

## Morphology and Viscoelastic Properties of Quarternized Poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) Three-Block Polymers

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**ABSTRACT:** Poly(4-vinylpyridine) (P4VP) blocks in solvent-cast films of poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) (SBP) three-block polymers were quarternized by a vapor phase reaction with CH<sub>3</sub>Br at 70°C (0.4 to 0.7 atm). The yield was nearly 100%. No changes in morphology were observed before or after quarternization in any SBP specimens cast from different solvents and hence of different morphology. The temperature-complex moduli curves of all the specimens in which isolated P4VP domains are wrapped with polybutadiene (PB) blocks surrounded by the polystyrene (PS) matrix (a "ball-in-a-box" morphology) received no effects from quarternization. Both unquarternized and quarternized specimens with this morphology exhibited only two mechanical transitions due to PB and PS phases (about 190 and 370 K, respectively). The unquarternized specimens having continuous P4VP domains ("three-layer-lamellar" morphology) exhibited three transitions due to the three components, and the quarternization significantly increased dynamic moduli above the glass transition temperature (430 K) of the P4VP phase.

**KEY WORDS** Block Polymer / Block Terpolymer / ABC Type Block Polymer / Poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) / Morphology / Viscoelastic Properties / Quarternization /

Our previous publications<sup>1-4</sup> described the synthesis, morphology and mechanical properties of poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) three-block polymers of ABC type, which are referred to as SBP polymers. We considered it interesting to ionize the poly(4-vinylpyridine) (P4VP) and polystyrene (PS) blocks of these SBP polymers to prepare a charge mosaic membrane, utilizable as an active transport membrane. As the first step to this end, we tried to quarternize P4VP blocks. However, according to Fielding-Russel *et al.*,<sup>5</sup> the morphology of PS-polybutadiene (PB)-poly(2-vinylpyridine) (P2VP) three-block polymers is greatly altered by quarternization of

P2VP blocks with HCl. If such a change occurs, the definite morphological features of the SBP membranes would be lost. Therefore, efforts were made to quarternize P4VP blocks in SBP membranes without destroying the morphology. In this article, we report some results from such an attempt, especially the morphology and dynamic mechanical properties of SBP specimens before and after quarternization.

### EXPERIMENTAL

The methods of synthesis of SBP polymers<sup>2,4</sup> and poly(styrene-*b*-4-vinylpyridine)

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**Table I.** Characteristics of the polymer samples<sup>a,b</sup>

Code	Number average values $10^{-3} M_n$					Volume compositions		
	$M_n^S$	$(M_w/M_n)^S$	$M_n^B$	$M_n^P$	$M_{nt}$	$\phi_S$	$\phi_B$	$\phi_P$
SBP-1	20.2	(1.06)	22.0	32.3	74.5	0.26	0.34	0.40
SBP-10	30.1	(1.08)	14.3	28.5	72.9	0.41	0.23	0.36
SBP-11	23.3	(1.08)	14.2	19.7	57.2	0.40	0.29	0.32
SP-2	35.9	(1.22)	—	40.8	76.7	0.48	—	0.52
SBS <sup>c</sup>	13.2	—	53.8	—	80.3	0.29	0.71	—

<sup>a</sup>  $M_n^S$ ,  $M_n^B$ ,  $M_n^P$  and  $M_{nt}$  denote the number average molecular weights of PS, PB, and P4VP blocks, and the whole molecule, respectively. The  $(M_w/M_n)^S$  values were determined for the PS precursors.

<sup>b</sup> For the weight fractions  $x_S : x_B : x_P = M_n^S : M_n^B : M_n^P$ , while for the volume fractions

$$\phi_S : \phi_B : \phi_P = M_n^S/\rho_S : M_n^B/\rho_B : M_n^P/\rho_P$$

with the bulk densities  $\rho_S = 1.05$ ,  $\rho_B = 0.89$ , and  $\rho_P = 1.114 \text{ g cm}^{-3}$ .

<sup>c</sup> Shell Chemical Kraton 1101.

(SP) diblock copolymers and the preparation of specimens with different morphology have been reported elsewhere.<sup>3,4</sup> A styrene (S)–butadiene (B) block copolymer sample of SBS type (Kraton 1101, Shell Chem. Co.) was used as a reference. Table I lists the characteristics of the samples used in this study.

