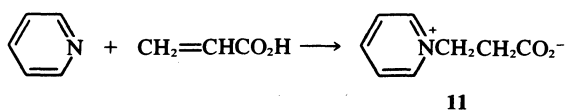
Copolymerizations of cyclic imino ethers with acrylic acid (Boxes Nos. 4 and 10) contain a new elementary reaction, i.e. the addition of a nucleophile to the double bond of acrylic acid followed by proton-transfer (eqn 8).



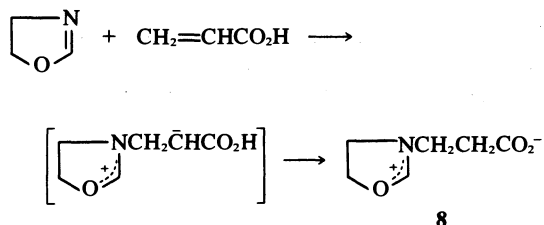
In fact, betaine 11 (m.p. 131-132°C), which used to be prepared from pyridine and BPL was produced from pyridine and acrylic acid.

Table 3. Combinations of  $M_N$  and  $M_E$  monomers

$M_N$	$M_E$		
		$CH_2=CHCO_2H$	$CH_2=CHCOCH_2CH_2OH$
1 (refs. 1-3) R = H (B) Me (C) Ph (C)	2 (ref. 4) R = H (A)	3 (ref. 5) R = H (C) Me (B)	4 (ref. 6) R = H (A) Me (A)
5 (ref. 7) R = H (A) Me (A)	6 (ref. 8) R = H (B)	7 (ref. 9) R = H (C) Me (C) Ph (C);	8 (ref. 10) R = H (A) Me (A) Ph (A)
9 (ref. 11) R = Me (C)	10 (ref. 12) R = Ph (A)	11 (ref. 13) R = Me (A)	12 (ref. 14) R = Ph (A)
13 (ref. 15) R = CH <sub>2</sub> Ph (B)	14 (ref. 16) R = CH <sub>2</sub> Ph (A)	15 (ref. 17) R = Me (A)	16 (ref. 18) R = Ph (A)
17 (ref. 19) R = Me (C)	18 (ref. 20) R = Me (C)	19 (ref. 21) R = Me (C)	20 (ref. 22) R = Me (C)
21 (ref. 23) R = Ph (A)	22 (ref. 24) R = Me (A)	23 (ref. 25) R = Me (A)	24 (ref. 26) R = Me (A)
25 (ref. 27) R = Me (A)	26 (ref. 28) R = Me (A)	27 (ref. 29) R = Me (A)	28 (ref. 30) R = Me (A)
29 (ref. 31) R = Me (C)	30 (ref. 32) R = Me (A)	31 (ref. 33) R = Me (C)	32 (ref. 34) R = Me (A)
33 (ref. 35) R = Me (C)	34 (ref. 36) R = Me (B)	35 (ref. 37) R = Me (A)	36 (ref. 38) R = Me (A)

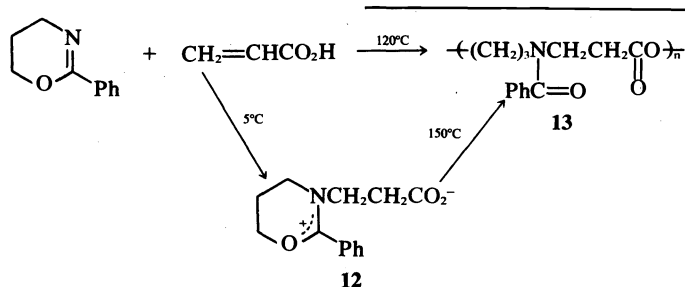


A mixture of OZO and acrylic acid in  $\text{CH}_3\text{CN}$  at  $50^\circ\text{C}$  produced the 1:1 alternating copolymers having the same structure 9 as that produced from OZO and BPL. The genetic zwitterion 8 was the same as that generated from OZO and BPL.

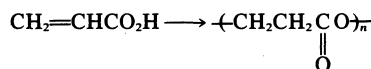


The above is an interesting example of the 1:1 alternating copolymer between a heterocyclic monomer and a vinyl compound.

