

## Mechanical Properties and Water Permeability of the A–B–A Tri-Block Copolymer Consisting of Poly( $\gamma$ -benzyl D,L-glutamate) or Poly( $\gamma$ -methyl D,L-glutamate) as the A Component and Polybutadiene as the B Component

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**ABSTRACT:** Membranes of A–B–A tri-block copolymers were prepared by polymerizing poly( $\gamma$ -benzyl D,L-glutamate) or poly( $\gamma$ -methyl D,L-glutamate) as the A component and polybutadiene as the B component. The mechanical properties of and the hydraulic permeability of water were examined and compared with those properties for A–B–A tri-block copolymers consisting of poly( $\gamma$ -benzyl L-glutamate) or poly( $\gamma$ -methyl L-glutamate) as the A component and polybutadiene as the B component. The temperature dependence of the dynamic modulus and the loss modulus were investigated based on Takayanagi's mechanical model. The mechanical properties led to the conclusion that the dynamic mechanical spectra could be well explained by the microheterophase structure observed with an electron microscope. In the case the shape of the inclusion phase was assumed to be spherical, the storage modulus  $E'$  calculated by means of Takayanagi's equation showed excellent agreement with the experimental data for D,L-type block copolymers, indicating that spherical inclusion phases exist in them in spite of their rather high volume fractions of the B portion. The hydraulic permeability coefficient  $K$  of water through D,L-type block copolymer membranes was remarkably lower than that of L-type membranes. This may indicate that the A domains are homogeneous in shape and dispersion state for the D,L-type block copolymer, owing to the existence of a molecular chain portion capable of forming interchain hydrogen bonds.

**KEY WORDS** Tri-Block Copolymer / Poly( $\gamma$ -benzyl D,L-glutamate) / Poly( $\gamma$ -methyl D,L-glutamate) / Polybutadiene / Mechanical Properties / Water Permeability /

In the previous paper,<sup>1</sup> we investigated the preparation, molecular characterization, and the microheterophase structure of A–B–A tri-block copolymers in which A was poly( $\gamma$ -benzyl D,L-glutamate) or poly( $\gamma$ -methyl D,L-glutamate) and B, polybutadiene. The  $\alpha$ -helix conformation was interrupted in D,L-copolypeptide chains. The microheterophase structure of these D,L-block copolymer membranes seemed spherical even though their volume fractions of the B portion were rather high.

In this paper, we discuss the mechanical

properties and water permeability of D,L-block copolymer membranes. The dynamic mechanical relaxation behavior and tensile properties of the present block copolymer membranes with a novel heterophase structure have been discussed on the basis of the equivalent mechanical model as proposed by Takayanagi,<sup>2</sup> in order to ascertain the heterophase structure pointed in our previous paper.<sup>1</sup>

Also, the permeability properties of the membranes have been investigated. The polybutadiene portion of the block copolymers is

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fully hydrophobic so that formation of the B domain is controlled only by dispersion force. Contrarily, the polypeptide chain portion includes NH and CO groups, and hence, formation of the A domain is governed not only by dispersion force but by polar and hydrogen bonding forces as well. The water permeability of these block copolymer membranes are discussed from the standpoint of conformation.

## EXPERIMENTAL

### Materials

The equimolar-D,L-copolypeptides, poly( $\gamma$ -benzyl D,L-glutamate) (PBDLG) and poly( $\gamma$ -methyl D,L-glutamate) (PMDLG) were prepared by polymerizing equimolar mixtures of D- and L-amino acid NCA under the same conditions for the corresponding homopolypeptides, PBLG and PMLG. A-B-A tri-block copolymers consisting of polybutadiene as the B component and poly( $\gamma$ -benzyl D,L-glutamate) (GBG-DL), poly( $\gamma$ -benzyl L-glutamate) (GBG-L), poly( $\gamma$ -methyl D,L-glutamate) (MBM-DL), or poly( $\gamma$ -methyl L-glutamate) (MBM-L) as the A component were synthesized as mentioned in the previous paper.<sup>1</sup> The molar content of the polypeptide component in the block copolymers was estimated by elemental analyses carried out at the Organic Microanalyses Center of Kyoto University and molecular weight was determined by ultracentrifugation.<sup>1</sup> In Table I, the copolymer composition, denoted by mol% of the component A, the helix content  $x_H$  of polypeptide component in the block copolymers in a solid state, and the degree of polymerization of A component, estimated in the previous paper,<sup>1</sup> are summarized.

