

# Copolymerization of Styrene-Divinylbenzene in the Presence of Hypalon-20

KENJI OKAMURA, YASUHIRO KAGIYAMA, KAZUO SHIKATA, and YUKIO MIZUTANI, *Tokuyama Soda Co., Ltd., Tokuyama City, 745, Japan*

## INTRODUCTION

Copolymers of styrene (St)-divinylbenzene (DVB) are widely used for the preparation of ion exchangers or gel beads gel permeation chromatography. Therefore, some studies have been reported with regard to the copolymerization of St-DVB,<sup>1-9</sup> in spite of the difficulties in the studies owing to the crosslinked structure of the copolymer. However, the details of the copolymerization have not yet been fully elucidated. The copolymers of St-DVB are hard but rather brittle, and this is a drawback in practical use. The incorporation of a linear polymer into the St-DVB copolymer is considered to be effective in overcoming this drawback, but no studies have yet been reported with regard to the copolymerization of St-DVB in the presence of the linear polymer. In this study, the copolymerizations of St-*m*-DVB and St-commercial DVB were investigated in the presence of Hypalon-20 (an elastomer manufactured by E. I. du Pont de Nemours & Co.) by means of the gravimetric method and differential scanning calorimetry.

## EXPERIMENTAL

### Materials

Styrene, *m*-DVB from Mitsubishi Gas-Chemical Co., Inc., and commercial DVB (com-DVB) were washed first with a dilute aqueous solution of sodium hydroxide and then with water, dried over anhydrous sodium sulfate, and distilled under reduced nitrogen atmosphere. The purity of *m*-DVB was 99.8% and the commercial DVB after the purification was a mixture of *m*- and *p*-diethylbenzene (4.6%), *m*- and *p*-ethylstyrene (42.6%), *m*-DVB (38.6%), and *p*-DVB (14.2%). Purity of benzoyl peroxide (BPO) was about 99% after reprecipitation using chloroform and methanol.

Hypalon-20 was selected as the elastomer because of its good solubility in the monomers. Hypalon-20 was twice purified by reprecipitation using benzene and methanol. The elemental analysis of Hypalon-20 was as follows: Cl, 29%, S, 1.7%. Specific gravity was 1.12, and the intrinsic viscosity was 0.58 dl/g in benzene at 25°C. The other reagents used were of chemical grade.

### Copolymerization by Gravimetric Method

Hypalon-20 was dissolved in the monomer mixture of St-*m*-DVB at room temperature in the dark. After adding BPO, the mixture (2 g) was put into a

glass ampoule (70 mm in length and 12 mm in diameter) and frozen by using Dry Ice-methanol. The ampoule was evacuated and flushed with nitrogen alternately three times and then sealed. The ampoule was dipped in an oil bath at a definite temperature for a definite time. The copolymerization was rapidly stopped by dipping the ampoule into Dry Ice-methanol. The ampoule was broken, and the resultant polymer was put into a 0.5% benzene solution of *p*-benzoquinone, and this mixture was subsequently poured into excess methanol. The precipitated copolymer was filtered by the use of a glass filter, washed with methanol, and dried at 60°C under vacuum. The conversion of the monomers was determined by subtracting the amount of Hypalon-20 added to the monomers from that of the resultant polymer mixture.

### Determination of Residual *m*-DVB

After the copolymerization for a definite time, the product was put into a 1% benzene solution of *p*-benzoquinone (25 ml) and kept overnight with stirring. Then, a 10% methanol solution of butylcellosolve (2 ml) was added as an internal reference for gas-chromatographic analysis, and the volume of the solution was adjusted to 250 ml by adding methanol. The solution thus prepared was used to determine the residual quantity of *m*-DVB with the aid of a Perkin-Elmer 900 gas chromatograph.