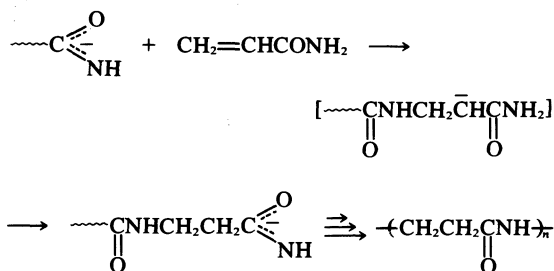
From a mixture of acrylic acid and 2-phenyl-5,6-dihydro-4H-1,3-oxazine 6 ( $\text{R} = \text{Ph}$ ) in  $\text{CH}_3\text{CN}$  at  $5^\circ\text{C}$ , a zwitterion 12 was isolated in a monohydrated form, m.p. 145–146. When 12 was heated at  $150^\circ\text{C}$ , it was converted into the 1:1 alternating copolymer 13 which was also produced directly from the two monomers at  $120^\circ\text{C}$ .



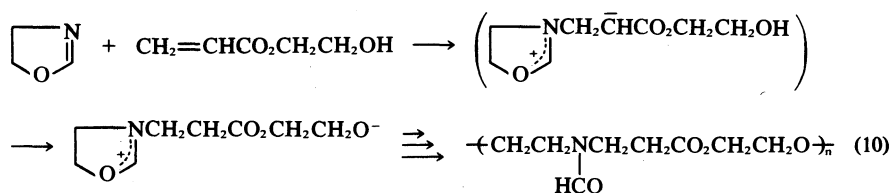
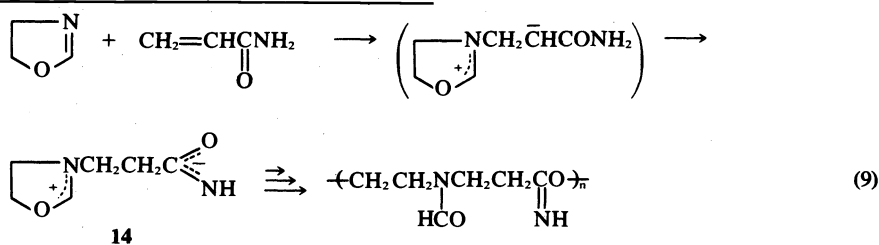
have various applications in organic synthesis, had not been known before the present series of studies. On the basis of this reaction, we found the hydrogen-transfer polymerization of acrylic acid to polyester at a higher temperature (e.g.  $120^\circ\text{C}$ ).<sup>17</sup> The product polymer is the same as that produced by the ring-opening polymerization of BPL.



The above pattern of polymerization of acrylic acid resembles that of the hydrogen transfer polymerization of acrylamide to poly- $\beta$ -alanine.<sup>18</sup>



The hydrogen-transfer process was assumed also in the formation of key intermediates 14 and 15, respectively, in the alternating copolymerizations of OZO with acrylamide (eqn 9) and with  $\beta$ -hydroxyethyl acrylate (eqn 10).



The above finding was taken as a strong support for the general scheme of our new copolymerization.

The elementary reaction of eqn (8) which may also

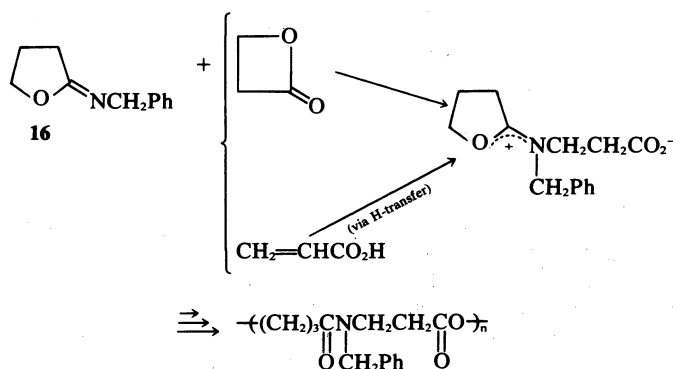
The reaction site of the anionic part of zwitterion 14 in eqn (9) is interesting. The amide anion reacts at its oxygen atom but not at nitrogen. This finding constitutes a sharp

contrast to the propagation of the anionic hydrogen-transfer polymerization of acrylamide in which the amide anion reacts at its nitrogen to produce poly- $\beta$ -alanine (*vide supra*).

