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Polymerization via Zwitterion. 12.[1] Novel 1:1:1 Alternating Terpolymerizations of 2-Phenyl-1,3,2-dioxaphospholane, Electron Deficient Vinyl Monomers of Acrylonitrile and Acrylate, and Carbon Dioxide

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ABSTRACT: This paper reports novel 1:1:1 alternating terpolymerizations of two systems composed of three monomers, i.e., 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO)–acrylonitrile (AN)–carbon dioxide (CO_2) and EPO–methyl acrylate (MA)–CO_2. The terpolymerizations took place without catalyst. Into an equimolar mixture of EPO–AN and EPO–MA, CO_2 was introduced under atmospheric or high pressure. A reaction occurred at a wide range of temperatures (room temperature–150 °C) to produce 1:1:1 alternating terpolymers having the structures of **7a** and **7b**, respectively. The structures of terpolymers **7a** and **7b** was established by NMR and ir spectroscopy and the elemental analyses as well as an alkaline hydrolysis experiment. A mechanism via zwitterion **18** was proposed for the terpolymerization. It is considered that **18** is formed by the reaction of a zwitterion **17** with CO_2, which was supported by the findings that analogous terpolymer **7b** was obtained from the reaction of phosphorane **16** with CO_2.

A series of our studies on the no-catalyst copolymerizations via zwitterion intermediate have revealed the importance of combination between a nucleophilic monomer (M_N) and an electrophilic one (M_E) in order to achieve alternating copolymerizations.[1-12] The M_N monomers which have hitherto been studied are 2-oxazolines,[3-5,8,9] 5,6-dihydro-4*H*-1,3-oxazine,[8] 2-benzyliminotetrahydrofuran,[6] 1,3,3-trimethylazetidine,[7] Schiff base,[10] and 2-phenyl-1,3,2-dioxaphospholane.[1,11,12] The M_E monomers are β-propiolactones,[3-6] acrylic acid,[5-7] acrylamide,[8] acrylate,[1] vinyl ketone,[1] 3-hydroxypropanesulfonic acid sultone,[9] and ethylenesulfonamide.[12] In these copolymerizations two monomers react at first to produce a zwitterion **1**, which is a key intermediate responsible for initiation as well as for propagation.

$$M_N + M_E \longrightarrow \underset{\mathbf{1}}{{}^+M_N\text{-}M_E{}^-} \rightleftharpoons \underset{\mathbf{2}}{{}^+M_N\!\left(M_EM_{N_N}\right)_n\!M_E{}^-} \qquad (1)$$

It is to be noted that the polymerization occurs without added catalyst to yield a 1:1 alternating copolymer **2**. Up to now, we have explored seven kinds of M_N and eight kinds of M_E monomers.[1-12] As an extension of these studies, the possibility of 1:1:1 alternating terpolymerization via a zwitterion formed from three monomer components has been examined.

As for the way of this ternary zwitterion formation two types of combination are conceivable as formulated in eq 2 and 3, i.e., zwitterion **4a** from one M_N and two M_E (M_{E_1}, M_{E_2}) and **4b** from two M_N (M_{N_1}, M_{N_2}) and one M_E, respectively.

$$M_N \xrightarrow{M_{E_1}} \underset{\mathbf{3a}}{{}^+M_N\text{-}M_{E_1}{}^-} \xrightarrow{M_{E_2}} \underset{\mathbf{4a}}{{}^+M_N\text{-}M_{E_1}\text{-}M_{E_2}{}^-} \qquad (2)$$

$$M_E \xrightarrow{M_{N_1}} \underset{\mathbf{3b}}{{}^+M_{N_1}\text{-}M_E{}^-} \xrightarrow{M_{N_2}} \underset{\mathbf{4b}}{{}^+M_{N_2}\text{-}M_{N_1}\text{-}M_E{}^-} \qquad (3)$$

