This work when coupled with the studies of vinylferrocene (2)[9-12,24] and vinylcynichrodene (3)[6,7] provides the first detailed examples of the homopolymerization behavior of vinyl organometallic monomers. Interest in such monomers is growing rapidly.[27]

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Polymerization via Zwitterion. 18. Alternating Cooligomerizations of Ethylenesulfonamide with Cyclic Phosphorus Compounds

Takeo Saegusa,* Shiro Kobayashi, and Jun-ichi Furukawa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received April 20, 1978*

ABSTRACT: Alternating cooligomerization of ethylenesulfonamide (ESAm) with cyclic phosphorus compounds, i.e., 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite, EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite, EPI), took place without any added initiator to produce 1:1 alternating cooligomers from ESAm–EPO and ESAm–EPI. The structures of the cooligomers were established by IR and NMR spectra, elemental analyses, as well as the alkaline hydrolysis experiments. The reaction scheme of the cooligomerization via zwitterion (eq 4–6) was proposed.

A series of the new alternating copolymerizations between nucleophilic monomers (M_N) and electrophilic monomers (M_E) via zwitterion intermediates has been found by us.[1] All of these copolymerizations are characterized by the fact that they take place without added catalyst. Recently we have reported the cooligomerization of ethylenesulfonamide (ESAm) with a cooligomer of an amide–sulfonamide structure.[2] In this case ESAm provided a very stable anionic part of a zwitterion derived from a combination of ESAm and 2-methyl-2-oxazoline (M_N), and hence, the key intermediate of genetic zwitterion could even be isolated.[2] In the present study we have adopted two cyclic phosphorus compounds as M_N monomers. They are 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite, EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite, EPI).

Results and Discussion

Cooligomerization and Characterization of Cooligomers. An equimolar mixture of EPO and ESAm (5 mmol each) in benzonitrile (1.5 mL) containing 0.02 mmol of *N*-phenyl-2-naphthylamine as a radical inhibitor was heated at 100 °C under nitrogen. After 42 h the reaction mixture was poured into a large amount of diethyl ether to precipitate the oligomeric product. The cooligomer was dried in vacuo to give 1.06 g of glassy, white, and hygroscopic solids (77% yield).

The structure of the cooligomer was examined by IR and NMR spectroscopy, elemental analysis, and the alkaline hydrolysis experiment of the cooligomer. The IR spectrum

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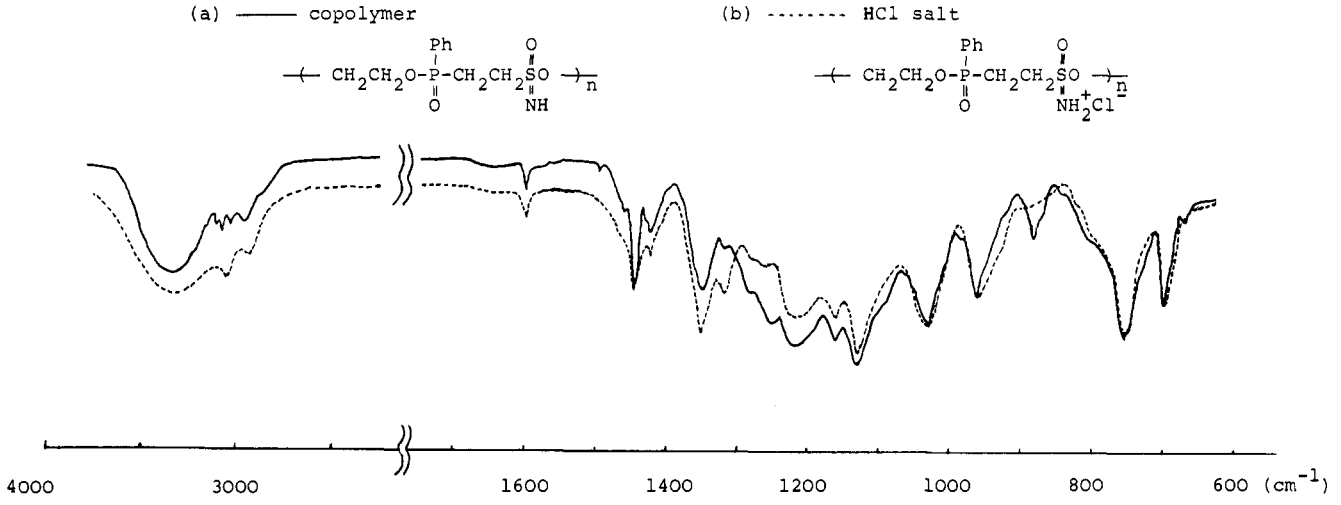
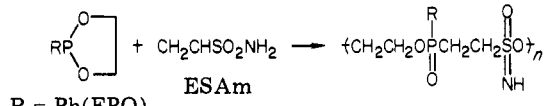
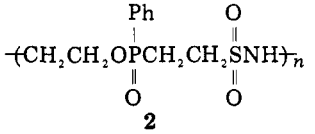


