

인산디에틸 이소프로페닐과 초산비닐 및 아크릴로니트릴의 혼성중합

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Copolymerization of Diethyl Isopropenyl Phosphate with Vinyl Acetate and Acrylonitrile

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요 약. 자유 라디칼 개시체에 의한 인산디에틸이소프로페닐 (DEIPA)과 초산비닐 (VAc) 및 아크릴로니트릴 (AN)의 혼성중합 연구를 행하여 단위체 반응성비를 얻었다. 개시제로는 과산화벤조일을 사용하였으며 중합온도는 60°C이었다. 단위체 반응성비는 $r_1(\text{VAc})=1.56$, $r_2(\text{DEIPA})=0.44$ 및 $r_1(\text{AN})=15.2$, $r_2(\text{DEIPA})=0.031$ 이었다. 이 값으로부터 DEIPA의 Alfrey-Price 상수 $Q=0.015$, $e=0.39$ 및 $Q=0.014$, $e=0.34$ 를 얻었으며 α 위치에 있는 메틸기가 반응성을 감소시킴을 알았다. 공중합체중 DEIPA의 함량이 증가함에 따라 공중합체의 고유점성도 및 수평균 분자량이 감소함도 알았다.

ABSTRACT. Free radical-initiated copolymerization of diethyl isopropenyl phosphate (DEIPA) 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: $r_1(\text{VAc})=1.56$, $r_2(\text{DEIPA})=0.44$; $r_1(\text{AN})=15.2$, $r_2(\text{DEIPA})=0.031$. The values of the Alfrey-Price constants, Q and e , for DEIPA were calculated to be 0.015 and 0.39, respectively, from the VAc system, and 0.014 and 0.34, respectively, from AN/DEIPA pair. These results indicate that α -methyl substituent of vinyl phosphate monomer decreases the general reactivity in free radical copolymerization. The intrinsic viscosity and number-average molecular weight of copolymers decreased as their content of DEIPA units increased, indicating a high degree of chain transfer caused by DEIPA, as previously learned in DEVPA system.

INTRODUCTION

Even though polymers and copolymers derived from phosphorus containing vinyl monomers are of great interest for various applications, there have not been much systematic copoly-

merization study of those monomers.¹⁻³

Murray⁴ reported high conversion free radical-initiated homopolymerization of DEIPA and its copolymerization with methyl methacrylate and vinyl acetate. According to his results, molecular weights of polymers, especially those

of homopolymers, were relatively low. However, he did not quantitatively analyze the reactivity of the monomer.

Levin *et al.*⁵ reported the copolymerizations of dimethyl- and diethyl vinyl phosphate with vinyl acetate and styrene, but they did not include DEIPA in their study.

We recently reported the study on free radical-initiated copolymerizations of diethyl vinyl phosphate (DEVPA) with VAc and AN.⁶ The values of Alfrey-Price constants, Q and e , of DEVPA were found to be 0.025 and 0.14, respectively. These results were not in complete agreement with the values earlier reported by Levin *et al.*⁵ The thermal behavior and flammability of DEVPA and AN copolymers were also studied by us and compared with those of polyacrylonitrile and polyacrylonitrile-tributyl phosphate mixtures.⁷

As a continuing effort to delineate further the structure-reactivity relationship of phosphorus-containing vinyl monomers, we have studied the free radical-initiated copolymerization of DEIPA, which has a methyl substituent at vinyl functional group, with VAc and with AN. The monomer reactivity ratios for the monomer pairs and reactivity parameters of DEIPA were determined.

EXPERIMENTAL

Chemicals and Instruments. The monomer DEIPA was synthesized by reacting chloromercury acetone with triethyl phosphite, following the method developed by Magee.⁸ The reaction was conducted in refluxing chlorobenzene.



Chloromercury acetone used in the above reaction was prepared from mercury (II) acetate, isopropenyl acetate, and potassium chloride according to the procedure of Nesmeyanov

*et al.*⁹ DEIPA 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 82 °C at 4 torr, in agreement with that given by Allen.¹⁰

Analysis: Percentage composition of P in $C_7H_{15}PO_4$: Calculated, 15.95 %: Observed, 15.78 %.

IR spectrum(neat): 3120, 1655, 1220~1300 and 940~1170 cm^{-1} : NMR spectrum (δ) in $CDCl_3$: 1.30 triplet (6H, CH_3), 1.90 singlet (3H, $C=C-CH_2$), 4.08 octet (4H, OCH_2), 4.46 triplet (1H, $C=CH$) and 4.68 triplet (1H, $C=CH$). Instruments used were a Jasco DS701G diffraction grating IR spectrophotometer and a Varian EM 360A NMR spectrophotometer. 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 of 1.0 torr. All other chemicals employed in the present investigation were of reagent grade and used as received.

Copolymerization of Diethyl Isopropenyl Phosphate(DEIPA) and Vinyl Acetate(VAc).

Copolymerization of DEIPA and VAc was conducted in bulk. Given amounts of 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 nitro-

gen 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. Recation times ranged from 45 to 200 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 dissolution-precipitation cycles using acetone and petroleum ether. The polymers obtained were dried under vacuum at 35 °C to a constant weight. Conversions ranged from about 2.8 to 6.5 wt. % (Table 1).

