Makromol. Chem. **179**, *1753–1763 (1978)*

Radical Polymerization and Copolymerization of Some Vinyl Phosphates

Kazuko Hayashi

Government Industrial Research Institute, Osaka,
Midorigaoka 1, Ikeda-shi, Osaka, Japan

(Date of receipt: May 21, 1977)

SUMMARY:

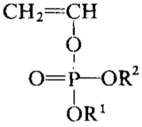
Diethyl vinyl phosphate (**1**), diphenyl vinyl phosphate (**2**), and phenyl divinyl phosphate (**3**) were prepared, and their polymerization and copolymerization behaviors as well as the hydrolysis of the polymers obtained were investigated. The monomers **1** and **2** were homopolymerized to give low molecular weight polymers, probably as a result of high chain transfer reactivity to monomer. Although the monomer **3** gave a cross-linked polymer, this polymerization was found to proceed mainly by a cyclopolymerization mechanism to give a polymer with a five-membered ring unit which was readily hydrolyzed. The alkaline hydrolysis of poly(**1**) occurred only partly and thus pure polyvinyl alcohol was not obtained. From the copolymerizations of **1** and **2** with vinyl monomers such as vinyl chloride, the reactivities of these monomers were found to be somewhat lower than that of vinyl acetate.

Introduction

Synthesis and polymerization of some vinyl phosphates have been reported briefly by several workers[1–5]. However, no systematic and detailed studies regarding their polymerization behavior and the hydrolysis of their polymers have been made.

In the previous paper[6], we have studied the relationship between the structure of vinyl carboxylates and their radical reactivities.

In the present work, three vinyl phosphates, diethyl vinyl phosphate (**1**), diphenyl vinyl phosphate (**2**), and phenyl divinyl phosphate (**3**), were prepared, and their radical polymerization and copolymerization behaviors were investigated and compared with those of vinyl acetate. The hydrolysis of poly(**1**) under mild conditions was also studied.



$CH_2{=}CH{-}O{-}P({=}O)(OR^2)(OR^1)$

1: $R^1 = R^2 = C_2H_5$
2: $R^1 = R^2 = C_6H_5$
3: $R^1 = C_6H_5, R^2 = CH{=}CH_2$

Experimental Part

Preparation of vinyl phosphates

Diethyl vinyl phosphate (**1**): This monomer was prepared from the equimolar reaction of chloroethylene carbonate with triethyl phosphite according to the method of Selms et al.[5]. The pure monomer was obtained in 42,7% yield by a fractional distillation under reduced pressure: bp 67–68 °C (4 Torr); $d_4^{25} = 1{,}176$; $n_D^{25} = 1{,}4017$ (lit.[5] $n_D^{25} = 1{,}4109$).

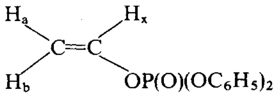
IR: 1643 (s: $CH_2{=}CH$) and 1271 cm^{-1} (vs; P=O).

Diphenyl vinyl phosphate (**2**): This monomer was not obtained by the same method as described above, but by the method of Gefter et al.[2]. To the mixture of diphenyl phosphorochloridate and excess triethylamine, three times excess amount of acetaldehyde was added dropwise at 10°C, and allowed to stand at 2°C for a week. The resulting brownish heterogeneous solution was filtered, and then the filtrate was distilled under reduced pressure: yield 42,1%, bp 160,5–161,0°C (3 Torr); $d_4^{25}=1{,}2062$; $n_D^{20}=1{,}5338$.

$C_{14}H_{13}O_4P$ 276,2	Calc.	C 60,78	H 4,74	P 11,42
	Found	C 60,80	H 4,72	P 11,43

IR: 1649 (s; $CH_2{=}CH$), 1593 (s; C_6H_5), and 1265 cm^{-1} (vs; P=O).

^1H NMR: $\delta=4{,}56$ (dq; H_a), 4,91 (dq; H_b), 6,62 (dq; H_x), and 7,18 ppm (m; C_6H_5); $J_{ab}=2{,}1$, $J_{ax}=5{,}9$, $J_{bx}=13{,}0$, $J_{ap}=2{,}8$, $J_{bp}=1{,}0$, and $J_{xp}=6{,}5$ Hz.



Phenyl divinyl phosphate (**3**): This monomer was prepared similarly to **2**, except the use of phenyl phosphorodichloridate: yield 53,0%, bp 99,1°C (1,5 Torr); $d_4^{25}=1{,}175$; $n_D^{25}=1{,}4885$.