Thus, an example is presented here, in which the reaction site of an ambident anion changes according to the nature of the electrophile.

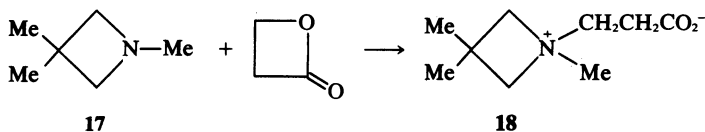
#### 4. COPOLYMERIZATIONS OF 2-IMINOTETRAHYDROFURAN WITH BPL AND WITH ACRYLIC ACID (Boxes Nos. 13 and 16)<sup>10</sup>

2-Benzyliminotetrahydrofuran **16** also contains an imino ether as the group responsible for ring-opening. Its copolymerizations with BPL and with acrylic acids are formulated as follows.

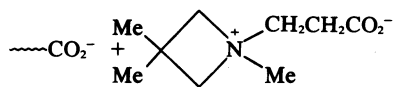


#### 5. COPOLYMERIZATIONS OF AZETIDINE WITH BPL AND WITH ACRYLIC ACID (Boxes Nos. 19 and 22)<sup>11</sup>

The pair of 1,3,3-trimethylazetidine **17** and BPL gave a copolymer consisting mostly of the BPL unit. The genetic



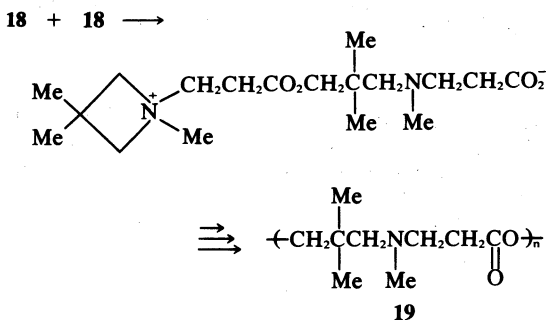
zwitterion **18** may reasonably be assumed, but the anionic homo-propagation of BPL from **18** predominates over the successive additions of the genetic zwitterions onto the carboxylate anion. The production of the BPL-rich copolymer is due to the decreased reactivity of the cyclic ammonium of the genetic zwitterion.



The results were quite similar to those of the experiments of Wilson *et al.*<sup>19</sup> in which pivalolactone was polymerized by a cyclic tertiary amine to produce a copolymer consisting mostly of the pivalolactone units.

Unlike BPL, acrylic acid gave the 1:1 alternating copolymer of **19** with **17**. Hydrogen transfer after the addition of **17** to the electron-deficient olefinic bond of acrylic acid gives rise to the generation of zwitterion **18**. Then the addition of **18** onto the propagating zwitterion

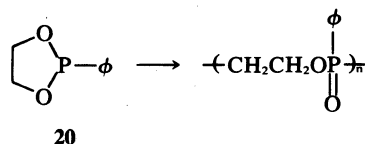
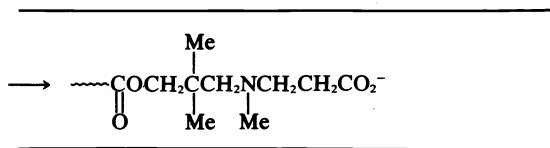
occurs exclusively to produce **19**, i.e.



The sequence of two units of acrylic acid is not formed because the addition of carboxylate anion onto acrylic acid hardly occurs at the temperature of copolymerization (80°C).