Copolymerization of Diethyl Isopropenyl Phosphate (DEIPA) and Acrylonitrile (AN).

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

Copolymerizations were terminated by quenching in liquid nitrogen, followed by transferal of the reaction mixture into DMF containing 2 % by weight of hydroquinone. Reaction

times ranged 80 to 240 min, depending on the feed composition. Polymers prepared from feed mixtures of more than 50 mol % DEIPA 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 0.77~2.65 wt % (Table 2).

High Conversion Polymerizations. Copolymerizations to high conversions (38.5~92.0 % by weight) were conducted in the same manner, with the exception that larger amount of benzoyl peroxide (0.4 mol %) and longer reaction times (12 h) were employed.

Characterization of Polymers. Copolymer compositions were determined colorimetrically from their phosphorus contents^{1,2,13} indicative of DEIPA 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 (Pye Unicam SP 500). Tri-para-cresyl phosphate was

Table 1. Copolymerization of VAc (M_1) and DEIPA (M_2)^a

Exp. No	1	2	5	4	5	6	7
M_1 (g)	0.6081	0.8228	1.5065	1.5137	2.0077	2.5078	3.0535
M_2 (g)	4.0653	3.6892	3.3802	1.3910	2.2618	1.9111	1.6945
M_1/M_2 (mole ratio) ^b	0.3373	0.5029	1.0050	1.0064	2.0014	2.9589	4.0634
Conversion (wt. %)	3.11	3.79	2.84	4.04	3.68	3.14	6.48
P content (wt. %)	12.35	11.29	8.81	8.79	6.31	4.88	4.01
m_1/m_2 (mole ratio) ^b	0.662	0.936	1.83	1.84	3.46	5.13	6.73

^a Copolymerized at 60.0 ± 0.1 °C using 0.1 mole % benzoyl peroxide as initiator. ^b M_1/M_2 designates the mole ratio of M_1 and M_2 in feed, and m_1/m_2 mole ratio of M_1 and M_2 units in copolymers formed.

Table 2. Copolymerization of AN(M_1) and DEIPA (M_2)^a

Exp. No.	1	2	3	4	5	6
M_1 (g)	0.5192	6.6203	1.0336	1.2035	1.5216	1.8635
M_2 (g)	4.4133	4.4656	3.1740	2.2943	2.3661	2.2140
M_1/M_2 (mole ratio) ^b	0.4304	0.5082	1.0182	1.9189	2.3530	3.0793
Conversion (wt. %)	0.772	0.446	1.93	1.87	2.65	2.06
P content (wt. %)	5.44	4.94	2.97	1.75	1.47	1.15
m_1/m_2 (mole ratio) ^b	7.09	8.20	16.0	29.8	36.1	47.2

^a Copolymerized at 60.0 ± 0.1 °C using 0.1 mole % benzoyl peroxide as initiator. ^b M_1/M_2 designates the mole ratio M_1 and M_2 in feed, and m_1/m_2 mole ratio of M_1 and M_2 units in copolymers formed.

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 (Herbert 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.

RESULTS AND DISCUSSION

The results of the copolymerization of DEIPA with VAc and AN are summarized in Tables 1 and 2. These data were analyzed by the Fineman-Ross method¹⁴ to determine the monomer reactivity ratios for the monomer pairs (Fig. 1 and 2). Using the method of least squares, well defined values were obtained from both systems:

$$\begin{aligned} r_1(\text{VAc}) &= 1.56 & r_2(\text{DEIPA}) &= 0.44 \\ r_1(\text{AN}) &= 15.2 & r_2(\text{DEIPA}) &= 0.031 \end{aligned}$$

These values indicate that the VAc monomer is more reactive than DEIPA toward both propagating species. The results for AN/DEIPA system also reveal that AN monomer is far more

reactive than DEIPA toward the both propagating radicals. Comparison of these data with those earlier reported by us for DEVPA/VAc and DEVPA/AN pairs leads us to the conclusion that DEIPA is significantly less reactive in free radical copolymerizations than DEVPA.⁶

The monomer reactivity ratios of the VAc/DEIPA pair lead to Alfrey-Price values¹⁵ of $Q = 0.015$ and $e = 0.39$ for DEIPA. The AN/DEIPA pair gives almost the same values: $Q = 0.014$ and $e = 0.34$. In these estimations, the following values were used for DEIPA's comonomers¹⁶.

$$\begin{aligned} Q(\text{VAc}) &= 0.026 & e(\text{VAc}) &= -0.22 \\ Q(\text{AN}) &= 0.20 & e(\text{AN}) &= 1.20 \end{aligned}$$

Judging by the Q value, the general reactivity or the degree of delocalization of the π electrons in the isopropenyl group of DEIPA is lower than that of DEVPA whose Q value was reported to be 0.025, in contradiction to the expectation that the methyl substituent would increase it. Almost all of the vinyl monomers possessing methyl substituent on α -position of vinyl group have higher Q values than those without the substituent. For instance, methyl acrylate has the value of $Q = 0.44$, while methyl methacrylate has a significantly higher value of $Q = 0.74$.

