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 (MN) and the other possesses electrophilic reactivity (ME).

\[ 	ext{MN} + \text{ME} \rightarrow \text{MN}^\equiv \text{ME} \]

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

\[ 1 + 1 \rightarrow \text{MN}^\equiv \text{ME} \]

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 MN monomers and six ME monomers have been investigated. As the MN monomer, cyclic imino ether, exo-imino cyclic ether, azetidine, Schiff base and cyclic phosphonite have been selected. As the ME 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 (MN) has nucleophilic reactivity and the other (ME) possesses electrophilic reactivity (eqn 1).

\[ 	ext{MN} + \text{ME} \rightarrow \text{MN}^\equiv \text{ME} \]

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.

\[ 1 + 1 \rightarrow \text{MN}^\equiv \text{ME} \]

\[ 2 + 1 \rightarrow \text{MN}^\equiv \text{ME} \]

In general,

\[ \text{MN}^\equiv \text{ME} + 1 \rightarrow \text{MN}^\equiv \text{ME} \]

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.

\[ \text{MN}^\equiv \text{ME} \rightarrow \text{MN}^\equiv \text{ME} \]

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 MN and ME units is disturbed by the following homo-propagation between the zwitterion and free monomer.

\[ \text{MN}^\equiv \text{ME} \rightarrow \text{MN}^\equiv \text{ME} \]

\[ \text{MN}^\equiv \text{ME} \rightarrow \text{MN}^\equiv \text{ME} \]

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.
### Table 1. Structures of MN monomers, cationic species and monomeric units

<table>
<thead>
<tr>
<th>MN monomers</th>
<th>Cationic species</th>
<th>Monomeric units</th>
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### Table 2. Structures of ME monomers, anionic species and monomeric units

<table>
<thead>
<tr>
<th>ME monomers</th>
<th>Anionic species</th>
<th>Monomeric units</th>
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<td><img src="image" alt="Structure 22" /></td>
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<td><img src="image" alt="Structure 24" /></td>
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<td><img src="image" alt="Structure 25" /></td>
<td><img src="image" alt="Structure 26" /></td>
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</tbody>
</table>

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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 co-polymerization 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. The results are summarized in Table 3. In all 20 combinations which have been 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 $M_N$ 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). 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. On the basis of various experimental findings, a reaction scheme involving a zwitterion 8 as the key intermediate was proposed.

$$\begin{align*}
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\text{5} & \quad \text{R} \\
\end{align*}$$

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

$$\begin{align*}
\text{CO}^- & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\text{8} & \\
\end{align*}$$

For the combination of OZO and succinic anhydride (Box No. 2), the following scheme was presented.

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.

$$\begin{align*}
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{Me} \\
\text{6} & \quad \text{R} \\
\end{align*}$$

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).

$$\begin{align*}
\text{Nu} & \quad + \text{CH}_2=\text{CHCO}_2\text{H} \quad \rightarrow \quad (\text{Nu}^+\text{CH}_2\text{CHCO}_2\text{H}) \\
\end{align*}$$

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 $\text{M}_n$ and $\text{M}_e$ monomers

<table>
<thead>
<tr>
<th>$\text{M}_n$</th>
<th>$\text{M}_e$ CH$_2$=CHCO$_2$H</th>
<th>CH$_2$=CHCNH$_2$</th>
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<td><img src="image4" alt="Structure" /></td>
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<td>1 (refs. 1-3)</td>
<td>2 (ref. 4)</td>
<td>3 (ref. 5)</td>
<td>4 (ref. 6)</td>
</tr>
<tr>
<td>R = H (B)</td>
<td>R = H (A)</td>
<td>R = H (C)</td>
<td>R = H (A)</td>
</tr>
<tr>
<td>Me (C)</td>
<td>Me (B)</td>
<td>Me (A)</td>
<td>Me (A)</td>
</tr>
<tr>
<td>Ph (C)</td>
<td>Ph (C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 (ref. 9)</td>
<td>8</td>
<td>9</td>
<td>10 (ref. 9)</td>
</tr>
<tr>
<td>R = H (C)</td>
<td>R = H (A)</td>
<td>R = H (A)</td>
<td>R = H (A)</td>
</tr>
<tr>
<td>Me (C)</td>
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<td>Me (A)</td>
<td>Me (A)</td>
</tr>
<tr>
<td>Ph (C)</td>
<td>Ph (A)</td>
<td></td>
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<tr>
<td>13 (ref. 10)</td>
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<td>16 (ref. 10)</td>
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<tr>
<td>19 (ref. 11)</td>
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<td>21</td>
<td>22 (ref. 11)</td>
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<tr>
<td>R = Me (C)</td>
<td>R = Me (A)</td>
<td>R = Me (A)</td>
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<tr>
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<td><img src="image8" alt="Structure" /></td>
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<tr>
<td>25 (ref. 12)</td>
<td>26</td>
<td>27</td>
<td>28 (ref. 12)</td>
</tr>
<tr>
<td>R = Ph</td>
<td>R = Me (A)</td>
<td>R = Me (A)</td>
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<td>31 (ref. 14)</td>
<td>32 (ref. 14)</td>
<td>33</td>
<td>34 (ref. 14)</td>
</tr>
<tr>
<td>PhCH=NPhe</td>
<td>PhCH=NPhe</td>
<td>PhCH=NPhe</td>
<td>PhCH=NPhe</td>
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</table>