#### 6. COPOLYMERS OF ETHYLENE PHENYLPHOSPHONITE WITH BPL, WITH ACRYLIC ACID AND WITH ACRYLAMIDE (Boxes Nos. 25, 28 and 29)<sup>12</sup>

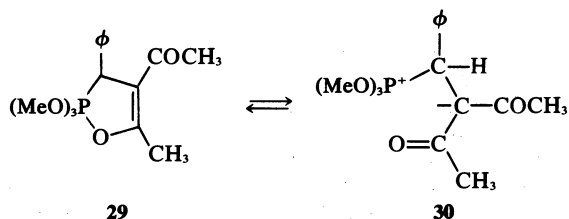
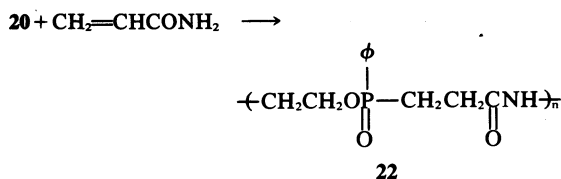
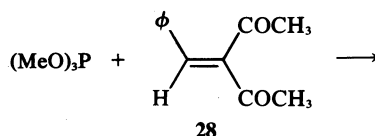
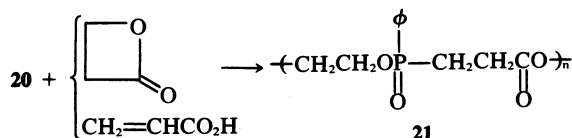
Homo-polymerization of ethylene phenylphosphonite (EPP) **20** is known, which proceeds through the propagation of an Arbusov type rearrangement.<sup>20,21</sup>



In this series of studies, EPP was employed as a nucleophilic monomer, which was successfully

copolymerized with BPL, with acrylic acid and with acrylamide to produce the respective alternating copolymers **21** and **22**.<sup>12</sup>

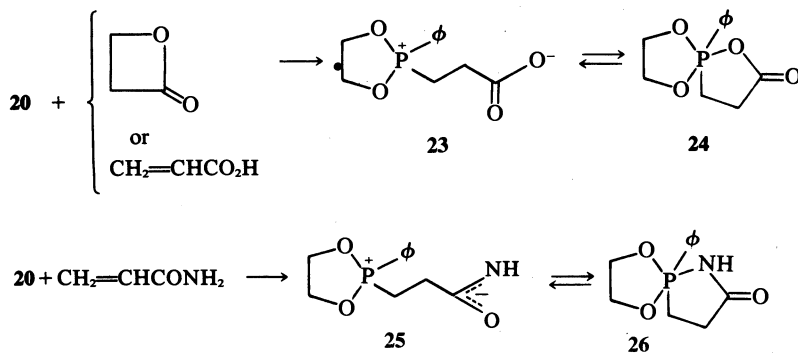
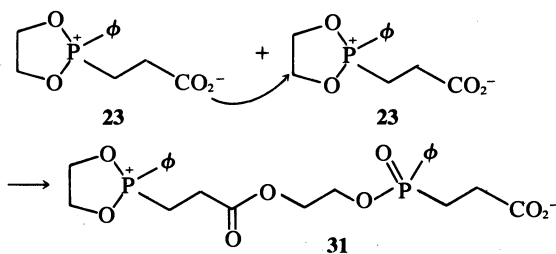
phosphite to an electron deficient olefin **28** is to be cited.<sup>22</sup> It is described that the adduct **29** is equilibrated with a zwitterion **30** at 140°C.



The copolymerization was performed in an aprotic polar solvent such as DMF, PhCN and CH<sub>3</sub>CN at higher temperatures (120–150°C). The structures of the alternating copolymers were established by i.r. and NMR spectra of the copolymer. In the case of **22**, the copolymer's structure was further confirmed by the NMR identification of its alkaline hydrolysis product. Similarly to the copolymerizations with cyclic imino ethers, the pairs of EPP-BPL and EPP-acrylic acid produce the same copolymers.

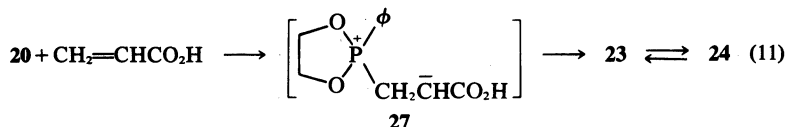
At lower temperatures (room temperature to ~50°C), the following adducts, **24** and **26** were isolated as hygroscopic crystalline solids in high yields (70–90%).

When the isolated adducts, **24** and **26**, were heated in bulk or in DMF at 150°C, the polymers **21** and **22** were produced, respectively, in almost quantitative yields.



The formation of **24** and **26** is explained by the addition of **20** to the acrylic olefin bonds followed by hydrogen-transfer, e.g.

