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Copolymerization of Diethyl Vinyl Phosphate with Vinyl Acetate and Acrylonitrile

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ABSTRACT

Free radical-initiated copolymerization of diethyl vinyl phosphate (DEVPA) with vinyl acetate (VAc) and acrylonitrile (AN) was studied. The monomer reactivity ratios for the monomer pairs, determined at 60°C using benzoyl peroxide as an initiator, are: r_1(VAc) = 0.95, r_2(DEVPA) = 0.93; r_1(AN) = 6.6, r_2(DEVPA) = 0.049. The values of the Alfrey-Price constants, Q and e, for DEVPA were calculated to be 0.025 and 0.13, respectively, from the VAc system, and 0.026 and 0.14, respectively, from the AN/DEVPA pair. These results indicate that the general reactivity of DEVPA is almost the same as that of VAc and that the

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diethylphosphate group is a stronger electron-attracting group than the acetoxy group. The intrinsic viscosity and number-average molecular weight of copolymers decreased as their content of DEVPA units increased, indicating a high degree of chain transfer caused by DEVPA.

INTRODUCTION

Very little has been published on the copolymerization characteristics of phosphorus-containing vinyl monomers, even though polymers of these monomers have been drawing a great deal of interest among various researchers [1-3]. Muray [4] reported high conversion copolymerizations of vinyl phosphates with various monomers such as methyl methacrylate, vinyl acetate, isopropenyl acetate, and styrene. However, one cannot quantitatively estimate reactivities of vinyl phosphates based on these data.

Levin et al. [5] determined the monomer reactivity ratios of dimethyl and diethyl vinyl phosphate in copolymerizations with VAc and styrene. But the results seem to be contradictory in that the values of Q and e reported for these monomers depend too much on the comonomer used and also that the e value of vinyl phosphate is almost as high as that of vinyl phosphonate.

We have recently reported the monomer reactivity ratios for free radical copolymerizations of bis (β-chloroethyl) vinyl phosphonate with VAc and AN [6, 7]. As a continuing effort to clarify further the structure-reactivity relationship of phosphorus-containing monomers, we have studied the free radical-initiated copolymerization of DEVPA with VAc and with AN. Copolymers containing different amounts of DEVPA were also prepared and characterized.

EXPERIMENTAL

Chemicals

DEVPA was synthesized by reacting chloromercury acetaldehyde with triethyl phosphite, following the method developed by Magee [8]. The reaction was carried out in refluxing chlorobenzene.

$$(C_2H_5O)_3P + ClHgCH_2CHO \longrightarrow CH_2{=}CHOPO(OC_2H_5)_2 + Hg + C_2H_5Cl$$

The chloromercury acetaldehyde used in the above reaction was prepared from mercury(II) acetate, vinyl acetate, and potassium chloride according to the procedure of Nesmeyanov et al. [9]. The DEVPA prepared was purified by fractional distillation. It was found to be more than 99.5% pure by gas chromatography and had a boiling point of 63°C at 2 torr, in agreement with that given by Muray [4].

Analysis: Percentage composition of P in $C_6H_{13}PO_4$: Calculated, 17.22%; Observed, 17.05%. IR spectrum (neat): 3000, 1645, 1250-1300, and 950-1150 cm^{-1}. NMR spectrum (δ), in $CDCl_3$: 1.32 triplet (6H, $-CH_3$), 4.08 octet (4H, $-OCH_2-$), 4.5-4.8 multiplet (2H, $=CH_2$), and 6.55 multiplet (1H, $=CH-O-$).

Instruments used were a Jasco DS701G diffraction grating IR spectrophotometer and a Varian EM360A NMR spectrometer. The spectral results are in complete agreement with literature data [8, 10, 11].

VAc (Merck A.G.) and AN (Merck A.G.) were purified by standard procedures. Afterwards, gas chromatographic analysis found the monomers to be better than 99.8% pure. N,N-Dimethylformamide (DMF, Merck A.G.), after being dried over anhydrous magnesium sulfate, was purified by distillation. Benzoyl peroxide (Fisher Scientific) was dissolved in chloroform and then precipitated with methanol. It was dried at room temperature at a pressure of 1.0 torr. All other chemicals employed in the present work were of reagent grade and used as received.

