

# Micro-Heterophase Structure in Membrane of Vinylpyridine-Styrene-Vinylpyridine Block Copolymers and their Quaternized Products

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A-B-A type block copolymers were synthesized by using 2-vinylpyridine and styrene as A and B components, respectively, and these copolymers were further quaternized with alkyl bromides. The micro-heterophase structures of solvent-cast A-B-A block copolymers and their quaternized products were investigated as functions of size and composition of copolymers, and of the kind of solvent. In particular, with block copolymers quaternized with lauryl bromide, a new type of micro-heterophase structure including intramolecular micelles formed by lauryl chains was found.

## INTRODUCTION

Since Sadron and co-workers<sup>1-4)</sup> discovered the occurrence of micro-heterophase structure in solutions of A-B and A-B-A type block copolymers consisting of homosequences A and B, and in particular in recent years, a number of works have been published on the formation mechanism and the structure of regular and periodic micro-heterophase produced by solvent casting from solutions of block or graft copolymers. Fine reviews on these topics have been presented by Molau,<sup>5)</sup> Kawai,<sup>6)</sup> and Sadron,<sup>7)</sup> recently.

The formation mechanism in connection with the structure was qualitatively investigated by Kawai,<sup>8-10)</sup> Krause,<sup>12,13)</sup> and Bianchi.<sup>14)</sup> Methods to determine the dimensions of domains in micro-heterophase structures were estimated and adopted to the liquid crystals,<sup>7,15-18)</sup> solvent-cast films<sup>1,2,20)</sup> and extruded pluges<sup>21-25)</sup> independently by Skoulios, Keller, Kim, and others. Samples used in these studies were mainly block copolymers composed of nonionic-A and nonionic-B sequences such as styrene-oxyethylene,<sup>1-4)</sup> styrene-isoprene,<sup>8-10)</sup> styrene-butadiene,<sup>21-25)</sup> isoprene-vinylpyridine,<sup>18)</sup> *etc.* However, little has been known on block copolymers composed of ionic block-sequences.

Experimental results on ionic block copolymers reported so far are on the preparation of block copolymers composed of styrene-methacrylic acid,<sup>26)</sup> of 2-vinylpyridine-methacrylic acid and some related comonomers,<sup>27,28)</sup> and on some properties as desalination membrane for 2-vinylpyridine-methacrylic acid<sup>27)</sup> and quaternized styrene-2-vinylpyridine block copolymers.<sup>29)</sup> Membranes of ionic block copolymers are prepared in two ways: one is by ionizing a solvent-cast nonionic membranes, and the other is by casting from solutions of ionic block copolymers. Kamachi<sup>27)</sup> has pointed out that the micro-heterophase structures were not observed with membranes prepared by casting from solution of 2-

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vinylpyridine-methacrylic acid block copolymer.

The aims of this report are to explore first the micro-heterophase structures of solvent-cast 2-vinylpyridine-styrene-2-vinylpyridine (A-B-A) block copolymer membranes as functions of size and composition of copolymers, and of the kind of solvent, and finally the domain structures in membranes of their quaternized products prepared by the two ways mentioned above.

## EXPERIMENTAL

### Synthesis of 2-Vinylpyridine-Styrene-2-Vinylpyridine A-B-A Type Block Copolymers

A-B-A type block copolymers composed of two 2-vinylpyridine (V) A-sequences and one styrene (S) B-sequence were synthesized using sodium biphenyl as the initiator by an anionic polymerization technique based on the method of Champetier, *et al.*<sup>30)</sup>

Commercial styrene was first washed several times with 10% NaOH aqueous solution to remove *p*-tert-butyl catechol, the inhibitor, then washed with water until the mixture becomes neutral, and dried over CaCl<sub>2</sub> for 24 hr. The dried styrene was then distilled at 20 mm Hg in N<sub>2</sub> atmosphere to collect 46–47°C fraction. The distillate was introduced into a flask involving CaH<sub>2</sub>, and the flask was connected to a vacuum line. After repeating evacuation and dehydration by usual way, the flask was sealed off from the vacuum line. Again the content was distilled in another flask involving fresh CaH<sub>2</sub> on the vacuum line under repeated flaming and evacuation, and again evacuated and dehydrated. Such distillation procedure was repeated until the color of the monomer became slightly pink. Finally, the monomer was collected under vacuum in separate ampoules with breakable seals, and stored in a refrigerator operating at –5°C.

With respect to 2-vinylpyridine monomer, the same procedure as that for styrene monomer was performed, after a commercial 2-vinylpyridine was distilled under reduced pressure in N<sub>2</sub> atmosphere. Distillations on the vacuum line were repeated same times as for styrene to accomplish the dehydration.

Purification of tetrahydrofuran(THF), the polymerization solvent, was carried out by the method of Fetters.<sup>31)</sup>

Figure 1 shows the apparatus for preparing sodium biphenyl complex, the initiator. Commercial biphenyl was recrystallized from an ethyl ether solution and dried in a desiccator over P<sub>2</sub>O<sub>5</sub>. A necessary amount of dried biphenyl was dissolved in purified THF in the vessel C equipped with a breakable tip. Purified THF was introduced in the vessel B. Vessel A is the reaction flask, and ampoules D<sub>1</sub>, D<sub>2</sub>, ..., D<sub>n</sub> were equipped to collect sodium biphenyl solutions prepared. The entire apparatus was connected to the vacuum line at b and c.