Films for later quarterization experiments were prepared by casting from 3 wt% solutions. The casting solvents were  $\text{CHCl}_3$ , mixtures of tetrahydrofuran (THF)/methanol (MeOH) (4/1 by volume ratio, v/v), THF/ethanol (EtOH) (4/1, v/v), or benzene (BZ)/EtOH (4/1, v/v). MeOH and EtOH are good solvents for P4VP, while  $\text{CHCl}_3$  and BZ are good solvents for PS and PB. THF is a good solvent for PS but somewhat poor for PB and P4VP. All the films obtained were tough and transparent.

Quarterization was carried out with  $\text{CH}_3\text{Br}$  by the vapor phase method reported by Platt and Schindler.<sup>6</sup> Usually, a film 0.2 to 0.5 mm thick was placed in a separable flask and dried under vacuum at room temperature for 24 h. After drying,  $\text{CH}_3\text{Br}$  was introduced into the flask for reaction with the film. Two sets of conditions were employed: at about 90°C, 1 atm  $\text{CH}_3\text{Br}$  vapor, 14 h; and at about 70°C, about 0.4 to 0.7 atm vapor, 48 h. Under the former conditions, the films changed color

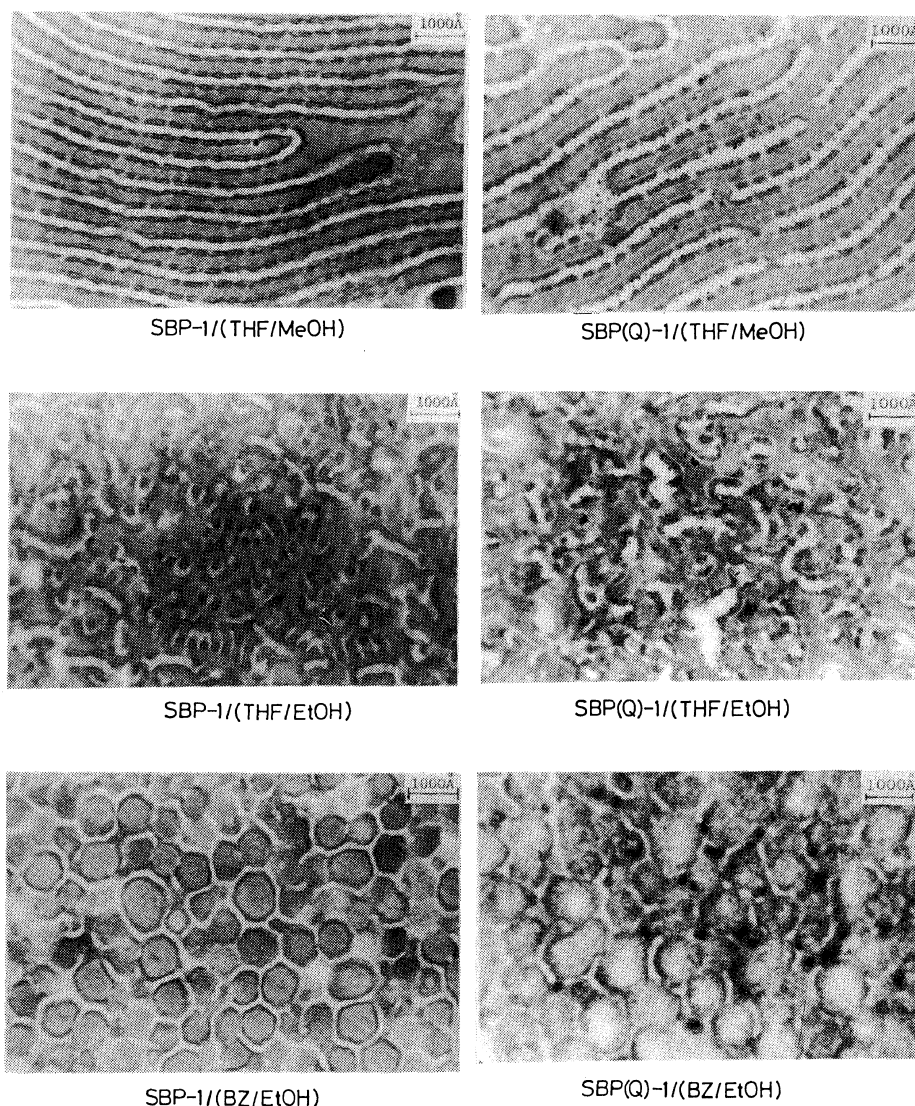
slightly. After the reaction, the film was dried under vacuum for several days to remove any unreacted  $\text{CH}_3\text{Br}$ . The degree of quarterization was determined by elemental analysis of bromine.

