

디페닐비닐산화포스핀과 아크릴로니트릴 및 초산비닐의 자유라디칼 공중합

진 정 일 · 심 홍 구*

고려대학교 화학과, *과학기술대학 화학과

(1985년 6월 4일 접수)

Free Radical Copolymerization of Diphenylvinylphosphine Oxide with Acrylonitrile and Vinyl Acetate

Jung-Il Jin and Hong-Ku Shim*

Department of Chemistry, Korea University, 1-Anam Dong, Seoul 132, Korea
Korea Institute of Technology, 400, Kusong dong, Taejon 300-31, Korea

(Received June 4, 1985)

Abstract: Free radical-initiated copolymerization of diphenylvinylphosphine oxide (DPVPO) with acrylonitrile (AN) and vinyl acetate (VAc) were studied. The monomer reactivity ratios for the monomer pairs determined at 70°C using benzoyl peroxide as an initiator were: $r_1(\text{AN})=3.8$, $r_2(\text{DPVPO})=0.16$ and $r_1(\text{VAc})=0.38$, $r_2(\text{DPVPO})=1.7$. The values of the Alfrey-Price constants, Q and e , for DPVPO were calculated to be 0.068 and 0.49, respectively, from the AN-DPVPO system, and 0.059 and 0.44, respectively, from VAc-DPVPO pair. The reduced viscosity of copolymers decreased as the content of DPVPO units increased for both systems.

1. INTRODUCTION

Very little information exists in the literature concerning free radical copolymerization characteristics of vinylphosphine oxides and their

derivatives. Even though polymers and copolymers derived from vinylphosphine oxides are of much interest for various applications, there have not been much systematic copolymerization studies of those monomers.

Berlin et al.¹ reported synthesis and free radical -initiated homopolymerization of diphenylvinylphosphine oxide. According to their results, degree of polymerization of the polymer was relatively low and the intrinsic viscosity value was only 0.047.

Rabinowitz and Pellon² reported the copolymerization of diphenylvinylphosphine oxide with styrene and methyl methacrylate. According to their results, the r_1 was 5 ± 1 for styrene and 11 ± 4 for methyl methacrylate, respectively. For both systems, the values of r_2 were zero. But because of the vast different in the reactivity of the comonomer pans and the high degree of error for the reported r_1 values, we can not deduce a quantitative information for copolymerization characteristics of diphenylvinylphosphine oxide from their work.

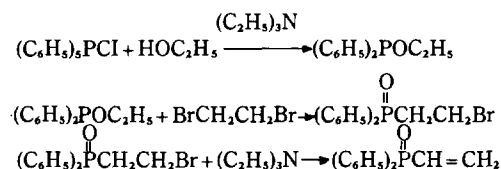
Levin et al.^{3,4} reported the copolymerizations of various phosphorus-containing vinyl monomers. However, they did not include diphenylvinylphosphine oxide in their study.

In order to establish the structure-reactivity relationship, we have investigated the monomer reactivity ratios and copolymerization characteristics of various phosphorus containing vinyl monomers. As a part of our continuing efforts toward this goal, we conducted a free radical-initiated copolymerization of diphenylvinylphosphine oxide with acrylonitrile and vinyl acetate. Especially monomer reactivity ratios of each monomer pairs were determined and the results are reported in this article.

2. EXPERIMENTAL

2-1. Chemicals and Instruments

Diphenylvinylphosphine oxide was synthesized via the following route developed by Rabinowitz and Pellon².



The yield of diphenylvinylphosphine oxide in the last step was 71% and had a melting point of 116-118°C, in agreement with that given by Rabinowitz and Pellon². Analysis: Percentage composition of P in $\text{C}_{14}\text{H}_{13}\text{PO}$; calculated, 13.59%; observed, 13.44%.

IR spectrum (KBr): 3000-3050 (phenyl C-H), 1600 and 1480 (C=C), 1160 cm^{-1} (P=O): NMR spectrum (CDCl_3): δ 5.75-6.25 (m, 2H, =CH₂), 6.45-6.71 (m, 1H, =CH), 7.28-7.80 ppm (m, 5H, -C₆H₅).

Instruments used were a Jasco DS 701 G diffraction grating IR spectrophotometer and a Vairan EM 360A NMR spectrophotometer.

