

## 비닐포스폰산 비스- $\beta$ -클로로에틸과 초산비닐의 혼성중합

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## Copolymerization of *Bis*( $\beta$ -chloroethyl) vinylphosphonate and Vinyl Acetate

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**요 약.** 비닐포스폰산 비스- $\beta$ -클로로에틸 (BCVP)과 초산비닐 (VAc)의 혼성중합을 50°C에서 행하여 단위체 반응성비를 구하였다. 이때 과산화벤조일을 개시제로 사용하였으며, 얻은 반응성비는 아래와 같다.

$$r_1(\text{VAc})=0.33, r_2(\text{BCVP})=0.47$$

이 값과 Alfrey-Price 식을 이용하여 비닐포스폰산 비스- $\beta$ -클로로에틸의  $Q$ 와  $e$  값을 계산하니  $Q=0.06$  및  $e=1.1$  을 얻었다.

이 두 단위체로 부터 얻어지는 혼성중합체중의 단위체 서열분포와 평균서열 길이를 통계적으로 분석한 결과 혼성중합체가 비교적 높은 교대경향을 갖고 있음을 알았다. 또한 혼성중합체중에 비닐포스폰산 비스- $\beta$ -클로로에틸의 함량이 많을 수록 열안정성이 나빠짐을 열시차분석에서 관찰하였다.

**ABSTRACT** The free radical initiated copolymerization of vinyl acetate (VAc) and *bis*( $\beta$ -chloroethyl) vinylphosphonate (BCVP) was studied. The monomer reactivity ratios for the monomer pair determined at 50°C using benzoyl peroxide as an initiator are:

$$r_1(\text{VAc})=0.33, r_2(\text{BCVP})=0.47$$

The values of Alfrey-Price's  $Q$  and  $e$  for the *bis*( $\beta$ -chloroethyl) vinylphosphonate were calculated to be 0.06 and 1.1, respectively.

The statistical analyses for the monomer sequence distribution and the mean sequence length show that the copolymer formed from these two monomers are of fairly alternating tendency.

Differential thermal analysis showed that thermal stability of the copolymers decreases as the content of BCVP in the copolymer increases.

### INTRODUCTION

Several studies on the free radical initiated

copolymerization of *bis*( $\beta$ -chloroethyl) vinylphosphonate (BCVP) have been reported, wherein the monomer reactivity ratios were determin-

ed for copolymerization with styrene (S)<sup>1,2,3</sup>, methacrylic acid (MA)<sup>1</sup> and methyl methacrylate (MMA)<sup>3</sup>. There are, however, considerable confusion as to the copolymerization reactivity of BCVP, because of wide discrepancy existing among the reported results.

Orlov and Tarakanov<sup>1</sup> reported that the monomer reactivity ratios for the free radical copolymerization of BCVP with styrene are  $r_1(\text{BCVP})=0.2$  and  $r_2(\text{S})=2.2$ , while those determined by Konya and Yokoyama<sup>2</sup> for the same pair are  $r_1=0.03$  and  $r_2=2.43$ . Fujii<sup>3</sup> studied  $\gamma$ -ray induced copolymerization of BCVP with styrene and found that the copolymerization proceeded via free radical mechanism. He reported the values of  $r_1(\text{BCVP})=0.16$  and  $r_2(\text{S})=2.3$ . Disaccord among the  $r$ 's values, especially among those of  $r_1(\text{BCVP})$  is significant.

