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SPONTANEOUS COPOLYMERIZATION OF P(III) COMPOUNDS VIA ZWITTERION INTERMEDIATES ———— REDOX COPOLYMERIZATION AND DEOXY POLYMERIZATION
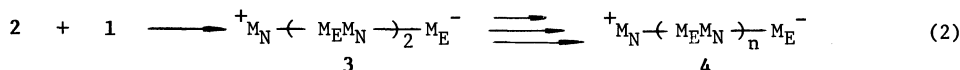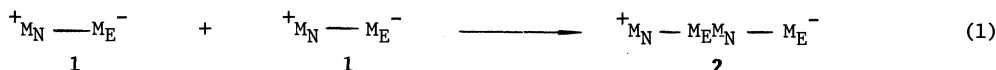
Takeo Saegusa

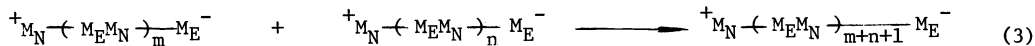Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Abstract – A group of new type copolymerizations have been explored on the basis of the combinations of P(III) compounds as one monomer with activated carbonyl compounds as another monomer which are exemplified by α-keto acid, o- and p-formylbenzoic acids, and p-benzoquinone. The P(III) compounds are cyclic and acyclic phosphonites and phosphites. These copolymerizations proceed without any added catalyst and produce 1:1 alternating copolymers. An important character is the fact that P(III) monomers are oxidized to the copolymer units consisting of P(V) groups, i.e., phosphonate and phosphate, whereas the carbonyl compounds are reduced to the units of the corresponding hydroxy derivatives. Thus, these copolymerizations have been called "Redox Copolymerization". In addition, "Deoxy Polymerization" and "Deoxy Copolymerization" are described, in which α-keto acid is incorporated into a homopolymer or a copolymer in the form of the ester of α-hydroxy acid with the elimination of the oxygen atom of its carbonyl group by non-polymerizable P(III) compounds.

1. INTRODUCTION

In these several years, a new pattern of polymerization has been developed by us, which proceeds without any added catalyst to produce 1:1 alternating copolymer (Ref. 1). This copolymerization consists of the combination of a nucelophilic monomer (M_N) and an electrophilic monomer (M_E), which are reacted with each other to generate a zwitterion 1 (^+M_N-M_E^-) ("Genetic Zwitterion") as the key intermediate of the reaction. Zwitterion 1 is first converted to its dimeric form 2 (eq. 1), which continues to grow by the successive reactions with 1 (eq. 2).

$$^+M_N \!-\! M_E^- \quad + \quad {}^+M_N \!-\! M_E^- \quad \longrightarrow \quad {}^+M_N - M_E M_N - M_E^- \tag{1}$$

$$112$$

$$2 \;+\; 1 \quad \longrightarrow \quad {}^+M_N \!\!+\!\! M_E M_N \!\!\xrightarrow{}_{2}\!\! M_E^- \quad \rightleftharpoons \quad {}^+M_N \!\!+\!\! M_E M_N \!\!\xrightarrow{}_{n}\!\! M_E^- \tag{2}$$

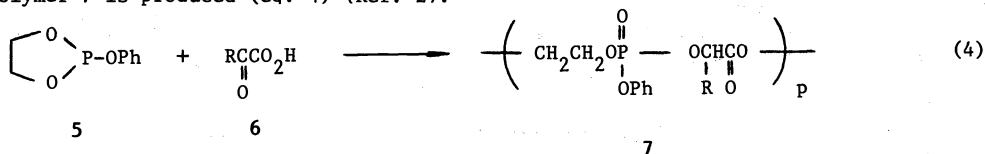$$34$$

At the stage of higher conversions where the concentration of propagating zwitterions ("macro-zwitterion") is high, the reaction between two moles of macro-zwitterion takes place to increase the chain length (the degree of polymerization) very sharply (eq. 3).

$$^+M_N \!\!+\!\! M_E M_N \!\!\xrightarrow{}_{m}\!\! M_E^- \quad + \quad {}^+M_N \!\!+\!\! M_E M_N \!\!\xrightarrow{}_{n}\!\! M_E^- \quad \longrightarrow \quad {}^+M_N \!\!+\!\! M_E M_N \!\!\xrightarrow{}_{m+n+1}\!\! M_E^- \tag{3}$$

On the basis of this concept, many new copolymerizations have been found by the combinations of various M_N and M_E monomers (Ref. 1).

