

COPOLYMERIZATION OF α -PHENYLVINYLPHOSPHINIC ACID WITH METHYL METHACRYLATE AND METHACRYLIC ACID*†

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VERY little attention has been paid to the polymerization and copolymerization of different α -substituted derivatives of vinylphosphinic acid. Patents report the possibility of the polymerization and copolymerization of α -carboxyvinylphosphinates [1], α -acetoxyvinylphosphinates or acetoxyalkenylphosphinates [2, 3] and their preparation on a base of refractory polymers. A recently published report describes the polymerization and copolymerization of the methylates, ethylates and *n*-propylates of α -acetoxyvinylphosphinic acid [4].

We have also reported on the polymerization of α -phenylvinylphosphinic acid (α -PVPA) and the polymeric chelate compound prepared on its base [5, 6]. Until now, the literature has contained no information on the preparation of α -PVPA copolymers with vinyl monomers, although the copolymers of this acid may be interesting due to the possibility of their being non-combustible, having ion-exchange properties and being capable of forming complexes with the ions of polyvalent metals.

The present work consisted of a study of the copolymerization of α -PVPA with methyl methacrylate (MMA) and methacrylic acid (MA).

The copolymerization was carried out on mixtures of the following molar ratios for α -PVPA : MMA and α -PVPA : MA: 0.1 : 0.9, 0.25 : 0.75, 0.5 : 0.5, 0.6 : 0.4, 0.75 : 0.25.

The copolymerization was carried out in the presence of 1 mol. % benzoyl peroxide, in sealed ampoules in a nitrogen atmosphere at $80 \pm 0.2^\circ$. The process was interrupted at an early stage of conversion by rapid cooling to -65° .

The α -PVPA-MMA copolymer was precipitated from the reaction medium by *n*-octane, and the α -PVPA-MA, by benzene.

The first copolymer was purified by two *n*-octane precipitations from solution in methylethylketone, and the α -PVPA-MA by precipitation by benzene from solution in ethyl alcohol and subsequent extraction in toluene for 20 hours. The copolymers precipitated were vacuum dried at 50° to constant weight. The composition was analysed for phosphorus content. To get the best possible

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purification, after choosing the solvent-precipitation agent system the separation range of the pure copolymer was found by fractional precipitation in a centrifuge at 4000 r.p.m. Thus, in the case of α -PVPA-MMA the best solvent-precipitation agent system was found to be methylethylketone-*n*-octane, and the relation between the amount of copolymer precipitated and the precipitator:solvent ratio has not the typical "hump" usually found for homopolymer mixtures (Fig. 1).

Tables 1 and 2 show the results of the copolymerization experiments.

TABLE 1. YIELD AND COMPOSITION OF COPOLYMERS OF α -PVPA (M_1) WITH MMA (M_2)

Experiment, No.	Molar composition of monomeric mixture		Initial amount of monomers, mmole		Polymer yield, %	Unreacted monomers, mmole		Phosphorus content (mean), %	Composition of copolymers, mol. %	
	PVPA	MMA	M_1^0	M_2^0		M_1	M_2		m_1	m_2
1	—	1	—	20	94.0	—	1.22	—	—	100
2*	0.10	0.90	2	18	43.4	1.63	9.28	2.12	7.38	92.7
3	0.25	0.75	5	15	41.6	3.76	6.79	5.68	21.7	78.3
4	0.50	0.50	10	10	30.3	8.87	3.47	6.22	24.2	75.8
5*	0.60	0.40	12	8	24.9	10.82	2.63	7.12	28.5	71.5
6*	0.75	0.25	15	5	13.8	14.03	6.05	9.18	39.4	60.6

Note: Asterisks indicate the experiments of which the results were used for determining the copolymerization constants.

TABLE 2. YIELD AND COMPOSITION OF COPOLYMERS OF α -PVPA (M_1) AND MA (M_2)

Experiment, No.	Molar composition of monomeric mixture		Initial amount of monomers, mmole		Polymer yield, %	Unreacted monomers, mmole		Phosphorus content (mean), %	Composition of copolymers, mole. %	
	PVPA	MA	M_1^0	M_2^0		M_1	M_2		m_1	m_2
1	—	1	—	20	93.0	—	1.41	—	—	100
2*	0.10	0.90	2	18	38.6	1.68	10.06	2.60	7.9	92.1
3*	0.25	0.75	5	15	32.1	2.24	8.37	5.82	19.8	80.2
4	0.50	0.50	10	10	25.2	7.88	6.62	10.20	41.8	58.2
5*	0.60	0.40	12	8	18.6	10.29	5.37	12.65	52.3	41.7
6	0.75	0.25	15	5	14.1	12.94	4.17	13.36	64.5	35.5

Note: Asterisks indicate the experiments of which the results were used for determining the copolymerization constants.