Thus, the adducts are reasonably deemed as the key intermediates, which react in the forms of zwitterions, **23** and **25**. The reaction between two molecules of **23** is



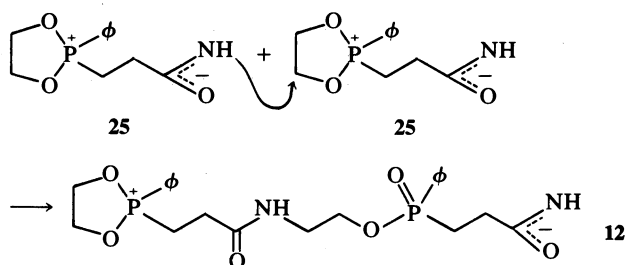
The structures of **24** and **26** were established by i.r. and <sup>1</sup>H NMR spectra as well as elemental analysis. The IR spectrum of **24** (KBr pellet) showed no absorption due to carboxylate anion (in the vicinities of 1600 and 1400 cm<sup>-1</sup>). The amide linkage of **26** is supported by the IR absorptions at 3400 cm<sup>-1</sup> (ν<sub>NH</sub> weak and broad), 3175 cm<sup>-1</sup> (ν<sub>NH</sub> of lactam, medium intensity and broad), 1680 cm<sup>-1</sup> (ν<sub>C=O</sub> of amide, strong) and 1065 cm<sup>-1</sup> (ν<sub>O-C</sub>, strong). As to the scheme of eqn (11), the addition of trimethyl

formulated according to the scheme of the Arbusov reaction.

Thus the propagating zwitterion **31** is formed.

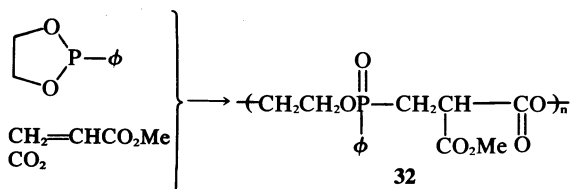
In a similar fashion, the scheme for reaction **25** is given below, in which the amide anion of one zwitterion reacts at its nitrogen atom with the phosphonium ring of another zwitterion.

The reaction site of the amide anion in eqn (12) is different from that in eqn (9) where the oxygen of the amide

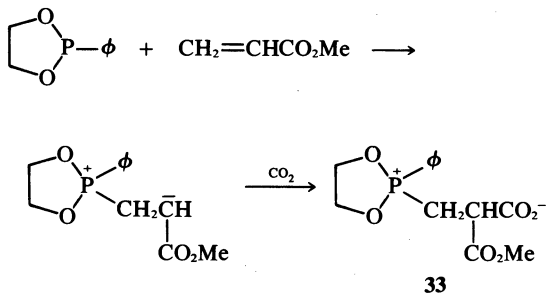


anion is the reaction site. Rationalization of this difference is the subject of future interest.

An interesting extension of the above copolymerizations of **20** is the 1:1:1 alternating terpolymerization of the combination of three monomers of **20**, methyl acrylate and  $\text{CO}_2$ .<sup>23</sup> In DMF or PhCN, an equimolar mixture of **20** and methyl acrylate under a 50 kg/cm<sup>2</sup> pressure of  $\text{CO}_2$  at 120–150°C gave the terpolymer **32** (molecular weight 1000–2000).

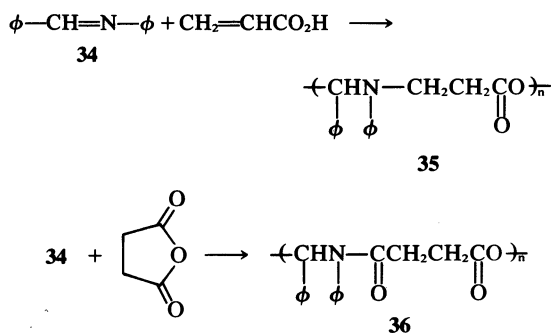


The phosphonium-carboxylate zwitterion **33** consisting of the three components may be assumed as the key intermediate of this new terpolymerization.