The responsible atoms of M_N monomers are nitrogen and phosphorus(III), which are reacted with diverse electrophilic groups of M_E monomers such as ester (lactone), sulfone ester (sultone), and vinyl groups having electron-withdrawing substituents (Ref. 1).

This article describes a group of interesting copolymerizations of P(III) compounds as the M_N component in combination with several M_E monomers having specific reactivity of carbonyl group toward P(III) site of M_N. In these copolymerizations, the trivalent phosphorus atom in M_N monomers is oxidized to a pentavalent form in the copolymer, whereas the carbonyl group of M_E monomer is reduced to a derivative of the hydroxyl group. Therefore a term "Redox Copolymerization" has been proposed to define the new category of copolymerization.

2. REDOX COPOLYMERIZATION

A typical example of "Redox Copolymerization" is seen in the combination of a cyclic phosphite **5** and an α-keto acid **6**. At temperatures above about 120°C, an alternating copolymer **7** is produced (eq. 4) (Ref. 2).

$$
\begin{array}{c}
\text{(phosphite 5)} \quad P\text{-OPh} \quad + \quad RCCO_2H \quad \longrightarrow \quad \left(CH_2CH_2OP - OCHCO\right)_p
\end{array}
\tag{4}
$$

5   **6**

7

The reduction-oxidation system is very clear. Thus, the form of phosphite in the M_N monomer **5** has been oxidized to the form of phosphate in the copolymer **7**. On the other hand, the carbonyl group in the M_E monomer **6** has been reduced to the form of ester of α-hydroxy acid in **7**. A zwitterion **9** below has been assumed in the above copolymerization, thought to be produced by the hydrogen transfer in the first   generated zwitterion **8** (eq. 5).
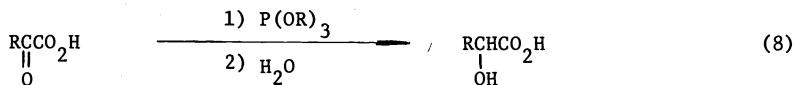
$$
\textbf{5} \ + \ \textbf{6} \quad \longrightarrow \quad \left[\ \right] \quad \longrightarrow \quad \tag{5}
$$

8   **9**

$$
\tag{6}
$$

9   **9**   **10**
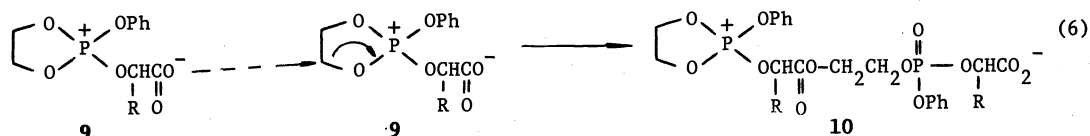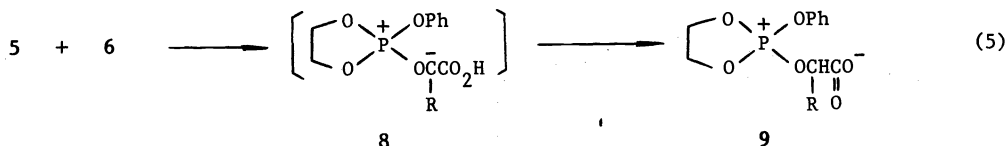
In the reaction between two moles of **9**, the five-membered phosphonium ring of **9** is opened by the nucleophilic attack of the carboxylate anion (eq. 6). This ring-opening reaction follows the pattern of the Arbusov reaction. The chain growth of macro-zwitterion proceeds through the patterns of polyaddition (eq. 2) and of polycondensation (eq. 3), whose elementary reaction is also comprised of the opening of phosphonium ring of one zwitterion by the nucelophilic attack of carboxylate of another zwitterion.
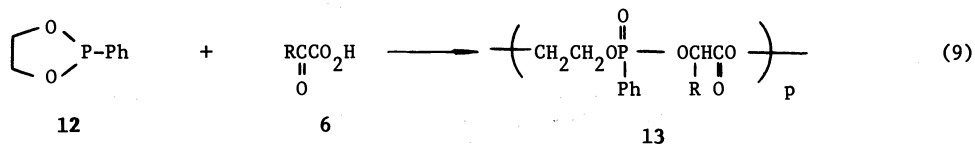
$$
\tag{7}
$$