Copolymerization of Diethyl Vinyl Phosphate (DEVPA) and Vinyl Acetate (VAc)

Copolymerization of DEVPA and VAc was conducted in bulk. Given amounts of the two monomers and 0.1 mol% of benzoyl peroxide (based on the total monomer mixture) were placed in a polymerization tube. The tube then was connected to a vacuum line and degassed by the usual freeze and thaw cycles, using liquid nitrogen. Next, the tube was filled with predried nitrogen and placed in a water bath at 60.0 ± 0.1°C. Polymerization was stopped by immersing the tube in a Dry Ice-acetone bath, followed by the transfer of the frozen mixture into 10 mL of acetone containing 2% by weight of hydroquinone. Reaction times ranged from 35 to 126 min, depending on the feed composition.

The copolymers formed were precipitated when the acetone solution was transferred to a large volume of petroleum ether (bp 30-70°C). The precipitated polymers were separated by centrifugation and purified by solution-precipitation cycles using acetone and petroleum ether. The polymers obtained were dried under vacuum at 35°C to a constant weight. Conversions ranged from 0.65 to 3.54 wt% (Table 1).

Copolymerization of Diethyl Vinyl Phosphate (DEVPA) and Acrylonitrile (AN)

Copolymerization of DEVPA and AN was performed in DMF. The total monomer concentration was kept at 50% by weight for all runs. The amount of initiator used was 0.1 mol% of the total amount of

TABLE 1. Copolymerization of Vinyl Acetate (M_1) and Diethyl Vinyl Phosphate (M_2)[a]

	Expt. no.							
	1	2	3	4	5	6	7	8
M_1 (g)	0.5250	0.6141	0.8637	0.8707	1.5498	2.2382	2.2476	2.6039
M_2 (g)	4.3226	3.8134	3.6051	3.6048	3.2471	3.3698	2.3699	1.8858
M_1/M_2 (mole ratio)[b]	0.2540	0.3368	0.5011	0.5052	0.9983	1.9755	1.9837	2.8888
Conversion (wt%)	2.50	2.91	2.01	3.54	2.33	1.80	2.85	0.65
P content (wt%)	15.28	14.79	13.85	13.82	11.67	8.82	8.80	7.30
m_1/m_2 (mole ratio)[b]	0.266	0.344	0.509	0.515	0.995	1.99	2.00	2.84

[a] Copolymerized at 60.0 ± 0.1°C using 0.1 mol% benzoyl peroxide as initiator.

[b] M_1/M_2 designates the mole ratio of M_1 and M_2 in the feed, and m_1/m_2 the mole ratio of M_1 and M_2 units in the copolymer formed.

monomer. Degassing and polymerization procedures were the same as those described for the copolymerization with VAc.

Copolymerizations were terminated by quenching in liquid nitrogen, followed by transferral of the reaction mixture into DMF containing 2% by weight of hydroquinone. Reaction times ranged from 90 to 120 min, depending on the feed composition.

Polymers prepared from feed mixtures of more than 50 mol% DEVPA were first precipitated into a large volume of distilled water and further purified using acetone and petroleum ether as a solvent-nonsolvent pair. Copolymers obtained from other feeds were precipitated in methanol and purified by successive precipitations using a DMF-methanol pair. The purified polymers were dried under vacuum at 35°C. Polymer yields were 2.14-5.87 wt% (Table 2).

High Conversion Polymerizations

Copolymerizations to high conversions (44.3-92.0% by weight) were conducted in the same manner, with the exception that larger amounts of benzoyl peroxide (0.4 mol%) and longer reaction times (12 h) were employed. The homopolymer of DEVPA, made in bulk, was isolated and purified by the same procedures used for VAc copolymers.

Characterization of Polymers

Copolymer compositions were determined colorimetrically from their phosphorus contents [12, 13], indicative of DEVPA units. A small quantity (10-20 mg) of copolymer first was oxidized in a hot 1:1 mixture of concentrated nitric and sulfuric acids. Further oxidation with perchloric acid and then with hydrogen peroxide resulted in a colorless solution. Reaction with ammonium molybdate and hydrazine sulfate produced a colored solution. Its absorbance was measured at 830 nm using a UV-VIS spectrophotometer (Unicam SP 500). Tri-para-cresyl phosphate was used as a standard for the construction of a calibration curve. Blank tests were run side by side with actual experiments.