### Copolymerization by Means of Differential Scanning Calorimetry

The sample was put into an A<sub>1</sub>-capsule, and its weight was measured before and after the copolymerization in order to confirm that the loss of the monomers was less than a few per cent. The calorimeter used was Perkin-Elmer DSC-1B. It is noteworthy that *t*-butylcatechol (*t*-BC) was added to the monomer mixture to delay the onset of the reaction (*t*-BC/monomers = 0.1% by weight), because the copolymerization without adding *t*-BC started so soon that precise measurement was difficult. Here, it was preliminarily confirmed that the addition of *t*-BC was effective in delaying the onset of the copolymerization without any serious change in the time-conversion curves. The copolymerization was carried out at a definite temperature, and after the exothermal phenomenon had ceased, the temperature was elevated at a speed of 10°C/min. The thermograms obtained show the change in the differential copolymerization rate at a definite temperature. The conversion was determined as follows:

$$\text{conversion} = \frac{\text{heat evolved for reaction time } t}{\text{total heat evolved}} = \frac{a}{A}$$

where *a* and *A* were determined by weighing the recording papers of the areas corresponding to *a* and *A*, respectively.

## RESULTS AND DISCUSSION

### Copolymerization by Gravimetric Method

Figure 1 shows an example of the time-conversion curve showing the effect of Hypalon-20. The copolymerization proceeded slowly at first, then accelerated,

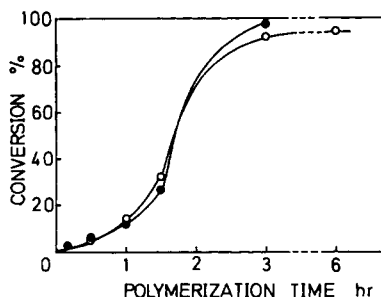


Fig. 1. Time-conversion curves of St-*m*-DVB systems in the presence (O) or absence (●) of Hypalon-20 at 70°C: *m*-DVB/(St + *m*-DVB) = 0.10; BPO/(St + *m*-DVB) = 0.10 and Hypalon-20/(St + *m*-DVB + Hypalon-20) = 0.15 by weight.

and slowed down to the final conversion. It was preliminarily confirmed that the temperature of the reactant itself rose over a definite temperature at the accelerating polymerization stage because of the unavoidable accumulation of the polymerization heat and then decreased to a definite temperature; but the reactant temperature was substantially constant for about 30 min after the onset of the copolymerization at 80°C. It is important to understand the time-conversion curves obtained by the gravimetric method in this study. When Hypalon-20 was used, the autoaccelerating effect was observed at an earlier stage, and the final conversion was a little less than that in the other case. Furthermore, the more Hypalon-20 was used, the more slowly the copolymerization proceeded at first and the earlier the autoacceleration began. This result can be explained as follows: the autoaccelerating effect is due to the retardation of the biradical termination of the copolymerization, the combination of the propagating radicals by the increase in the viscosity of the copolymerizing system. This is supported by the fact that the bulk polymerization rate of methyl methacrylate at the earlier stage increases with increase in the conversion because of the increase in the viscosity of the polymerization system.<sup>11</sup>

Figure 2 shows the effect of the BPO quantity on the time-conversion curve. The result is reasonable, and the initial rate of the copolymerization was arbitrarily determined, as Bamford and Jenkins did,<sup>12</sup> from the conversion at a polymerization time of 30 min or less. Then, the conversions were smaller than 10%. Figure 3 shows the relation between the logarithms of the initial rate (%/min) and the BPO concentration (mole/l). The slope of the straight line

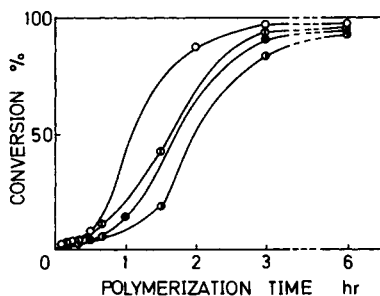


Fig. 2. Effect of BPO quantity on time-conversion curves at 70°C: *m*-DVB/(St + *m*-DVB) and Hypalon-20/(St + *m*-DVB + Hypalon-20) ratios are same as those shown in Fig. 1; BPO/(St + *m*-DVB): (●) 0.005; (●) 0.01; (○) 0.02; (○) 0.03 by weight.

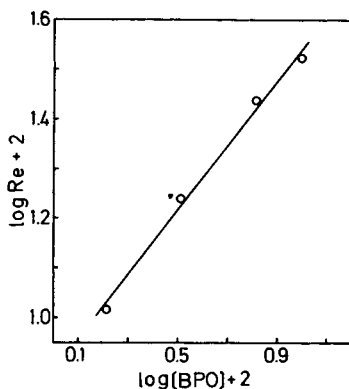


Fig. 3. Plot of log initial rate ( $Re$ ) of copolymerization vs. log BPO at 70°C.