$C_{10}H_{11}O_4P$ 226,2	Calc.	C 53,11	H 4,90	P 13,70
	Found	C 52,92	H 4,93	P 13,68

IR: 1695 (s; $CH_2{=}CH$), 1593 (s; C_6H_5), and 1290 cm^{-1} (vs; P=O).

^1H NMR: $\delta=4{,}57$ (dq; H_a), 4,90 (dq; H_b), 6,55 (dq; H_x), and 7,20 ppm (m; C_6H_5); $J_{ab}=2{,}0$, $J_{ax}=5{,}6$, $J_{bx}=12{,}5$, $J_{ap}=2{,}7$, $J_{bp}=1{,}0$, and $J_{xp}=6{,}4$ Hz.

The attempts to prepare other alkyl vinyl phosphates, such as methyl divinyl phosphate and ethyl divinyl phosphate, by this method were unsuccessful.

Other materials

Commercial vinyl acetate (VAc) and vinyl chloride (VC) were distilled just prior to use. Vinyl chloroacetate (VCAc) was prepared by vinyl interchange reaction[6]. Maleic anhydride (MA) and α,α'-azoisobutyronitrile (AIBN) were recrystallized twice from chloroform and ethanol, respectively. Acetone, benzene, ethyl acetate, and pyridine were purified by usual methods. The reagent-grade tetrahydrofuran and petroleum ether were used without further purification.

Homopolymerizations

The 50 vol.-% ethyl acetate solution polymerizations of vinyl phosphates were carried out in sealed tubes with AIBN ($5{,}0\cdot10^{-3}$ $mol\cdot l^{-1}$) under shaking in a thermostat. The required amounts of reagents were placed into glass ampoules and degassed several times by a freezing and thawing technique, and then sealed under vacuum. After polymerization, the content of the tubes was poured into a large amount of petroleum ether to isolate the polymer. The conversion was calculated from the weight of the dried polymer obtained.

Copolymerizations

The copolymerizations of vinyl phosphates **1–3** with VC and VCAc were carried out in sealed tubes with AIBN ($5{,}0\cdot10^{-3}$ $mol\cdot l^{-1}$) in benzene at 60°C. A similar method was used for the copolymerizations with MA except the use of ethyl acetate as solvent. After copolymerization for a given time, the polymerization mixture was poured into a large amount of methanol to isolate the copolymer.

The compositions of the copolymers were determined from the chlorine analysis by a flask combustion method for the copolymers with VC and VCAc, and from pH titration by a standard sodium hydroxide aqueous solution in pyridine-water mixed solvent for the copolymers with MA.

Hydrolysis of poly(diethyl vinyl phosphate) (poly(1))

Alkali and acid hydrolyses of poly(**1**) were carried out in sealed tubes at 60°C for 24 h. The ethanol solution of a required amount of poly(**1**) was charged into a glass ampoule, and sodium hydroxide or hydrochloric acid aqueous solution was added to give 3 M or 1 M solutions, respectively. Ethanol concentration was kept at 75%. Then this ampoule was sealed under nitrogen atmosphere, and allowed to shake at 60°C for 24 h.

In alkali hydrolysis, a coloration of the reaction mixture was observed even at room temperature and a brownish polymer was precipitated during the reaction at 60°C. The polymer was separated by decantation. Then it was dissolved in water, dialyzed, and finally converted into the free acid through a strong acidic cation-exchange resin column.

Analyses and measurements

The intrinsic viscosities, $[\eta]$, of the polymers and copolymers, were measured in acetone (except the copolymers with VC where THF was used), by using an Ubbelohde viscometer at 30°C. Number-average molecular weights ($\bar{M}_n$) of the polymers were determined by vapor pressure osmometry in acetone at 30°C.

Elementary analysis of the polymers containing phosphorus was done by a Yanagimoto CHN Coder using tungsten trioxide as an absorbent for phosphorus pentoxide. Phosphorus contents were determined by spectroscopic analysis using ammonium molybdate and ascorbic acid7) after decomposition by perchloric acid.

The check for residual vinyl and phenyl groups in poly(phenyl divinyl phosphate) (poly(**3**)) was performed from IR spectra (KBr disks) by using the calibration curves determined from **3**.

^{1}H NMR spectra were taken on a JEOL PS-100 apparatus at 100 MHz in carbon tetrachloride for monomers **1**–**3** and in DMSO-d_6 for the hydrolyzed poly(**1**).