Intrinsic viscosities of copolymers were measured at 25.0 ± 0.1°C with an Ubbelohde-type viscometer. The number-average molecular weights of the polymers were determined using a vapor pressure osmometer (Hebert Knauer Co., West Germany) equipped with an electronic universal temperature measuring instrument and an X-Y recorder (Griffin & George, Model 2700, Great Britain). Benzil (MW 210.13) was employed as a standard.

TABLE 2. Copolymerization of Acrylonitrile (M_1) and Diethyl Vinyl Phosphate (M_2)[a]

	Expt. no.						
	1	2	3	4	5	6	7
M_1 (g)	0.4380	0.7090	1.0937	1.1762	2.6205	2.3880	2.3899
M_2 (g)	4.4999	4.3576	4.6764	4.6718	4.2118	2.8608	2.8800
M_1/M_2 (mole ratio)[b]	0.3249	0.5226	0.7991	0.8547	2.1115	2.8326	2.8162
Conversion (wt%)	2.69	3.26	2.14	2.78	2.80	5.87	2.72
P content (wt%)	9.51	7.87	6.45	6.03	3.29	2.57	2.56
m_1/m_2 (mole ratio)[b]	2.75	4.03	5.67	6.30	14.4	19.3	19.4

[a] Copolymerized at 60.0 ± 0.1°C using 0.1 mol% benzoyl peroxide as initiator.

[b] M_1/M_2 designates the mole ratio of M_1 and M_2 in the feed, and m_1/m_2 the mole ratio of M_1 and M_2 units in the copolymers formed.

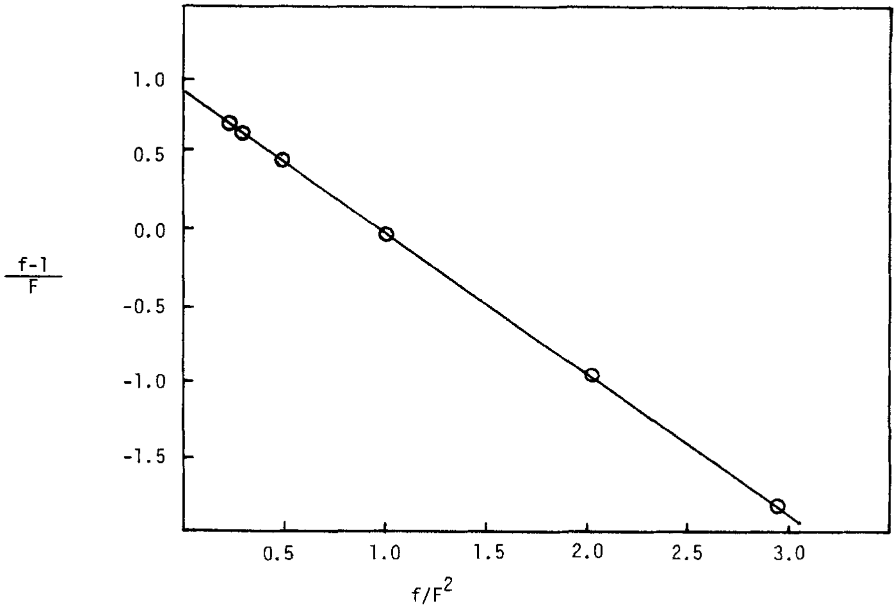


FIG. 1. Fineman-Ross plot for copolymerization of vinyl acetate (r_1 = 0.95) and diethyl vinyl phosphate (r_2 = 0.93) at 60.0 ± 0.1°C [$f = m_2/m_1$, $F = (M_2)/(M_1)$].