R
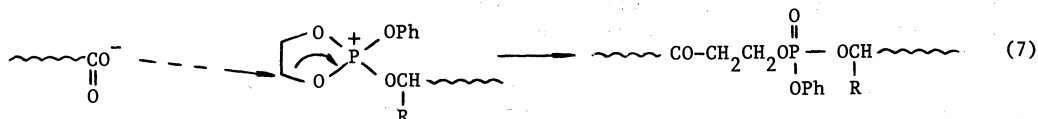
At lower temperatures, e.g., -20°C, the reaction of **5** and **6** in ether produces a spiro acylpentaoxyphosphorane **11** in high yields, which can be isolated in crystalline form, mp. 87°C (R=Me) and 60-62°C (R=Ph). The formation of **11** is reasonably understood by the cyclization through the covalent bonding between the phosphonium center and the carboxylate anion. On heating at 120°C, a spiro phosphorane **11** is polymerized to **7** through the form of a zwitterion **9**.

$$
\text{(spiro 11)} \quad \rightleftharpoons \quad \text{(zwitterion)} \quad \longrightarrow \quad \textbf{7}
$$

**11**   **9**
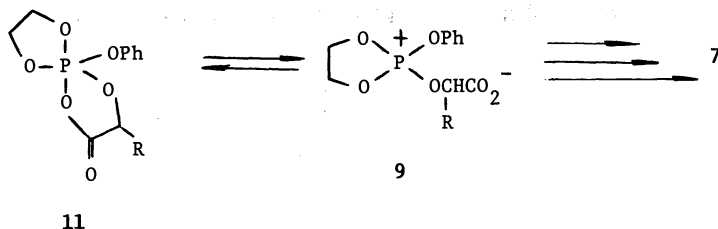
The above two findings, i.e., the isolation of **11** and its polymerization, are taken to support the mechanism of this copolymerization shown in the scheme of eqs. 5-7.
The redox system can be applied also to a synthetic method of the reduction of α-keto acid to the corresponding α-hydroxy acid by means of phosphite (eq. 8) (Ref. 3).

$$
RCCO_2H \quad \xrightarrow[\text{2) } H_2O]{\text{1) } P(OR)_3} \quad / \quad RCHCO_2H
\tag{8}
$$

with O and OH substituents.

For the purpose of the above synthesis, acyclic common phosphites such as trialkyl phosphites are conveniently utilized, and the isolation of the phosphorane intermediate is not necessary. Thus, α-keto acid is mixed with a phosphite, and after 10 minutes at room temperature the mixture is hydrolyzed to produce α-hydroxy acid.

A similar P(III) monomer **12** has also been copolymerized with α-keto acid **6** (R=CH$_3$ and R=Ph) in benzonitrile or acetonitrile at 100°-120°C (eq. 9) (Ref. 4). Trivalent phosphorus atom in the form of phosphonite in the monomer **12** is oxidized to a pentavelent form of phosphonate in the alternating copolymer **13**.

$$
\begin{array}{ccccc}
\text{[12]} & + & \text{RCCO}_2\text{H} & \longrightarrow & \text{[13]} \\
& & 6 & & \\
\end{array}
\qquad (9)
$$

12   **6**   **13**

A spiro acyltetraoxyphosphorane **14** has been isolated in a room temperature reaction. For the copolymerization, a mechanism similar to that of the 5-6 copolymerization is assumed.