First, the reaction vessel A was evacuated via V<sub>1</sub> up to 10<sup>-5</sup> mmHg under repeated flaming and sealed off at b. The THF solution of biphenyl was introduced in A, and then only THF was again returned to C by distillation. Finally, vessel C was sealed off at e. Now the purified THF was introduced into A, and vessel B was sealed off at a. By keeping the temperature of A at –78°C with dry ice-methanol mixtures, the sodium in the side-arm was melted by heating and introduced into A, by which the color of the solution in A was immediately turned into deep green. Next, ampoules D<sub>1</sub>, D<sub>2</sub>, ..., D<sub>n</sub> were

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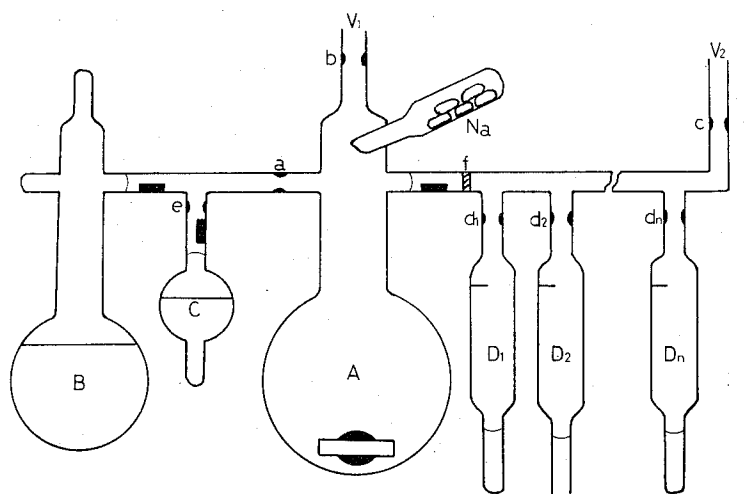


Fig. 1. Apparatus for preparing initiator.

evacuated via  $V_2$  up to  $10^{-5}$  mmHg under repeated flaming, and sealed off at c. Now the solution prepared in A was introduced in the ampoules through a glass filter f. The ampoules were finally sealed off at  $d_1, d_2, \dots, d_n$  and stored in a refrigerator.

Initiator solution used for cleaning of the polymerization vessel was prepared in a similar manner.

Figure 2 shows the polymerization apparatus. Polymerization was carried out in a round-bottomed flask A. Ampoules S, P, I, and  $T_1$  and  $T_2$  contain styrene, 2-vinylpyridine, sodium biphenyl solution, and methanol, the terminator, respectively. THF, the polymerization solvent, and the initiator solution for cleaning the vessel were introduced

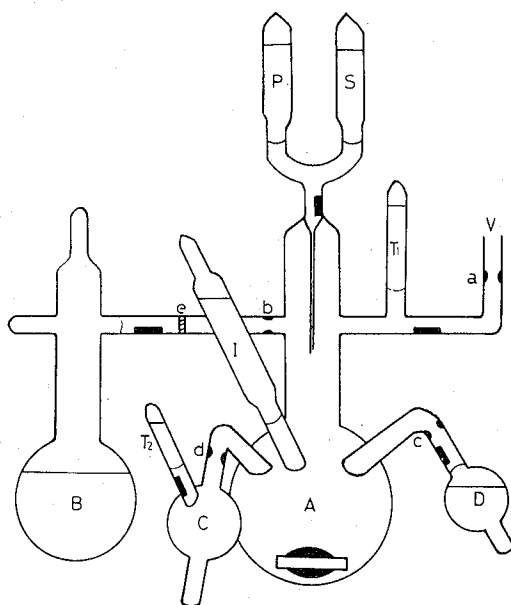


Fig. 2. Polymerization apparatus.

Table I. Preparation of Block Copolymers.

Sample	Sty (g)	2VP (g)	Initiator (molx10 <sup>4</sup> )	THF (cm <sup>3</sup> )	Yield (%)
V <sub>8</sub> -S <sub>84</sub> -V <sub>8</sub>	12.5	2.5	1.25	400	89
V <sub>12</sub> -S <sub>76</sub> -V <sub>12</sub>	10.5	3.1	1.25	340	78
V <sub>23</sub> -S <sub>54</sub> -V <sub>23</sub>	7.0	6.2	1.25	380	83
V <sub>37</sub> -S <sub>26</sub> -V <sub>37</sub>	3.5	9.7	1.25	410	85
V <sub>43</sub> -S <sub>14</sub> -V <sub>43</sub>	1.4	11.2	1.25	320	79
V <sub>24</sub> -S <sub>54</sub> -V <sub>23</sub> (H)	13.9	12.4	1.25	450	89

in vessels B and D, respectively. The vessel C was connected to take out the living polystyrene for characterization. The entire assembly was connected to the vacuum line via *v*, evacuated up to 10<sup>-5</sup> mm Hg under repeated flaming, and then sealed off at a from the vacuum line.

To begin with, the content in D was introduced in A to clean A, and then returned to D again. Next, only THF in D was distilled into A to remove the remaining initiator in A, and again returned to D. After repeating such procedure several times, the vessel D containing the solution was sealed off at *c*. Now fresh THF was introduced into A through a glass filter *e* from the vessel B, and the empty vessel B was sealed off at *b*. In the next place, solution of sodium biphenyl complex was introduced into A and stirred for about 10 min. Keeping the temperature of the vessel A at -30°C, styrene monomer was introduced into A through a capillary from ampoule S. By this process the color of the solution immediately turned into orange from deep green. Now the content of the vessel was cooled down to -78°C and allowed to stand for 2 hr under agitation for polymerization. After bringing back the temperature of the content to room temperature, a part of the living polystyrene produced was transferred to the vessel C, the vessel C was sealed off at *d* and killed with methanol in T<sub>2</sub>. The vessel A was again cooled down to -78°C, into which 2-vinylpyridine monomer was introduced from P through the capillary. By this operation, the color of the solution became slightly lighter. After the reaction at -78°C for 1 hr, polymerization was stopped by adding methanol from T<sub>1</sub>, by which the color of the solution was immediately disappeared.

In this way, we prepared A-B-A type block copolymers of different compositions as indicated in Table 1. The block copolymers and homopolystyrene obtained were precipitated in *n*-hexane and in methanol, and finally dried at 60°C for 24 hr.

### Characterization of 2-Vinylpyridine-Styrene-2-Vinylpyridine Block Copolymers

Before characterization, homopolymers which may be included in the polymerization products were removed by appropriate method. For example, with respect to the sample V<sub>23</sub>-S<sub>54</sub>-V<sub>23</sub>, poly-2-vinylpyridine homopolymer was first extracted with methanol, and then polystyrene homopolymer was extracted with cyclohexane. However, the amount of homopolymers included was negligibly small.