Electron micrographs were taken on a Hitachi HV-12 transmission electron microscope at an operating voltage of 75 kV. The films were trimmed and exposed to osmium tetroxide vapor over a 1% aqueous solution at room temperature for 4 days. The films were then microtomed into sections about 40 to 60 nm thick in two mutually perpendicular directions both normal to the film surface.

Complex tensile moduli  $E^*$  were measured with a Rheovibron DDV-II (Toyo Baldwin Co.) at 110 Hz over a temperature range from 150 to 450 K at a heating rate of about 1 K  $\text{min}^{-1}$ . The thermal properties were investigated with a differential scanning calorimeter (DSC; Rigaku Denki Co., Model 8055). Usually, data were taken in a temperature range from 150 to 473 K at a heating rate of 10 K  $\text{min}^{-1}$ . Measurements were sometimes made up to a polymer decomposition temperature of about 600 K.

## RESULTS AND DISCUSSION

For an SBP-1 sample, lamellar, complicated



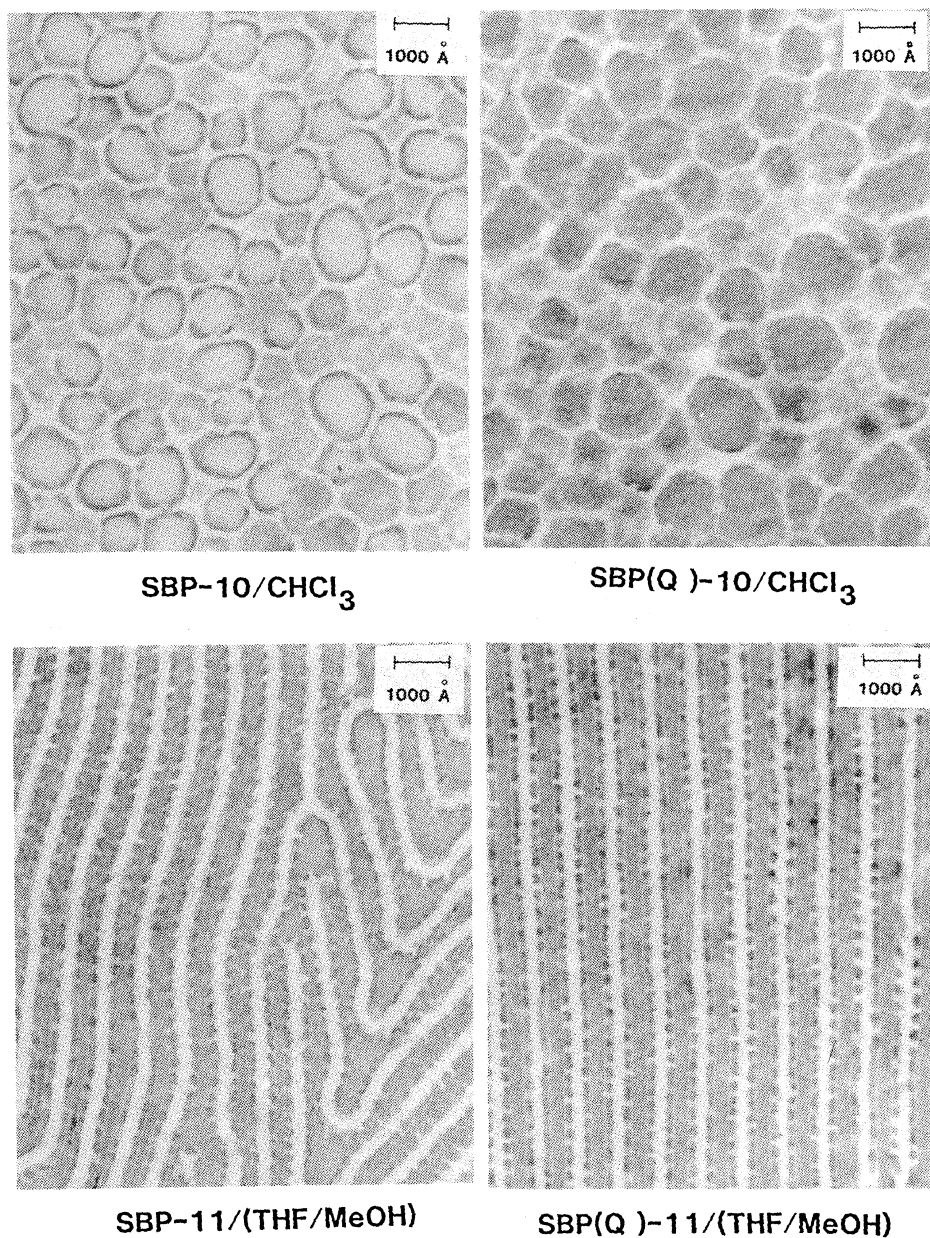
**Figure 1.** Electron micrographs of SBP-1 cast from THF/MeOH, THF/EtOH, and BZ/EtOH (left) and their quarternizates [SBP(Q)-1] (right) by  $\text{CH}_3\text{Br}$  vapor at  $90^\circ\text{C}$  for 14 h.