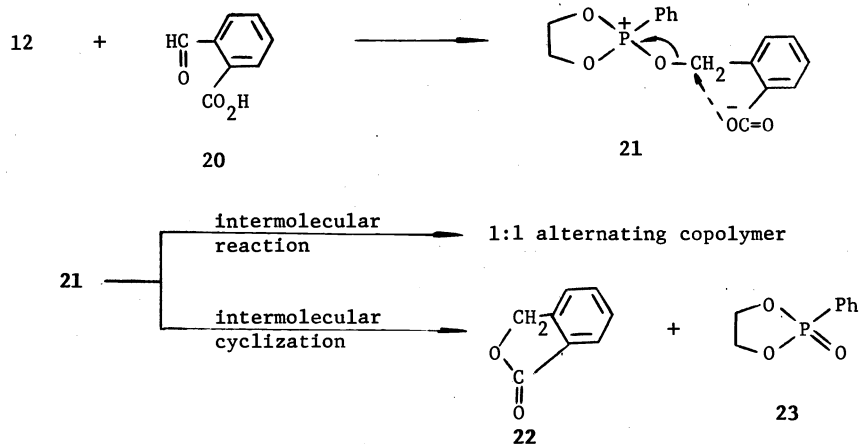**14** $\rightleftharpoons$ **15** $\Longrightarrow$ **13**
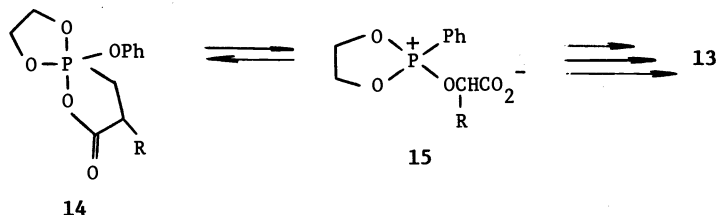
The copolymerization between a cyclic phosphonite **12** and p-formylbenzoic acid **16** is the second example of "Redox Copolymerization" (eq. 10) (Ref. 5).

$$
\begin{array}{ccccc}
\text{[12]} & + & \text{[16]} & \longrightarrow & \text{[17]}
\end{array}
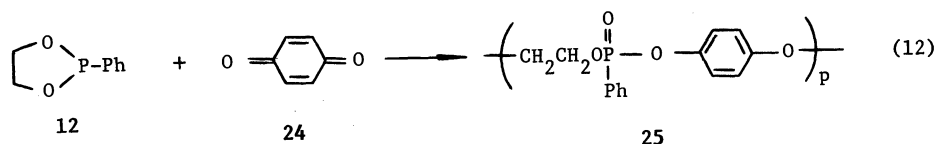\qquad (10)
$$

12   **16**   **17**
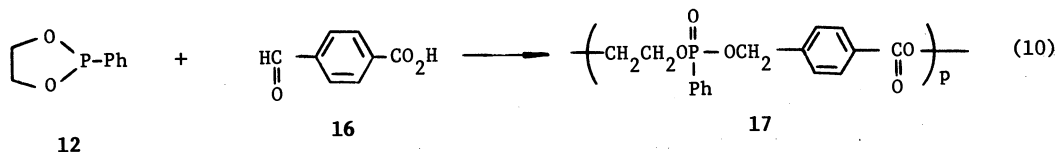
In this copolymerization, a phosphonite is oxidised to phosphonate, whereas the formyl group in **16** is reduced to an ester of methylol in **17**. A scheme of eq. 11 has been proposed, although no intermediate species has been isolated in this case.

$$
\text{12} + \text{16} \longrightarrow \left[\text{18}\right] \xrightarrow[\text{transfer}]{\text{hydrogen}} \text{19}
\qquad (11)
$$