In the preceding paper of this series of copolymerizations, we have reported the novel no-catalyst copolymerizations between 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO) and four vinyl monomers having an electron-withdrawing group, methyl acrylate (MA), phenyl vinyl ketone (PVK), methyl vinyl ketone (MVK), and acrylonitrile (AN).[1] For each of these copolymerizations a zwitterion **5** was involved, through which 1:1 alternating copolymer was produced except for the AN system. It is then considered that **5** is expected to react with a third monomer of M_E. In the present paper we disclose novel 1:1:1 terpolymerizations (eq 4), in which carbon dioxide (CO_2) was employed

Table I

1:1:1 Alternating Terpolymerization among EPO (M_N), Acrylic Monomers (M_{E_1}), and CO_2 (M_{E_2})[a]

No.	M_{E_1}[b]	M_{E_2} CO_2, atm	Solvent	Vol, ml	Temp, °C	Time, hr	Terpolymer yield, %	Mol wt[c]
1	AN	1[d]	Acetonitrile	2.0	r.t.	24	35	319
2	AN	10	Acetonitrile	3.0	r.t.	24	37	616
3	AN	50	Acetonitrile	1.0	50	25	67	1280
4	AN	50	Chlorobenzene	1.0	130	90	83	1710
5	AN	50	Toluene	1.0	95	70	92	2760
6[e]	MA[e]	1[d]	Acetonitrile	1.0	r.t.	24	20	560
7	MA	50	DMF	1.0	150	24	36	1320
8	MA	50	Benzonitrile	1.0	140	60	70	973
9	MA	50	Benzonitrile	0.5	120	300	61	1800

[a] $M_N = M_{E_1} = 3$ mmol. [b] AN, acrylonitrile; MA, methyl acrylate. [c] Determined by vapor pressure osmometry. [d] Atmospheric pressure. [e] A mixture of EPO–MA was allowed to form 1:1 adduct, **16**, before the reaction with CO_2.

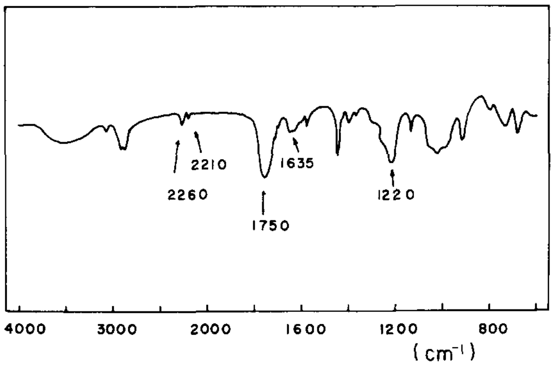
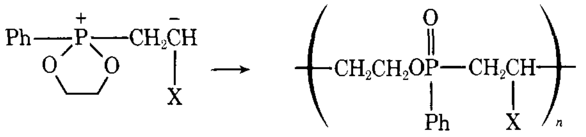


Figure 1. Ir spectrum of the 1:1:1 terpolymer **7a** (polymer sample No. 4) from the EPO–AN–CO_2 system (KBr).

as M_{E_2} in the reaction of eq 2.



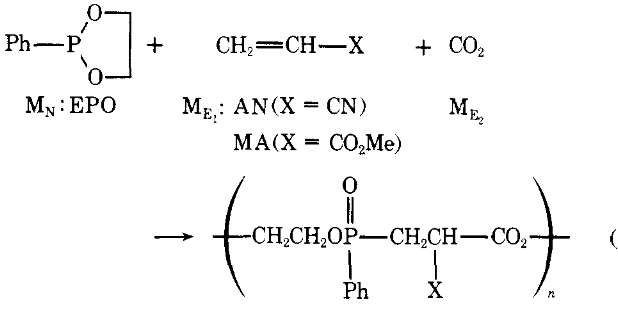
5a, X = CO_2Me
b, X = COPh
c, X = COMe
d, X = CN

6a, X = CO_2Me
b, X = COPh
c, X = COMe + other unit
d, X = CN + AN homo-unit

Results and Discussion

1:1:1 Terpolymerization of EPO–AN–CO_2. The polymerization of AN by the EPO catalysis has already been described.[1] The product polymer was poly(acrylonitrile) containing a small amount of EPO units of **6d** (eq 5).