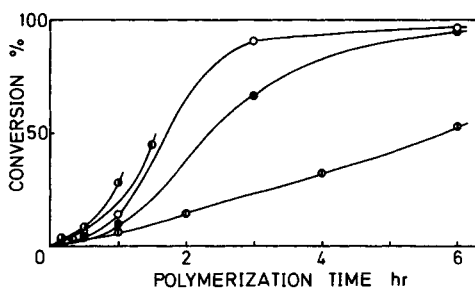


Fig. 4. Effect of DVB quantity on time-conversion curves at 70°C: BPO/(St + *m*-DVB) = 0.01; Hypalon-20/(St + *m*-DVB + Hypalon-20) = 0.15; *m*-DVB/(St + *m*-DVB): (○) 0; (●) 0.05; (○) 0.10; (●) 0.15, (●) 0.20 by weight.

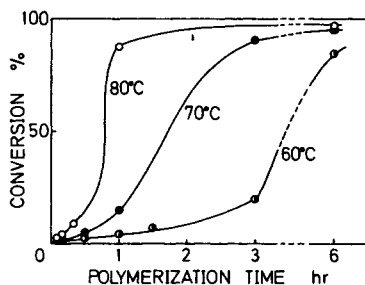


Fig. 5. Effect of copolymerization temperature on time-conversion curves. The recipe is same as that shown in Fig. 1; temperature: (●) 60°C; (●) 70°C; (○) 80°C.

shows the exponential relation to the term of the BPO concentration, and the exponential value was 0.61, larger than 0.5. This result also means that the biradical termination was retarded and that self-termination of the propagating radical occurred because the propagating radical was immobilized in the viscous media and also occluded in the resultant copolymer itself.<sup>12</sup> This is the cause of the autoacceleration phenomenon. Similar phenomena have been shown in the copolymerization of methyl methacrylate-ethylene glycol dimethacrylate<sup>13</sup> and the polymerization of acrylonitrile in aqueous solution.<sup>14</sup>

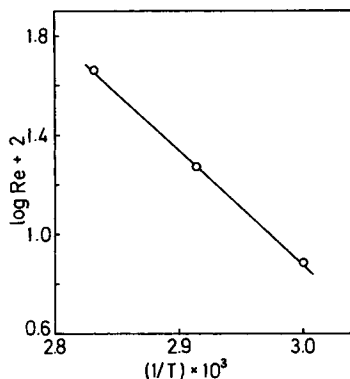


Fig. 6. Arrhenius plot.

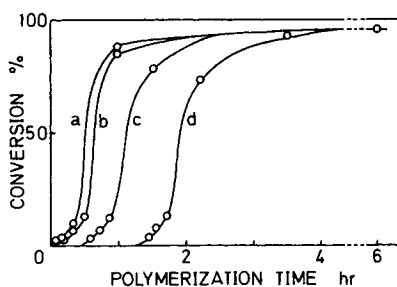


Fig. 7. Effect of *t*-BC on time-conversion curves at 80°C. The recipe is same as that shown in Fig. 1; *t*-BC/BPO: (a) 0; (b) 0.014; (c) 0.06; (d) 0.21 by weight.

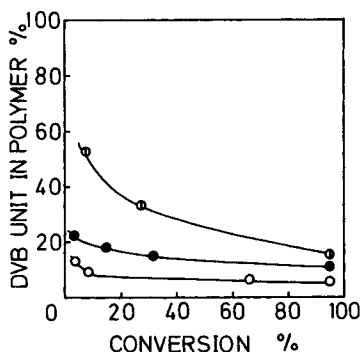


Fig. 8. Relation between conversion and quantity of *m*-DVB incorporated into the copolymer at 70°C: Hypalon-20/(St + *m*-DVB + Hypalon-20) = 0.15; BPO/(St + *m*-DVB) = 0.01; *m*-DVB/(St + *m*-DVB): (○) 0.05; (●) 0.10; (○) 0.15 by weight.