18   **19**
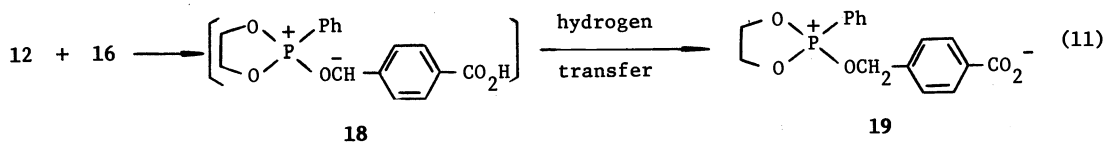
The key species is a zwitterion **19**, which is assumed to be formed by the hydrogen transfer in the first formed zwitterion **18**. In the copolymerization of **12** with the o-isomer (o-formylbenzaldehyde **18**), the copolymer is rather a minor product. The major product is an equimolar mixture of o-phthalide **21** and a cyclic phosphate **23** whose production rationalizes the lower yield of the copolymer and gives a support to the intermediacy of zwitterions **19** and **21**.

12   +   **20** $\longrightarrow$ **21**

21 $\left\{ \begin{array}{ll} \dfrac{\text{intermolecular}}{\text{reaction}} & \longrightarrow \quad \text{1:1 alternating copolymer} \\[2ex] \dfrac{\text{intermolecular}}{\text{cyclization}} & \longrightarrow \quad \text{22} \quad + \quad \text{23} \end{array} \right.$
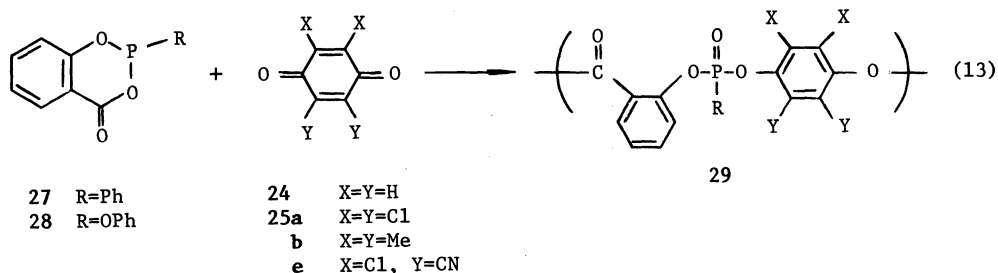
22   **23**

In zwitterion **21**, the intramolecular cyclization shown by arrows is favorable to the intermolecular reaction leading to the polymer production.

p-Benzoquinone **24** is known to be a reactive oxidant. Its copolymerization with a cyclic phosphonite **12** has been described in a patent literature (eq. 12) (Ref. 6).

$$\underset{\textbf{12}}{\left[\begin{matrix}O\\O\end{matrix}\right\rangle P-Ph} \quad + \quad \underset{\textbf{24}}{O=\!\!\left\langle\bigcirc\right\rangle\!\!=O} \quad \longrightarrow \quad \underset{\textbf{25}}{\left(\!CH_2CH_2O\overset{\overset{O}{\|}}{\underset{Ph}{P}}-O-\!\left\langle\bigcirc\right\rangle\!-O\right)_p} \qquad (12)$$
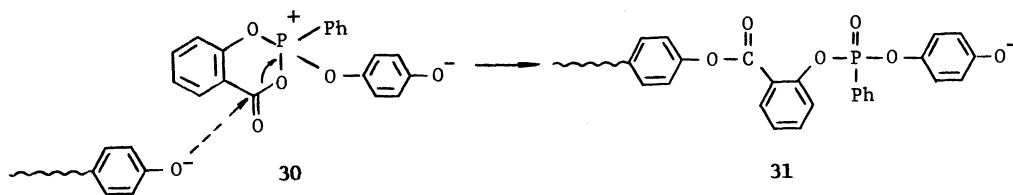
It belongs to the category of "Redox Copolymerization". The course of copolymerization is reasonably explained by the intermediacy of a phosphonium-phenolate zwitterion **26**. This copolymerization requires higher temperatures above 100°C. It is due to the fact that the Arbusov reaction of the opening of phosphonium ring of **26** by phenolate anion occurs only at higher temperatures.
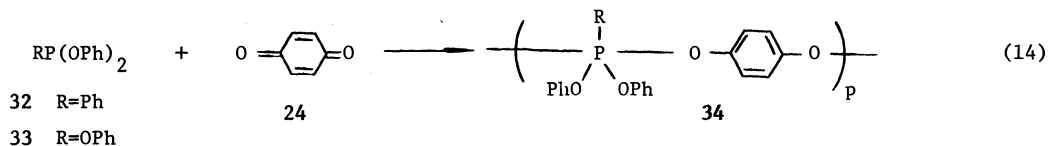
$$\underset{\textbf{26}}{\left[\begin{matrix}O\\O\end{matrix}\right\rangle \overset{+}{P}\overset{Ph}{\diagdown}O-\!\left\langle\bigcirc\right\rangle\!-O^-}$$
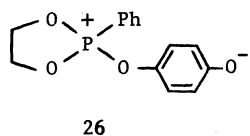
Cyclic acyl phosphonite **27** and phosphite **28** can be copolymerized with p-benzoquinone and its substituted derivatives **25** under much milder conditions (eq. 13) (Ref. 7). For example, the copolymerizations of **27** are possible even at room temperature.