### Membrane Preparation

To study their mechanical properties and water permeability, membranes from 30 to 100  $\mu$ m in thickness were cast onto glass plates from about 2 wt% solution in chloroform (CF) or a CF-trifluoroethanol (TFE) (2:1, v/v)

Table I. Molecular parameters of samples

Code	A	$P_A$	$x_H$
	mol%		
GBG-DL-1	51.9	33	0.71
GBG-DL-2	68.7	67	0.70
GBG-DL-3	81.1	131	0.70
GBG-DL-4	87.5	213	0.72
PBDLG-1	100.0	429	0.70
GBG-L-1	69.5	69	1.00
GBG-L-2	81.6	135	1.00
GBG-L-3	87.7	218	1.00
PBLG-1	100.0	899	1.00
MBM-DL-1	70.0	71	0.58
MBM-DL-2	86.0	187	0.58
PMDLG-1	100.0	716	0.60
MBM-L-1	67.8	64	1.00
MBM-L-2	80.2	124	1.00
MBM-L-3	91.9	346	1.00
PMLG-1	100.0	990	1.00

mixture. The residual solvent in the air-dried membranes was removed by exchanging the solvent with methanol and ether. The membranes were then dried *in vacuo* for 3 days at room temperature prior to the measurements.

### Mechanical Property Measurements

The dynamic mechanical relaxation behavior was measured with a Rheovibron DDV-II at a frequency of 110 Hz and heating rate of 0.3°C min<sup>-1</sup> over a temperature ranging from -20 to 200°C. The tensile properties were measured by a Tensilon UTM-II-20 (Toyo-Baldwin Co.) using dog-bone samples of 1.0  $\times$  0.4 cm from 30 to 50  $\mu$ m in thickness. All the samples were tested at an elongation rate of 40% per min at 25°C and 65%RH.

### Water Permeability Measurements

Water permeation through the membranes was measured with a low-pressure ultrafiltration cell from Bio-Engineering Co. (Model MC-II). The exposed membrane area was 12.57 cm<sup>2</sup>. The cell was immersed in a water bath whose temperature was controlled within

0.1°C. The measurements were carried out in a temperature range from 25 to 55°C, and a pressure range from 1 to 4 atm.

## RESULTS AND DISCUSSION

### *Estimation of Microheterophase Structures of D,L-Block Copolymer Membranes with an Equivalent Mechanical Model for Dynamic Viscoelastic Behavior*

Takayanagi<sup>3</sup> succeeded in representing the viscoelastic properties of heterogeneous polymer system in terms of a simple mechanical model comprising elements (assumed to have the viscoelastic properties of the constituent phases of the composite medium) connected partly in series and partly in parallel. In essence, this model represents an attempt to construct average response curves intermediate between the bounds given by simple series and parallel rules of mixing. Two parameters,  $\lambda$  and  $\psi$ , which express the mixing states of the system, were introduced in his model.<sup>3</sup> The relative magnitude of  $\lambda$  and  $\psi$  can be interpreted as representing the extent of the parallel and series elements, and  $\lambda\psi$  is equal to the volume fraction of the inclusion phase; *i.e.*,  $\lambda\psi = \phi_2$ . The dynamic Young's modulus  $E_c^*$  for such a model is given by

$$\frac{1}{E_c^*} = \frac{\psi}{\lambda E_2^* + (1-\lambda)E_1^*} + \frac{1-\psi}{E_1^*} \quad (1)$$

assuming the elastic Poisson's ratio  $\nu$  to be  $\nu = \nu_1 = \nu_2 = 0.5$  (the subscripts 1 and 2 refer to the matrix and inclusion phases, respectively). Equation 1 is equivalent to the modified Kerner's equation used by Dickie.<sup>4</sup>

Equation 1 may be applied to investigate the microheterophase structures formed in these block copolymers based on dynamic viscoelastic behavior of polypeptide and polybutadiene homopolymers. In this case, the inclusion phase is rubber-like and therefore, its elastic Poisson ratio is equal to 0.5. If the shape of the inclusion phase is spherical, the values of  $\lambda$  and