Figure 4 shows the effect of the *m*-DVB quantity on the copolymerization. When the content of *m*-DVB in the recipe was 15% or 20%, higher conversions could not be determined because the resultant copolymers were too tightly crosslinked to be swollen in benzene and the complete exclusion of the residual monomers was difficult. Use of the crosslinking agent renders the polymerization system viscous, develops a network of the resultant copolymer, and hinders biradical termination. So, the more *m*-DVB was used, the sooner and more distinctly the autoacceleration was observed. Similar phenomena were

previously observed in the copolymerizations of St-DVB<sup>6</sup> and methyl methacrylate-ethylene glycol dimethacrylate.<sup>13</sup>

Figure 5 shows the dependence of the copolymerization on temperature. The initial rate was determined as described before, and Figure 6 shows the Arrhenius plot. The activation energy was determined to be 21 kcal/mole from the slope of the straight line. Wiley et al.<sup>15</sup> reported that the activation energy for the copolymerization of St-*m*-DVB in *t*-butylbenzene was 15 kcal/mole.

Figure 7 shows the effect of adding *t*-BC (a radical scavenger) to the copolymerization system. The shapes of the time-conversion curves are similar and the final conversions were the same. It was observed that the length of the induction period was proportional to the molar ratio of *t*-BC/BPO.

Figure 8 shows the changes in the *m*-DVB quantity incorporated into the resultant copolymer with the conversion. The content of the *m*-DVB unit was calculated from the conversion and the *m*-DVB quantity determined by subtracting the quantity of the residual *m*-DVB from the initial quantity. The *m*-DVB quantity incorporated at the earlier stage was rather small, and the plots at the earlier stage might contain some error. However, the tendencies of the curves were unquestionable, and the copolymers resulting at the earlier stage evidently contain more *m*-DVB than those at the later stage. Namely, *m*-DVB polymerized more rapidly than St at the early stage. This result is similar to those by Schwachula,<sup>4</sup> Wiley et al.,<sup>5</sup> and Malinsky et al.,<sup>7</sup> and is the reason that the resultant copolymers consist of ingredients with various degrees of cross-linking, as will be described later.

### Copolymerization by DSC Method

Figures 9 and 10 show the time-conversion curves and the DSC thermograms of the St-com-DVB and St-*m*-DVB systems in the presence of Hypalon-20. The

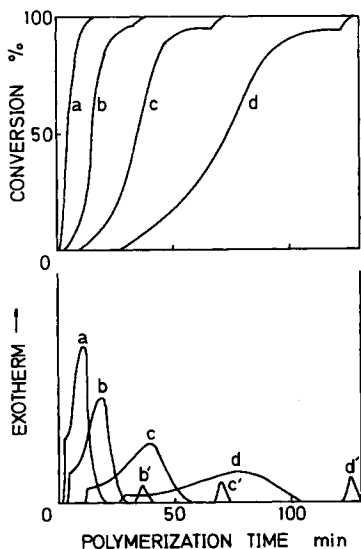


Fig. 9. DSC thermograms of St-com-DVB system: BPO/(St + com-DVB) = 0.01; *t*-BC/BPO = 0.1; com-DVB/(St + com-DVB) = 0.17; Hypalon-20/(St + com-DVB + Hypalon-20) = 0.15 by weight. Temperature: (a) 110°C; (b) 100°C; (c) 90°C; (d) 80°C.

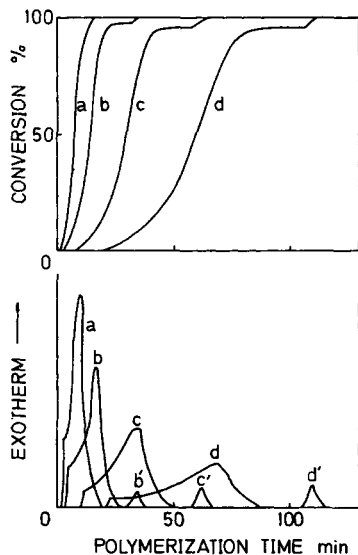


Fig. 10. DSC thermograms of St-*m*-DVB system: BPO/(St + *m*-DVB) = 0.01; *t*-BC/BPO = 0.1; *m*-DVB/(St + *m*-DVB) = 0.1; Hypalon-20/(St + *m*-DVB + Hypalon-20) 0.15 by weight. Temperature: (a) 110°C; (b) 100°C; (c) 90°C; (d) 80°C.