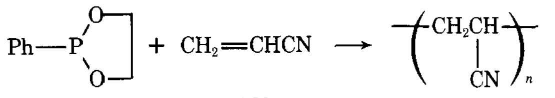
Into this binary system of EPO–AN, a third monomer of CO_2 was introduced with bubbling at room temperature. After the CO_2 had been added for 10 h, the mixture was kept standing for another 14 h. White precipitate, which was formed in the EPO–AN copolymerization system, was not produced; instead, the viscosity of the colorless system was increased greatly. The product was a colorless grease that was shown by ir spectroscopy to contain all three monomer components. Strong absorptions were observed at 1750 cm⁻¹ for ester, 1220 cm⁻¹ for P=O, and 2260 cm⁻¹ for nitrile. As shown in Table I (No. 1–5), a higher temperature and a higher CO_2 pressure were favorable for obtaining terpolymers of higher molecular weights, which are white powdery polymers having melting points of 40–50 °C. They are soluble in polar solvents like DMF, methanol, acetonitrile, and chloroform but insoluble in diethyl ether, benzene, and water.



M_N:EPO M_{E_1}: AN(X = CN) MA(X = CO_2Me) M_{E_2}

(4)

7a, X = CN
b, X = CO_2Me



(5)

EPO AN **8**

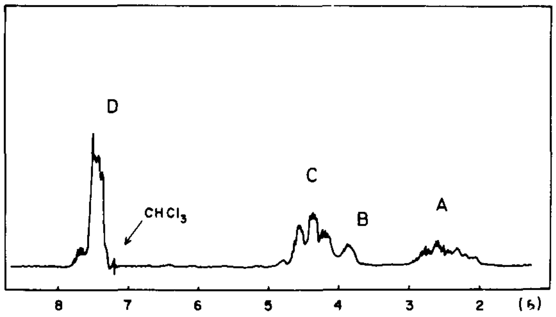


Figure 2. NMR spectrum of the 1:1:1 terpolymer **7a** (polymer sample No. 4) of EPO–AN–CO_2 (in $CDCl_3$).

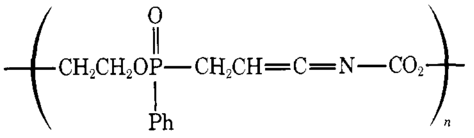
Elemental analysis of the polymers agrees quite well with the calculated values for a 1:1:1 terpolymer of EPO–AN–CO_2. The lower molecular weight polymer (sample No. 1, Table I) was hygroscopic and it was very difficult to remove occluded water from it. Figure 1 shows an ir spectrum for the terpolymer (sample No. 4), which is typical for these products. In addition to the strong characteristic absorptions, there are weak absorptions at 2210 cm⁻¹ ($\nu_{C \equiv N}$) and at 1635 cm⁻¹ ($\nu_{C=O}$ in CO_2^-), which indicate these groups to be on the polymer ends, i.e., $\sim\!\sim CH_2CH(CN)CO_2^-$. Figure 2 shows a ^1H NMR spectrum (in $CDCl_3$) of the terpolymer (sample No. 4). Four kinds of signals are observed. Peaks A (δ 2.0–3.0), B (δ 3.8), C (δ 4.0–4.7), and D (δ 7.5) are assigned respectively to methylene protons ($P\text{-}CH_2$, 2 H), methyne proton ($CH(CN)\text{-}CO_2$, 1 H), two methylene protons ($CO_2\text{-}CH_2\text{-}CH_2\text{-}O$, 4 H), and phenyl protons ($C_6H_5\text{-}P$, 5 H). No olefinic signal was detected. From these findings the structure **7a** was assigned to the 1:1:1 terpolymer. The production of the phosphinate unit in **7a** from

Table II
Characteristics of 1:1:1 Terpolymer Samples

Polymer sample No.	Characters: Polymer appearance	Characters: Mp, °C	Polymer structure
1	Colorless grease		**7a**
2	Colorless grease		**7a**
3	White powder		**7a**
4	White powder	38–42	**7a**
5	White powder	50–54	**7a**
6	Colorless grease		**7b**
7	White powder		**7b**
8	Colorless gum		**7b**
9	White powder	48–49	**7b**

EPO is similar to that of the cationic homopolymerization[13] of EPO in which the Arbusov type reaction took place.