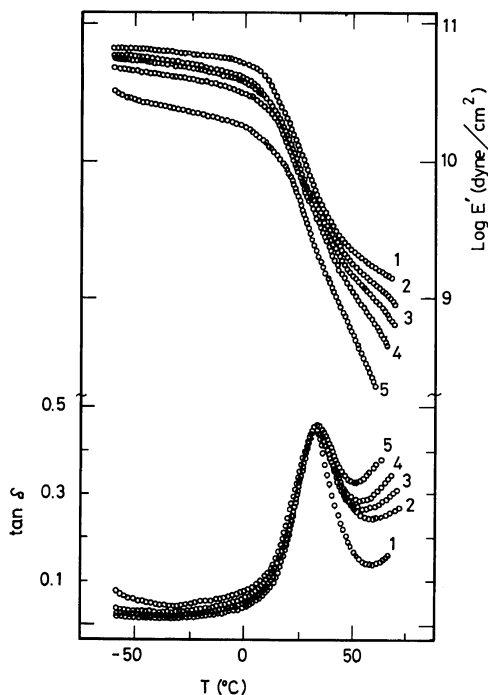
$\psi$  are given by<sup>4</sup>

$$\lambda = (2 + 3\phi_2)/5 \quad (2)$$

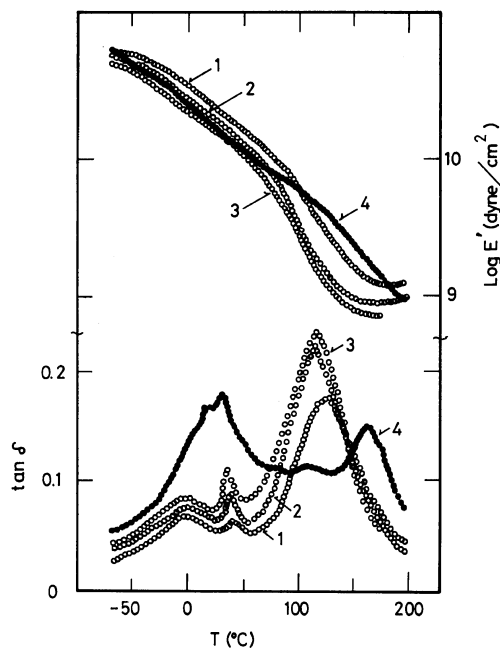
$$\phi = 5\phi_2/(2 + 3\phi_2) \quad (3)$$

Figures 1 and 2 illustrate the temperature dependence of the loss tangent,  $\tan \delta$ , and the dynamic elastic modulus  $E'$  for GBG-DL and MBM-DL block copolymer membranes and the corresponding D,L-copolypeptides, PBDLG and PMDLG membranes, respectively.

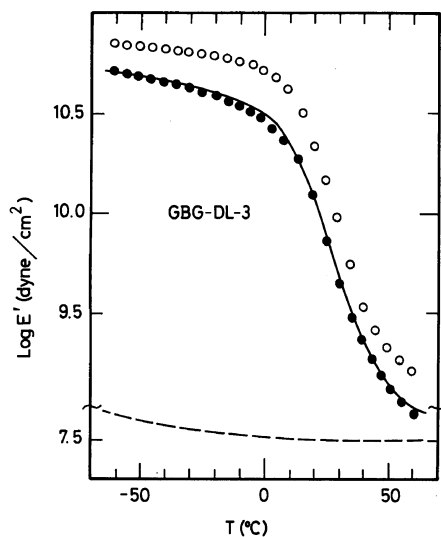
In Figures 3 and 4, the  $E'$  values calculated by eq 2 and 3, assuming the shape of the inclusion phase, B-portion, to be spherical, are compared to the experimental values for GBG-DL-3 and MBM-DL-1, respectively. The data of polybutadiene was taken from the work of Keskkula.<sup>5</sup> The calculated curves clearly show excellent agreement with the ex-



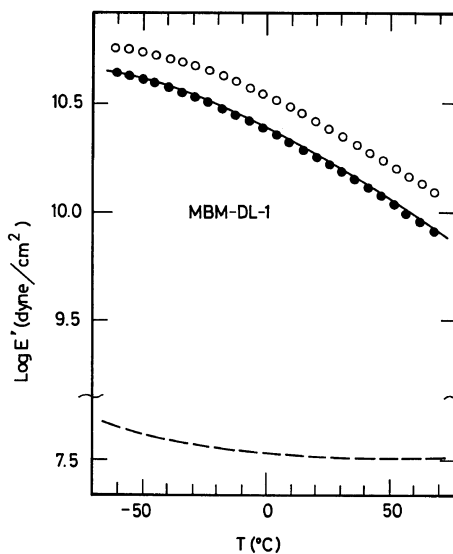
**Figure 1.** Temperature dependence of  $\tan \delta$  and  $\log E'$  for sample membranes cast from CF: (1) PBDLG-1; (2) GBG-DL-4; (3) GBG-DL-3; (4) GBG-DL-2; (5) GBG-DL-1.