Acrylonitrile (Merck A.G.) and vinyl acetate (Merck A.G.) were purified by standard procedures^{5,6}. Afterwards, gas chromatographic analysis found the monomers to be better than 99.9% pure. N,N-Dimethyl formamide (DMF, Merck A.G.), after being dried over anhydrous magnesium sulfate, was purified by distillation. Benzoyl peroxide (Fisher Scientific) used as an initiator throughout the present work was dissolved in chloroform and then precipitated with ethanol. It was dried at room temperature under vacuum. All other chemicals employed in the present investigation were of reagent grade and used as received.

2-2. Copolymerization of Diphenylvinylphosphine Oxide (DPVPO) and Acrylonitrile (AN)

Copolymerization of DPVPO and AN was performed in DMF. Given amounts of two monomers and 0.5 mole % 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. Next, the tube was filled with predried nitrogen and placed in a water bath at $70.0 \pm 0.1^\circ\text{C}$. 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 DMF containing 2% by weight of hydroquinone. Reaction time ranged from 20 min. to 5 hours depending on the feed composition. The copolymers formed were precipitated when the DMF solution was transferred to a large volume of diethyl ether. The precipitated polymers were separated by centrifugation and purified by dissolution-

precipitation cycles using DMF and diethyl ether. The polymers obtained were dried under vacuum at 35°C to a constant weight. Conversions ranged from about 2.9 to 5.2 wt.% (Table 1).

2-3. Copolymerization of Diphenylvinylphosphine Oxide (DPVPO) and Vinyl Acetate (VAc)

Copolymerization of DPVPO and VAc was performed in benzene. Given amounts of two monomers and 0.5 mole % of benzoyl peroxide (based on the total monomer mixture) were placed in a polymerization tube. Benzene was added in a tube until the mixture became an homogeneous solution. Degassing and polymerization procedures were the same as those described above for the copolymerization with acrylonitrile. Polymerization was stopped by immersing the tube in a dry ice-acetone bath, followed by the transfer of the frozen mixture into benzene containing 2% by weight of hydroquinone. Reaction time ranged 20 to 25 hours depending on the feed composition. The copolymers formed were precipitated into a large volume of n-hexane and further purified using benzene and n-hexane as a solvent-nonsolvent pair. The purified copolymers were dried under vacuum at 35°C . Conversions ranged from about 1.9 to 5.2 wt.% (Table 2).

Table 1. Copolymerization of Acrylonitrile (M_1) and Diphenylvinylphosphine Oxide (M_2) *1

Exp. No.	1	2	3	4	5	6	7
M_1 (g)	0.260	0.361	0.398	0.457	0.652	0.506	0.414
M_2 (g)	1.143	0.798	0.572	0.433	0.908	0.942	0.964
M_1/M_2 (mole ratio) **	1.02	1.95	2.99	4.09	5.99	8.01	9.89
Conversion (wt. %)	2.9	3.6	5.2	4.4	4.4	3.1	3.0
P content (wt. %)	6.38	4.83	3.67	2.96	2.21	1.66	1.37
m_1/m_2 (mole ratio) **	4.87	7.81	11.7	15.4	22.2	30.9	38.3

* 1 Copolymerized at 70°C using 0.5 mole% benzoyl peroxide as initiator.

* 2 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.

2-4. High Conversion Polymerizations

Copolymerizations to high conversion (DPVPO-AN: 5.00-17.5%, DPVPO-VAc: 11.0-16.5%) were conducted in the same manner, with the exception that larger amount of benzoyl peroxide (1.0 mole %) and longer reaction

times (DPVPO-AN: 40 min-5 hrs., DPVPO-VAc : 33-50 hrs.) were employed.

2-5. Characterization of Polymers

Copolymer compositions were determined colorimetrically from their phosphorus contents indicative of DPVPO units⁷. A small quantity (10-20 mg) of copolymers 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. Tripara-cresyl phosphate was used as a standard for the construction of a calibration curve. Blank tests were run side by side with actual experiments. Reduced viscosities of copolymers were measured at $25.0 \pm 0.1^\circ\text{C}$ using an Ubbelohde-type viscometer.

Table 2. Copolymerization of Vinyl Acetate (M_1) and Diphenylvinylphosphine Oxide (M_2)^{*1}

Exp. No.	1	2	3	4	5	6
M_1 (g)	0.427	0.564	0.686	0.376	0.758	0.882
M_2 (g)	1.135	0.754	0.457	0.325	0.255	0.209
M_1/M_2 (mole ratio) ^{*2}	0.996	1.98	3.98	6.00	7.87	11.18
Conversion (wt. %)	1.9	2.3	5.2	2.6	3.6	3.5
P content (wt. %)	11.36	10.07	8.22	6.92	6.08	5.01
m_1/m_2 (mole ratio) ^{*2}	0.516	0.927	1.74	2.56	3.27	4.55

* 1 Copolymerized at 70°C using 0.5 mole % benzoyl peroxide as initiator.