Although a structure **9** might be conceivable as an alternative for the terpolymer, the possibility of such a unit was ruled out by ir and NMR spectra; i.e., no absorption of $\nu_{C=C=N}$ and no olefinic signal of HC=C=N were observed.



$$\left(\mathrm{CH_2CH_2O\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Ph}{|}}{P}}{-}CH_2CH{=}C{=}N{-}CO_2}\right)_n$$

9

The maximum molecular weight of the terpolymer is 2760, which was obtained by the polymerization in toluene.

1:1:1 Terpolymerization of EPO-MA-CO$_2$. An electron deficient vinyl monomer as M_{E_1} is not limited to AN. MA can also be employed for the terpolymerization. When CO$_2$ was introduced into the equimolar mixture of EPO and MA in a polar solvent, polymerization took place at the wide range of temperature and CO$_2$ pressure. The terpolymer (sample No. 9) is a white powder (mp 48–49 °C) and soluble in polar solvents like DMF and chloroform but insoluble in diethyl ether, benzene, and water. The molecular weight was less than 2000 in all cases (No. 6–9 in Table I).

The structure of the terpolymer was established by ^{1}H NMR and ir spectroscopy as well as by alkaline hydrolysis of the polymer. Figure 3a shows the ir spectrum (sample No. 7). A strong absorption due to $\nu_{C=O}$ at 1740 cm^{-1} is observed with characteristic absorptions of $\nu_{P=O}$ at 1220 cm^{-1} and of $\nu_{P\text{-}O\text{-}C}$ at 1040 cm^{-1}. When the ir spectrum of the terpolymer is compared with that of 1:1 EPO-MA copolymer **6a**[1] (Figure 3b), the difference is certainly obvious. Absorption at 1635 cm^{-1} can reasonably be ascribed to $\nu_{C=O}$ of the CO$_2^-$ group at the polymer end (vide supra). The increase of the intensity was brought about by the decrease of the degree of polymerization. Results of elemental analyses are in accord with the calculated value for the 1:1:1 composition of EPO-MA-CO$_2$ (Table III).

In Figure 4 an NMR spectrum of the terpolymer is illustrated. Peak A at δ 2.35 is ascribed to methylene protons (2 H) of P-CH$_2$. A small signal B around δ 3.40 is due to the methyne proton (1 H) of CH(CO$_2$Me)-CO$_2$. A sharp singlet C at δ 3.55 is assigned to the methoxy group (3 H) of ester, CO$_2$-CH$_3$. A broad peak D around δ 4.10 is ascribed to two methylene protons (4 H) of O-CH$_2$-CH$_2$-O. Peak E at δ 7.48 is assigned to the phenyl group (5 H). These data are quite compatible with the structure **7b**. A rather high field shift of peaks A, B, and D, in comparison with corresponding peaks of **7a**, is explained by the difference of electronegativity, i.e., the CO$_2$Me group is less electronegative than the CN group.

The structure of **7b** was further confirmed by an alkaline hydrolysis experiment of the terpolymer. **7b**, on the hydrolysis with aqueous NaOH, should give a tribasic acid of **10** which probably induces decarboxylation to form **11** and **12** under the present conditions of experiment. Accordingly, the production of an equimolar mixture of **11**, **12**, **13**, and **14** is expected (eq 6). Therefore, NaOH is consumed in a quantity of three moles by one molar unit of **7b**. The hydrolysis in 2 N NaOH was carried out and the residual NaOH was titrated by a 1 N HCl solution (thymolphthalein indicator). The consumption of NaOH was found to be 3.11 equiv/mol of the unit of the terpolymer (sample No. 7). This fact is quite compatible with the incorporation of CO$_2$ in the polymer. In the same hydrolysis mixture after it was neutralized, the productions of ethylene glycol (**13**) and methanol (**14**) were indicated by means of gas chromatography. The mixture was then dried and from the residue the disodium salt of **11** was isolated. **11** was confirmed by comparison of the NMR spectrum with a reference sample of **11** (vide infra). Any other product was not found at all. All these data strongly support the structure of **7b**. A possible