The number-average molecular weight  $M_{ABA}$  of block copolymers was determined with a Knauer Membrane Osmometer in THF at 30°C. The molecular weight  $M_B$  of polystyrene B-block was estimated from viscosity measurements on polystyrene, taken

out of the polymerization vessel before the addition of 2-vinylpyridine monomer, by using the equation:<sup>32)</sup>

$$[\eta] = 8.81 \times 10^{-5} M^{0.75} \quad (1)$$

where  $[\eta]$ (dl/g) is the limiting viscosity number of polystyrene in toluene at 30°C, and  $M$  the molecular weight of polystyrene. This equation was obtained for homologous polystyrene prepared by anionic polymerization at -78°C from light scattering measurements. Therefore, the molecular weight obtained by the light scattering measurements, in this case, is approximated by that obtained by osmotic pressure measurements.

The content of 2-vinylpyridine units in copolymers was determined by elemental analysis on nitrogen.

### Quaternization of V-S-V Block Copolymers

As mentioned above, two methods were used for quaternization. In the first method, quaternization was carried out on the dry films of V-S-V block copolymers cast from THF solutions. Films V<sub>23</sub>-S<sub>54</sub>-V<sub>23</sub>(H) and V<sub>37</sub>-S<sub>26</sub>-V<sub>37</sub> were quaternized with HBr and transformed into QV<sub>23</sub>-S<sub>54</sub>-QV<sub>23</sub>(H) and QV<sub>37</sub>-S<sub>26</sub>-QV<sub>37</sub>. In these cases, poly-2-vinylpyridine block portions were wholly quaternized with HBr.

The second is to quaternize V-S-V block copolymers in solution. The polymer sample and the alkyl halide used were V<sub>43</sub>-S<sub>14</sub>-V<sub>43</sub> and lauryl bromide, respectively. The polymer sample was dissolved in dimethyl formamide (DMF) so as to make a 0.5% solution. To this solution, lauryl bromide was added by twice the molar quantity of 2-vinylpyridine residues. The solution was divided and sealed in five tubes under nitrogen atmosphere and kept in a thermostat at 85°C for different reaction times. The quaternized products obtained were purified and then subjected to elemental analysis to determine the contents of bromine and nitrogen. In Table II, the degrees of quaternization calculated from Br and N contents were shown as a function of reaction time. It has been known<sup>33,34)</sup> that, during the quaternization, a part of lauryl bromide is decomposed and produces HBr. Thus, the degrees of quaternization indicates the total molar quantity of 2-vinylpyridine residues quaternized by lauryl bromide and hydrogen bromide referred to the molar quantity of initially existed 2-vinylpyridine residues. According to Inoue,<sup>33)</sup> about 60% of the degrees of quaternization may be attributed to lauryl bromide.

### Preparation of Specimens for Electron Microscopy

The polymer samples were dissolved in solvent so as to form 0.1% solutions. A sheet mesh for electron microscope equipped with a carbon membrane was put on a slide

Table II. Quaternization of V<sub>43</sub>-S<sub>14</sub>-V<sub>43</sub> with Lauryl Bromide.

Reaction Time (hr)	Br (meq·g <sup>-1</sup> )	N (meq·g <sup>-1</sup> )	Deg. of Quaterniz. (%)
0	0	8.14	0
2.5	1.96	7.84	25.0
6.5	2.97	7.42	40.0
24	4.21	7.35	57.2
48	4.49	7.19	62.4
71	4.62	7.12	64.8

glass placed in a glass dish. Now a drop of the polymer solution was introduced onto the mesh by a pipette and allowed to form thin film. In the case of solvent quickly evaporizes, a small amount of the solvent was added in the glass dish to reduce the vaporization velocity. Quaternization on the dry films was performed with the film formed on the sheet mesh. The films were stained with osmium tetroxide vapor for 24 hr to take electron micrographs. The thickness of the films is expected to be about 500~1000Å.

## RESULTS AND DISCUSSION

### Micro-Heterophase Structure in V-S-V Block Copolymer Membranes

From experimentally obtained molecular weights,  $M_{ABA}$  (obs) of copolymer, and the value of N% of copolymer, we estimate the molecular weight  $M_B$  (cal, 2) of the B-block chain. Also we can calculate  $M_A$  (cal, 1) from the value of N% of copolymer together with  $M_B$  (obs). Table III indicates the results of characterization performed in these ways. We point out that  $M_B$  (cal, 2) is in good agreement with  $M_B$  (obs). This may mean that the copolymers are sufficiently homologous with respect to both molecular weight- and composition-distribution. Hereafter, we shall use the numerical values of  $M_{ABA}$  (obs) and  $M_A$  (cal, 1) for discussion. Copolymer samples except V<sub>23</sub>-S<sub>54</sub>-V<sub>23</sub> (H) were designed and synthesized so as to have almost same  $M_{ABA}$ . The molecular weight of V<sub>23</sub>-S<sub>54</sub>-V<sub>23</sub> (H) is about twice of V<sub>23</sub>-S<sub>54</sub>-V<sub>23</sub>. Micro-heterophase structure for these samples will be discussed below.

In the first place, domain structures were investigated with films cast from THF, a solvent acts as good solvent for both V- and S-component. Solubilities of V- and S-block chains in THF are not strictly equal but solubility of V-component in THF is slightly better than that of S-component.

Electron micrographs of these films were illustrated in Fig. 3. The dark portions in these photographs correspond to the domains composed of 2-vinylpyridine block chain portions stained with osmium tetroxide. Micro-heterophase structures are observed systematically as a function of copolymer composition, the weight fraction  $\phi_A$  of A-component. With  $\phi_A=0.151$ , V-domains are cylindrical in the matrix of S-component, and packed vertically to the film surface (Fig. 3a). Increase of V-content results in the formation of lamellar structure as shown in Fig. 3c. Further increase of V-content leads to an inverted structure, in which S-component forms cylindrical domains in the matrix of V-component as indicated in Fig. 3d. Finally, with large value of V-content, S-

Table III. Characterization of 2-Vinylpyridine-Styrene-2-Vinylpyridine (A-B-A) Block Copolymers.