Results and Discussion

1. *Homopolymerizations*

The results of radical polymerizations of vinyl phosphates **1**–**3** are summarized in Tab. 1, in which the results for vinyl acetate (VAc) as a typical vinyl ester are also included. From this table, it is found that the monomers can homopolymerize in the presence of a radical initiator, and that the polymerization rates (R_p) decrease in the order of VAc, **1**, **3**, and **2**. Namely, it is noted that monomers **2** and **3** polymerize much slower than monomer **1** which polymerizes almost as readily as VAc. The resulting polymers from **1**–**3** are a transparent viscous oil, a colored powder, and a brownish-colored insoluble mass, respectively. The molecular weights ($\bar{M}_n$) and intrinsic viscosities $[\eta]$ of poly(**1**) and poly(**2**) are very small in comparison with the poly(vinyl acetate) (PVAc) from VAc, as follows:

For poly(**1**): $[\eta] = 0{,}1\text{–}0{,}2\ \text{dl}\cdot\text{g}^{-1}$; $\bar{M}_n = 1\text{–}2\cdot 10^4$
For poly(**2**): $[\eta] = 0{,}01\ \text{dl}\cdot\text{g}^{-1}$; $\bar{M}_n = 1\cdot 10^3$
For PVAc: $[\eta] = 0{,}7\ \text{dl}\,\text{g}^{-1}$

From these results it may be anticipated that the chain transfer reaction to monomer is more important in the radical polymerizations of these phosphate monomers than with VAc, probably due to the abstraction of the tertiary hydrogen in the backbone and the α-hydrogen atom of the alkyl phosphate ester group by growing polymer radicals, as has been pointed out in the polymerization of alkyl vinyl phosphonates8). Furthermore, the lower R_p observed in the polymerization of **2** compared with **1** may be due to the steric effect by a phenyl

Tab. 1. Results of polymerizations of vinyl phosphates **1**–**3** and vinyl acetate (VAc). [M] = 50 vol.-%; [AIBN] = 5,0 · 10^{-3} mol · l^{-1}; solvent: ethyl acetate[a]

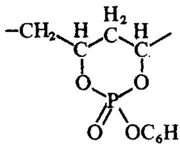
Vinyl ester	$\frac{[M]}{mol \cdot l^{-1}}$	Temp. in °C	Time in min	Conversion in %	$10^4 \cdot R_p$ in $\% \cdot s^{-1}$	$\frac{0{,}239 \cdot E_a}{kJ \cdot mol^{-1}}$	$\frac{A_a}{l \cdot mol^{-1} \cdot s^{-1}}$
1	3,28	70	70	23,6	56,2	22,7 ± 0,7	2,5 · 10^{11}
		60	120	16,8	23,3		
		50	180	8,2	7,6		
		40	1200	17,2	2,4		
2	2,23	80	480	1,0	0,35	11,9 ± 0,3	1,1 · 10^2
		60	1620	1,1	0,11		
		40	8680	2,1	0,04		
3	2,58	80	480	7,4	2,5	22,7 ± 7,1	3,3 · 10^8
		60	540	5,4	1,8		
		40	8680	2,2	0,04		
VAc	5,43	70	10	13,7	228	23,8 ± 1,1	5,0 · 10^{12}
		60	15	6,5	72		
		50	60	10,7	30		
		40	95	4,4	7,7		

[a] R_p: rate of polymerization; E_a: apparent activation energy; A_a: apparent frequency factor.

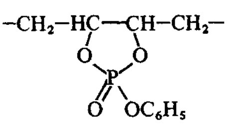
group or the formation of a π-complex between a phenyl group and a growing polymer radical, as was assumed in the radical polymerization of vinyl benzoate[9].

From Tab. 1, the apparent activation energies (E_a) and frequency factors (A_a) evaluated for **1** are found to be almost identical to those of VAc. The unusual values for **2** and **3**, however, are concluded to be unreliable, because of the small conversions for **2** and of poorness in linearity of the Arrhenius plot for **3**.

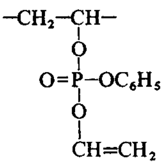
Although cyclopolymerization is expected to occur in the polymerization of **3**, the polymers obtained contained some insoluble fractions in most solvents examined. In fact, the brownish-colored polymer was precipitated in the early stage of polymerization, indicating that some intermolecular propagation to cross-linked polymer also occurred. Thus, the polymerization of **3** seems to involve intra- and intermolecular propagation steps to give polymers mainly consisting of the following three repeating units **4**–**6**.



4



5



$$\begin{array}{c} -CH_2-CH- \\ | \\ O \\ | \\ O=P-OC_6H_5 \\ | \\ O \\ | \\ CH=CH_2 \end{array}$$

6

It was also found that the resulting insoluble polymer was very sensitive to moisture, and the phenol odour was observed during treatments like filtration. This finding also agreed with the result of the IR spectrum of this polymer, which showed absorption bands at 3400 (m; C—OH) and 2670 cm^{-1} (P—OH), as seen in Fig. 1(A).

