

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

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## Copolymerization of Bis( $\beta$ -chloroethyl) Vinylphosphonate and Acrylonitrile

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**요약** : 비닐포스폰산 비스- $\beta$ -클로로에틸 (BCVP) 과 아크릴로니트릴 (AN) 의 혼성중합을 50°C 에서 행하여 단위체 반응성 비를 구하였다. 이때 과산화벤조일을 개시제로 사용하였으며 용매로는 DMF 를 사용하였고 얻은 반응성비는 아래와 같다.

$$r(\text{AN}) = 7.3$$

$$r(\text{BCVP}) = 0.13$$

이 값과 Alfrey-Price 식을 이용하여 비닐포스폰산 비스- $\beta$ -클로로에틸의  $Q$  와  $e$  값을 계산하니  $Q=0.06$  및  $e=0.98$  을 얻었다.

이 두 단위체로 얻어지는 혼성중합체 중의 단위체 서열분포와 평균서열길이를 통계적으로 분석한 결과 혼성중합체가 짧은 BCVP block과 긴 AN 의 block으로 되어 있음을 알았다. 또한 혼성중합체의 열안정성을 열시차분석법으로 조사하였다.

**Abstract:** The monomer reactivity ratios determined at 50°C for the free-radical copolymerization of bis ( $\beta$ -chloroethyl) vinylphosphonate (BCVP) and acrylonitrile (AN) are:

$$r(\text{AN}) = 7.3$$

$$r(\text{BCVP}) = 0.13$$

The values of Alfrey-Price's  $Q$  and  $e$  for BCVP were found to be 0.06 and 0.98, respectively.

The statistical analysis for the monomer sequence distribution and the mean sequence length shows that the copolymers formed from this monomer pair are composed of short blocks of BCVP and long blocks of AN.

Thermal stability of copolymers were also examined by differential thermal analysis and they were compared with those of homopolymers.

## INTRODUCTION

We have reported in the previous paper the results of the free radical copolymerization of bis-( $\beta$ -chloroethyl) vinylphosphoante (BCVP) and vinyl acetate (VAc).<sup>1</sup> According to the work the monomer reactivity ratios for the copolymerization of BCVP and VAc were  $r_1$  (VAc)=0.33 and  $r_2$  (BCVP)=0.47 and the Alfrey-Price's  $Q$  and  $e$  values for BCVP were estimated to be 0.06 and 1.1, respectively. The reactivity parameters of BCVP obtained were not too close to those derived from other works.<sup>2,3,4</sup> We also estimated, from the linear relationship existing between  $\sigma$  and  $e$  values, the Hammett  $\sigma$  value of bis( $\beta$ -chloroethoxy) phosphono group to be 0.61. We have conducted the copolymerization of BCVP with acrylonitrile (AN), a vinyl monomer with a fairly strong -I group which is in conjugation with the vinyl group and would like to report our results in this paper.

## EXPERIMENTAL

*Preparation of BCVP.* BCVP was prepared from tris( $\beta$ -chloroethyl) phosphite as described in the previous paper.<sup>1</sup>

*Other Chemicals.* Acrylonitrile (reagent grade from Fluka AG, Switzerland) was dried over anhydrous calcium chloride and distilled under  $N_2$  atmosphere. Only the fraction which distilled over at  $77\sim 78^\circ C$  was used for copolymerization. Benzoyl peroxide (reagent grade from Kanto Chemical Co., Japan) was purified by precipitation from concentrated chloroform solution adding excess amount of methanol. The precipitates were washed with methanol and vacuum dried. Other reagents used in this work were reagent grade supplied by Merck AG., Germany and were used as received 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. And then 10 ml of freshly distilled  $N,N$ -dimethylformamide was added to the mixture. The mixture was frozen in a dry-ice acetone bath and the air in the empty space of the reaction tube was replaced with dry nitrogen. The mixture was polymerized at  $50\pm 0.1^\circ C$  in a water bath. The polymerization was stopped by freezing the mixture in a dry-ice/acetone bath after 2 to 3 hours to give copolymer yields of 0.4~2% by the weight of the initial feed mixture (see Table 1). The frozen mixture was transferred into a cold methanol solution containing 5 wt. % hydroquinone precipitating the copolymer formed. The reaction tube was thoroughly washed with  $N,N$ -dimethylformamide and the washings were also poured into the methanol solution. The copolymer obtained was purified by dissolution and precipitation using the solvent and nonsolvent pair of  $N,N$ -dimethylformamide and methanol. This procedure was repeated four more times and the copolymer was finally dried at  $50\sim 60^\circ C$  under reduced pressure (10 mmHg).