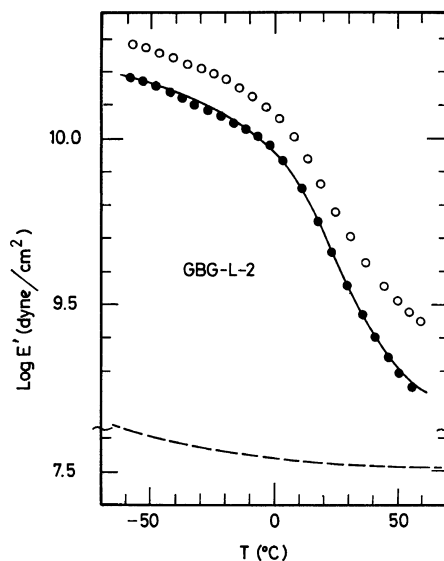
**Figure 2.** Temperature dependence of  $\tan \delta$  and  $\log E'$  for sample membranes cast from CF-TFE mixture: (1) PMDLG-1; (2) MBM-DL-2; (3) MBM-DL-1; (4) MBM-L-2.



**Figure 3.** Temperature dependence of  $\log E'$  for GBG-DL-3 (●) and PBDLG-1 (○) membranes. The solid curve was calculated from eq 1 using the values of  $\lambda=0.50$ ,  $\psi=0.32$ , and  $\phi_2=0.16$ . The broken curve denotes the experimental result for polybutadiene by Keskkula.<sup>5</sup>



**Figure 4.** Temperature dependence of  $\log E'$  for MBM-DL-1 (●) and PMDLG-1 (○) membranes. The solid curve was calculated from eq 1 using the values of  $\lambda=0.53$ ,  $\psi=0.42$ , and  $\phi_2=0.22$ . The broken curve denotes the experimental result for polybutadiene by Keskkula.<sup>5</sup>



**Figure 5.** Temperature dependence of  $\log E'$  for GBG-L-2 (●) and PBLG-1 (○) membranes. The solid curve was calculated from eq 1 using the values of  $\lambda=0.56$ ,  $\psi=0.34$ , and  $\phi_2=0.19$ . The broken curve denotes the experimental result for polybutadiene by Keskkula.<sup>5</sup>

perimental data. This indicates that these D,L-block copolymer membranes include a spherical inclusion phase in spite of their rather high volume fractions of the B-portion.

In Figure 5, the dynamic modulus  $E'$  calculated using eq 1 was compared with observed data for the GBG-L-2 block copolymer membrane. The solid curve in Figure 5 was obtained using  $\phi_2=0.19$ ,  $\lambda=0.56$ , and  $\psi=0.34$ , the latter two values being determined by trial and error, based on the experimental data. If a value larger than 0.56 is used, the calculated value of the  $E'$  is smaller than the calculated value obtained above, and if  $\lambda$  decreases, the calculated value of the  $E'$  increases. As obvious from Figure 5, a rather satisfactory agreement was obtained between the observed and calculated curves on the basis of a reasonable values of  $\lambda$ . On using  $\phi_2=0.19$  in eq 2, we obtained  $\lambda=0.51$ . The best-fit  $\lambda$ -value of 0.56 estimated for the GBG-L-2 block copolymer was somewhat larger than the value for a spherical inclusion, suggesting the lines of force in the membrane passing through the matrix component to be smaller than that for a spherical inclusion model. One possible explanation for this is that the shape of the inclusion phase deviates from the sphere; in other words, the ellipsoidal or cylindrical inclusion phase (domain) is expected for the polybutadiene component in this block copolymer membrane. It should be added that the  $\phi_2$  values used in these calculations were obtained from the copolymer composition, assuming the chain conformation of polybutadiene as well as that of polypeptides to be in an unperturbed state.<sup>6</sup> The domain structures investigated by the mechanical model analyses are quite comparable with previous electron micrograph observations.<sup>1</sup>