RESULTS AND DISCUSSION

The results of the copolymerization of DEVPA with VAc and AN are summarized in Tables 1 and 2. These data were analyzed by the Fineman-Ross method [14] to determine the monomer reactivity ratios for the monomer pairs (Figs. 1 and 2). Using the method of least squares, well-defined values were obtained from both systems:

r_1(VAc) = 0.95 r_2(DEVPA) = 0.93

r_1(AN) = 6.6 r_2(DEVPA) = 0.049

These values indicate that the two monomers in the DEVPA/VAc system show about equal reactivities toward both propagating radicals: $r_1 \simeq r_2 \simeq 1$. As expected in such a system, copolymer compositions are very close to those of the feed (see Table 1). However, AN is much more reactive than DEVPA toward both propagating species.

The monomer reactivity ratios of the VAc/DEVPA pair lead to Alfrey-Price values [15] of Q = 0.025 and e = 0.13 for DEVPA. The

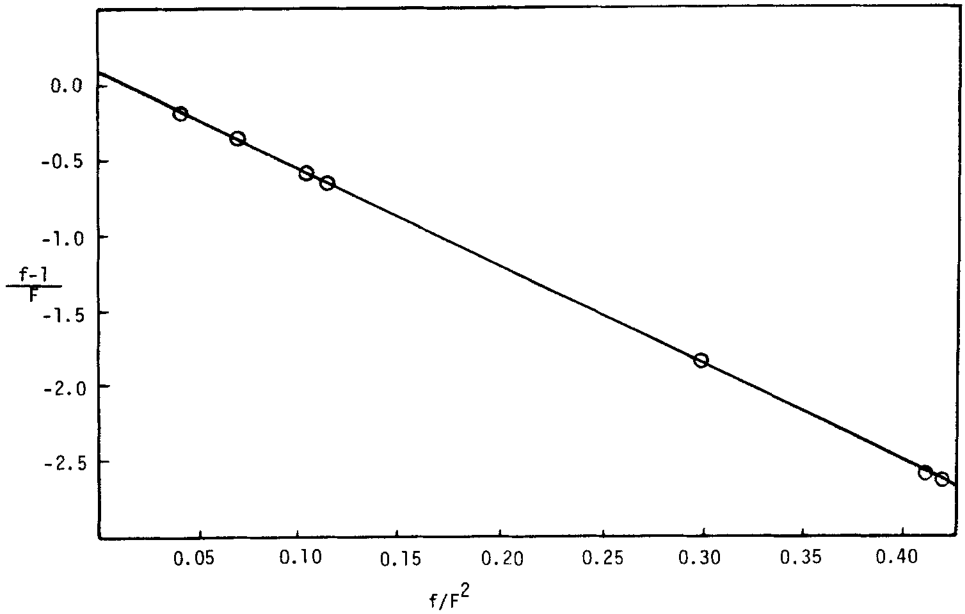


FIG. 2. Fineman-Ross plot for copolymerization of acrylonitrile (r_1 = 6.6) and diethyl vinyl phosphate (r_2 = 0.049) at 60.0 ± 0.1°C [$f = m_2/m_1$ and $F = (M_2)/(M_1)$].

AN/DEVPA pair give almost the same values: Q = 0.026 and e = 0.14. In these estimations, the following values were used for DEVPA's comonomers [16]:

Q(VAc) = 0.026	e(VAc) = -0.22
Q(AN) = 0.20	e(AN) = 1.20

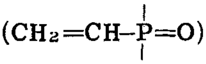
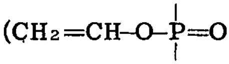
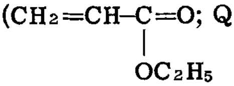
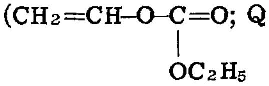
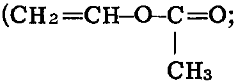
Judging by the Q values, the general reactivity or the degree of delocalization of the π-electrons in the vinyl group of DEVPA is very low, approximating that of VAc. Muray [4] has also pointed out the resemblance of the charge distribution in the two monomers. The e value of DEVPA indicates that the diethoxyphosphato group ($-OPO(OC_2H_5)_2$) is a slightly stronger electron attractor than the acetyloxy group ($-OCOCH_3$). This is in agreement with the diethoxyphosphono group's ($-PO(OC_2H_5)_2$) being a stronger electron attractor (σ_p = 0.60) [17] than the acetyl group (σ_p = 0.50) [18].