*Determination of Copolymer Composition.* The composition of copolymers was determined by the colorimetric analysis of the phosphorus content of the copolymers following the literature procedure.<sup>5</sup> About 10 to 20 mg of a copolymer was oxidatively decomposed in a mixture of concentrated sulfuric and nitric acids. The solution was developed using ammonium molybdate-hydrazine sulfate solution. The absorbance was measured at 830  $m\mu$ . A calibration curve was constructed using poly[bis( $\beta$ -chloroethyl) vinylphosphonate] as the standard material.

*Thermal Analysis of Copolymers.* Thermal behaviors of copolymers and homopolymers

were studied by differential thermal analysis. Thermograms were obtained by Automatic Recording Differential Analysis system, Model 4-442 of American Instrument Co.. Glass powders were used as reference material.

**RESULTS and DISCUSSION**

*Copolymerization of BCVP and AN.* The data for the copolymerization of BCVP and AN from Table 1 are presented in direct curve fitting (Fig. 1)<sup>6</sup> and Fineman-Ross<sup>7</sup> (Fig. 2) plots.

The curve fits reasonably well the experimental

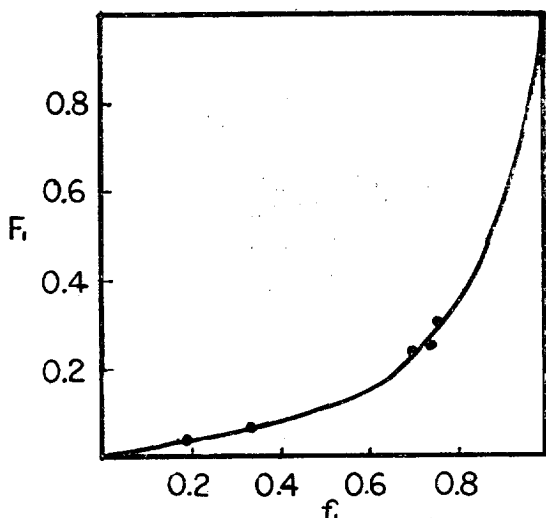
data and the points fit the linear plot well. The least-squares analysis for the linear plot gives values of  $r$  (AN)=7.3 and  $r$  (BCVP)=0.13. The  $Q$  and  $e$  values for BCVP monomer calculated by the Alfrey-Price equations with these data are  $Q=0.06$  and  $e=0.98$ . These values are reasonably close to those reported earlier by us<sup>1</sup>:  $Q=0.06$ ,  $e=1.1$ . The  $Q$  and  $e$  values for AN were taken to be 0.6 and 1.20, respectively, as reported in the literature.<sup>8</sup>

The newly estimated  $Q$  and  $e$  values for BCVP are in the same range as those for methyl vinyl sulfoxide ( $Q=0.057$ ,  $e=0.98$ )<sup>9</sup> and phenyl