* 2 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.

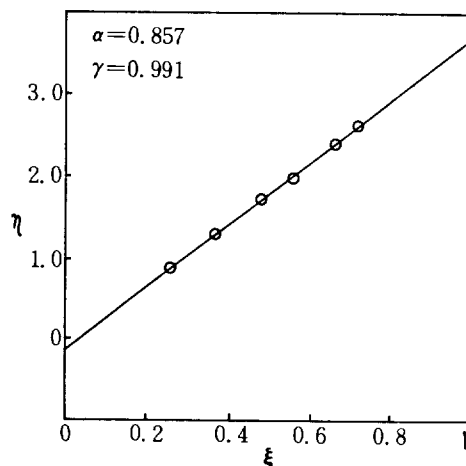


Fig. 1. Kelen-Tüdös plot for copolymerization of acrylonitrile and diphenylvinylphosphine oxide ($r_1=3.8$, $r_2=0.16$). α stands for the constant of Kelen-Tüdös equation and r for the coefficient of correlation.

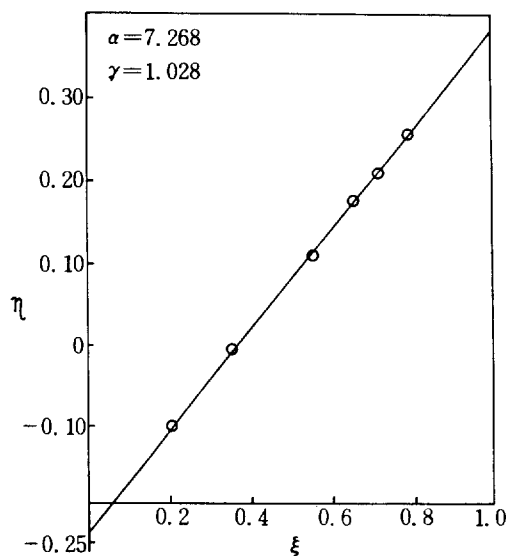


Fig. 2. Kelen-Tüdös plot for copolymerization of vinyl acetate and diphenylvinyl phosphine oxide ($r_1=0.38$, $r_2=1.7$). α stands for the constant of Kelen-Tüdös equation and r for the coefficient of correlation.

3. RESULTS AND DISCUSSION

The results of the copolymerization of DPVPO with AN and VAc are summarized in Table 1 and 2.

These data were analyzed by the Kelen-Tüdös⁸ method to determine the monomer reactivity ratios for the monomer pairs (Fig. 1 and 2). From the intercepts at $\xi = 0$ and $\xi = 1$, well defined values were obtained from both systems;

$$r_1(\text{AN}) = 3.8, \quad r_2(\text{DPVPO}) = 0.16$$

$$r_1(\text{VAc}) = 0.38 \quad r_2(\text{DPVPO}) = 1.7$$

These values indicate that the AN monomer is more reactive than DPVPO toward both propagation species. But the results for VAc/DPVPO system reveal that DPVPO monomer is more reactive than VAc toward the both propagating radicals. The monomer reactivity ratios of the AN/DPVPO pair lead to Alfrey-Price values of $Q = 0.068$ and $e = 0.49$ for DPVPO. The VAc/DPVPO pair gives almost the same results; $Q = 0.059$ and $e = 0.44$. Judging by the Q values obtained, the general reactivity or the degree of delocalization of the π -electrons in the vinyl group of DPVPO is very low, approximately same as those of bis (β -chloroethyl) vinyl phosphonate and sodium ethenesulfonate whose Q values are known to be 0.06⁹ and 0.064¹⁰, respectively.

Certainly conjugation between $\text{CH}_2 = \text{CH}$ - and $\text{P} = \text{O}$ groups of the compound is not as facile as that between $\text{CH}_2 = \text{CH}$ - and $> \text{C} = \text{O}$ groups in vinyl ketones or acrylates. For example, the Q value of

Table 3. Reduced Viscosities of the Copolymers of Diphenylvinylphosphine Oxide (DPVPO: M_2) with Acrylonitrile (AN: M_1) and Vinyl Acetate (VAc: M_1)^{*1}