On the basis of the results set out in Tables 1 and 2 the copolymerization coefficients of α -PVPA with MMA and MA were determined by the Mayo and

Lewis intersection method [7]. The copolymerization coefficients for the system α -PVPA (M_1)-MMA(M_2) were: $r_1 = 0.06 \pm 0.04$ and $r_2 = 3.30 \pm 0.2$, and for α -PVPA (M_1)-MA (M_2): $r_1 = 0.36 \pm 0.12$ and $r_2 = 3.50 \pm 0.2$.

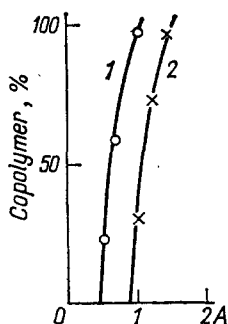


FIG. 1

FIG. 1. Amount of α -PVPA-MMA copolymer precipitated (in % of original amount) *v.* precipitator : solvent volumetric ratio (*A*): 1—solvent—methanol, precipitator—water, 2—solvent—methylethylketone, precipitator—*n*-octane.

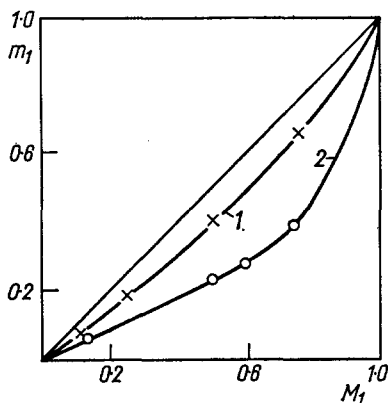


FIG. 2

FIG. 2. Composition of product copolymer *v.* composition of original monomer mixture: 1— α -PVPA-MA, 2— α -PVPA-MMA.

From the figures obtained, and analysis of the composition curves of the copolymers plotted from the calculated copolymerization coefficients (Fig. 2), it can be seen that copolymers of α -PVPA with MMA and MA have a much lower concentration of the first component than do the original monomeric mixtures. Since in this case $r_1 < 1$, and $r_2 > 1$, there can be no azeotropic mixtures for these systems.

As we know, the product of the copolymerization constants gives the alternating tendency of the radicals. For the system α -PVPA-MMA the product $r_1 \times r_2 = 0.19$, which shows a definite tendency to alternate and formation of a copolymer with quite an ordered chain structure.

The product copolymers, which contain a small amount (up to 20 mol. %) α -PVPA, dissolve in the same solvents as polymethylmethacrylate or polymethacrylic acid, but their solubility deteriorates as the α -PVPA concentration rises. α -PVPA-MMA copolymers in which the concentration of the first component is more than 20 mol. % have good solubility in acetone, methanol, methylethylketone, dimethylformamide, dioxane; and poor solubility in sulphate and hot toluene; they do not dissolve in water, dichloroethane, chloroform and fatty hydrocarbons.

CONCLUSIONS

The copolymerization of α -phenylvinylphosphinic acid with methyl methacrylate and methacrylic acid in the presence of benzoyl peroxide has been studied. The composition of the product copolymers has been established and the copolymerization constants determined.

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KINETICS OF THE COPOLYMERIZATION OF GLYCIDYL METHACRYLATE AND STYRENE*

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KINETIC studies of the copolymerization of different monomers not only make it possible to establish the optimum conditions for synthesizing the copolymers, but also to determine a number of kinetic parameters (rate constants of the reaction for instance), typical of the process of copolymerization.

The purpose of the present work was to make a kinetic study of the radical copolymerization of glycidyl methacrylate (GMA) with styrene in bulk and in solvents. Definite theoretical and practical interest attaches to the determination of the principal relationships of the copolymerization of these monomers, since there is the possibility of producing polymeric products containing different amounts of epoxy groups which are capable of subsequent chemical conversions.

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