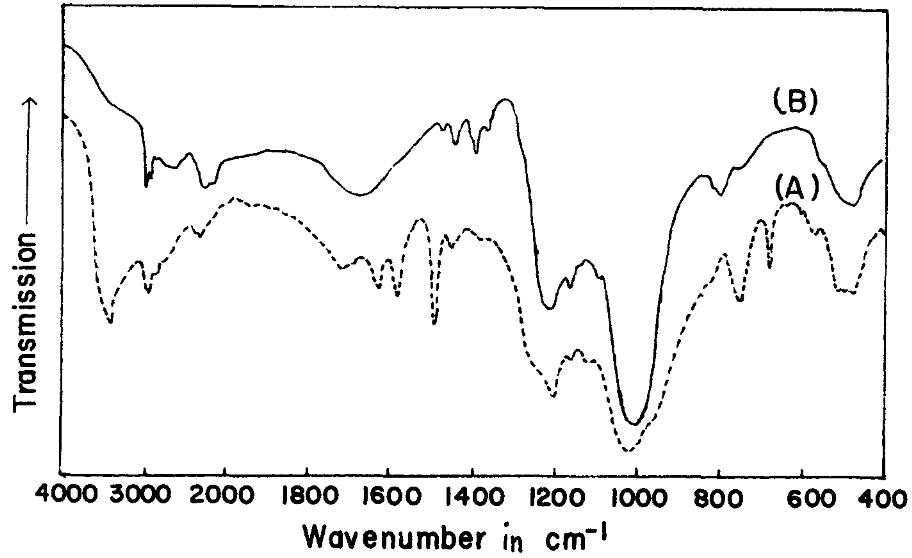
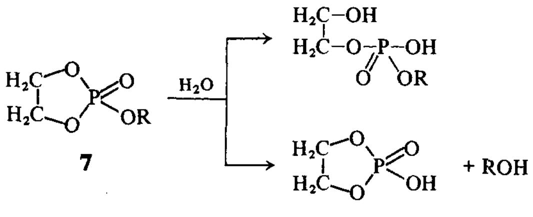
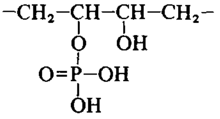


Fig. 1. IR spectra of partly hydrolyzed poly(vinyl phosphate)s. (A): poly(**3**) (sample A), KBr method; (B): alkali-hydrolyzed poly(**1**) (acid-form), film method

The fact that poly(**3**) was unstable towards water might indicate that this polymer included a considerable amount of five-membered rings **5**. This can be anticipated from the finding that the low molecular model compound **7** hydrolyzes 10^6–10^8 times faster than the respective six-membered and linear phosphoric esters[10,11], according to the following equation.

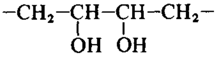


Therefore, when poly(**3**) was allowed to stand in air the five-membered unit **5** seemed to be readily hydrolyzed to the units **8** and **9**.



$-CH_2-CH(O-P(=O)(OH)_2)-CH(OH)-CH_2-$

8



$-CH_2-CH(OH)-CH(OH)-CH_2-$

9

Thus, the insoluble poly(**3**) isolated in this study seemed to consist of the repeating units **4**, **6**, **8**, and **9**. The content of these units might be determined approximately by elementary analyses of carbon and phosphorus. The results are shown in Tab. 2.

Tab. 2. Results of analyses of poly(**3**) partly hydrolyzed by moisture[a)]

Poly(**3**) sample[b)]	% C	% P	Content of five-membered ring in mole-%		Phenyl content in mmol · g^{-1}		Residual vinyl[c)] content in mole-%	1,2-Glycol[d)] content in mole-%
			8	**9**	(found)[c)]	(calc.)		
A	41,14	16,1	55,9	0,7	1,80	2,25	15,3	9,4
B	39,19	15,7	59,8	11,0	1,42	1,66	13,8	8,1

[a)] Based on (**4**+**6**+**8**+**9**) = 100%.

[b)] Polymerized at 60°C. Conversions were 0,9 (A) and 5,8% (B).

[c)] Determined from IR spectra.

[d)] Determined by the periodate method[14)] after acid-hydrolysis.

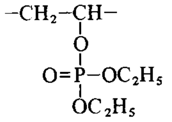
From this table, the observed phenyl content determined by elementary analysis was in fairly good agreement with that by IR determination. As also shown in Tab. 2, the actual content of unit **6** (vinyl) should be higher than that evaluated from the residual vinyl group as the result of the formation of cross-linked polymer, and hence, the content of unit **4** (six-membered ring) should be lower than that calculated from the sum of **5** (i.e. **8**+**9**) and residual vinyl content. Therefore, it was concluded that the cyclopolymerization to the five-membered ring occurs easier than to the six-membered ring in the polymerization of **3**.