wormlike, and “ball-in-a-box” structures were observed in specimens cast from THF/MeOH, THF/EtOH, and BZ/EtOH mixtures, respectively.<sup>3</sup>

$\text{CHCl}_3$  cast specimens of SBP-10 and -11 exhibited a “ball-in-a-box” structure, the ball varying in size roughly in proportion to the  $2/3$  power of the number-average molecular weight  $M_n^P$  of P4VP blocks.<sup>4</sup> SBP-10 and -11 specimens cast from THF/MeOH (4/1, v/v)

exhibited three-layer lamellar type structures. The lamellar structures of THF/MeOH cast specimens were usually incomplete and in them, PB blocks formed dotted-line-like layers between the PS and P4VP lamellae.<sup>4</sup> The details are described in our previous articles.<sup>1-4</sup>

SBP specimens having different composition and morphology were subjected to vapor phase quarternization with  $\text{CH}_3\text{Br}$ . The re-

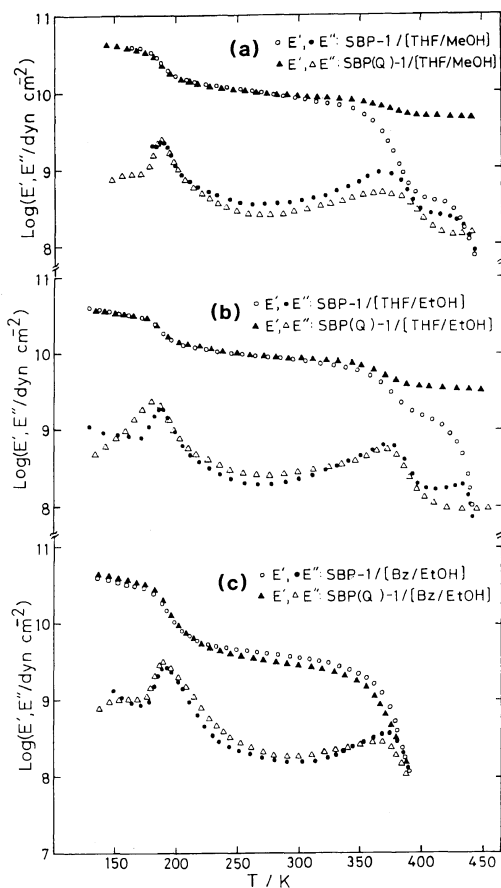


**Figure 2.** Electron micrographs of SBP-10 cast from CHCl<sub>3</sub> and SBP-11 cast from THF/MeOH (left) and their quarternizates [SBP(Q)-10 and -11] (right) by CH<sub>3</sub>Br at 70°C for 24 h.

action yield was about 91% for those quarternized at 90°C for a 14 h reaction, while that for those quarternized at 70°C for 24 h was nearly 100%, regardless of the composition or morphology of the SBP specimens before the

reaction. No bromine was detected in the SBS control.

Figure 1 shows electron micrographs for three SBP-1 specimens, coded as SBP-1 and SBP(Q)-1, respectively, before and after the



**Figure 3.** Temperature dependence of storage Young's moduli  $E'$  and loss moduli  $E''$  at 110 Hz of SBP-1 cast from (a) THF/MeOH, (b) THF/EtOH, and (c) Bz/EtOH and their quarternized SBP(Q)-1 films.

quarternization at 90°C for 14 h. Figure 2 shows similar micrographs for SBP-1 cast from  $\text{CHCl}_3$  and SBP-11 cast from THF/MeOH (4/1), and then quarternized at 70°C for 24 h.

