CONCLUSIONS

The effect of conditions on the degree of estrification was studieed with PVA and benzoyl chloride as the esterifying agent. The characteristics of the processes involved are described.

Translated by K. A. ALLEN

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α-PHENYLVINYLPHOSPHINIC ACID (α-PVP) COPOLYMERIZATION WITH ACRYLIC ACID AND ACRYLONITRILE*†

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THE copolymers of α-phenylvinylphosphinic acid (α-PVP) are of special interest because they can be expected to have good ion-exchanging and complex-forming properties. Nevertheless, this copolymerization has hardly been studied and very little can be found about it in the literature.

We have tested the possibility of producing an α-PVP homopolymer in the presence of radical polymerization initiators (benzoyl peroxide, azobisisobutyronitrile, cyclohexylperoxycarbonate), but without success. It was found, however, that α-PVP will copolymerize in the presence of these initiators with methylmethacrylate and methacrylic acid [1]. This report is about the study of the α-PVP copolymerization with acrylic acid (AA) and acrylonitrile (AN). The copolymerization constants (r_1 and r_2) were determined and the parameters Q and e were calculated for the α-PVP monomer.

EXPERIMENTAL

α-PVP was purified by double recrystallization from hot chloroform; m.p. 113–114°C.

AA was purified by double distillation and the fraction boiling at 40°C/22 mm, n_D^{20} 1·4224 was taken.

AN was purified by double distillation and the fraction boiling at 77°C, n_D^{20} 1·3911 was taken.

The benzoyl peroxide was precipitated twice from chloroform by methanol.

The copolymerization was carried out in sealed ampoules at 70°C using different rations of the monomer components in the presence of 1 mole % benzoyl peroxide on total monomers; the duration of the reaction was 8 hr.

The α-PVP–AA copolymer was dissolved in dimethylformamide and then precipitated with methylethylketone (MEK). The α-PVP–AN copolymer was dissolved in methanol and precipitated with ethyl ether. The copolymers were vacuum dried to constant weight at 40–45°C.

In the diagram are given the curves for the potentiometric titration of the monomers α-PVP and AA and the copolymer α-PVP–AA with AN. The composition of the copolymers is defined by the percentage of phosphorus. The results obtained are given in Tables 1 and 2.

The copolymerization constats (r_1 and r_2) were determined by the "intersect" method using the Mayo and Lewis integrations [2–4]. The results can be found in Table 3.

The activity factors Q and e were calculated for the α-PVP–AA and α-PVP–AN copolymers from the available results [5]. These are given in Table 4.

RESULTS

Tables 1 and 2 show that an α-PVP content in the starting component mixture higher than 20–30% decreased its amount in the copolymer. The curves plotted on the basis of the found copolymerization constants in "monomer content–copolymer composition" ordinates indicated that azeotropic mixtures of the monomers should have been present. The α-PVP content in its copolymer with AA should have been 20 mole % if present as an azeotropic mixture, and 27 mole % in its copolymer with AN. The results given in Tables 1 and 2 are in good agreement with these values.

TABLE 1. THE COPOLYMERIZATION OF α-PVP WITH AA

Test number	Molar content of α-PVP in starting mixture, M_1^0	Conversion, %	P-content in copolymer (% average)	Molar content of α-PVP in copolymer, m_1
1	0·50	6·0	5·78	0·17
2*	0·33	6·0	8·50	0·29
3*	0·25	7·0	8·10	0·27
4*	0·20	6·0	6·54	0·20
5*	0·17	6·0	6·01	0·18

Remark: The stars in Tables 1 and 2 denote the tests from which the copolymerization constants were calculated.

Table 3 shows that $r_1 < 1$ and $r_2 < 1$ in both cases, i.e. the terminal free radical of the growing polymer chain reacted dominantly with the "alien" monomer, i.e. $M_1^\cdot$ with M_2 and $M_2^\cdot$ with M_1. The relative reactivity $(1/r_2)$ of α-PVP is greater towards the AN- than the AA- radical, while the relative reactivity of the α-PVP radical $(1/r_1)$ is greater towards AN than AA.
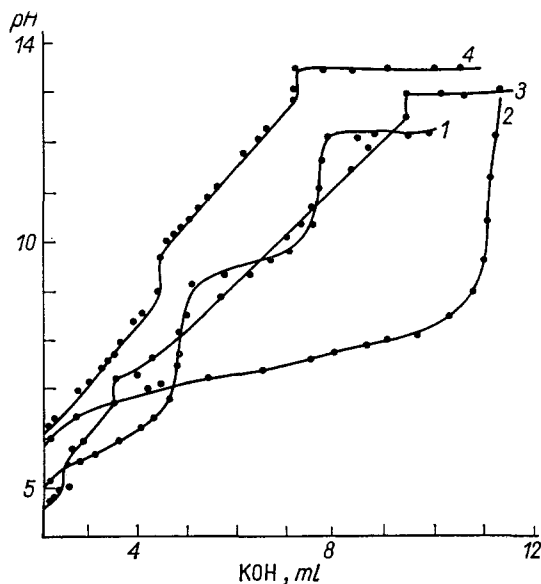
Potentiometric titration curves: 1 — α-PVP, 2 — AA, 3 — α-PVP–AA copolymer, 4 — α-PVP–AN copolymer.

The product of the copolymerization constants $(r_1 \cdot r_2)$ is 0·43 for the system α-PVP–AA and 0·22 for the system α-PVP–AN; this indicates a greater tendency towards an alternation of chain elements and an orderly st ucturation of the α-PVP–AN copolymer.

TABLE 2. THE COPOLYMERIZATION OF α-PVP WITH AN

Test number	Molar content of α-PVP in starting mixture, M_1^0	Conversion, %	P-content in copolymer (% average)	Molar content of α-PVP in copolymer, m_1
1	0·60	4·0	11·20	0·37
2*	0·50	8·0	11·58	0·40
3*	0·33	9·0	8·95	0·24
4*	0·25	9·0	9·54	0·27
5*	0·20	6·0	10·20	0·31
6*	0·17	6·0	9·30	0·27

The Q_1 and e_1 values found from copolymerization of α-PVP with AA compared favourably with those for AN. It is thought that $Q = 0.80 \pm 0.02$ and $e = 0.76 \pm 0.04$ for α-PVP.

TABLE 3. COPOLYMERIZATION CONSTANTS

M_1	M_2	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$
α-PVP	AA	0.44 ± 0.03	0.98 ± 0.08	0.43	2.27	1.02
α-PVP	AN	0.32 ± 0.07	0.69 ± 0.18	0.22	3.12	1.45

TABLE 4. ACTIVITY FACTORS

M_1	Q_1	e_1	M_2	Q_2	e_2	Q_2 and e_2 from:
α-PVP	0.78	0.72	AA	1.45	0.01	
α-PVP	0.82	0.80	AN	0.44	1.20	[6]*

* The activity factors of AA were calculated from the results of its copolymerization with styrene ($r_1 = 0.15$; $r_2 = 0.25$ [7]).

CONCLUSIONS

The copolymers of α-phenylvinylphosphinic acid with acrylic acid or acrylonitrile were synthesized by radical copolymerization. This process was studied and the respective copolymerization constants were determined. The Q- and e-value of α-phenylvinylphosphinic acid was calculated.

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