The lower Q value for DEIPA than for DEVPA can be explained by the fact that vi-

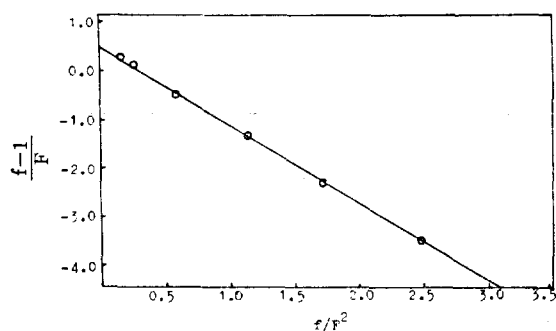


Fig. 1. Fineman-Ross plot for copolymerization of VAc ($r_1=1.56$) and DEIPA ($r_2=0.44$) at 60.0 ± 0.1 °C ($f=m_2/m_1$ and $F=M_2/M_1$; coefficient of correlation was -0.999).

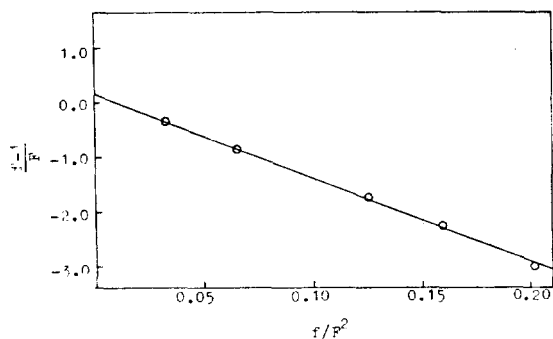


Fig. 2. Fineman-Ross plot for copolymerization of AN ($r_1=15.2$) and DEIPA ($r_2=0.031$) at 60.0 ± 0.1 °C ($f=m_2/m_1$ and $F=M_2/M_1$; coefficient of correlation was -0.997).

nyl phosphate monomers have fairly bulky phosphate ester groups which would cause a steric hindrance between the propagating radical and approaching monomer. Such a steric effect is expected to increase even further by the presence of the methyl substituent on the vinyl group. Another point of importance is the fact that Q-e scheme has the very drawback of not accommodating steric effects.

We can find a similar example in α -methyl styrene and styrene pair. The value of $Q=0.98$ for α -methyl styrene is slightly lower than that ($Q=1.0$) of styrene. The e values of vinyl monomers are known to decrease by the elec-

tron donating methyl substituent on α -position of vinyl groups, but the e value of DEIPA is increased by methyl substituent from 0.14 to 0.39 as if the substituent were the electron withdrawing group. Even though there is controversies as to the nature of inductive effect of methyl group, we do not have a concrete explanation for this unexpected observation.

Recently, Pros and Rodon¹⁷ have reported the electronic inductive effect of methyl group by using *ab initio* molecular orbital theory. They showed that the inductive effect of methyl group depends on environment. Bartmess¹⁸ and Hehre¹⁹ have showed experimentally that methanol is more acidic than water in gas phase.

The results for high conversion copolymerizations of DEIPA with VAc and AN are summarized in Table 3. One can see from the table that the percentage of DEIPA units incorporated into AN copolymers is much lower than that incorporated into VAc as expected from the difference in their reactivities. The copolymerization with VAc consistently produced higher yields than that with AN under the same reaction condition described in experimental section (Table 3).

Intrinsic viscosity and the number-average molecular weight of copolymers steadily decreased as the content of DEIPA increased. We observed similar effect in DEVPA copolymers. This suggests that either the chain transfer constant of DEIPA is higher than VAc and AN or steric effect hinders propagation reactions or both.

Muray⁴ polymerized DEIPA in bulk or in hexane at $70 \sim 160$ °C using diisopropenyl peroxy-carbonate and found that the number-average molecular weights of the homopolymers obtained were only 400, which strongly indicates the high chain transfer activity or steric hind-

Table 3. Intrinsic viscosities and molecular weights of the copolymers of DEIPA (M_2) with VAc(M_1) and AN(M_1)

Copolymer	VAc/DEIPA				AN/DEIPA		
M_1/M_2 (mole ratio)	0.5191	0.9973	2.0037	100/0	1.0216	2.0006	100/0
Conversion (wt. %)	71.4	70.2	76.3	92.0	38.5	39.7	44.3
P content (wt. %)	11.24	8.84	6.30	0	2.95	1.73	0
m_1/m_2 (mole ratio)	0.952	1.818	3.448	100/0	16.129	30.303	100/0
Intrinsic viscosity ^a	0.262 ^a	0.453 ^a	0.557 ^a	0.753 ^a	0.605 ^c	0.767 ^c	0.690 ^b
Molecular wt. (No. Av) ^b	7,200 ^a	9,800 ^a	12,000 ^a	20,300 ^a	12,200 ^c	15,900 ^c	20,800 ^b

^a Determined using chloroform a, DMF b or acetonitrile c as a solvent. ^b Determined by vapor pressure osmometer.

rance or both effects of this monomer. Further research is needed to clarify this point.

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