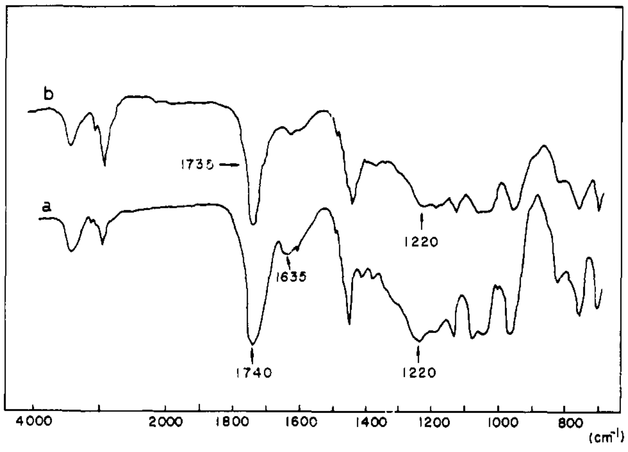


Figure 3. Ir spectra of (a) the EPO-MA-CO$_2$ terpolymer **7b** and (b) the EPO-MA copolymer **6a** (KBr).

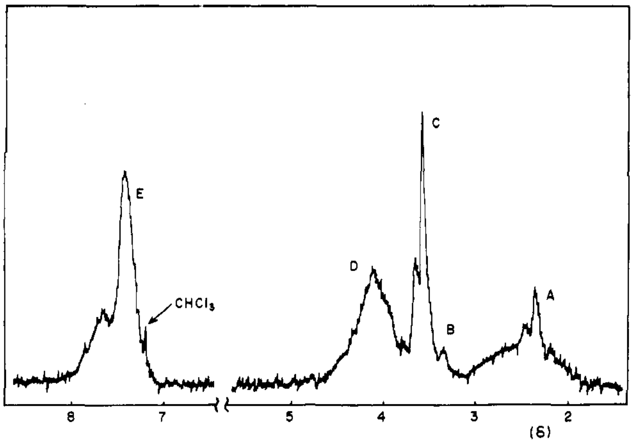
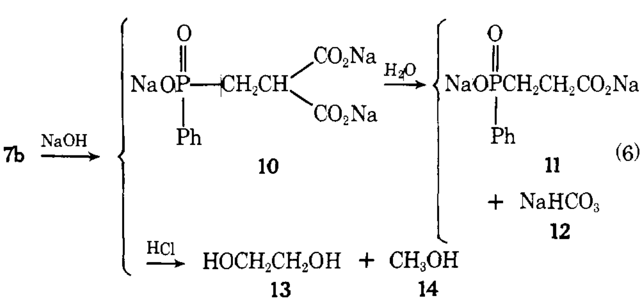


Figure 4. NMR spectrum of the EPO-MA-CO$_2$ terpolymer **7b** (CDCl$_3$).

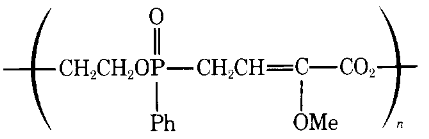


(6)

Table III
Analytical Data of 1:1:1 Terpolymer Samples

Polymer sample No.	Formula	Calcd for 1:1:1 composition C	H	N	P	Found C	H	N	P
1	$C_{12}H_{12}NO_4P(H_2O)_{0.50}$	52.57	4.78	5.11	11.30	52.53	5.39		11.60
3	$C_{12}H_{12}NO_4P$	54.35	4.56		11.68	54.30	4.85		12.01
4	$C_{12}H_{12}NO_4P$	54.35	4.56	5.28	11.68	54.37	4.84	4.93	11.66
6	$C_{13}H_{15}O_6P(H_2O)_{0.30}$	51.42	5.18		10.20	51.34	6.09		10.16
7	$C_{13}H_{15}O_6P$	52.36	5.07		10.39	52.37	5.46		10.23