According to the same report by Fujii the monomer reactivity ratios for the BCVP and MMA pair are  $r_1(\text{BCVP})=0.26$  and  $r_2(\text{MMA})=29.9$ . The product of  $r_1$  and  $r_2$  are much greater than 1 and it is well known that there are only few established instances of a free-radical-propagated copolymerization for which  $r_1 \times r_2 > 1$ .<sup>4</sup>

The  $Q$  and  $e$  values estimated for BCVP from the reported  $r$ -values vary widely. Orlov and Tarakanov's results for the copolymerization of BCVP and styrene suggest the  $Q$  and  $e$  values for BCVP to be 0.22 and 0.11, respectively, while those for BCVP/MMA pair predict  $Q=0.58$  and  $e=-0.68$  for the same monomer. The differences between the two sets of values are obviously outside the range of simple experimental error. Moreover, Konya and Yokoyama<sup>2</sup> estimated the  $Q$  and  $e$  values for the vinylphosphonate monomer to be  $Q=0.11$  and  $e=0.8$ , of which the magnitude of the latter is considerably higher than those mentioned above. Fujii<sup>3</sup> reported the values of  $Q=0.2$  and  $e=0.2$ ,

which are relatively close to those estimated from the copolymerization results of BCVP and styrene by Orlov and Tarakanov<sup>1</sup>.

The above explained discrepancies existing among the  $r$  as well as  $Q$  and  $e$  values hamper the correct prediction for the reactivity of BCVP in vinyl copolymerizations. Moreover, the substituent effect of *bis*( $\beta$ -chloroethoxy)phosphono group on the vinyl functional group can not be defined at all due to the same reason. We have, therefore, performed the copolymerization studies of BCVP with vinyl acetate (VAc) in order to clarify the copolymerization reactivity of BCVP and the substituent effect of *bis*( $\beta$ -chloroethoxy)phosphono group.

## EXPERIMENTAL

**Preparation of BCVP.** BCVP was prepared by the method reported by Konya and Yokoyama<sup>2</sup>. Purified *tris*(2-chloroethyl)phosphite (Aldrich Chemical Co. Inc.) was thermally rearranged to *bis*( $\beta$ -chloroethyl)vinylphosphonate at 180~190°C, which was subsequently dehydrochlorinated in the presence of triethylamine to give *bis*( $\beta$ -chloroethyl)vinylphosphonate. The desired product, having a b. p of 136~137°C (4.0 mmHg) and  $n_D^{20}$  1.4779, was obtained in about 60% yield counted from the phosphite; literature value<sup>2</sup>, b. p 135~137°C (4.0 mmHg) and  $n_D^{20}$  1.4780.

**Other Chemicals.** Vinyl acetate (reagent grade from Wako Chemical Co., Japan) was dried over calcium chloride and distilled under nitrogen right before use. Only the fraction which was distilled over at 72.5~73°C was used for copolymerization. Benzoyl peroxide (reagent grade of Kanto Chemical Co., Japan) was purified by methanol precipitation from concentrated chloroform solution and vacuum dried. Other reagents used in this work were reagent grade supplied by E. Merck AG., Germany and

were used without further purification.

**Copolymerization.** The monomer mixture including benzoyl peroxide (0.5 % by weight of the monomer mixture) was placed in a glass tube with a screw cap. The mixture was placed in a dry-ice/acetone bath and air in the empty space of the tube was replaced with nitrogen. The copolymerizations were carried out at  $50 \pm 0.1^\circ\text{C}$  in a water bath and were stopped after 45 to 60 minutes to give copolymer yields of 3 ~ 6 %. At the end of a copolymerization the reaction tube was immersed in a dry-ice/acetone bath to be frozen. After the mixture had been frozen, the tube was removed from the bath and 2 ml of acetone containing 5 wt. % of the inhibitor, hydroquinone, was added. This was thoroughly mixed and the mixture was poured into cold diethyl ether precipitating the copolymer formed. The reaction tube was thoroughly washed with acetone and the washings were also poured into the ether. The copolymer obtained was purified by dissolution and precipitation using acetone and ether. This procedure was repeated four more times and the copolymer was finally dried at  $50 \sim 60^\circ\text{C}$  under reduced pressure (15 mmHg).