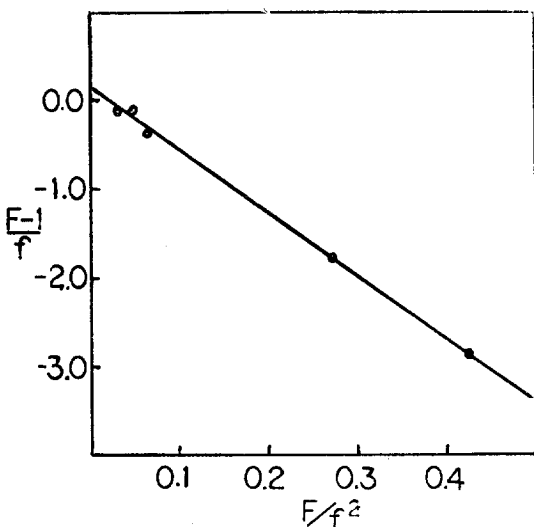
**Table 1.** Copolymerization of bis (β-chloroethyl) vinylphosphonate (M<sub>1</sub>) and acrylonitrile (M<sub>2</sub>)

Eap. No.	1	2	3	4	5
M <sub>1</sub> (g)	3.0067	4.0008	5.0014	5.2748	4.6606
M <sub>2</sub> (g)	2.5084	1.8262	0.4687	0.4172	0.4192
m <sub>1</sub> /m <sub>2</sub> (mole ratio)	0.3331	0.4988	2.427	2.882	2.571
Conversion (wt. %)	1.00	0.40	1.20	0.91	1.02
P Content (wt. %)	2.33	3.05	7.88	8.97	8.85
M <sub>1</sub> /M <sub>2</sub> (mole ratio)	0.0484	0.0678	0.352	0.472	0.453

\*Copolymerized at 50 °C using 0.5 wt. % benzoyl peroxide as initiator.



**Fig. 1.** Incremental copolymer composition (mole fraction of BCVP,  $F_1$ ) plotted against the monomer feed composition (mole fraction of BCVP,  $f_1$ ).



**Fig. 2.** Fineman-Ross plot for the copolymerization of BCVP ( $r=0.13$ ) and AN ( $r=7.3$ ).

vinyl sulfone ( $Q=0.069$ ,  $e=1.18$ )<sup>10</sup>, similar to the conclusion that was previously made from the results of the copolymerization of BCVP and vinyl acetate.<sup>1</sup>

*Statistical Analysis of the Sequence Distribution of Copolymers.* The mean length ( $\bar{n}$ ) of the the sequences of BCVP and AN monomers in the copolymer was computed using the Miller-Nielson equation<sup>11</sup> and are presented in Fig. 3. This figure shows how the mean length ( $\bar{n}$ ) of the sequence of each comonomer units in the instantaneously formed copolymer changes as the mole fraction of BCVP or AN in the feed increases. According to the figure  $\bar{n}$  of BCVP unit remains below 2 until the mole fraction of BCVP in the feed mixture reaches 0.8, while  $\bar{n}$  of AN increases rapidly as its mole fraction in the feed increases.

Using Sakaguchi-Berger equation<sup>12,13</sup> the fraction of polymer existing in the blocks of  $n$  unit length was calculated for the arbitrarily chosen 3 different feed compositions and the results are presented in Fig. 4.

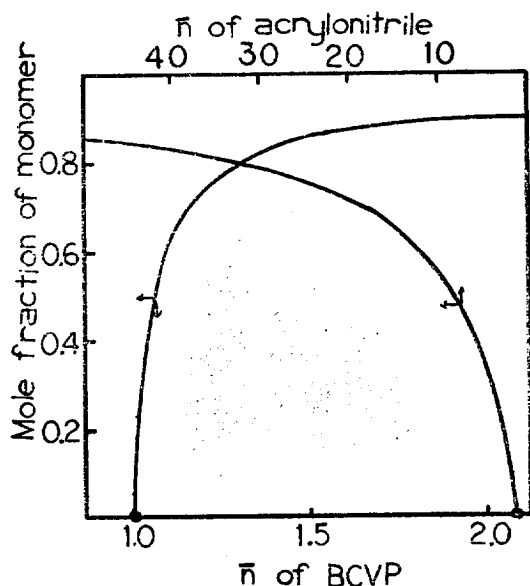


Fig. 3. Dependence of mean lengths of the sequences of each monomers on its mole fraction in feed.