R = H (A) Me (B) Ph (C)
No catalyst copolymerization by spontaneous initiation mechanism

A mixture of OZO and acrylic acid in CH\textsubscript{3}CN at 50°C produced the 1:1 alternating copolymers having the same structure as that produced from OZO and BPL. The genetic zwitterion 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 \( R = \text{Ph} \) in CH\textsubscript{3}CN at 5°C, a zwitterion 12 was isolated in a monohydrated form, m.p. 145-146. When 12 was heated at 150°C, it was converted into the 1:1 alternating copolymer 13 which was also produced directly from the two monomers at 120°C. 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)$^{10}$

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.

![Chemical structure of 16 and reaction equation](image)

5. COPOLYMERIZATIONS OF AZETIDINE WITH BPL AND WITH ACRYLIC ACID (Boxes Nos. 19 and 22)$^{11}$

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.

![Chemical structure of 17 and reaction equation](image)

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)$^{12}$

Homo-polymerization of ethylene phenylphosphonite (EPP) 20 is known, which proceeds through the propagation of an Arbusov type rearrangement.$^{20,21}$

![Chemical structure of 20 and reaction equation](image)

The results were quite similar to those of the experiments of Wilson et al.$^{19}$ 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.

![Chemical structure of 18 and reaction equation](image)
Nocatalyst copolymerization by spontaneous initiation mechanism

Copolymerized with BPL, with acrylic acid and with acrylamide to produce the respective alternating copolymers 21 and 22. 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 CH₃CN 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%).

![Chemical structure](https://example.com/structure)

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

\[
\begin{align*}
20 + & \xrightarrow{\phi} 21 \\
20 + & CH_2=CHCONH_2 \rightarrow 22 \\
20 + & CH_2=CHCO_2H \rightarrow 23 \\
20 + & CH_2=CHCONH_2 \rightarrow 24
\end{align*}
\]

The structures of 24 and 26 were established by i.r. and \(^1\)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\(^{-1}\)). The amide linkage of 26 is supported by the IR absorptions at 3400 cm\(^{-1}\) (\(\nu_{NH}\) weak and broad), 3175 cm\(^{-1}\) (\(\nu_{NH}\) of lactam, medium intensity and broad), 1680 cm\(^{-1}\) (\(\nu_{CO}\) of amide, strong) and 1065 cm\(^{-1}\) (\(\nu_{PO}\) of amide, strong). As to the scheme of eqn (11), the addition of trimethyl phosphite to an electron deficient olefin 28 is to be cited.

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.

\[
\begin{align*}
20 + & CH_2=CHCO_2H \rightarrow 25 \\
20 + & CH_2=CHCONH_2 \rightarrow 26
\end{align*}
\]

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 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

\[
\begin{align*}
20 + & CH_2=CHCONH_2 \rightarrow 27
\end{align*}
\]
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 CO2. In DMF or PhCN, an equimolar mixture of 20 and methyl acrylate under a 50 kg/cm² pressure of CO₂ 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.

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 has been mentioned already. Kagiya et al. 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 described a co-oligomer from a bicyclic phosphate and acrylic or methacrylic acid in the presence of acetic anhydride. A phosphonium zwitterion was suggested as the key intermediate, although complex reactions were assumed besides simple zwitterion propagation.

A Japanese patent claims the alternating copolymerization between a cyclic phosphite and p-benzoquinone, for which the intermediacy of a zwitterion may be postulated.
The "death-charge" polymerization\(^2\) of 43 is also to be referred to here, which starts with the isolated monomer of a zwitterion 43.

![](image)

The alternating copolymerization between tetrahydronofuran and 1,4-diazophenoxide 43\(^3\) is another instance which is related to our copolymerization.

REFERENCES


\(^2\) 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).