$$\underset{}{\left\langle\bigcirc\right\rangle\!\!\begin{matrix}O\\{}\\O\end{matrix}\!\!\overset{P-R}{\underset{O}{}}} \quad + \quad \underset{}{O=\!\!\left\langle\overset{X\ X}{\underset{Y\ Y}{\bigcirc}}\right\rangle\!\!=O} \quad \longrightarrow \quad \underset{\textbf{29}}{\left(\!\!\begin{matrix}O\\\|\\C\end{matrix}\!\left\langle\bigcirc\right\rangle\!O-\overset{O}{\underset{R}{\overset{\|}{P}}}-O-\!\left\langle\overset{X\ X}{\underset{Y\ Y}{\bigcirc}}\right\rangle\!-O\right)} \qquad (13)$$

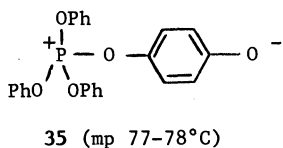|		
27 R=Ph	**24**	X=Y=H
28 R=OPh	**25a**	X=Y=Cl
	b	X=Y=Me
	e	X=Cl, Y=CN

The easiness of the copolymerization is due to the high reactivity of the phosphonium ring of zwitterion **30**, which is being activated by acyl group as well as phosphonium cation.

$$\underset{\textbf{30}}{\cdots\cdots\left\langle\bigcirc\right\rangle\!\!\begin{matrix}O\\{}\\C\\\|\\O\end{matrix}\!\!\overset{\overset{+}{P}\diagdown Ph}{\underset{O-\left\langle\bigcirc\right\rangle-O^-}{}} \cdots\cdots\left\langle\bigcirc\right\rangle\!-O^-} \quad \longrightarrow \quad \underset{\textbf{31}}{\sim\!\!\left\langle\bigcirc\right\rangle\!-O-\overset{O}{\overset{\|}{C}}\!\left\langle\bigcirc\right\rangle\!O-\overset{O}{\underset{Ph}{\overset{\|}{P}}}-O-\!\left\langle\bigcirc\right\rangle\!-O^-}$$

p-Benzoquinone **24** can be copolymerized even with acyclic P(III) compounds, a phosphonite **32** and a phosphite **33**, at temperatures above 130°C, to produce phosphorane type polymers **34** (eq. 14) (Ref. 8).

$$\underset{\substack{\textbf{32}\ \ R=Ph\\\textbf{33}\ \ R=OPh}}{RP(OPh)_2} \quad + \quad \underset{\textbf{24}}{O=\!\!\left\langle\bigcirc\right\rangle\!\!=O} \quad \longrightarrow \quad \underset{\textbf{34}}{\left(\!\!\begin{matrix}R\\|\\P\\\diagup\ \diagdown\\PhO\ \ OPh\end{matrix}\!\!-O-\!\left\langle\bigcirc\right\rangle\!-O\right)_p} \qquad (14)$$

A zwitterion **35** has been isolated, which is assumed to play a role of the key species.