From these micrographs, we see that, in all the samples examined, the original domain shape remain unchanged, but the domain spacings or size of the P4VP balls slightly increased by quarternization. It appears that  $\text{CH}_3\text{Br}$  molecules selectively reacted with P4VP segments and increased the volume of the P4VP domains. Although osmium tetroxide does not react with quarternized pyri-

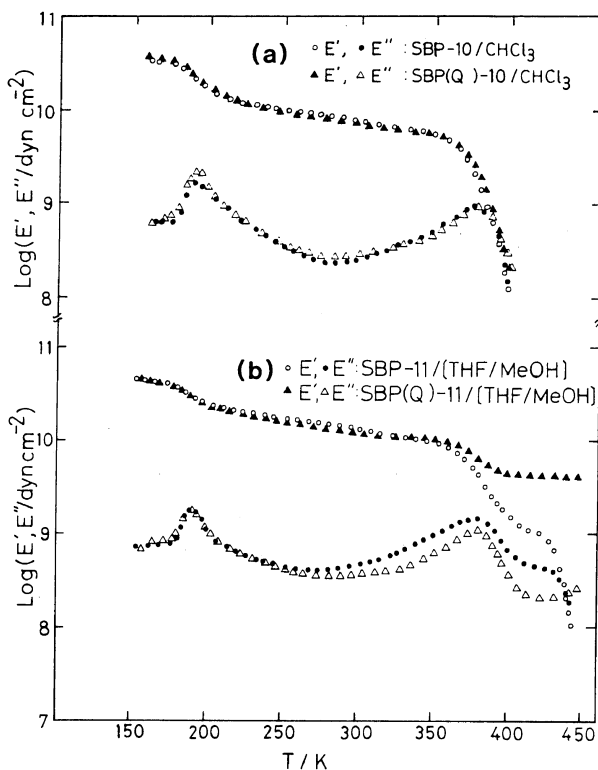
dine rings, the quarternized P4VP domains appeared grey. This is presumably due to scattering of electron beams by bromium counter ions.

Figure 3 shows the temperature dependence of dynamic Young's moduli  $E'$  and loss moduli  $E''$  for unquarternized SBP-1 and quarternized SBP(Q)-1 specimens. Figure 4 compares the temperature dependence of  $E'$  and  $E''$  for  $\text{CHCl}_3$ -cast SBP-10 and THF/MeOH (4/1)-cast SBP-11 specimens and their quarternized salts.

The SBP(Q) specimens having "three-layer-lamellar" type morphology did not flow even above the glass transition temperature  $T_g$  of P4VP (about 430 K).<sup>2</sup> However, the transitions due to PS (about 370 K) and PB (about 190 K) phases did not change, indicating that  $T_g$  of P4VP domains rose to a temperature considerably higher than  $T_g$  of the corresponding unquarternized specimens and also that of the P4VP homopolymers. The quarternized P4VP domains appeared to gain the thermomechanical resistance characteristic of ionically-crosslinked polymers known as *ionomers*.<sup>7</sup> Recently, Isono *et al.*<sup>8</sup> also found similar hardening by quarternization of multiblock copolymers containing PS, polyisoprene (I), and poly[(4-vinylbenzyl) dimethylamine] (A) of SAI or ISIAI type, in which A segments were quarternized.

Quarternization had no effect on the moduli-temperature curves of  $\text{CHCl}_3$ -cast SBP specimens having "ball-in-a-box" morphology, as can be seen from the two examples in Figures 3c and 4a. Only two glass transitions assignable to the PS and PB phases were observed for these specimens. It should be noted that even unquarternized specimens having a similar "ball-in-a-box" morphology showed no viscoelastic transition assignable to the P4VP phase.<sup>2-4</sup>

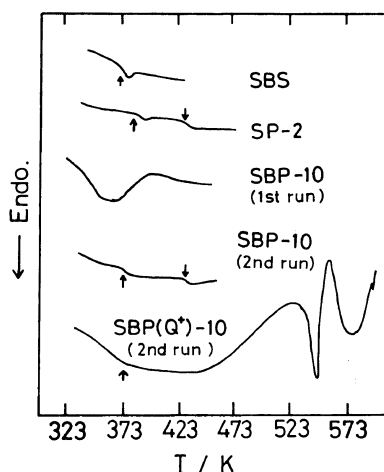
These results were interpreted<sup>9</sup> as indicating that the isolated P4VP domains surrounded by the soft PB phase contribute little to the bulk tensile moduli at small strain, in contrast to the