shapes of the time-conversion curves are almost similar to those obtained by the gravimetric method. However, after copolymerization at a definite temperature and the evolution of heat had ceased, the copolymerization proceeded again accompanied by heat evolution by further elevating the temperature at a speed of 10°C/min. The latter heat evolutions are shown in Figures 9 and 10 as (b'), (c'), and (d'), corresponding to (b), (c), and (d). In the case of (a), no further heat evolution was observed. The elevation of the temperature surely made it possible for the residual monomers to diffuse to the active centers and to polymerize, because of the more active thermal motion of the resultant copolymer network and the residual monomers. This is insignificant from the practical viewpoint because complete conversion of the monomers can thus be attained. The copolymerization of St-*m*-DVB was more rapid than that of St-com-DVB. Because the com-DVB was a mixture as described before and the copolymerizing behavior of ethylstyrene is presumed to be similar to that of St from the fact that the copolymerizability ratios of *p*-methylstyrene and *p*-ethylstyrene with St are

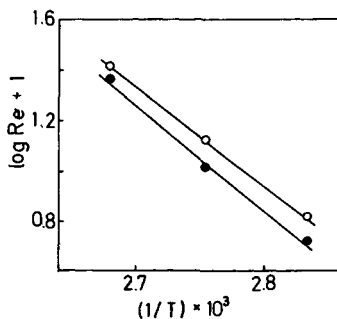


Fig. 11. Plot of  $\log Re$  vs.  $1/T$ .

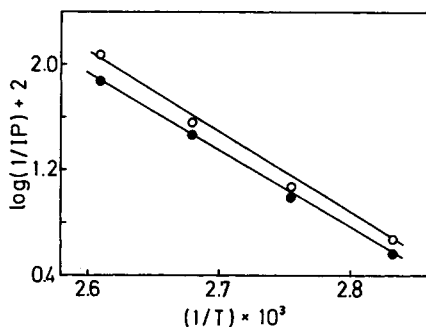


Fig. 12. Plot of  $\log(1/IP)$  vs.  $1/T$ .

nearly unity.<sup>16,17</sup> Thus, the amount of *m*-DVB in the St-*m*-DVB system was more than that of divinylbenzene in the St-com-DVB system. As described before, the larger amount of divinylbenzene was more effective in accelerating the copolymerization, which explains the difference in the copolymerization rates shown in Figure 11.

Figures 11 and 12 show the Arrhenius plots of the initial copolymerization rate and the reciprocal of the induction period, respectively. The latter represents the average rate of the reaction during the induction period. Here, the induction period is the length of time from placing the capsule into the apparatus to the point of heat rise, and the initial rate of the copolymerization was determined as described before. From the slopes of the straight lines in Figure 11, the activation energies were calculated to be 20 kcal/mole and 19 kcal/mole for the

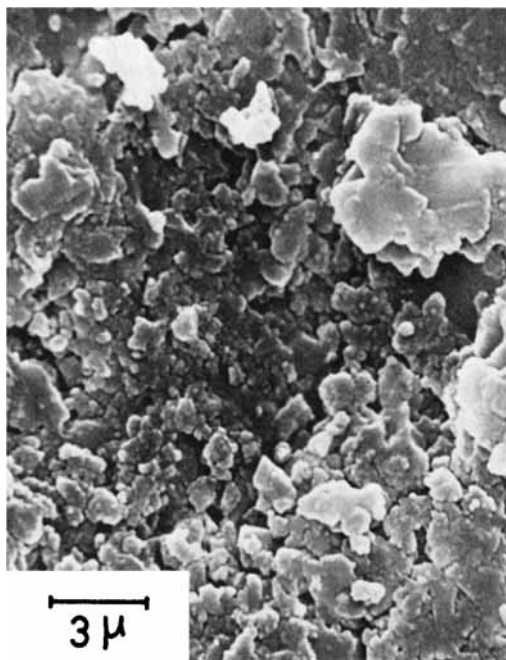


Fig. 13. Cross section of the copolymer prepared without using Hypalon-20: com-DVB/(St + com-DVB) = 0.10 and BPO/(St + com-DVB) = 0.01 by weight. Temperature, 80°C; polymerization time, ca. 10 hr.