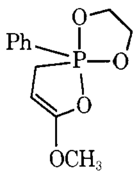
alternative for **7b**, the structure of **15**, was ruled out by NMR analysis, i.e., no olefinic proton -CH=C- was detected.



$$\left(-CH_2CH_2O\overset{O}{\underset{Ph}{P}}-CH_2CH=\underset{OMe}{C}-CO_2-\right)_n$$

15

An attempt was made to modify the procedure of terpolymerization under atmospheric pressure of CO_2 (sample No. 6), since the rate of reaction between EPO and MA was much slower than that of EPO-AN. From the binary reaction of EPO-MA at 50 °C, the pentacovalent phosphorane **16** was successfully isolated as previously described.[1] **16** is a 1:1 adduct which is an intermediate of alternating copolymerization of EPO-MA. At first, an equimolar mixture of EPO and MA in acetonitrile was kept at 50 °C for 10 h to prepare **16**. The formation of **16** was confirmed by NMR spectroscopy. To this mixture CO_2 was then introduced and a slow reaction occurred. A usual work-up gave a terpolymer of colorless grease having a structure of **7b**.



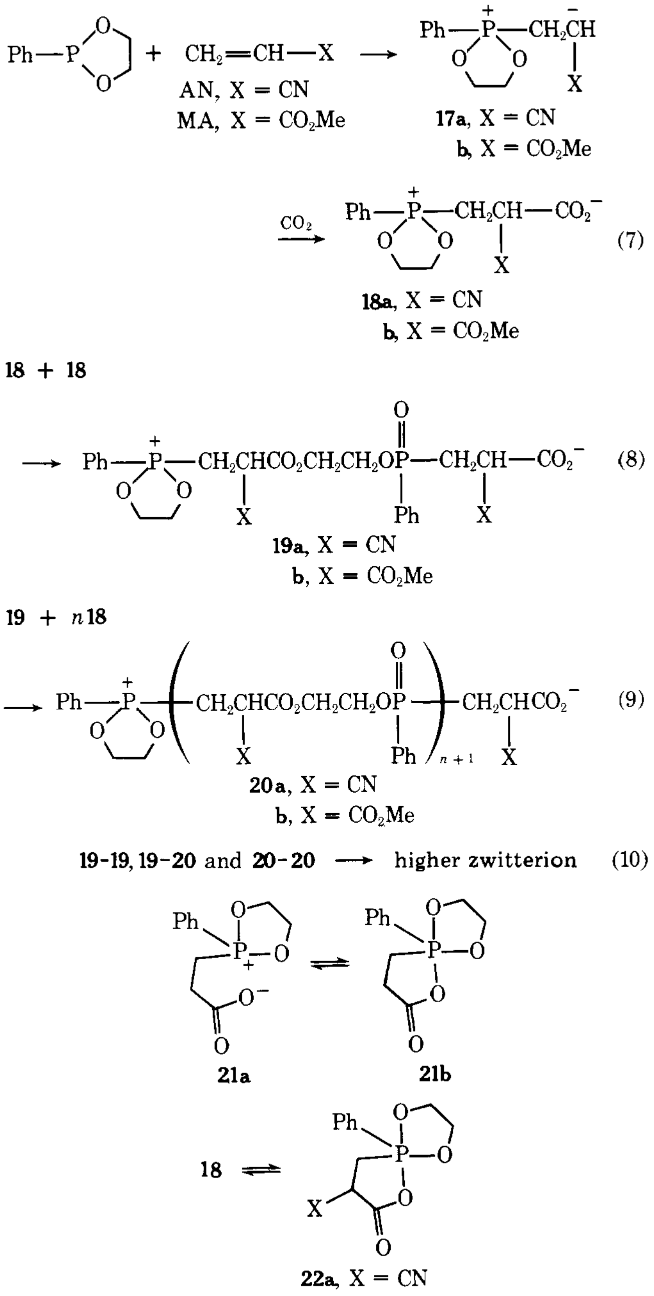
16

By the combination of EPO-MVK-CO_2, a terpolymer was not obtainable but only a binary copolymer **6c** was produced.