#### Determination of Copolymer Composition.

The composition of copolymers was determined by the gravimetric analysis of the phosphorous content of the copolymers following the procedure reported in the literature<sup>5</sup>. About 20 mg of a copolymer was first combusted wet in a mixture of concentrated sulfuric and nitric acids. The solution was treated with ammonium molybdate to obtain precipitates of ammonium phosphomolybdate, which were collected by filtration, washed, and dried. The phosphorous content was calculated from the weight of precipitates obtained.

**Thermal Analysis of Polymers.** Thermal properties of polymers were studied by differential thermal analysis. Thermograms were obtained

by Automatic Recording Differential Analysis System, Model 4~4442 of American Instrument Co.. Glass powders were used as reference material.

## RESULTS AND DISCUSSION

**Copolymerization of BCVP and Vinyl Acetate.** The data for the copolymerization of BCVP and vinyl acetate from Table 1 are presented in intersect (Fig. 1)<sup>6</sup> and Fineman-Ross (Fig. 2)<sup>7</sup> plots. The intersect is reasonably definitive and the points fit the linear plot well. The least-squares analysis for the linear plot gives values of  $r_1$  (VAc) = 0.33 and  $r_2$  (BCVP) = 0.47. The  $Q$  and  $e$  values for BCVP calculated by Alfrey-Price equations<sup>8</sup> with these data are  $Q=0.06$  and  $e=1.1$ . The  $Q$  and  $e$  values for vinyl acetate were taken to be 0.026 and  $-0.22$ , respectively, as reported in the literature<sup>9</sup>. These values are not far from those reported by Konya and Yokoyama<sup>2</sup>, but they are not too close to the values reported by or expected from other works<sup>1,3</sup>.

We believe all the earlier workers cited in the "Introduction" for the copolymerization of BCVP have common uncertainty in obtaining  $r$  values, thus  $Q$  and  $e$  values for BCVP, because the comonomers selected were too reactive in comparison with reactivity of BCVP resulting in very low  $r$ -values for BCVP. It is well known that experimental error can be significant, especially when  $r$  value lies near to zero<sup>10</sup>. The  $Q$  and  $e$  values for BCVP obtained in the present work are in the same range as those for methyl vinyl sulfoxide ( $Q=0.057$ ,  $e=0.98$ )<sup>11</sup> and phenyl vinyl sulfone ( $Q=0.069$ ,  $e=1.18$ )<sup>12</sup>.

The low  $Q$  value for BCVP indicates that this monomer has low copolymerization reactivity and there is very little direct conjugation between vinyl and phosphonate group. The

Table 1. Copolymerization of vinyl acetate ( $M_1$ ) and *bis*( $\beta$ -chloroethyl)vinylphosphonate ( $M_2$ )\*

Exp. No.	1	2	3	4	5	6
$M_1$ (g)	3.0025	1.4679	1.0200	0.6496	0.6513	0.6188
$M_2$ (g)	2.7110	4.0050	5.4208	4.6934	4.9998	5.0455
$M_1/M_2$ (mole ratio)	3.001	1.001	0.507	0.350	0.354	0.332
Conversion (wt. %)	3.81	5.53	6.11	3.51	4.12	3.32
P. Content (wt. %)	8.12	10.01	10.86	11.29	11.32	11.38
$m_1/m_2$ (mole ratio)	1.75	0.885	0.610	0.478	0.472	0.457

\*Copolymerized at 50 °C using 0.5 wt. % benzoyl peroxide as initiator.  $m_1$  and  $m_2$  designate mole fraction of  $M_1$  and  $M_2$  in the copolymer.