**Figure 4.** Temperature dependence of storage  $E'$  and loss  $E''$  moduli at 110 Hz of unquarternized (a) SBP-10/CHCl<sub>3</sub> and (b) SBP-11/[THF/MeOH] and their quarternized specimens, SBP(Q)-10/CHCl<sub>3</sub> and SBP(Q)-11/[THF/MeOH].

continuous P4VP lamellae. In a specimen having the "ball-in-a-box" type structure, the mechanical excitation of the matrix phase may not be transmitted to the isolated P4VP domains (having the highest  $T_g$ ), but be absorbed and dissipated in the interconnecting PB phase (having the lowest  $T_g$ ).<sup>9</sup> Therefore, the hardening of the P4VP domains by quarternization does not affect the bulk viscoelastic properties of such specimens.

If this interpretation is correct, it should be possible to find the  $T_g$  of the P4VP phase by DSC, since the thermal excitation is transmitted to the P4VP phase no matter how the PB phase intervenes. Figure 5 shows typical DSC traces for SBS, SP-2, SBP-10/CHCl<sub>3</sub> and SBP(Q)-10/CHCl<sub>3</sub> in a temperature range above 300 K. The samples containing P4VP blocks exhibited unusual behavior (see the



**Figure 5.** Typical DSC thermograms of SBS, SP-1, SBP-10/CHCl<sub>3</sub> and SBP(Q)-10/CHCl<sub>3</sub>. The arrows (↑) denote the  $T_g$  of PS phase and (↓) that of P4VP phase.

curve for SBP-10 in the figure): an extremely broad endothermic peak in the temperature region from 310 to 370 K in the first heating process (first run). However, it disappeared in the 2nd run, and the  $T_g$  corresponding to the PS and P4VP phases appeared. This broad peak in the first run may be attributed to the presence of moisture in the specimen. All other unquarternized as well as quarternized SBP specimens (cast from different solvents and hence having different morphology) exhibited essentially similar thermograms.

Two facts are worthy of note. As indicated by one example of a  $\text{CHCl}_3$ -cast SBP-10 specimen in Figure 5, the  $T_g$  of the P4VP phase was detected in all the (unquarternized) SBP specimens regardless of the casting solvent used. However, for quarternized SBP(Q) specimens of any structure, no clear  $T_g$  corresponding to the P4VP phase could be observed up to about 530 K, at which the specimen began to decompose. This latter finding may be other evidence for the hardening of P4VP domains by quarternization.

Fielding-Russel *et al.*<sup>5</sup> Reported that the plateau modulus of a quarternized PS-PB-P2VP:HCl specimen was approximately one order of magnitude higher than that of an as-cast unquarternized specimen. However, in all our SBP(Q) specimens cast from any solvent, the plateau moduli between the glass transitions of PS and PB remained unchanged before and after vapor phase quarternization. Summarizing our morphological observations

and viscoelastic measurements, we may argue that quarternization does not change the morphology of as-cast films of SBP polymers. This should facilitate the morphological control and increase the scope of applications of SBP polymers.

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## REFERENCES

1. K. Arai, T. Kotaka, Y. Kitano, and K. Yoshimura, *Macromolecules*, **13**, 455 (1980).
2. K. Arai, T. Kotaka, Y. Kitano, and K. Yoshimura, *Macromolecules*, **13**, 1670 (1980).
3. K. Arai, C. Ueda-Mashima, T. Kotaka, K. Yoshimura, and K. Murayama, *Polymer*, in press (1983).
4. I. Kudose and T. Kotaka, *Macromolecules*, submitted (1983).
5. G. S. Fielding-Russel and P. S. Pillai, *Polymer*, **18**, 859 (1977).
6. K. L. Platt and A. Schindler, *Angew. Makromol. Chem.*, **19**, 135 (1971).
7. A. Eisenberg, "Ion-Containing Polymers," Academic Press, New York, 1977.
8. Y. Isono, H. Tanisugi, K. Endo, T. Fujimoto, H. Hasegawa, T. Hashimoto, and H. Kawai, *Macromolecules*, **16**, 5 (1983).
9. H. Watanabe and T. Kotaka, *Polym. J.*, **13**, 149 (1981).