Terpolymerization Mechanism. The present novel terpolymerizations without added catalyst are best represented by the following scheme of polymerization via a ternary zwitterion intermediate **18**. In these three component polymerizations, EPO acts as M_N and an electron deficient olefin of AN or MA plays a role of M_{E_1}. CO_2 reacts with the zwitterion **3a** as M_{E_2} (eq 2).

As indicated in Scheme I, zwitterion **17** is first formed by a Michael type addition of EPO and vinyl monomer. It should be mentioned here that in the binary system between EPO and CO_2 or between AN and CO_2 no reaction took place. The anion site of zwitterion **17** is trapped by CO_2 to produce **18**, where the anion site is replaced by more stable carboxylate anion. This might be one of the driving forces of the reaction of CO_2. **18** has the structure corresponding to **4a**, i.e., a phosphonium ion from EPO, an alkyl chain formed by the opening of vinyl group of AN or MA, and a carboxylate anion from CO_2. The subsequent initiation (eq 8) and propagation (eq 9) proceed via zwitterion **18** as in a similar manner of alternating copolymerizations.[2] Evidence involving macrozwitterions **19** and **20** is partly provided by the detection of CO_2^- in the isolated terpolymer as was mentioned above.

Scheme I

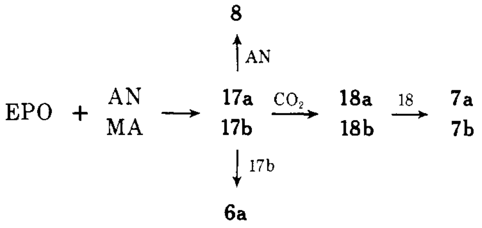


The mode of the reaction is similar to that of the EPO-AA system[11] in which **21a** was considered as a transient species. **21a** was formed by the equilibrium with pentacovalent acylphosphorane (**21b**) at higher temperatures. Analogously **18** may be present in equilibrium with **22**. Isolation of **22**, however, has not been accomplished yet. The terpolymerization via **18** occurred even at room temperature, while the copolymerization via **21a** needed a higher temperature than 100 °C.[1]

The intermediacy of **17** was actually proved in the case of MA. As has been described[1] **17b** can readily isomerize to phosphorane **16** and an equilibrium **17b** $\rightleftharpoons$ **16** was established, where the isolation could be achieved in the form of **16.** The isolated **16** gave the 1:1 alternating copolymer **6a** when heated under nitrogen.[1] **16** could also produce 1:1:1 alternating terpolymer **7a** when it was allowed to react with CO_2 (No. 6 in Table I), indicating that **17b** reacts with CO_2 to yield **18b.** On the contrary, **17a** cannot be stabilized with isomerization but induced the AN homopolymerization at room temperature. Under the presence of CO_2, **17a** is readily quenched to form **18a,** and hence the homopolymerization of AN was not induced. It is reasonable that CO_2^- does not initiate the vinyl polymerization of AN or MA.

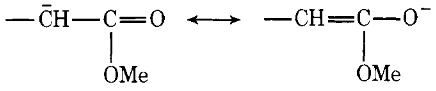
A simple representation of these reactions is given in Scheme II. The success of terpolymerization is due to the fast and selective reaction between binary zwitterion **17** and CO_2.

Scheme II



The anion sites of both **17a** and **17b** are ambident as is indicated by eq 12 and 13. Quenching of the anions occurs at the carbanion form regiospecifically, i.e., **23a** and **24a** attacks CO_2 exclusively. Reactions of CO_2 with **23b** and **24b,** leading to **9** and **15**, respectively, did not occur at all.

$$\underset{\mathbf{23a}}{—\bar{C}H—C{\equiv}N} \longleftrightarrow \underset{\mathbf{23b}}{—CH{=}C{=}N^-}$$



$$\underset{\mathbf{24a}}{—\bar{C}H—\underset{OMe}{\underset{|}{C}}{=}O} \longleftrightarrow \underset{\mathbf{24b}}{—CH{=}\underset{OMe}{\underset{|}{C}}—O^-}$$

24a **24b**

In summary, present terpolymerizations have shown that no-catalyst copolymerization via zwitterion could be extended to a three-component system: M_N (EPO), M_{E_1} (electron deficient vinyl monomer, e.g., AN or MA), and M_{E_2} (CO_2). Furthermore the present reaction provides a novel example of polymerizations using CO_2 as a monomer.