$$\underset{\substack{\textbf{35 (mp 77-78°C)}}}{\overset{OPh}{\underset{PhO\ \ OPh}{\overset{|}{\underset{\diagup\ \diagdown}{\overset{+}{P}}}}}-O-\!\left\langle\bigcirc\right\rangle\!-O^-}$$
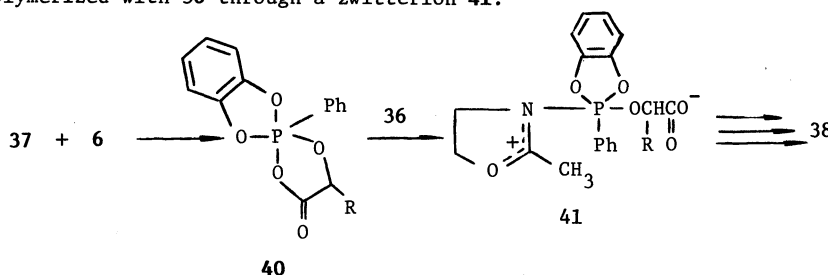
3. SEQUENCE-REGULATED 1:1:1 TERPOLYMERIZATION

A sequence-regulated 1:1:1 terpolymerization involving a redox reaction has been discovered as an extention of the binary redox copolymerization. A ternary mixture of 2-methyl-2-oxazoline 36, o-phenylene phenyl phosphonite 37, and α-keto acid 6 in acetonitrile was kept first at 0°C for 10 hrs, and then at room temperature for 1 day and finally heated at 90°C. The polymeric product 39 was isolated after the treatment of the reaction mixture with water, which had resulted from the hydrolysis of the initially formed terpolymer 38 (Ref. 9).
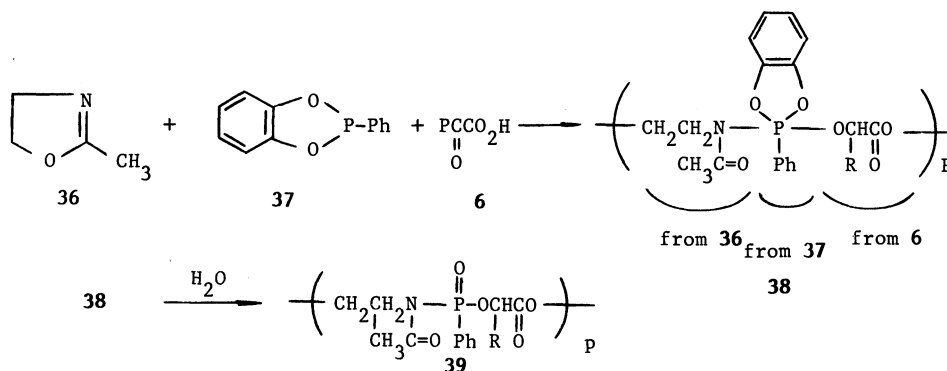
The above terpolymerization involves a combination of two M_N monomers (36 and 37) and one M_E monomer (6). In the terpolymer three different units are being arranged in a regular pattern of ···ABCABCABC···. The regulation of the monomeric units' arrangement is due to the specific order of the sequence of reactions. In the first stage, the reaction between 37 and 6 takes place to produce a spiro-bicyclic phosphorane 40. Then, in the second stage, 40 is copolymerized with 36 through a zwitterion 41.
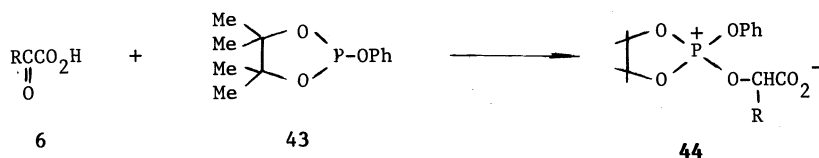