Earlier, we reported values of Q = 0.06 and e = 1.1 for bis (β-chloroethyl) vinyl phosphonate [6, 7]. Changing the structure from

TABLE 3. High Conversion Copolymerizations of Diethyl Vinyl Phosphate (M_2) with Vinyl Acetate (M_1) and Acrylonitrile (M_1)

Copolymer	VAc/DEVPA				AN/DEVPA			
M_1/M_2 (mole ratio)	0/100	0.5612	1.0010	1.9767	100/0	1.0051	2.0049	100/0
Conversion (wt%)	76.0	90.9	87.3	84.8	92.0	45.2	47.8	44.3
P content (wt%)	17.15	13.67	11.69	8.81	0	5.70	3.42	0
m_1/m_2 (mole ratio)	0/100	0.543	0.990	2.00	100/0	6.67	13.5	100/0
Intrinsic viscosity[a]	0.125[a]	0.381[a]	0.503[a]	0.607[a]	0.753[a]	0.664[c]	0.708[c]	0.690[b]
Number-average molecular weight[b]	5,200[a]	9,800[a]	13,800[a]	15,200[a]	20,300[a]	15,400[c]	18,600[c]	20,800[b]

[a] Determined using chloroform (a), DMF (b), or acetonitrile (c) as the solvent.
[b] Determined by vapor pressure osmometer.

phosphonate ( $CH_2{=}CH{-}\overset{|}{\underset{|}{P}}{=}O$) to phosphate ( $CH_2{=}CH{-}O{-}\overset{|}{\underset{|}{P}}{=}O$) results in lowering both the Q and e values. Similar substitution effects can be found in ethyl acrylate ( $CH_2{=}CH{-}\underset{OC_2H_5}{\underset{|}{C}}{=}O$; Q = 0.52, e = 0.22) [19] and vinyl carbonate ( $CH_2{=}CH{-}O{-}\underset{OC_2H_5}{\underset{|}{C}}{=}O$; Q = 0.025, e = -0.26) [20] or vinyl acetate ( $CH_2{=}CH{-}O{-}\underset{CH_3}{\underset{|}{C}}{=}O$; Q = 0.026, e = -0.22) [16].

Levin et al. [5] have reported $r_1(VAc) = 1.59$ and $r_2(DEVPA) = 0.25$, and for DEVPA Q = 0.03 and e = 1.18. We believe that there is no reason why DEVPA should be so much less reactive than VAc. Moreover, the e value reported for DEVPA seems unreasonably high for a vinyl ester. Levin also concluded that the monomer reactivity of DEVPA was unpredictable due to the marked behavioral differences dependent on the structure of the comonomer used, styrene or vinyl acetate. Our results, however, clearly indicate that the copolymerization characteristics of DEVPA can be properly described by classical analysis of the copolymerization kinetics as well as by the Alfrey-Price scheme.

The results for high conversion copolymerizations of DEVPA with VAc and AN are summarized in Table 3. Here again, one can see that the composition of vinyl acetate copolymers is almost identical to those of the feed due to the similarity in reactivity of the two monomers involved. On the other hand, the percentage of DEVPA units incorporated into AN copolymers is much lower than that in the feed, as expected from AN's much higher reactivity. Copolymerization with VAc showed consistently higher yields than with AN (see Table 3).

Intrinsic viscosity and the number-average molecular weight of copolymers steadily decreased as the content of DEVPA increased. This suggests that the chain transfer constant of DEVPA is higher than that of either VAc or AN. At 60°C the chain transfer constant reported for DEVPA is 8.9×10^{-3} [5], which indeed is much larger than that of VAc, $1.75\text{-}2.8 \times 10^{-4}$ [21]. Acrylonitrile is known to be much less susceptible to chain transfer reactions [22]. The fact that the average molecular weight of the DEVPA homopolymer is only 5200 also leads to the same conclusion. This value agrees well with Muray's 5500 [4]. He prepared the DEVPA homopolymer in hexane at 70°C using diisopropenyl peroxycarbonate as the initiator. Even though the site of chain transfer in DEVPA is not yet known, it is reasonable to assume the transfer reactions occur mainly at the α-carbon atom, as in VAc monomer [23].

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