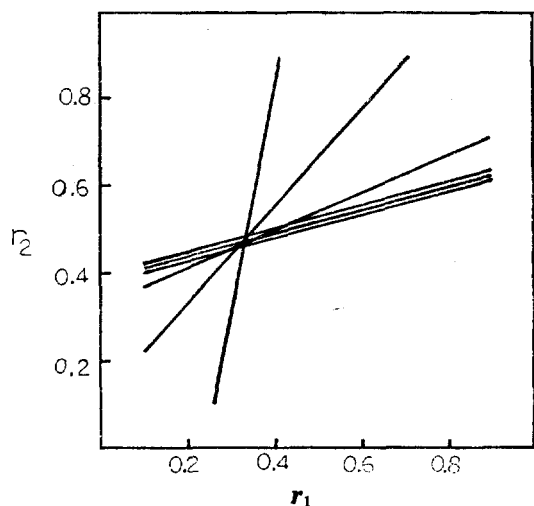


Fig. 1. Intersect plot for copolymerization of vinyl acetate ( $r_1=0.33$ ) and *bis*( $\beta$ -chloroethyl)vinylphosphonate ( $r_2=0.47$ ) at 50 °C.

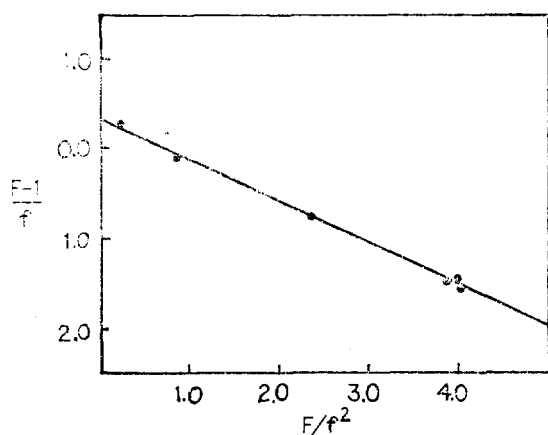


Fig. 2. Fineman-Ross plot for copolymerization of vinyl acetate ( $r_1=0.33$ ) and *bis*( $\beta$ -chloroethyl)vinylphosphonate ( $r_2=0.47$ ) at 50 °C ( $f=M_1/M_2$  and  $F=m_1/m_2$ ).

magnitude of  $e$  of the vinylphosphonate suggests that the *bis*( $\beta$ -chloroethyl)phosphonate group exerts a fairly strong -I effect onto the vinyl group.

According to Furukawa and Tsuruta<sup>13</sup> there is a linear relationship between  $e$  values of vinyl monomers and Hammett's  $\sigma$  values of the corresponding substituents attached to the vinyl group. This linearity between  $e$  and  $\sigma$  values predicts that, when the  $e$  value of 1.1 for BCVP is located on the  $e$ - $\sigma$  plot and the corresponding  $\sigma$  value is read, the  $\sigma$  value of *bis*( $\beta$ -chloroethoxy)phosphono group be about 0.61. This value is very close to that reported for diethylphosphono group ( $\sigma_p=0.60$ )<sup>14</sup>.

**Statistical Analysis of the Sequence Distribution of Copolymers.** The mean length ( $\bar{n}$ ) of the sequences of BCVP and VAc monomers in the BCVP/VAc copolymer was computed using the equation of Miller and Nielson<sup>15</sup> and are presented in Fig. 3. This figure shows how the mean length of the sequence of BCVP or VAc changes as the mole fraction of BCVP or VAc in the feed increases. According to the figure  $\bar{n}$  of BCVP remains below 2 until the mole fraction of BCVP in the feed reaches 0.7. When the mole fraction of BCVP in the feed mixture is 0.9,  $\bar{n}$  of BCVP in the copolymer to be formed at the feed composition is only 4.8. Similar trend can be observed for VAc unit in the copolymers.