The first stage reaction is the formation of 40, and the second stage is a binary copolymerization between 36 as M_N monomer and 40 as M_E monomer. Other reactions do not take place, and the sequence regulation is secured.
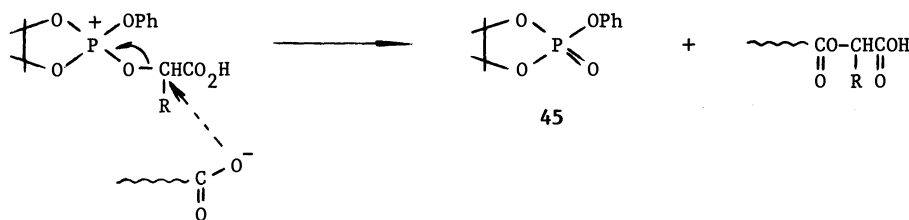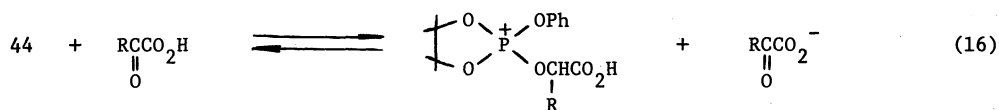
4. DEOXY POLYMERIZATION AND DEOXY COPOLYMERIZATION

On the basis of the binary redox copolymerization, an interesting homopolymerization of α-keto acid 6 producing a polyester has been realized (eq. 15) (Ref. 1).


In the polymerization, one oxygen atom of 6 is eliminated by the assistance of a tetramethylated cyclic phosphite 43. Firstly a reaction takes place between 6 and 43 to generate a zwitterion 44. The subsequent reaction of 44 with the carboxyalte anion of another zwitterion occurs at the external carbon atom which is being located at a β-position after oxygen from the phosphonium center. The nucleophilic attack to open the phosphonium ring in 44 is hampered by severe steric hindrance due to methyl groups. The final result is the transfer of one oxygen atom from 6 to 43. The stoichiometric amount of the cyclic phosphate 45 was actually isolated. (see the scheme of the next page).

$$44 \ + \ \underset{\overset{\|}{O}}{R}CCO_2H \ \rightleftharpoons \ \left[\begin{array}{c}O\\O\end{array}\right]\overset{+}{P}\begin{array}{c}OPh\\OCHCO_2H\\|\\R\end{array} \ + \ \underset{\overset{\|}{O}}{R}CCO_2^- \qquad (16)$$

"Dexoy Copolymerization" has been developed on the basis of "Deoxy Polymerization". A typical example is the combination of a cyclic imino ether **46** with the system of a sterically hindered cyclic phosphite **43** and an α-keto acid **6**. The copolymerization was performed in two stages. First, the three components in acetonitrile were kept at a lower temperature, e.g., 0°C, for 5 hrs and then the mixture was heated at 90°C. An alternating copolymer **47** was produced.
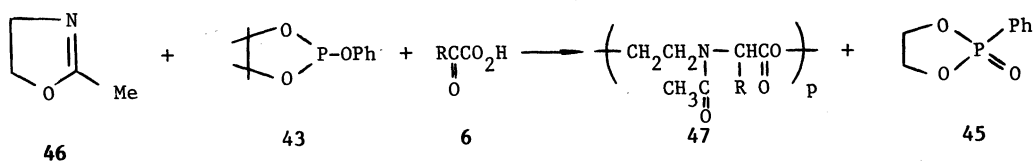
The monomer of α-keto acid has been incorporated into the copolymer with reduction. One oxygen atom of **6** has been transfered to a phosphite. The reaction scheme involving the nucleophilic displacement at the external carbon atom of a sterically hindered cyclic phosphonium with **46** has been proposed (Ref. 1).
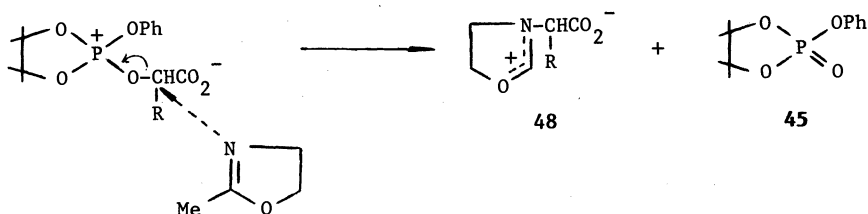
A zwitterion **48** is the key intermediate, which leads to the production of **47**.

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