Figure 1. Infrared spectra of the EPO–ESAm cooligomer (a, solid line) and its HCl salt (b, dotted line) (neat).

of the cooligomer (Figure 1a) shows strong absorption bands at 1215 (due to $\nu_{P=O}$), at 1340 and 1130 (due to ν_{SO}), at 1250 (due to $\nu_{S=N}$), and at 1030 cm^{-1} (due to ν_{C-O}).

As to the structure of the cooligomer unit derived from ESAm, there are two possibilities, i.e., the phosphinate sulfilimine **1a** and phosphinate sulfonamide **2** structures.





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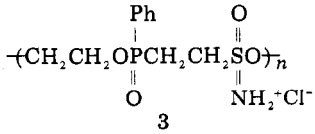
The IR data (the band of $\nu_{S=N}$ at 1250 cm^{-1}) strongly suggest structure **1**. To confirm this, the cooligomer was treated with dry HCl gas. Into a 5 mL $CHCl_3$ solution of cooligomer (0.20 g) dry HCl gas was introduced at room temperature until the solution no longer absorbed HCl. The copolymer–HCl salt precipitated as waxy material (0.18 g after drying). The extent of the salt formation was found by the chlorine analysis to be about 27%. Anal. Calcd for $C_{10}H_{15}NO_4PSCl$ (1:1 addition product of **1** and HCl): Cl, 11.37. Found: Cl, 3.11. The IR spectrum of the cooligomer salt is shown in Figure 1b (dotted line). The absorption at 1250 cm^{-1} of the cooligomer has become very weak after salt formation. The structure of the cooligomer–HCl salt is reasonably given by **3**. Thus, this



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finding is taken to support the sulfilimine unit structure **1a**, but not the sulfonamide unit structure **2**.

The NMR spectrum of the EPO–ESAm cooligomer in $CDCl_3$ (Figure 2) shows four kinds of broad signals at δ 8.2–7.2 (due to C_6H_5 (5 H)), 6.4–5.8 (due to NH (1 H)), 4.7–3.5 (due to OCH_2CH_2O (4 H)), and 3.5–2.2 (due to PCH_2CH_2 (4 H)).

The result of the elemental analysis supports the 1:1 composition of EPO and ESAm. Anal. Calcd for $(C_{10}H_{14}NO_4PS)_n$: C, 43.64; H, 5.13; N, 5.09; P, 11.25.

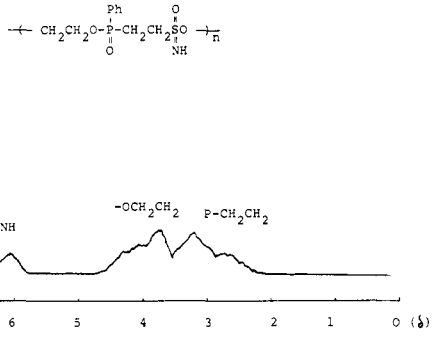


Figure 2. NMR spectrum of the EPO–ESAm cooligomer in $CDCl_3$.