Copolymer	AN/DPVPO				VAc/DPVPO			
M_1/M_2 (mole ratio)	1.941	4.061	7.899	100/0	1.987	3.986	8.106	100/0
Conversion (wt. %)	10.2	17.5	5.00	9.50	11.0	13.2	16.5	59.3
P content (wt. %)	4.84	3.04	1.84	0	9.91	8.18	5.93	0
m_1/m_2 (mole ratio)	7.79	15.0	27.7	100/0	0.988	1.75	3.43	100/0
Reduced viscosity ^{*2} (dl/g)	0.183 ⁰	0.408 ⁰	0.689 ⁰	0.721 ⁰	0.042 ⁰	0.064 ⁰	0.081 ⁰	0.366 ⁰

* 1 Copolymerized at 70°C using 1.0 mole % benzoyl peroxide as initiator. Reaction time: AN/DPVPO; 40 min. - 5 hrs, VAc/DPVPO; 33-50 hrs.

* 2 Determined using DMF (a) or chloroform (b) as a solvent.

phenylvinyl ketone is 0.66, which is much greater than that of DPVPO. However, the reactivity of DPVPO seems to be much higher than that of diethylvinyl phosphate whose Q value is 0.025¹². The e value of DPVPO is comparable to those of methacrylic esters (0.4-0.5)¹³ and sodium ethenesulfonate (0.41)¹⁰ indicating that the diphenylphosphine oxide group is a moderate electron attractor. Electron withdrawing capacity of the group is higher than that of diethyl phosphate function, but significantly lower than that of phosphonate group. According to our earlier reports, the e values of diethylvinyl phosphate and bis(β -chloroethyl)vinyl phosphonate are 0.13¹³ and 1.1¹², respectively.

The results for high conversion copolymerization of DPVPO with AN and VAc are summarized in Table 3. One can see from the table that the percentage of DPVPO units incorporated into AN copolymers is much lower

than that incorporated into VAc copolymers as expected from the difference in their reactivities. Reduced viscosities of copolymers steadily decreased as the content of DPVPO increased. This suggests that either the chain transfer constant of DPVPO is higher than VAc and AN or steric effect by the bulky diphenylphosphine oxide group hinders propagation reactions or both. Further study is needed to quantify the chain-transfer characteristics of DPVPO in free radical-initiated copolymerizations.

4. CONCLUSION

From the present investigation the following conclusion can be drawn:

1. Free-radical copolymerization of diphenylvinylphosphine oxide (DPVPO) with acrylonitrile (AN) and vinyl acetate (VAc) produced well-defined values of monomer reactivity ratios of the monomer pairs: r_1 (AN)=3.8, r_2 (DPVPO)=0.16 and r_1 (VAc)=0.38, r_2 (DPVPO)=1.7.
2. General reactivity of DPVPO was found to be rather low as judged by its Q value of 0.06-0.07. The e value of the monomer was estimated to be about 0.4-0.5, indicating an electron withdrawing property of the diphenylphosphine oxide group.
3. Copolymerization of DPVPO with either AN or VAc resulted in lowering solution viscosity of the copolymers suggesting a higher chain-transfer capacity of DPVPO compared with those of AN and VAc.

REFERENCES

1. K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **26**, 2537(1961).
2. R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4623(1961).
3. Ya. A. Levin, G. B. Fridman, and B. E. Ivanov, *Vysokomol. Soed.*, **A17(4)**, 845(1975).
4. S. V. Shulyndin, Ya. A. Levin, and B. E. Ivanov, *Russian Chemical Reviews*, **50(9)**, 865(1981).
5. M. Windholz, S. Budavari, L. Y. Stroumstos, and M. N. Fertig, "The Merck Index," Merck & Co., Inc., N. J., 1976, p. 127.
6. Quoted in ref. 5, p. 9649.
7. I. M. Kolthoff *et al.*, "Quantitative Chemical Analysis", 4th ed., p. 1126, MacMillan, London, 1971.
8. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem.*, **A9(1)**, 1(1975).
9. J.-I. Jin, H. S. Byun, and Y. M. Park, *J. Korean Chem. Soc.*, **21(3)**, 219(1977); *Polymer (Korea)*, **1(3)**, 139 (1977).
10. J. Brandrup and E. H. Immergut, "Polymer Handbook", 2nd ed., John Wiley & Sons, New York, 1975, p. II-392.
11. T. Otsu, J. Ushirone, and M. Imoto, *Kogyo Kagaku Zasshi*, **69**, 516(1966).
12. J.-I. Jin, H. S. Byun, and S. M. Lee, *J. Macromol. Sci. Chem.*, **A16(5)**, 953(1981).
13. J. Brandrup and E. H. Immergut, "Polymer Handbook", 2nd ed., John Wiley & Sons, New York, 1975, pp. II 391-392.