Sample	wt%, N in Copoly,	$\phi_A$	$M_{ABA} \times 10^{-4}$ (obs)	$M_B \times 10^{-4}$ (obs)	$M_B \times 10^{-4}$ (cal, 2)	$2M_A \times 10^{-4}$ (cal, 1)	$2M_A \times 10^{-4}$ (cal, 2)
V <sub>8</sub> -S <sub>84</sub> -V <sub>8</sub>	2.1	0.151	42.4	36.0	35.8	6.4	6.6
V <sub>12</sub> -S <sub>76</sub> -V <sub>12</sub>	3.2	0.243	53.5	39.0	40.7	12.5	12.8
V <sub>23</sub> -S <sub>54</sub> -V <sub>23</sub>	6.2	0.465	47.6	24.0	25.4	20.9	22.2
V <sub>37</sub> -S <sub>26</sub> -V <sub>37</sub>	9.7	0.730	35.8	10.2	9.6	27.5	26.2
V <sub>43</sub> -S <sub>14</sub> -V <sub>43</sub>	11.4	0.858	42.8	6.2	6.2	37.4	36.6
V <sub>23</sub> -S <sub>54</sub> -V <sub>23</sub> (H)	6.3	0.474	105.0	60.0	56.4	54.0	48.6

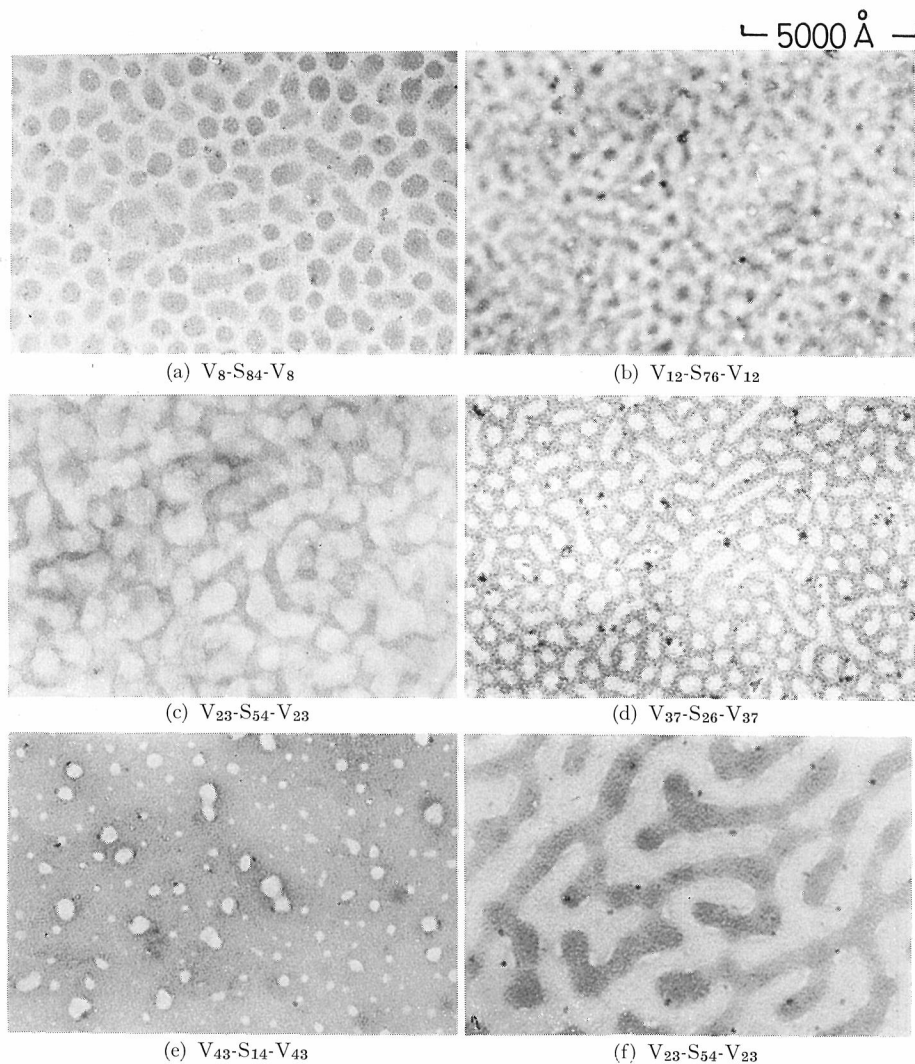


Fig. 3. Electron micrographs of V-S-V block copolymer films cast from 0.1% solutions in tetrahydrofuran.

component forms spherical domains in the matrix of V-component (Fig. 3e). Dimensions of the domains, such as the diameter  $D'_A$  of A-cylinder and the lamellar thickness  $L_A$  of A-component, are expected to increase with increasing block length of the corresponding component. Comparison of Fig. 3c for  $V_{23}\text{-}S_{54}\text{-}V_{23}$  with Fig. 3f for  $V_{23}\text{-}S_{54}\text{-}V_{23}$  (H) gives an answer to this expectation. The Gibbs free energy per unit volume,  $\Delta G$ , for the formation of various kinds of micelles is given by

$$\Delta G = A\Delta W - N(T\Delta S) \quad (2)$$

where  $A$  is the area of interface between the two components per unit volume of the micelles.  $\Delta W$  is the interfacial contact energy per unit area,  $\Delta S$  is the entropy change per chain for the micelle formation and  $N$  is the number of copolymer chains per unit volume.  $\Delta S$  for