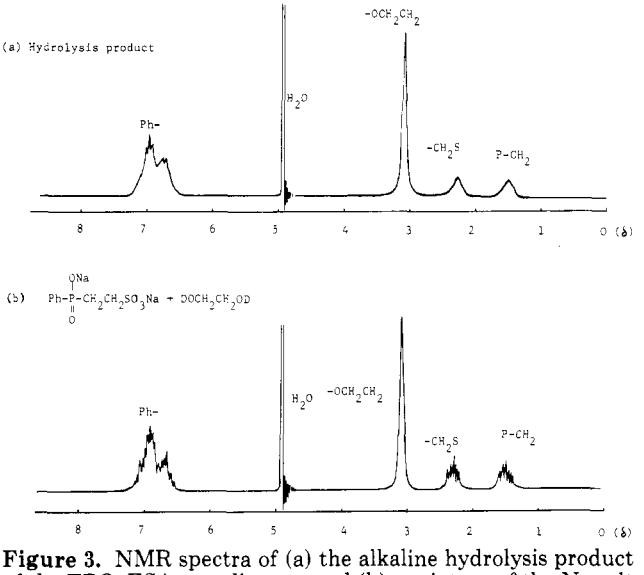


Figure 3. NMR spectra of (a) the alkaline hydrolysis product of the EPO–ESAm cooligomer and (b) a mixture of the Na salt of **4** and ethylene glycol in D_2O.

Found: C, 43.12; H, 5.31; N, 5.24; P, 10.98.

The alkaline hydrolysis of the cooligomer was carried out to confirm the above structure. To 50 mg of the cooligomer was added 0.5 mL of a 10% solution of NaOH in D_2O. The reaction of the hydrolysis mixture at 90 °C for 5 h gave an equimolar mixture of the disodium salt of 2-(phenylphosphono)ethanesulfonic acid (**4**) and ethylene glycol (Figure 3a), i.e., NMR peaks at δ 7.2–6.5 (broad, 5 H), 3.1 (singlet, 4 H), 2.5–2.1 (broad, 2 H), 1.7–1.3 (broad, 2 H) are assigned respectively to the protons of C_6H_5 and

$-OCH_2CH_2O-$, CH_2S, and PCH_2.

$$\mathbf{1a} \xrightarrow[D_2O]{NaOH} \underset{\text{disodium salt of 4}}{Ph-\overset{\overset{ONa}{|}}{\underset{\underset{O}{\|}}{P}}-CH_2CH_2SO_3Na} + DOCH_2CH_2OD \quad (1)$$

The assignment was further confirmed by the comparison of Figure 3a with the NMR spectrum (Figure 3b) of an equimolar mixture of the disodium salt of an authentic sample of dimethyl ester of **4** and ethylene glycol in $NaOH-D_2O$ solution. It is evident that these two spectra (Figure 3a and 3b) resemble each other.

Dimethyl ester of **4** was obtained by the reaction of dimethoxyphenylphosphine with ethylenesulfonic acid as a colorless, slightly viscous liquid: IR (neat) 1235 ($\nu_{P=O}$), 1325 and 1150 (ν_{SO_2}), 1060 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 8.2–7.4 (multiplet, C_6H_5, 5 H), 3.9 (singlet, OSO_3CH_3), 3.8 and 3.6 (doublet, $P-OCH_3$, 3 H), 3.6–3.2 (multiplet, CH_2S, 2 H), 2.8–1.9 (multiplet, $P-CH_2$, 2 H). Anal. Calcd for $C_{10}H_{15}O_5PS$: C, 43.16; H, 5.43; P, 11.13. Found: C, 43.06; H, 5.67; P, 10.93.

As to the structure of the cooligomer unit derived from ESAm, there are two possibilities as mentioned above, i.e., **1a** and **2**. However, the absence of monoethanolamine in the alkaline hydrolysis products is taken to exclude the possibility of the phosphinate sulfonamide structure **2**.

$$-\{CH_2CH_2O\overset{\overset{Ph}{|}}{\underset{\underset{O}{\|}}{P}}CH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{NH}{|}}{SO}}\}_n- \rightarrow NaO\overset{\overset{Ph}{|}}{\underset{\underset{O}{\|}}{P}}CH_2CH_2SO_3Na + \quad \mathbf{1a}$$

$$HOCH_2CH_2OH\ (+\ NH_3) \quad (2)$$

$$-\{CH_2CH_2O\overset{\overset{Ph}{|}}{\underset{\underset{O}{\|}}{P}}CH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{SNH}}\}_n- \rightarrow NaO\overset{\overset{Ph}{|}}{\underset{\underset{O}{\|}}{P}}CH_2CH_2SO_3Na + \quad \mathbf{2}$$

$$H_2NCH_2CH_2OH \quad (3)$$

Moreover, the alkaline hydrolysis liberated ammonia gas which was detected by Nessler's reagent. Thus, the structure **1a** was supported.