To obtain directly the content of five-membered ring, the content of 1,2-glycol units for the sample B (cf. Tab. 2) was determined through hydrolysis by boiling in 0,5 M H_2SO_4 for 24 h, followed by the periodate method[14)]. The value obtained (0,705 mmol · g^{-1}; 12,4 mole-%) was only slightly over that without hydrolysis, which is shown in Tab. 2. The hydrolyzed products (gels) were still stained with basis dye and had the absorption of the phosphoric ester group in the IR spectrum. However, it is obscure if the low value above may be only due to incompletion of hydrolysis.

2. *Hydrolysis of poly*(**1**)

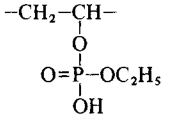
The vinyl phosphate polymers of **1** and **2** are expected to convert to polyvinyl alcohol through hydrolysis. However, pure polyvinyl alcohol was not obtained by both acid- and alkali-hydrolyses under the present conditions.

To study the hydrolysis of these polymers and to evaluate the structure of the hydrolyzed products, poly(**1**) was used, which was relatively high in molecular weight. Acid-hydrolysis of poly(**1**) was performed heterogeneously. The resulting polymer showed an almost identical NMR spectrum to poly(**1**). However, alkali-hydrolysis easily occurred to give a brownish-colored powder. This polymer was very hygroscopic in its salt-form, but its acid-form had a film-forming ability. The IR spectrum of this film showed absorption bands at 2675 (m; P—OH), 1225 (s; P=O), 1012 (s; POC), 1394 (w; CH_3), and 3400 cm^{-1} (w; C—OH), as shown in Fig. 1(B). From this the polymer seemed to consist of the repeating units **10**–**13**.



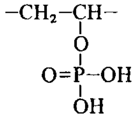
$$-CH_2-\underset{\substack{| \\ O \\ | \\ O=P-OC_2H_5 \\ | \\ OC_2H_5}}{CH}-$$

10



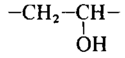
$$-CH_2-\underset{\substack{| \\ O \\ | \\ O=P-OC_2H_5 \\ | \\ OH}}{CH}-$$

11



$$-CH_2-\underset{\substack{| \\ O \\ | \\ O=P-OH \\ | \\ OH}}{CH}-$$

12



$$-CH_2-\underset{\substack{| \\ OH}}{CH}-$$

13

The results of elementary analysis of this polymer for carbon and phosphorus were C 30,36% and P 20,4%. These values are in fairly good agreement with those (C 31,59% and P 20,4%) calculated for **11**.

Both pH titration and conductimetric titration curves for the same sample clarified that the hydrolyzed product was a strong acidic polyanion, as can be seen in Fig. 2. The curves (A) and (B) gave the values of 6,10 and 7,06 meq·g^{-1} (mmol $H^+ \cdot g^{-1}$), respectively, as acid content, while the calculated one for the unit **11** was 6,58 meq·g^{-1}. No clear neutralization point in the conductimetric titration curve (C) in Fig. 2 could be obtained because of its large rounded tendency. From the result of ^1H NMR, as shown in Tab. 3, it was found that the number of methyl and oxymethylene groups decreased to 33 and 32%, respectively, and the formation of hydroxyl groups (that is unit **13**) was suggested by the change of the peak of the methylene group in the backbone to a broad one with a shoulder at the side of high magnetic field. The mole ratio, **11**:**12**:**13** = 69,7:18,6:11,7, which was calculated from carbon and phosphorus contents on the assumption that the hydrolyzed poly(**1**) consisted of these units, was found to be in fair agreement with the ^1H NMR data as shown in Tab. 3, and in that case, 7,96 meq·g^{-1} was calculated as total acid content.

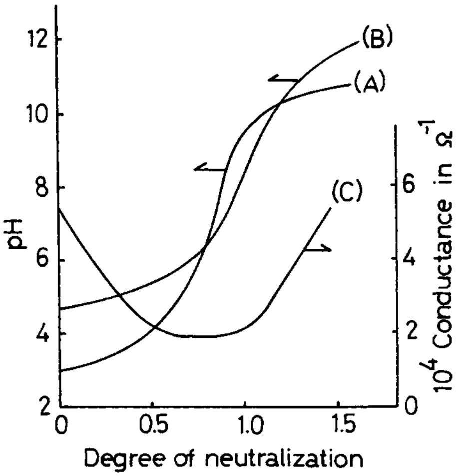


Fig. 2. Titration curves for the alkali-hydrolyzed poly(**1**) (acid-form). (A): pH titration with 0,05 M NaOH in water; (B): do. in the pyridine-water (1:3) system; (C): Conductimetric titration with 0,1 M NaOH in water