A-B-A block copolymer having equal A-block chain length may be approximated by

$$\Delta S = 2\Delta S_A + \Delta S_B \quad (3)$$

where  $\Delta S_A$  and  $\Delta S_B$  are the entropy changes for A-block and B-block chains, respectively. Kawai<sup>6,11)</sup> has adopted the equation by assuming that the copolymer chain is composed of Gaussian chains of A and B block chains. On the other hand, Leary<sup>35,36)</sup> has assumed a mixed region for the junction between A and B block chains, in addition to A and B pure domains. With either model,  $\Delta G$  is formulated according to the shapes of domain, such as sphere, cylinder, and lamellar. By differentiating  $\Delta G$  with respect to the size of domain, one obtains the equilibrium size of the domain as functions of the copolymer composition, the dimensions of A and B block chains at critical micelle concentration, and the interfacial energy. The root mean square radii of gyration,  $\langle S_A^2 \rangle^{1/2}$  and  $\langle S_B^2 \rangle^{1/2}$ , A and B block chains, respectively, were estimated from the viscosity data for poly-2-vinylpyridine-THF and polystyrene-THF systems by using the equation:

$$\langle S^2 \rangle^{1/2} = \frac{[\eta]^{1/3} M^{1/3}}{6^{1/2} \Phi^{1/3}} \quad (4)$$

where  $[\eta]$  is the limiting viscosity number in dl/g,  $M$  the molecular weight, and  $\Phi = 2.5 \times 10^{21}$ . Numerical values of  $\langle S_A^2 \rangle^{1/2}$  and  $\langle S_B^2 \rangle^{1/2}$  for corresponding block chains were shown in Table IV, together with the domain dimensions measured from the electron micrographs illustrated in Fig. 3. Domain dimensions are not uniform, so the mean values are given in Table IV.  $D'_A$  denotes the diameter of A-cylinder suspended in B-matrix,  $D_B$  the diameter of B-sphere suspended in A-matrix, and  $L_A$  and  $L_B$  respectively denote the thickness of A and B-lamellae. If the chain dimension at the critical micelle concentration is kept even in the film, then the diameters  $D$  and  $D'$  of sphere and cylinder, respectively, may be approximated by  $4\langle S^2 \rangle^{1/2}$ . Table IV indicated that this is roughly true for  $D'_A$ ,  $D'_B$ , and  $D_B$ . With respect to  $L_A$  and  $L_B$ , observed relations were  $4\langle S_B^2 \rangle^{1/2} = L_B$  and  $2\langle S_A^2 \rangle^{1/2} = L_A$ . These results may lead to the chain packing as shown in Fig. 4.

Micro-heterophase structure of V-S-V cast from benzene, a selective solvent for the polymer, is illustrated in Fig. 5. Benzene is a good solvent for polystyrene but acts as a poor solvent for poly-2-vinylpyridine block chains. In such case, poly-2-vinylpyridine block portions tend to shrink compared with polystyrene block portions. Such trend is obviously observed in Fig. 5. In V<sub>12</sub>-S<sub>76</sub>-V<sub>12</sub> film (Fig. 5a), poly-2-vinylpyridine forms

Table IV. Dimensions of Domains in Micro-heterophase Structures of V-S-V Block Copolymers.

Sample	Domain Structure	$\langle S_B^2 \rangle^{1/2}$ (Å)	$\langle S_A^2 \rangle^{1/2}$ (Å)	Domain Dimension	
				PS <sub>t</sub> (Å)	PVP (Å)
V <sub>8</sub> -S <sub>84</sub> -V <sub>8</sub>	PVP, Cylind.	—	93	Matrix	$D'_A = 500 \text{Å}$
V <sub>12</sub> -S <sub>76</sub> -V <sub>12</sub>	PVP, Cylind.	—	131	Matrix	$D'_A = 350 \text{Å}$
V <sub>23</sub> -S <sub>54</sub> -V <sub>23</sub>	Lamellar	160	169	$L_B = 470 \text{Å}$	$L_A = 320 \text{Å}$
V <sub>37</sub> -S <sub>26</sub> -V <sub>37</sub>	PS <sub>t</sub> , Cylind.	98	—	$D'_B = 430 \text{Å}$	Matrix
V <sub>43</sub> -S <sub>14</sub> -V <sub>43</sub>	PS <sub>t</sub> , Sphere	79	—	$D_B = 300 \text{Å}$	Matrix
V <sub>23</sub> -S <sub>54</sub> -V <sub>23</sub> (H)	Lamellar	246	380	$L_B = 900 \text{Å}$	$L_A = 750 \text{Å}$



Micro-hetero Structure of A-B-A Block Copolymers

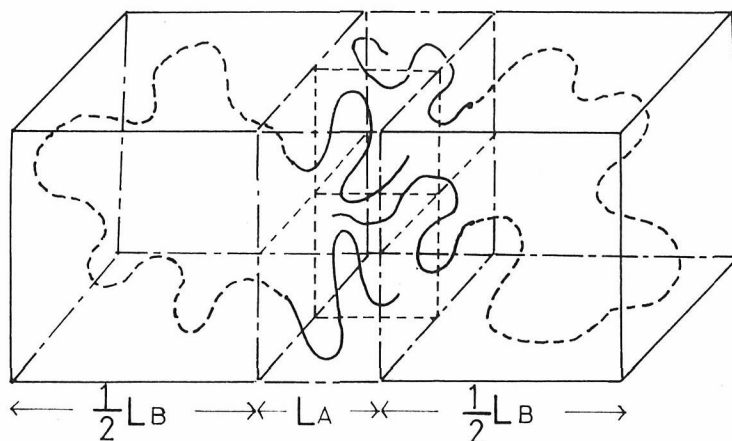


Fig. 4. Chain packing in lamellar structure.