All the above findings support the phosphinate sulfilimine structure **1a**. Similarly, the structure of the cooligomer obtained from the EPI–ESAm was established as the phosphonate sulfilimine **1b**.

Effects of the reaction solvents and temperatures were examined (Table I). In all cases, 1:1 alternating cooligomers were obtained. All cooligomers are soluble in chloroform, methanol, acetonitrile, and DMF whereas they are insoluble in water, benzene, and diethyl ether. The molecular weights of reaction products were not high, and therefore, they are termed as cooligomers.

Cooligomerization Mechanism. On the basis of the above data as well as the previous observations in the relevant copolymerizations of ESAm with 2-methyl-2-oxazoline (MeOZO) and of acrylamide with EPO,[2,4] Scheme I is proposed here. The first step is the formation of zwitterion **6** by the addition of EPO with ESAm followed by the proton-transfer process. Then, two molecules of **6** afford a dimeric zwitterion **7**. The propagation proceeds via the successive attack of **6** onto **7** to form an oligozwitterion **8**.

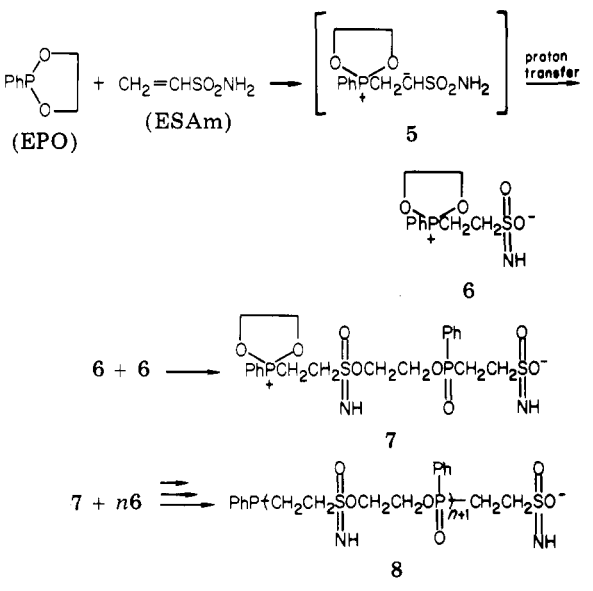
The present cooligomerization is interestingly compared with the cooligomerization of ESAm with MeOZO, which gave a cooligomer of the amide sulfonamide structure **10**, via the regiospecific reaction at the nitrogen anion **9**.[2]

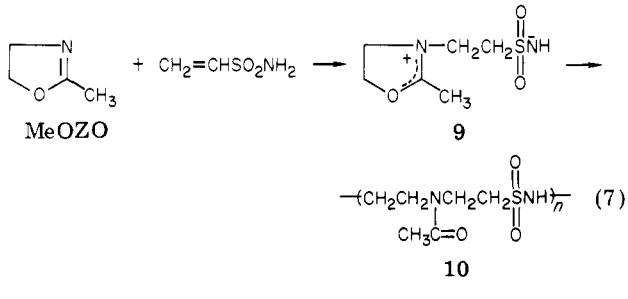
Table I
Cooligomerization of ESAm with EPO and EPI[a]

M_N	solvent	temp, °C	time, h	cooligomer[b] yield, %[c]	cooligomer[b] mol wt[d]
EPO	PhCN	100	42	77	1120
EPO	CH_3CN	50	23	64	630
EPO	Et_2O	20	170	48	530
EPI	PhCN	80	65	74	870
EPI	PhCN	120	24	69	1110

[a] The charged ESAm and M_N were 5.0 mmol each in 1.5 mL of solvent. [b] The ESAm/M_N ratio of the cooligomer was in all cases 1:1 determined by NMR. [c] [(Cooligomer obtained, g/(total initial monomers, g)] × 100. [d] Determined by vapor pressure osmometry in DMF at 55 °C.

