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Polymerization via Zwitterion. 20. Alternating Copolymerizations of 2-Phenyl-1, 3, 2-dioxaphospholane with p- and o-Formylbenzoic Acids

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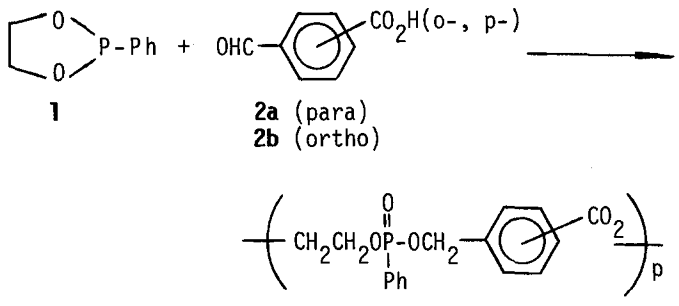
Introduction

Spontaneous alternating copolymerization, a new category of polymerization, has been developed by us (SAEGUSA, 1975 and 1977; SAEGUSA et al., 1975, 1976, and 1977). In this copolymerization a monomer (M_N) having nucleophilic reactivity is combined with the second monomer (M_E) having electrophilic reactivity. By the interaction between these two monomers a zwitterion ($^+M_N-M_E^-$) is formed which is the key intermediate in the copolymerization. In the present paper we wish to report an extention of this copolymerization, i.e., copolymerizations of a cyclic phosphonite (M_N), 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite **1**) with p- and with o-formylbenzoic acids (M_E, **2a** and **2b**) whose formyl group is reactive toward trivalent phosphorus compounds. The copolymerization takes place without added catalyst to produce 1:1 alternating copolymers **3** consisting of both phosphonate and ester groups in the main chain. In this copolymerization, phosphonite monomer **1** is oxidized to phosphonate unit and the formyl group of monomer **2** is reduced to a methylol phosphonate group. Therefore, it falls under the category of a new type of copolymerization named "redox copolymerization" (SAEGUSA et al., 1977d).



1

2a (para)
2b (ortho)

3a (para)
3b (ortho)

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In relation to the copolymerization combination of the present study, we have already reported the alternating copolymerizations of **1** with several M_E monomers such as acrylic acid, β-propiolactone, acrylamide (SAEGUSA et al., 1976b), and γ-hydroxypropane sulfonic acid ester (sultone) (SAEGUSA et al., 1977c), as well as a 1:1:1 alternating terpolymerization of **1**, acrylic monomers, and carbon dioxide (SAEGUSA et al., 1977b).

Experimental

Copolymerization of **1** with **2**. An example of copolymerization procedure was as follows. In a sealed tube, an equimolar (3 mmol each) amount of **1** and **2a** were mixed in 1.5 ml benzonitrile under nitrogen. After it was kept at 130° for 20 hrs, the reaction mixture was poured into a large excess of diethyl ether to precipitate the polymeric products, which were then purified by several reprecipitation from chloroform (solvent) to diethyl ether (precipitant) and then dried *in vacuo*. The obtained copolymer, yielding 0.906g (95%), was then submitted to the structure analysis.

TABLE 1

Alternating Copolymerizations of 2-Phenyl-1,3,2-dioxaphospholane(M_N*) with p- and o-Formylbenzoic Acids (M_E*).

No.	M_E	Solvent**	Temp (°C)	Time (hr)	Yield (%)	Molecular Weight***
1	**2a**	Benzonitrile	130	20	95	4390
2	〃	〃	145	24	99	3460
3	**2b**	Toluene	140	90	25	920
4	〃	Benzonitrile	130	93	17	910

* 3 mmol each.
** 1.5 ml.
*** Determined by vapor pressure osmometry in DMF (at 55°).

Results and Discussion

Copolymerization of **1** with **2a**. Some typical results of the copolymerization are shwon in TABLE 1 (No.1 and 2). A white powdery copolymer was produced in yields higher than 95% with the highest molecular weight of 4390. The structure was established by spectrometric analyses and by elemental analysis, as **3a** : ^{1}H NMR ($CDCl_3$)

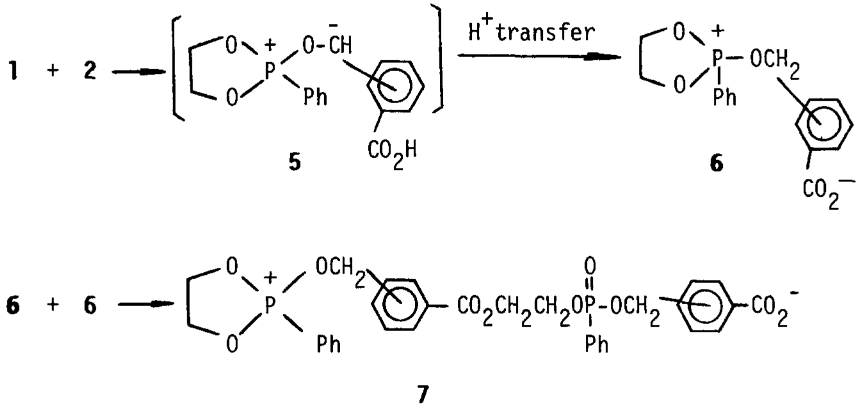
δ 4.0-4.6 (broad m, O-CH_2CH_2-O and P-O-CH_2-⌬- , 6H), 6.9-8.0 (broad m, aromatic protons, 9H); IR (KBr) 1720 ($\nu_{C=O}$ of ester), 1250 ($\nu_{P=O}$), 1040 (ν_{P-O-R}) cm^{-1}, etc. Anal. Calcd. for the 1:1 copolymer $(C_{16}H_{15}O_5P)_p$: C, 60.38; H, 4.75; P, 9.73. Found for sample No. 2 in TABLE 1 : C, 59.70; H, 4.89; P, 8.90.