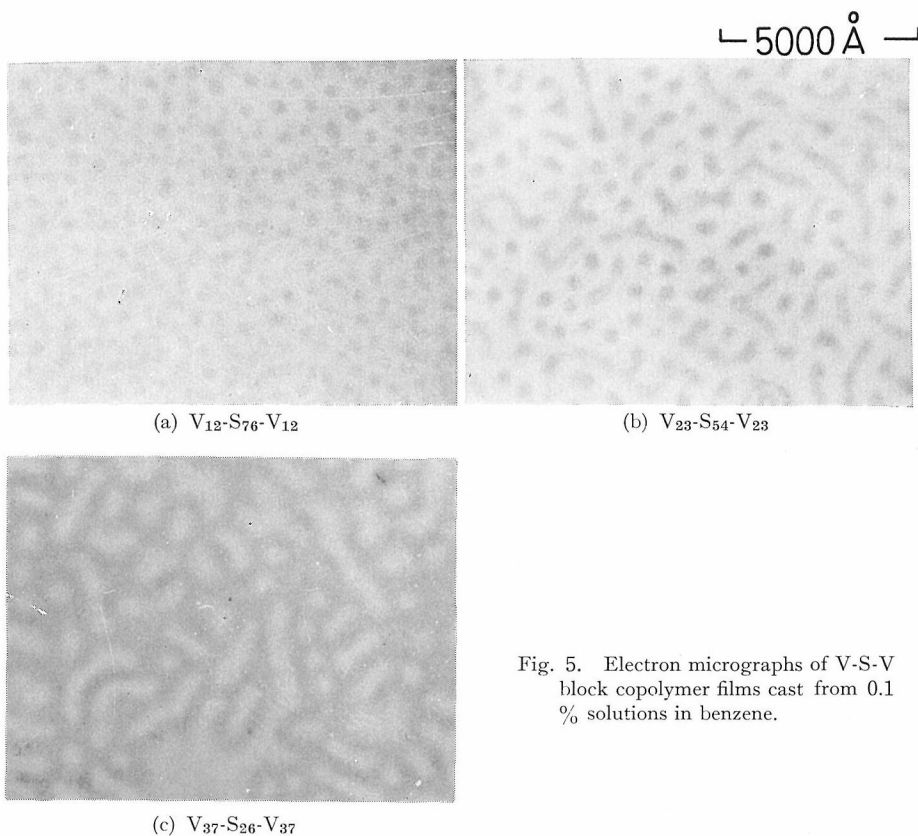


Fig. 5. Electron micrographs of V-S-V block copolymer films cast from 0.1 % solutions in benzene.

cylindrical domains of about 300 Å in diameter. With increasing chain length of V-component, the diameter of cylinder increases, thus  $D'_A$  is about 700 Å for  $V_{23}\text{-}S_{54}\text{-}V_{23}$  (Fig. 5b). Further increase of V-component results in a heterophase structure in which cylindrical domains ( $D'_B=400$  Å) of polystyrene component coexist with lamellar structure of about 500 Å ( $=L_B$ ) in thickness as shown in Fig. 5c.

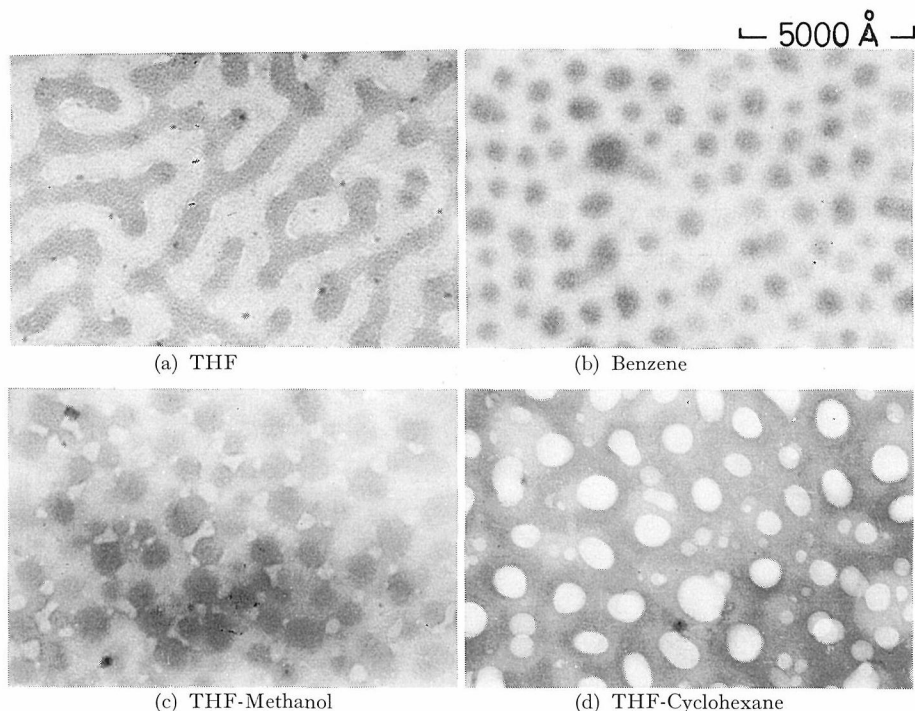


Fig. 6. Electron micrographs of  $V_{23}$ - $S_{54}$ - $V_{23}$  (H) films cast from various solvents.

In the next place,  $V_{23}$ - $S_{54}$ - $V_{23}$  (H) films cast from 0.1% solutions in THF-methanol (4 : 1) and THF-cyclohexane (4 : 1) mixtures were investigated (Fig. 6). Figure 6c and 6d are the electron micrographs of films cast from THF-methanol and THF-cyclohexane systems, respectively. As mentioned above, THF (bp., 66°C) is good solvent for both components. On the other hand, methanol (bp., 64.65°C) is poor solvent for poly-2-vinylpyridine, and non-solvent for polystyrene; cyclohexane (bp., 81.4°C) is poor solvent for polystyrene and non-solvent for poly-2-vinylpyridine.

In THF-methanol system, presumably methanol is predominantly removed from polystyrene portions but remains in poly-2-vinylpyridine portions, and thus the film is formed in such a situation as that THF is selectively adsorbed to polystyrene portions. Accordingly, V-spheres are suspended in S-matrix (Fig. 6c).

On the other hand, in THF-cyclohexane system, it is expected that THF evaporizes earlier, but cyclohexane is selectively adsorbed to polystyrene portions. Thus the ratio of THF to cyclohexane in poly-2-vinylpyridine portions is larger than that in polystyrene portions at critical micelle concentration. Such behavior may lead to the formation of S-domain in V-matrix (Fig. 6d).