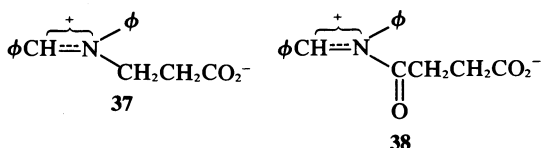
#### 7. COPOLYMERIZATIONS OF SCHIFF BASE WITH $\text{M}_2$ MONOMERS (Boxes Nos. 31, 32 and 34)<sup>14</sup>

A Schiff base of *N*-benzilidenaniline **34** was successfully copolymerized with acrylic acid and with succinic anhydride, a cyclic acid-anhydride.



Alternating copolymers **35** and **36** (molecular weight ~900) were obtained in moderate yields. The following

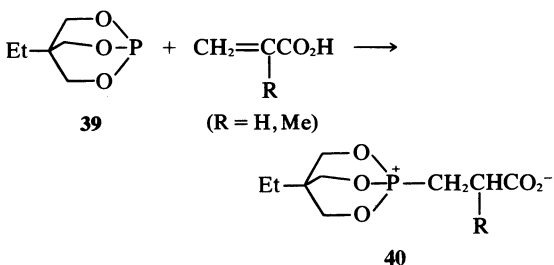
two zwitterions, **37** and **38**, may be taken to explain the structures of the respective copolymers.



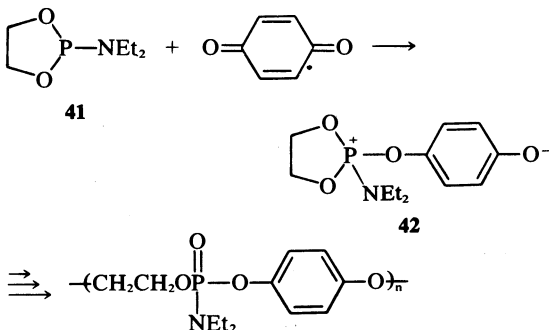
The combination of **34** and BPL produced polymers consisting mostly of the BPL units.

The new concept has been very useful in the explorative studies of new copolymerizations. On the basis of this concept, various new copolymerizations have been discovered. In the literature, there are several interesting studies which should be mentioned here in relation to the present concept. Copolymerization of cyclic amine and pivalolactone reported by Wilson and Beaman<sup>19</sup> has been mentioned already. Kagiya *et al.*<sup>24</sup> reported the alternating copolymerization of *N*-acetylaziridine with BPL without added catalyst, for which the zwitterion mechanism was presented.

A patent of Rohm and Haas<sup>25</sup> described a co-oligomer from a bicyclic phosphite **39** and acrylic or methacrylic acid in the presence of acetic anhydride. A phosphonium zwitterion **40** was suggested as the key intermediate, although complex reactions were assumed besides simple zwitterion propagation.



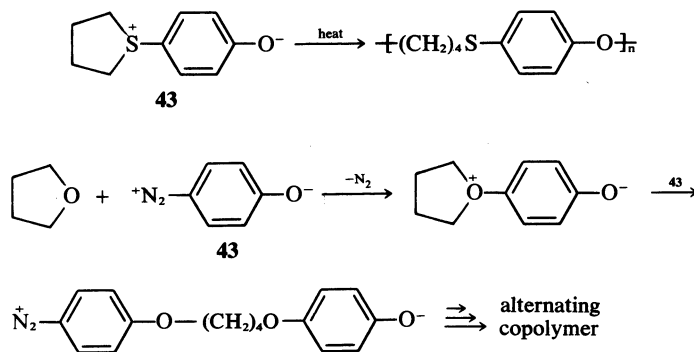
A Japanese patent<sup>26</sup> claims the alternating copolymerization between a cyclic phosphite **41** and *p*-benzoquinone, for which the intermediacy of a zwitterion **42** may be postulated.





The "death-charge" polymerization<sup>27</sup> of **43** is also to be referred to here, which starts with the isolated monomer of a zwitterion **43**.

The alternating copolymerization between tetrahydrofuran and 1,4-diazophenoxide **43**<sup>28</sup> is another instance which is related to our copolymerization.



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- <sup>15</sup>Results at an early stage of studies on this copolymerization have been summarized in an article, T. Saegusa, S. Kobayashi, Y. Kimura and H. Ikeda, *J. Macromol. Sci., Chem.* **A9** (1975).
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