Consequently, in this alkali-hydrolysis, it seems to be probable that the first cleavage occurred at the ethyl ester bond in the side chain and at the ester bond linking with the backbone, but that the hydrolysis for the resultant monoethyl ester bond was difficult because of the large differences among the three dissociation constants of phosphoric acid ($pK_1 = 2{,}1$, $pK_2 = 7{,}2$,

Tab. 3. Comparison of the data of ^1H NMR spectrum[a] with the results calculated from elemental analyses for the alkali-hydrolyzed poly(**1**)

Peak			Relative area	
shape	δ in ppm	assignment	found	calc.[b]
S[c]	6,05[d]	POH, COH, H_2O	2,70	1,19
Broad	4,26–4,75	—CH—	1,0	1,0
Dq	4,02	—CH_2O—	1,32	1,39
Broad	1,47–2,23	—CH_2—	2,0	2,0
T	1,28	—CH_3	1,92	2,09

[a] Measured in ca. 10% solution in DMSO-d_6 at 85 °C.

[b] Calculated from the carbon and phosphorus contents (30,36 and 20,4%, respectively) by assuming that the polymer includes the repeating units **11**, **12**, and **13**.

[c] S = singlet, Dq = double quartet, T = triplet.

[d] $\delta = 6{,}49$ ppm at room temperature.

and $pK_3 = 12{,}3$) and also because of the repulsion between the catalyst (OH^-) and the phosphoric acid group formed. Prolonged reaction using 3 M NaOH still gave similar analytical data.

3. *Copolymerization*

The results of the radical copolymerizations of vinyl phosphates **1–3** and of VAc with VC and VCAc (M_1) are shown in Tabs. 4 and 5. Both the rates of copolymerization and intrinsic viscosities of the resulting copolymers were found to decrease with increasing of

Tab. 4. Copolymerizations of vinyl chloride (VC) (M_1) with vinyl phosphates **1–3** (M_2) at 60 °C. $[M_1] + [M_2] = 91{,}0$ vol.-%, $[AIBN] = 4{,}5 \cdot 10^{-3}$ mol·l^{-1}; solvent: benzene

M_2	Content of M_1 in feed in mole-%	Polym. time in min	Conv. in %	Polym. rate in %·s^{-1}	Copolymer		
					% Cl	content of M_1 in mole-%	$\frac{[\eta]}{dl \cdot g^{-1}}$
1	91,3	45	4,0	$1{,}5 \cdot 10^{-3}$	52,4	97,2	0,56
	79,7	45	4,4	$1{,}6 \cdot 10^{-3}$	46,8	93,2	0,52
	63,5	45	3,9	$1{,}4 \cdot 10^{-3}$	39,3	86,7	0,46
	39,5	65	5,5	$1{,}4 \cdot 10^{-3}$	26,3	71,4	0,34
	22,5	80	4,1	$0{,}9 \cdot 10^{-3}$	16,4	54,0	0,30
2	90,1	180	9,2	$8{,}5 \cdot 10^{-4}$	48,3	96,3	0,52
	79,6	380	11,0	$4{,}8 \cdot 10^{-4}$	40,6	91,8	0,42
	62,6	240	0,3	$0{,}2 \cdot 10^{-4}$	30,4	83,6	0,33
	49,3	2470	5,6	$0{,}4 \cdot 10^{-4}$	22,4	73,9	0,24
	30,3	2550	5,7	$0{,}4 \cdot 10^{-4}$	12,3	55,1	
3	79,2	120	5,4	$7{,}5 \cdot 10^{-4}$			
	62,0	100	4,9	$4{,}5 \cdot 10^{-4}$			
	41,1	210	2,3	$1{,}8 \cdot 10^{-4}$			
	28,9	240	2,6	$1{,}8 \cdot 10^{-4}$			
	15,4	330	2,3	$1{,}2 \cdot 10^{-4}$			

Tab. 5. Copolymerizations of vinyl chloroacetate (VCAc) (M_1) with vinyl phosphates **1**–**3** and vinyl acetate (VAc) (M_2) at 60°C. $[M_1]+[M_2]=91{,}0$ vol.-%, $[AIBN]=5{,}0\cdot10^{-3}$ mol·l^{-1}, solvent: benzene