Also reproduced are the photographs (Figs. 6a and 6b) of films cast from THF and benzene. Comparison of these four photographs tells us that the shape of domains predominantly depends on the kind of solvent and the casting procedure.

#### Micro-Heterophase Structure of QV-S-QV Membrane Quaternized with HBr on V-S-V Membranes

Figures 7a and 7b, respectively, show the electron micrographs of films which trans-

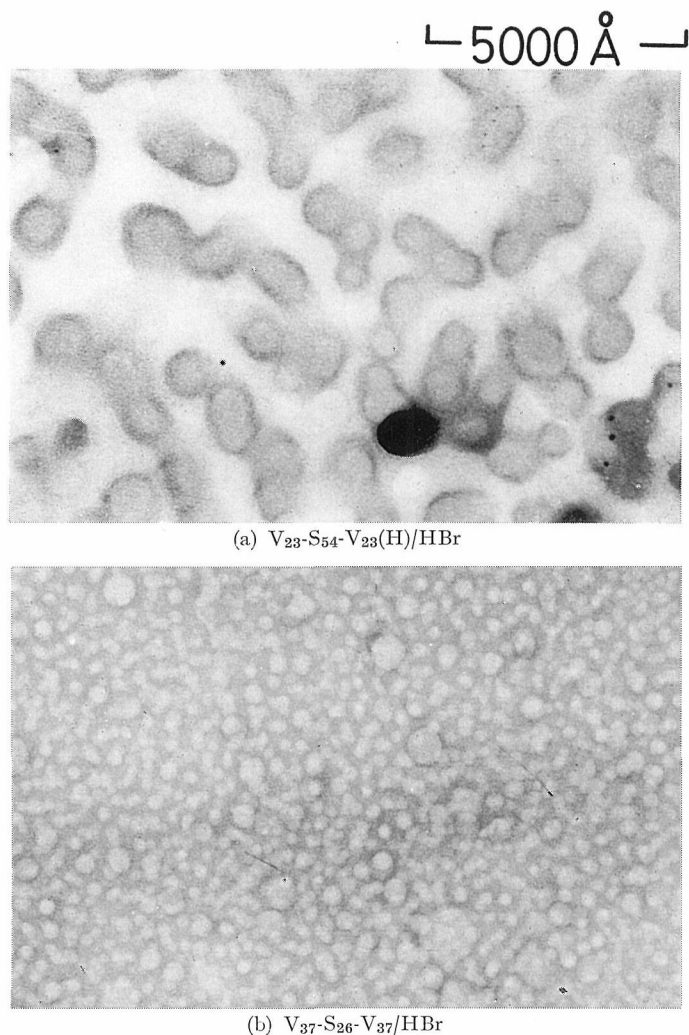


Fig. 7. Electron micrographs of films quaternized with HBr on films cast from THF.

formed into  $QV_{23}\text{-}S_{54}\text{-}QV_{23}(\text{H})$  and  $QV_{37}\text{-}S_{26}\text{-}QV_{37}$  by quaternization with HBr on  $V_{23}\text{-}S_{54}\text{-}V_{23}(\text{H})$  and  $V_{37}\text{-}S_{26}\text{-}V_{37}$  films. The photographs 7a and 7b are compared with the photographs 3f and 3d, respectively. The domain structures of parent films are not fully destroyed with quaternization. However, the domain dimension of V-component is considerably enlarged by the quaternization. Such membranes as shown here may be useful as ionic membranes possessing micro-heterophase structure in the field of desalination and biomaterials.

#### Micro-Heterophase Structure of Solvent-Cast QV-S-QV Membrane

Quaternization of V-S-V block copolymers with HBr or  $\text{CH}_3\text{Br}$  in THF solution resulted in precipitate which did not dissolve in solvent. But longer alkyl bromides produced some quaternized block copolymers which soluble in solvent on account of their long hydrophobic side chains. Thus,  $V_{43}\text{-}S_{14}\text{-}V_{43}$  was quaternized with lauryl bromide

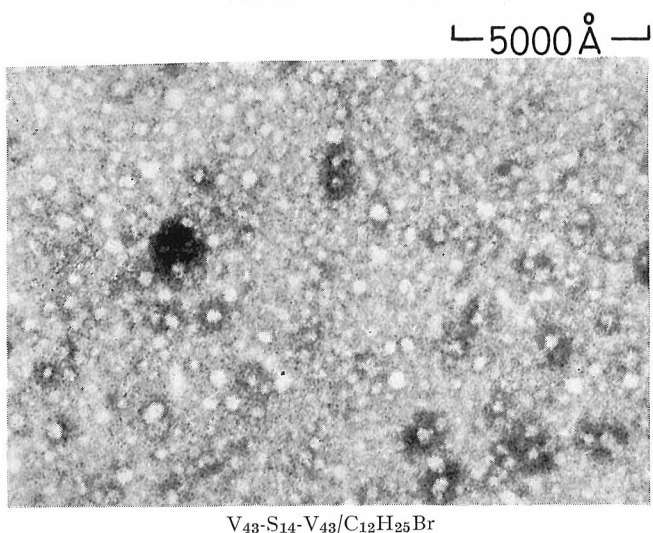


Fig. 8. Electron micrograph of quaternized V<sub>43</sub>-S<sub>14</sub>-V<sub>43</sub> cast from 0.1% solution in DMF.

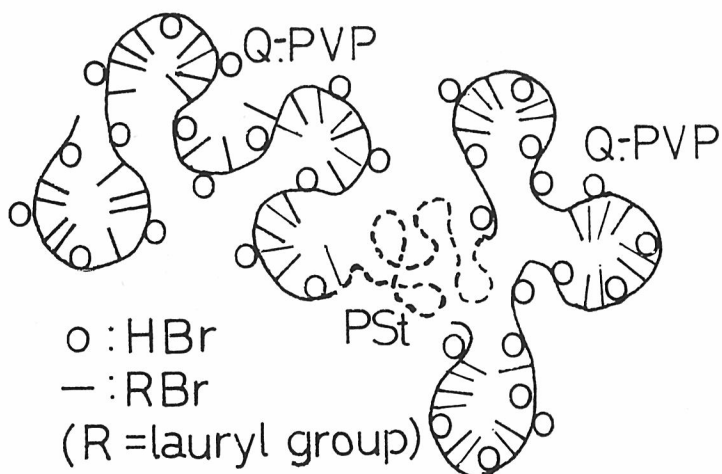


Fig. 9. Intramolecular micelles in copolymer quaternized with lauryl bromide.