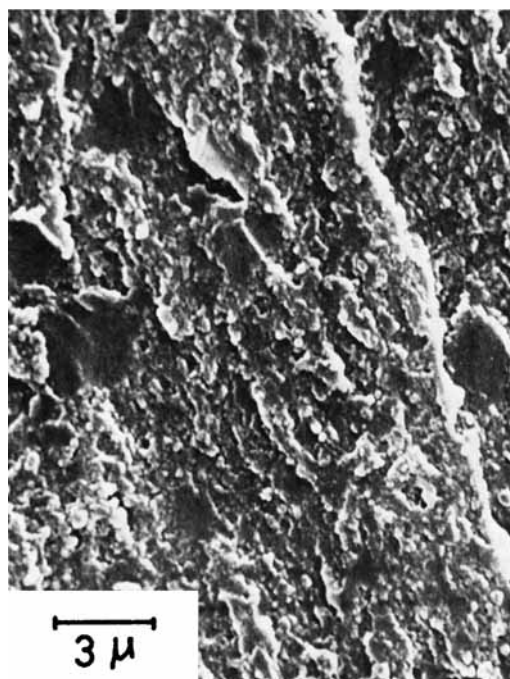


Fig. 14. Cross section of the copolymer prepared by using Hypalon-20: Hypalon-20/(St + com-DVB + Hypalon-20) = 0.14. Other conditions are same as those shown in Fig. 13.

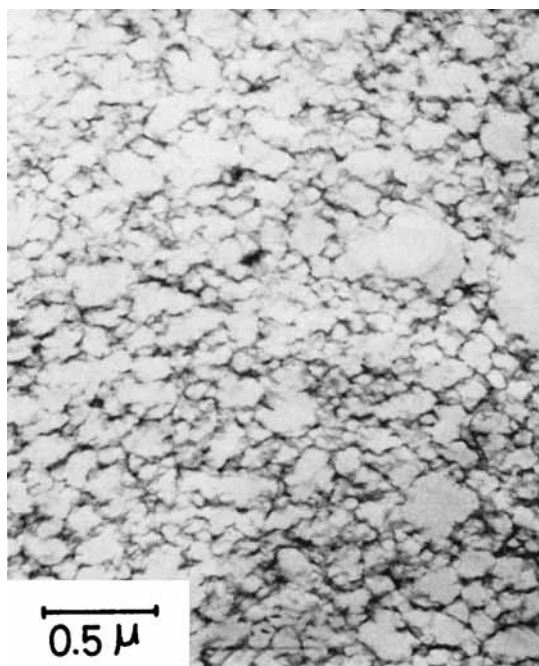


Fig. 15. Cross section of the copolymer prepared by using SBR instead of Hypalon-20. Conditions are same as those in Fig. 14.

copolymerization of the St-com-DVB and St-*m*-DVB systems at the initial stages, respectively. Here, the initial copolymerization rates at 110°C were too fast to be determined exactly, so these values were omitted. The activation energies are approximately consistent with the value determined from Figure 6. Aptova et al.<sup>9</sup> reported that the activation energies were 20–24 kcal/mole for the bulk polymerization of St, *m*-DVB, *p*-DVB, or com-DVB at lower conversion when the polymerization temperatures were 50°–80°C. From the comparison of the values described above, it was difficult to clarify the effect of Hypalon-20 on the activation energies. From the slopes of the straight lines in Figure 12, the activation energies were calculated to be 27 kcal/mole and 29 kcal/mole for the reaction during the induction period of the St-com-DVB and St-*m*-DVB systems, respectively. Both values are pretty well consistent with each other. Now, it can be presumed that the rate-determining process during the induction period might be the decomposition of BPO, provided that *t*-BC could very rapidly scavenge the radicals generated from BPO. This presumption might be supported by the good consistency of the values described above with the activation energy for the spontaneous decomposition of BPO in cyclohexane (29.2 kcal/mole).<sup>18</sup>

### Morphology of the Copolymer

The copolymerization of St-DVB results in a crosslinked copolymer which is insoluble in the monomer mixture, so phase separation of the resultant copolymer should occur. The cross sections of the copolymers were observed by using a scanning electron microscope, JSM-50A from JEOL Ltd., as shown by the microphotographs in Figures 13 and 14. Evidently, the cross sections are neither homogeneous nor gel-like but heterogeneous, showing that the copolymerization of St-com-DVB resulted in the successive phase separation of the resultant copolymer. When Hypalon-20 was added, the dimension of the phase separation was smaller, and this means that the propagating copolymer was separated out of the monomer mixture earlier than in the other case. Therefore, the difference in the dimensions of the microheterogeneity, shown in Figures 13 and 14, shows that Hypalon-20 promoted phase separation.