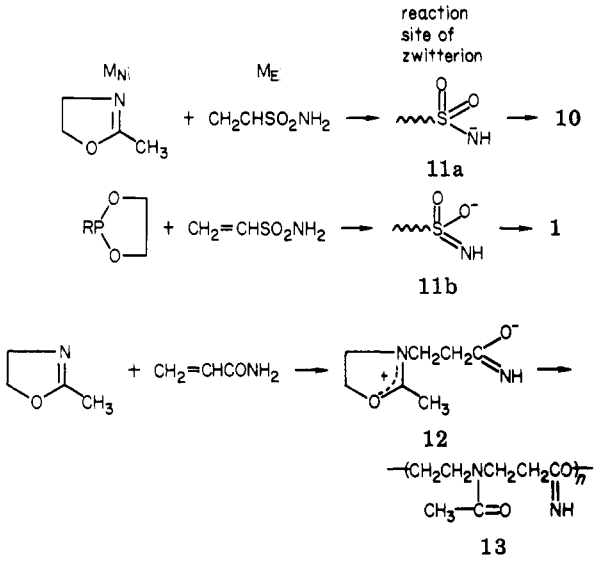
Scheme I



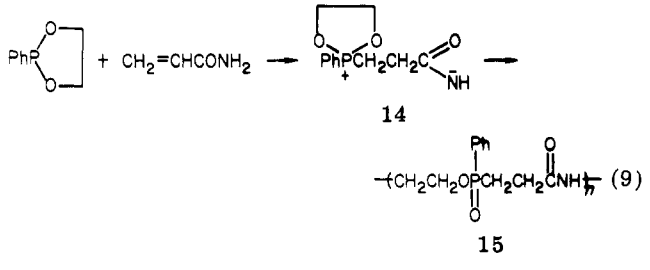


When ESAm was combined with EPO and with EPI in the present study, ESAm gave the sulfilimine unit of the structure **8** via the regiospecific reaction at the oxygen anion **6**. The sulfonamide anion of ESAm is an ambident anion of nitrogen (**11a**) and of oxygen (**11b**). The site of reaction of the sulfonamide anion changes according to the difference of the nature of the gegencation derived from M_E. These are summarized as follows.

Furthermore, this is also interestingly compared with the copolymerization of acrylamide (AM) with MeOZO or EPO(EPI).[3] In the copolymerization of AM with MeOZO, it is known that this combination gives a copolymer of the amide imidate structure **13** via the regiospecific reaction at the oxygen anion in **12**.[3]



In addition, the AM–EPO copolymerization gave a copolymer of the phosphinate amide structure **15** via a regiospecific reaction at the nitrogen atom in the ambident anion **14**.[4]



It should be noted that the reaction site of the ambident anion changes according to the nature of the cationic part in zwitterions derived from M_N. Sulfonamide anion from ESAm reacts at the oxygen atom with a cation of phosphonium (generated from EPO or EPI), whereas it reacts at nitrogen with oxazolinium cation (from MeOZO). On the contrary, the amide anion from AM reacts at a reverse position, i.e., reacting at the nitrogen atom with phosphonium and at the oxygen atom with the oxazolinium cation.

Experimental Section

Reagents. EPO[4,5] and EPI[6,7] were prepared by the reaction of ethylene glycol with phenyldichlorophosphine in the presence of triethylamine and by the reaction of triphenyl phosphite with ethylene glycol.

ESAm was synthesized according to a well-known method,[8] mp 24 °C (lit.[8] mp 24 °C). All solvents were purified by distillation in the usual manners.

Methyl-2-(phenylmethoxyphosphono)ethane sulfonate (dimethyl ester of **4**) was prepared by the reaction of dimethoxyphenylphosphine with ethylenesulfonic acid at 80 °C for 3 h and obtained by preparative gas chromatography as a colorless, slightly viscous liquid.

Cooligomerization Procedue. To 1.5 mL of solvent in a test tube EPO (or EPI) and ESAm (5.0 mmol each) were added at room temperature under nitrogen and the tube was sealed. Then the mixture was kept at a desired temperature. After the reaction the tube was opened and the reaction mixture was poured into a large amount of diethyl ether to precipitate the cooligomer. A white, glassy material was obtained after drying in vacuo.

Hydrolysis of Cooligomer. To 0.05 g of cooligomer was added 0.5 mL of a 10% D_2O solution of NaOH at room temperature and the mixture was heated at 90 °C for 5 h. Then, the reaction mixture was subjected to NMR measurement.

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