As can be seen from the figure most of the copolymers are existing in fairly long blocks of

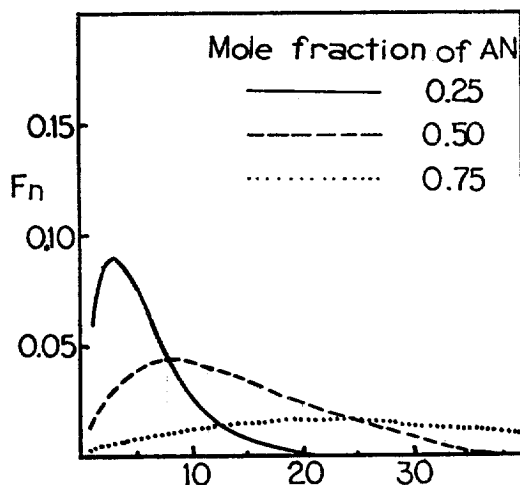


Fig. 4. Fraction of copolymer existing in  $n$ -long blocks of acrylonitrile.

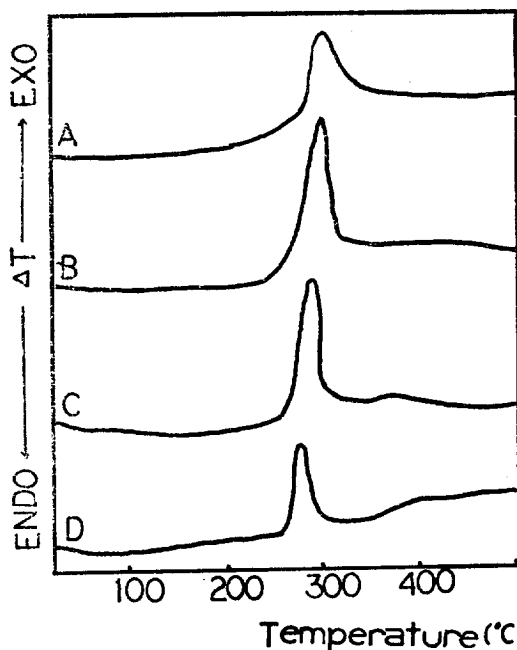


Fig. 5. Thermogram of polyacrylonitrile (A), poly (BCVP-co-AN) (B, AN/BCVP=15.7), poly (BCVP-co-AN) (C, AN/BCVP=4.46), and poly bis ( $\beta$ -chloroethyl vinylphosphonate) (D) obtained in air (heating rate,  $16^\circ\text{C}/\text{min.}$ ).

AN indicating that their alternating tendency is very low. This result in combination with the above statistical analysis shows that the copolymers are consisted of short blocks of BCVP unit and longer blocks of AN units.

*Thermal Properties of Copolymers.* Thermograms of two copolymers and two homopolymers are shown in Fig. 5.

Copolymers and homopolymer of BCVP seem to be a little poorer in thermal stability than polyacrylonitrile. All the polymers left thick chars in the cell well when heated to 500 °C.

### CONCLUSION

The monomer reactivity ratios for the free radical copolymerization of bis ( $\beta$ -chloroethyl) vinylphosphonate and acrylonitrile determined at 50°C in *N,N*-dimethylformamide are  $r(\text{AN}) = 7.3$  and  $r(\text{BCVP}) = 0.13$ . Copolymerization parameters of BCVP were estimated to be  $Q = 0.06$  and  $e = 0.98$ . These values are in good agreement with previously determined values from the copolymerization of BCVP with vinyl acetate :  $Q = 0.06$ ,  $e = 1.1$ .

Statistical analysis of the copolymer sequences indicates that BCVP/AN copolymers exist in longer blocks of AN units and shorter blocks of BCVP. Thermal stability of the copolymers seems to be reduced as the content of BCVP unit increases.

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