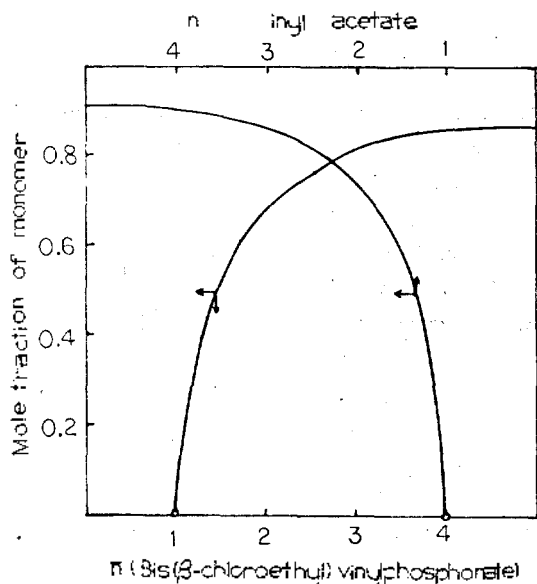


Fig. 3. Dependence of mean length of the sequence of each monomers on their mole fractions in feed.

Sakaguchi<sup>16</sup> statistically analyzed the sequential distribution of syndiotactic and isotactic units in a polymer, and later Berger<sup>17</sup> applied Sakaguchi's approach to the statistical analysis of copolymer sequences and proposed following equation.

$$F_n = \frac{F_1 \cdot n}{\{1 + (M_1/M_2) r_1\}^2 \left[ \frac{(M_1/M_2) r_1}{1 + (M_1/M_2) r_1} \right]^{n-1}}$$

where  $M_1$  and  $M_2$  are moles or mole fractions of monomers in the feed and  $F_1$  the mole fraction of  $M_1$  in the growing chain or copolymer formed.  $F_n$  means the fraction of copolymer existing in the blocks of  $M_1$  units  $n$  long.

Such calculations for the BCVP monomer unit were conducted for BCVP/VAc copolymers at three different feed compositions using the observed monomer reactivity ratios and the results are presented in Fig. 4. As can be seen from the figure most of the copolymers are existing in very short blocks of BCVP or VAc indicating that the copolymers have relatively

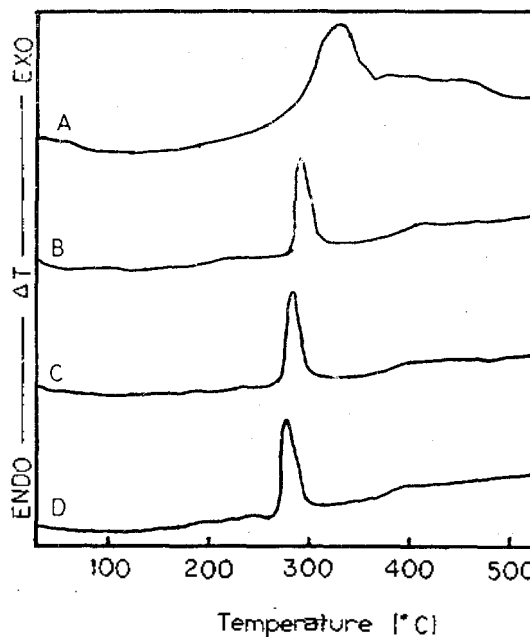


Fig. 4. Fraction of copolymer existing in  $n$  long blocks of bis( $\beta$ -chloroethyl) vinylphosphonate (BCVP).

high alternating tendency of the two monomers, which is in accord with the results of the analysis of the mean length of the sequence mentioned above.

**Thermal Properties of Copolymers.** Thermal behaviors of the two BCVP/VAc copolymers and homopolymers of BCVP and VAc were examined by differential thermal analysis and are shown in Fig. 5. As the copolymer contained more BCVP unit, its decomposition temperature decreased accordingly.

While the BCVP homopolymer and copolymers showed substantial amount of charry residues in the cells when heated to 500°C, VAc homopolymer left practically no residue. Certainly BCVP units in the copolymer modify the thermal degradation mechanism in such a way that char formation is favored. There are many reported results that phosphorus and halogen compounds promote char formation during the thermal degradation of polymers<sup>18</sup>.