In order to elucidate the role of Hypalon-20, an ultrathin film of the copolymer prepared by using SBR instead of Hypalon-20 was observed, as shown in Figure 15, with the aid of an electron microscope (HU-12 from Hitachi Ltd.) SBR could be stained with osmium tetroxide but Hypalon-20 could not. Clearly, SBR is observed at the boundary among the particles. As suggested by the fact that the polymerization of St in a poly(vinyl chloride) film resulted in a graft copolymer,<sup>19</sup> Hypalon-20 containing C-Cl bonds could participate in the formation of the graft copolymer. On the other hand, SBR contains double bonds which can participate in the formation of the graft copolymer. Therefore, though the behavior of SBR should be a little different from that of Hypalon-20, Figure 15 might suggest the approximate behavior of Hypalon-20.

As described above, the copolymerization of St-DVB in the presence or absence of other polymers inevitably results in microheterogeneity owing to the promotion of the phase separation during the copolymerization. This microheterogeneity is also the cause of the microheterogeneity in ion exchangers prepared from St-DVB copolymer, the localized distribution of ion exchange groups.<sup>20–22</sup> Thus,

the addition of an elastomer to St-DVB system is effective both in rendering the dimension of the microheterogeneity finer and in improving the brittleness of the ion exchangers derived from the resultant copolymer.

### References

1. R. H. Wiley, W. K. Mathews, and K. F. O'Driscoll, *J. Macromol. Sci., Chem.*, **A-1**, 503 (1967).
2. R. H. Wiley, J. K. Allen, S. P. Chang, K. E. Musselman, and T. K. Venkatachalam, *J. Phys. Chem.*, **68**, 1776 (1964).
3. R. H. Wiley, *Chim. Ind.*, **94**, 602 (1965).
4. G. Schwachula, *J. Polym. Sci., Symp. No. 53*, 107 (1975).
5. R. H. Wiley and E. E. Sale, *J. Polym. Sci.*, **42**, 491 (1960).
6. G. Schwachula, F. Wolf and H. Kathe, *Plaste Kautsch.*, **19**, 731 (1972).
7. J. Malinský, J. Klaban, and K. Dušek, *J. Macromol. Sci.*, **A5**, 1071 (1971).
8. W. L. Sederel and G. J. DeJong, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).
9. T. A. Aptova, Yu. Ya. Babushkin, Ye. A. Gukasova, B. R. Smirnov, and T. M. Chernyavskaya, *Vysokomol. Soed.*, in **A12**, 1246 (1970).
10. J. Malavašič, I. Vizovišek, S. Lapanje, and A. Moze, *Macromol. Chem.*, **175**, 873 (1974).
11. P. Hayden and H. Melville, *J. Polym. Sci.*, **43**, 201 (1960).
12. C. H. Bamford and A. D. Jenkins, *Proc. R. Soc. (London)*, **216**, 515 (1953).
13. P. Hayden and H. Melville, *J. Polym. Sci.*, **43**, 215 (1960).
14. F. S. Dainton, P. H. Seeman, D. G. L. James, and R. S. Eaton, *J. Polym. Sci.*, **34**, 209 (1959).
15. R. H. Wiley and G. Devenuts, *J. Polym. Sci.*, **3**, 1959 (1965).
16. R. H. Wiley and B. Davis, *J. Polym. Sci.*, **46**, 423 (1960).
17. G. E. Ham, in *Copolymerization*, Interscience, New York, 1964, p. 786.
18. P. F. Hartman, H. G. Sellers, and D. Turnbull, *J. Am. Chem. Soc.*, **69**, 2416 (1947).
19. D. Reichenberg and D. J. McCauley, *J. Chem. Soc.*, 2741 (1955).
20. E. Glueckauf and R. E. Watts, *Nature*, **191**, 904 (1961).
21. D. Koschel and R. Schlogl, *Z. Phys. Chem. N. F.*, **11**, 137 (1957).
22. Y. Mizutani, *Kogyo Kagaku Zasshi*, **65**, 1124 (1962).

Received September 24, 1976

Revised November 5, 1976