M_2	Content of M_1 in feed in mole-%	Polym. time in min	Conv. in %	Polym. rate in %·s^{-1}	Copolymer			
					% Cl	content of M_1 in mole-%	$\frac{[\eta]}{\text{dl}\cdot\text{g}^{-1}}$	$10^{-3}\cdot M_n$
1	86,2	50	11,7	$3{,}9\cdot10^{-3}$	26,3	92,7	0,23	
	69,4	50	10,3	$3{,}4\cdot10^{-3}$	22,2	82,1	0,24	
	50,2	50	9,3	$3{,}1\cdot10^{-3}$	17,1	67,4	0,24	
	36,2	50	8,9	$3{,}0\cdot10^{-3}$	12,9	53,9	0,23	7,4
	14,5	50	5,6	$1{,}9\cdot10^{-3}$	6,6	30,2	0,27	
2	90,1	90	2,3	$4{,}3\cdot10^{-4}$	25,1	93,0	0,12	
	77,2	140	1,6	$1{,}9\cdot10^{-6}$	19,9	82,8	0,10	
	60,1	210	1,1	$0{,}9\cdot10^{-6}$	15,0	70,5	0,08	
	36,1	330	0,8	$0{,}4\cdot10^{-6}$	8,4	47,8	0,05	
	20,1	330	0,5	$0{,}3\cdot10^{-6}$				
3	79,8	80	3,4	$7{,}1\cdot10^{-4}$				
	58,8	100	2,2	$3{,}7\cdot10^{-4}$				
	38,8	100	1,2	$2{,}0\cdot10^{-4}$				
	19,2	100	1,0	$1{,}7\cdot10^{-4}$				
VAc	78,5	15	1,9	$2{,}1\cdot10^{-3}$	24,5	78,2		
	57,8	15	2,4	$2{,}7\cdot10^{-3}$	19,1	56,9		
	37,8	15	2,5	$2{,}8\cdot10^{-3}$	14,2	39,9		
	18,6	10	1,8	$3{,}1\cdot10^{-3}$	8,1	21,2		

the M_2 concentration in the feed, except the case of **1** with VCAc. It was also observed that the rates at identical feed monomer mixture decreased in the order of **1**, **3**, and **2**, which coincided with that observed in the homopolymerization. These results might be explained from the degradative chain transfer reactivities of vinyl phosphates.

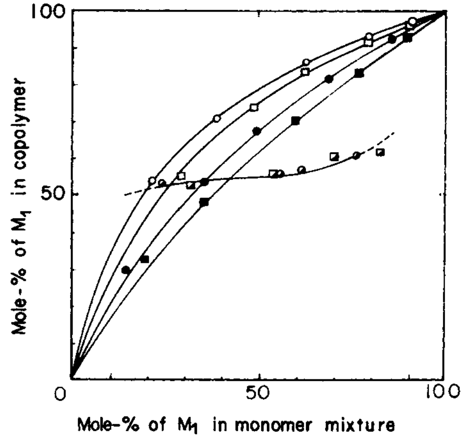


Fig. 3. Monomer-copolymer composition curves for the copolymerizations of **1** and **2** (M_2) with vinyl chloride (VC), vinyl chloroacetate (VCAc), and maleic anhydride (MA) (M_1), initiated with AIBN in benzene at 60°C.
(○): **1** – VC; (□): **2** – VC
(●): **1** – VCAc; (■): **2** – VCAc
(◑): **1** – MA; (◪): **2** – MA
(——): Curves obtained from the reactivity ratios r_1 and r_2 determined by the Fineman-Ross method

All copolymers obtained from **1** were almost colorless, but those from **2** were colored powders whose coloration increased with increasing content of **2**. All copolymers obtained from **3** were insoluble in most solvents, and had residual double bonds, indicating that the cross-linking reaction occurred during the copolymerization. Since these copolymers were also sensitive to moisture and the phenol odour was observed similarly to the homopolymer of **3**, the cyclopolymerization to five-membered ring units seemed to occur.

Tab. 6. Parameters for the copolymerizations of the vinyl phosphates **1** and **2** and VAc (M_2) with vinyl chloride (VC), vinyl chloroacetate (VCAc), and maleic anhydride (MA) (M_1)

M_1	M_2	Reactivity ratios		Q_2	e_2
		r_1	r_2		
VC[a]	**1**	3,3	0,20	0,012	−0,44
	2	2,8	0,25	0,014	−0,40
	VAc	2,0	0,28	0,020[b]	−0,59[b]
VCAc[c]	**1**	2,0	0,43	0,014	−0,68
	2	1,4	0,50	0,020	−0,88
	VAc	0,95	0,86	0,030	−0,73
MA	**1**	0,2	0,0	—	—
	2	0,2	0,0	—	—
	VAc	0,01[d]	0,07[d]	—	—

[a] $Q_1 = 0{,}044$ and $e_1 = 0{,}20$[12].