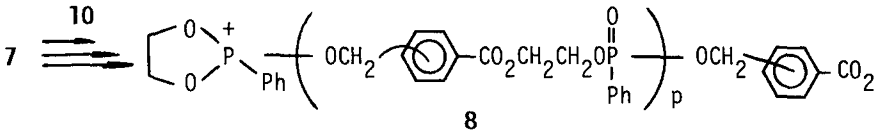
Copolymerization of **1** with **2b**. A similar copolymer **3b** was prepared from **1** and **2b** in poorer yields (TABLE 1, No. 3 and 4). The yield was 25% at highest and the molecular weight did not reach 950 which corresponded to trimer of the alternating units. The structure **3b** was supported by the following data; ^1H NMR ($CDCl_3$) δ 3.4-4.7 (m, O-CH_2CH_2-O and -O-CH_2-⌬ ,6H) 7.0-8.0 (m, aromatic protons, 9H); IR (KBr) 1720 ($\nu_{C=O}$ of ester), 1250 ($\nu_{P=O}$), 1040 (ν_{P-O-R}) cm^{-1}, etc.

The low yield of the copolymer **3b** was rationalized by the reaction scheme shown later. The copolymer was a by-product, and the main product was phthalide **4** (lactone), which was isolated by glpc (silicon 200°); ^1H NMR ($CDCl_3$) δ 5.4 (s, -OCH_2-, 2H) 7.4-7.9 (m, C_6H_4, 4H), these data being in good agreement with the Sadtler's standard NMR spectra v 496.

In a copolymerization in nitrobenzene at 150° after 92 hr, the yield of the copolymer **3b** isolated by the above reprecipitation was 18% and that of **4** was determined as 87% by glpc (hexamethylphosphoric triamide standard). In toluene (130°, 92hr), **3b** and **4** were produced respectively in 24% and 70% yeilds.

Scheme of Copolymerization. The scheme of the present alternating copolymerization is constructed on the basis of the general pattern of the "No Catalyst Copolymerization" (SAEGUSA, 1975 and 1977) together with the scheme of related copolymerizations (SAEGUSA et al., 1976b, 1977b, 1977c, and 1977d) as well as the experimental findings of the present study.





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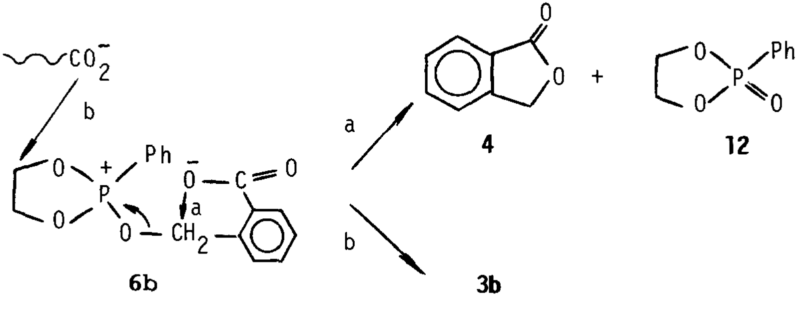
The reaction between **1** and **2** leads to a transient species **5** by the bond formation between the phosphorus atom of **1** and the formyl oxygen atom of **2**. The detailed mechanism of this reaction is not clear now, which is closely related to a controversial problem of the mechanism of the reaction of P(3) compounds with carbonyl functions (RAMIREZ, 1974).

Hydrogen transfer in **5** occurs through either intramolecular or intermolecular mechanism to produce the key intermediate of a zwitterion **6**. Then, the reaction between two molecules of **6** produces the initial propagating zwitterion **7** (macrozwitterion), which continues to grow by successive reactions with **6**. The reaction between macrozwitterions also occurs. The elemental reaction of these propagations is the opening of phosphonium ring by the nucleophilic attack of carboxylate of other zwitterions onto the ring carbon atom located at the position of ⋗P^+-O-C-. The mode of this reaction falls into the category of the Arbusov reaction.

In the copolymerization with the ortho isomers **2b**, the linear copolymer **3b** is a by-product. A lactone **4** is the main product. This finding is reasonably explained by a zwitterion **6b**, in which carboxylate anion is located at a convenient site for the intramolecular nucleophilic attack onto the exocyclic methylene carbon of benzyl group. Intramolecular reaction leads to the production of lactone **4**. The concurrent formation of cyclic phosphonate **12** was actually observed, although the quantification of **12** was not made because it was decomposed during the process of glpc analysis.



Summary

Spontaneous alternating copolymerizations of 2-phenyl-1,3,2-dioxaphospholane (M_N) with p- and with o-formylbenzoic acids (M_E) were examined. The copolymerizations took place without catalysts affording the copolymer **3** via zwitterion **6**. The copolymerizations involve the oxidation of the phosphorus monomer and the reduction of formylbenzoic acid. The scheme of the copolymerizations was presented. The yields of copolymers were quite different between these two copolymerizations. With ortho acid, the copolymer yield was low due to producing phthalide **4**.

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