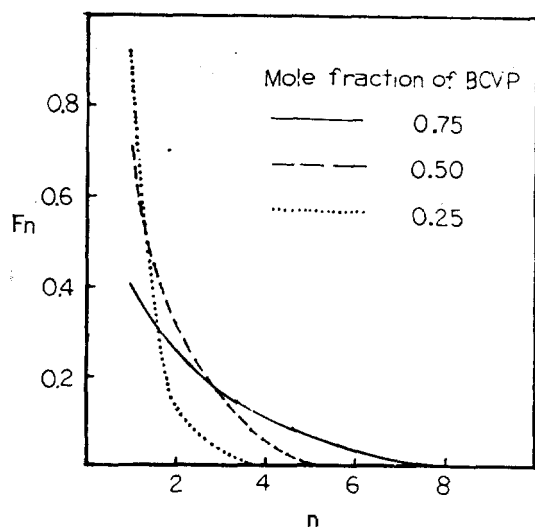


Fig. 5. Thermogram of poly(vinyl acetate) (A), poly(*bis*( $\beta$ -chloroethyl)vinylphosphonate-co-vinylacetate) (B),  $m_1/m_2=10.6$ ; (C),  $m_1/m_2=0.82$ , and poly(*bis*( $\beta$ -chloroethyl)vinylphosphonate) (D) (obtained in air:heating rate  $16^\circ\text{C}/\text{min.}$ ).

### CONCLUSION

The monomer reactivity ratios for the free radical copolymerization of *bis*( $\beta$ -chloroethyl)vinylphosphonate and vinyl acetate determined at  $50^\circ\text{C}$  in bulk are  $r_1(\text{VAc})=0.33$  and  $r_2(\text{BCVP})=0.47$ . Copolymerization parameters of BCVP were estimated to be  $Q=0.06$  and  $e=1.1$ .

It was also found that *bis*( $\beta$ -chloroethoxy)-phosphono group is a fairly strong -I group whose Hammett's  $\sigma$  value is about 0.61.

Statistical analysis of the copolymer sequences indicates that BCVP/VAc copolymers are of relatively high alternating tendency. Thermal stability of the copolymers seems to be reduced as the content of BCVP unit increases.

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### REFERENCES

1. V. A. Orlov and O. G. Tarakanov, *Plasticheski Massy*, **6**, 6 (1964); *Chem. Abstr.*, **61**, 8412k (1964).
2. S. Konya and M. Yokoyama, *Kogyo Kagaku Zasshi*, **68**(6), 1080 (1965).
3. S. Fujii, *Radiation Res.*, **33**, 249 (1968).
4. J. Brandrup and E. H. Immergut (Ed.), "Polymer Handbook," II 141~II 289. Interscience Publishers, New York, 1966.
5. W. T. Smith and R. L. Shriner, "The Examination of New Organic Compound", P. 56, John Wiley & Sons, Inc., New York, 1956.
6. F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).
7. M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).
8. T. Alfrey, Jr. and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).
9. J. Brandrup and E. H. Immergut (Ed.), "Polymer Handbook", P. II-360, Interscience Publishers, New York, 1996.
10. C. Walling, "Free Radicals in Solution," P. 142, John Wiley & Sons,
11. J. Brandrup and E. H. Immergut (Ed.), "Polymer Handbook," P. II-349, Interscience Publishers, New York, 1966.
12. J. Brandrup and E. H. Immergut (Ed.), "Polymer Handbook," P. II-350, Interscience Publishers, New York, 1966.
13. J. Furukawa and T. Tsuruta, *J. Polymer Sci.*, **40**, 457 (1959).
14. L. D. Freedman and H. H. Jaffe, *J. Amer. Chem. Soc.*, **77**, 920 (1955).
15. R. L. Miller and L. E. Nielson, *J. Polymer Sci.*, **46**, 303 (1960).
16. Y. Sakaguchi, *Kobunshi Kagaku*, **17**, 333 (1960).
17. M. Berger, *J. Polymer Sci.*, **A1**, 1601 (1963).
18. P. C. Warren, *SPE Journal*, **27**, 17 (1971) and references cited therein.