[b] Results of Hayashi et al.[6].

[c] $Q_1 = 0{,}025$ and $e_1 = -0{,}28$[6].

[d] Results of Young[13].

Tab. 7. Copolymerizations of vinyl phosphates (M_2) with maleic anhydride (MA) (M_1) at 60°C. $[M_1]+[M_2]=91{,}0$ vol.-%, $[\mathrm{AIBN}]=5{,}0\cdot10^{-3}$ mol·l^{-1}, solvent: benzene

M_2	Content of M_1 in feed in mole-%	Polym. time in min	Conv. in %	$10^3\cdot$Polym. rate in $\%\cdot s^{-1}$	Copolymer			
					MA content in wt.-%	MA content in mole-%	$\frac{[\eta]}{dl\cdot g^{-1}}$	$10^{-3}\cdot M_n$
1	76,0	210	3,2	2,5	43,2	60,3	0,09	
	61,3	210	11,0	8,7	39,9	56,7	0,17	
	55,8	210	12,0	9,6	39,2	55,9	0,26	2,7
	24,2	150	18,9	21,0	37,1	53,5	0,62	4,6
2	82,5	150	0,5	0,6	36,0	61,3		
	70,3	210	4,1	3,3	34,9	60,1	0,13	4,3
	46,1	210	6,0	4,8	31,8	56,8	0,16	
	31,7	210	2,4	1,9	28,4	52,8	0,11	
3	79,4	390	14,1	6,0				
	58,9	300	16,2	9,0				
	38,9	390	19,4	8,3				
	19,3	480	16,8	5,8				
	7,0	480	8,7	3,0				

Fig. 3 shows the monomer-copolymer composition curves for these copolymerizations except for those with **3**. The monomer reactivity ratios (r_1 and r_2) which were obtained by the Fineman-Ross method are shown in Tab. 6, in which the Q and e values are also indicated.

As can be seen from Tab. 6, in both copolymerizations with VC and VCAc, the observed r_1 values were found to decrease in the order of **1**, **2**, and VAc, whereas the values of r_2, Q_2, and e_2 increased in the same order, although the difference was very small. From this follows that the radical reactivities of the vinyl phosphates **1** and **2** are somewhat lower than that of VAc. Moreover, the slight difference in reactivities between **1** and **2** may be caused by the different ester groups, because the polar effect of the substituents in the acyl group can affect the radical reactivities of vinyl carboxylates[6].

Tab. 7 shows the results of radical copolymerizations of vinyl phosphates with MA (M_1), from which copolymer composition curves are also indicated in Fig. 3. The compositions of the resulting copolymers remained nearly 1:1 (mol/mol) independent of the feed monomer composition, indicating that these systems undergo alternating copolymerization. However, these copolymers were light brown- or pink-colored powders of low molecular weight.

The author wishes to thank Prof. *T. Otsu* for many helpful suggestions and Mr. *J. Iyoda* for NMR studies.

[1] R. W. Upson, J. Am. Chem. Soc. **75**, 1763 (1953)
[2] E. L. Gefter, M. I. Kabachnik, Dokl. Akad. Nauk SSSR **114**, 541 (1957)
[3] S. G. Matsoyan, G. M. Pogosyan, M. A. Ekiazyan, Vysokomol. Soedin. **5**, 777 (1963)
[4] B. J. Muray, J. Polym. Sci., Part C, **16**, 1869 (1967)
[5] C. De Selms, T. Lin, J. Org. Chem. **32**, 2023 (1967)
[6] K. Hayashi, T. Otsu, Makromol. Chem. **127**, 54 (1969)
[7] D. N. Fogg, N. T. Wilkinson, Analyst **83**, 406 (1958)
[8] R. M. Pike, R. A. Cohen, J. Polym. Sci. **44**, 531 (1960)
[9] G. F. Santee, R. H. Marchessault, H. G. Clark, J. J. Kearny, V. Stannett, Makromol. Chem. **73**, 177 (1964)
[10] F. Covitz, F. H. Westheimer, J. Am. Chem. Soc. **85**, 1773 (1963)
[11] J. Kumamoto, J. R. Cox, Jr., F. H. Westheimer, J. Am. Chem. Soc. **78**, 4858 (1956); P. C. Haake, F. H. Westheimer, ibid. **83**, 1102 (1961)
[12] C. C. Price, J. Polym. Sci. **3**, 772 (1948)
[13] L. J. Young, J. Polym. Sci. **54**, 411 (1961)
[14] H. E. Harris, J. G. Pritchard, J. Polym. Sci., Part A, **2**, 3673 (1964)