(see Table II). The sample quaternized for 71 hr was cast from dimethyl formamide solution to obtain thin film.

Figure 8 is the electron micrograph of this film. As mentioned earlier, the degree of quaternization of this sample is 64.8%, and about 60% of which is expected<sup>(33)</sup> to be lauryl residues. This means that about 40% of the total 2-vinylpyridine residues is quaternized with C<sub>12</sub>H<sub>25</sub>Br and about 25% is in the form of HBr. Thus, we expect the formation of intramolecular micelles due to lauryl residues.

The white domains in Fig. 8 correspond to S-domains. We can also distinguish existence of "polysoap" produced by intramolecular micelle formation in the matrix. Further noticed is that the white (S-)domains are not round but somewhat distorted by surrounding intramolecular micelles. These characteristic figures are not distinguished

in the parent polymer (Fig. 3e) prior to quaternization. In conclusion, we propose a model as indicated in Fig. 9 for the formation of intramolecular micelles in QV-S-QV copolymer obtained by quaternization with lauryl bromide.

## REFERENCES

- (1) A. Skoulios, G. Finaz, and J. Parrod, *C. R. Acad. Sci. [Paris]*, **251**, 739 (1960).
- (2) A. Skoulios and G. Finaz, *ibid.*, **252**, 3467 (1961).
- (3) C. Sadron, *Pure and Appl. Chem.*, **4**, 347 (1962).
- (4) C. Sadron, *Angew. Chem.*, **75**, 472 (1963).
- (5) G. E. Molau, "Block Polymers", Aggarwal, ed., Plenum Press, New York, 1970, pp. 79-106.
- (6) H. Kawai, T. Soen, T. Inoue, T. Ono, and T. Uchida, *Memoirs Faculty Engineering, Kyoto University*, **33**, 383 (1971).
- (7) C. Sadron and B. Gallot, *Makromol. Chem.*, **164**, 301 (1973).
- (8) T. Inoue, T. Soen, H. Kawai, M. Fukatsu, and M. Kurata, *J. Polymer Sci.* **B-6**, 75 (1968).
- (9) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *J. Polymer Sci.*, **A-2**, **7**, 1283 (1969).
- (10) T. Soen, T. Inoue, K. Miyoshi, and H. Kawai, *ibid.*, **10**, 1757 (1972).
- (11) T. Uchida, T. Soen, T. Inoue, and H. Kawai, *ibid.*, **10**, 101 (1972).
- (12) S. Krause, *ibid.*, **7**, 249 (1969).
- (13) S. Krause, *Macromolecules*, **3**, 84 (1970).
- (14) U. Bianchi, E. Pedemonte, and A. Turturro, *Polymer*, **11**, 268 (1970).
- (15) A. Skoulios and G. Finaz, *J. Chim. Phys.*, 473 (1962).
- (16) A. Douy, R. Mayer, J. Rossi, and B. Gallot, "Liquid Crystals 2", Part 1, G. H. Brown, ed., Gordon and Breach Science Pub. London, 1969, p. 119.
- (17) P. Grosius, Y. Gallot, and A. Skoulios, *Makromol. Chem.*, **127**, 94 (1969).
- (18) A. Douy, R. Mayer, J. Rossi, and C. Sadron, *Mol. Cryst. Liq. Cryst.*, **7**, 103 (1969).
- (19) P. Grosius, Y. Gallot, and A. Skoulios, *Makromol. Chem.*, **132**, 35 (1970).
- (20) B. Gallot, R. Mayer, and C. Sadron, *C. R. Acad. Sci. [Paris]*, **C263**, 42 (1966).
- (21) A. Keller, E. Pedemonte, and F. M. Willmouth, *Nature*, **225**, 538 (1970).
- (22) A. Keller, E. Pedemonte, and F. M. Willmouth, *Koll-Z. u. Z. Polymere*, **238**, 385 (1970).
- (23) J. Dlugosz, A. Keller, and E. Pedemonte, *ibid.*, **242**, 1125 (1970).
- (24) M. J. Folkes and A. Keller, "Physics of Glassy Polymers", Haword, ed., Elsevier, 1972.
- (25) Hyo-gun Kim, *Macromolecules*, **5**, 594 (1972).
- (26) C. W. Brown and I. F. White, *J. Appl. Polymer Sci.*, **16**, 2621 (1972).
- (27) M. Kamachi, M. Kurihara, and J. K. Stille, *Macromolecules*, **5**, 161 (1972).
- (28) M. Kurihara, M. Kamachi, and J. K. Stille, *J. Polymer Sci., Chem. ed.*, **11**, 587 (1973).
- (29) H. Yasuda, C. E. Lamaze, and A. Schindler, *J. Polymer Sci.* **A-2**, **9**, 1579 (1971).
- (30) G. Champetier, M. Fontanille, A.-C. Korn, and P. Sigwalt, *J. Polymer Sci.*, **58**, 911 (1962).
- (31) L. J. Fetters, *J. Res. Natl. Bur. Standard*, **70A**, 421 (1966).
- (32) A. Yamamoto, M. Fujii, G. Tanaka, and H. Yamakawa, *Polymer J.*, **2**, 799 (1971).
- (33) H. Inoue, *Koll-Z. u. Z. Polymere*, **195**, 102 (1964).
- (34) U. P. Strauss and E. G. Jackson, *J. Polymer Sci.*, **6**, 649 (1951).
- (35) D. Leary and M. C. Williams, *J. Polymer Sci.*, **11**, 345 (1973).
- (36) D. Leary and M. C. Williams, *ibid.*, **8**, 335 (1970).