Other related polymerizations should be cited. A report by Hsieh disclosed the first 1:1:1 alternating terpolymerization among tetrahydrofuran, epichlorohydrine, and phthalic acid anhydride.[14] Inoue, Koinuma, and Tsuruta have reported an interesting alternating copolymerization between ethylene oxide and CO_2 by use of diethylzinc–H_2O catalyst.[15]

Experimental Section

Materials. Solvents of benzonitrile, DMF, acetonitrile, chlorobenzene, and toluene were purified as described.[1] A monomer EPO was prepared according to Mukaiyama et al.[13] and purified as before.[1,11] AN and MA were commercial reagents and purified by a careful distillation under nitrogen. CO_2 from a gas bomb (Seitetsu Kagaku Co., Japan) was used without further purification. An authentic compound of disodium salt of 3-(phenylphosphono)propionic acid (**11**) was prepared by the previous method.[11]

Terpolymerization of EPO–AN–CO_2. EPO and AN (3 mmol each) were mixed in 2.0 ml of acetonitrile under nitrogen at −78 °C. Into this solution CO_2 was introduced through a syringe needle as soon as the system was allowed to be warmed. The bubbling of CO_2 was continued for 10 h. After standing in the dark for another 14 h, the mixture was poured into a large amount of a mixed solvent of diethyl ether–pentane (50/50) to precipitate the polymeric material. The product was then isolated and further purified by reprecipitation with a chloroform–*n*-hexane system. The polymer was then dried in vacuo. The result is given in Table I (No. 1).

A typical polymerization under a high pressure of CO_2 was as follows. In a 50 ml pressure tube, 3 mmol each of EPO and AN were mixed in 1.0 ml of chlorobenzene at −78 °C under nitrogen. CO_2 was then introduced into the tube up to a pressure of 50 atm. It was then slowly heated to 130 °C. After 90 h the tube was opened and the copolymer was isolated as above. The results are shown in Table I (No. 2–5).

Terpolymerization of EPO–MA–CO_2. The polymerization at atmospheric pressure was as follows; 3 mmol each of EPO and MA were reacted in 1.0 ml of acetonitrile at 50 °C for 10 hr under nitrogen. To this reaction system CO_2 was introduced by bubbling for 10 h. After standing for 14 h the copolymer was isolated (No. 6 in Table I). A polymerization under high CO_2 pressure was of similar manner as EPO–AN–CO_2 (No. 7–9).

Alkaline Hydrolysis of 1:1:1 Terpolymer of 7b. To 0.306 g (1.02×10^{-3} units' mol) of **7b** was added 4.00 ml of aqueous 2 N NaOH solution. After the mixture was kept at 95 °C for 7 h, it was diluted with water to 10.0 ml. A 2.00-ml portion out of the diluted solution was titrated twice by aqueous 1 N HCl solution by use of a microburet, where 1.02 ml of 1 N HCl was required (thymolphthalein indicator) as an average. From these findings the alkali consumed was calculated as 3.18×10^{-3} mol which was 3.11 equiv of the units' mol of **7b.** The neutralized mixture was then subjected to gas chromatography. Ethylene glycol and methanol were detected.

Then, water was evaporated to dryness and the residue was washed by a diethyl ether and by a chloroform solvent. **11** was then extracted with 10 ml of ethanol from the residue. The NMR spectrum of **11** was the same with that of the authentic sample, i.e., δ 2.25 (m, P–CH_2–CH_2–CO_2, 4 H), 7.70 (m, C_6H_5–P, 5 H).[11]

Molecular Weight Determination. The molecular weight of the polymer was measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in chloroform at 35 °C.

References and Notes

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