#### *Dynamic Mechanical Properties Relating to the Molecular Conformation of A Blocks*

For GBG-DL block copolymers and PBDLG membranes, the tangent spectra (see Figure 1) show similar techniques and a large

$\beta$ -peak at about 30°C. The  $E'$  curves of these membranes are also similar and show a fairly large modulus drop at the  $\beta$ -peak. The  $\beta$ -temperature for GBG-DL block copolymers and PBDLG membranes is somewhat lower than that for GBG-L and PBLG membranes (40°C) reported earlier.<sup>7</sup> The  $\beta$ -process should be influenced by crystals in the chain molecules,<sup>8</sup> and it is evident from DSC<sup>9</sup> and dielectric relaxation studies<sup>10</sup> that the  $\beta$ -process more closely resembles the glass-rubber transition of the side chains of a polypeptide component. This may indicate that rather short  $\alpha$ -helix portions in the D,L-copolypeptide chains make the glass-rubber transition temperature lower than that of longer  $\alpha$ -helix portions in the L-isomers.

In regard to MBM-DL block copolymers and PMDLG membranes, there are notable differences for the temperature dependence of  $E'$  and  $\tan \delta$ , compared to those of L-isomers (Figure 2). MBM-DL block copolymers and PMDLG membranes showed two absorption in the temperature range from -10 to 50°C and a large absorption at around 120°C. The lower two were termed  $\beta_1$ - and  $\beta_2$ -dispersions in the order of increasing temperature. The MBM-L block copolymer membrane showed only one absorption ( $\beta_2$ -peak) at around 40°C and an  $\alpha$ -absorption at around 160°C. Watanabe *et al.*<sup>11</sup> suggest that the  $\beta_2$ -dispersion is attributable to the motion of the side chains in the hexagonal crystalline phase, and the  $\beta_1$ -dispersion to that of the disoriented side chains in the main chains with interchain hydrogen bonds and/or in the disordered part of the main chains, on the basis of dielectric and X-ray measurements for PMDG and PMDLG membranes. Thus, it is concluded that the formation of interchain hydrogen bonds in D,L-copolypeptide chains is also confirmed by these relaxation curves. From X-ray measurements, a hexagonal crystalline phase was found to disappear for PMDLG and MBM-DL block copolymer membranes.<sup>1</sup> This may be due to the breakdown of the  $\alpha$ -helix

Table II. Tensile properties of membranes

Code	A	Cast <sup>a</sup> solvent	E	$\sigma_B$	$\epsilon_B$
	mol%		dyn cm <sup>-2</sup>	dyn cm <sup>-2</sup>	%
MBM-DL-1	70.0	CF-TFE (2:1)	$4.0 \times 10^9$	$1.35 \times 10^8$	92
MBM-DL-2	86.0	CF-TFE (2:1)	$6.0 \times 10^9$	$1.75 \times 10^8$	90
PMDLG-1	100.0	CF-TFE (2:1)	$8.7 \times 10^9$	$2.30 \times 10^8$	55
MBM-L-1	67.8	CF-TFE (2:1)	$2.3 \times 10^9$	$0.84 \times 10^8$	120
MBM-L-3	91.9	CF-TFE (2:1)	$3.2 \times 10^9$	$1.14 \times 10^8$	90
PMLG-1	100.0	CF-TFE (2:1)	$5.0 \times 10^9$	$2.05 \times 10^8$	98
PMDLG-1	100.0	FA-TFA (9:1)	$15.8 \times 10^9$	$4.15 \times 10^8$	6
PMLG-1	100.0	FA-TFA (9:1)	$12.1 \times 10^9$	$3.71 \times 10^8$	11

<sup>a</sup> FA=formic acid; TFA=trifluoroacetic acid; CF=chloroform; TFE=trifluoroethanol.

conformation of the main chains, as is also supported from an infrared absorption measurement,<sup>1</sup> and followed by the partial formation of a  $\beta$ -chain structure.<sup>12</sup>

The relaxation process above 100°C may be attributable to the motion of  $\alpha$ -helices in the region having different molecular packings and to a mutual displacement of crystallites.<sup>13,14</sup> The large absorption peak at 160°C observed for the MBM-L block copolymer membrane may indicate the existence of a crystalline structure similar to that of PMDG in the solid membrane cast from DMF as reported by Watanabe *et al.*<sup>15</sup> The large peaks obtained with MBM-DL and PMDLG membranes should differ basically from those of the L- and D-isomers. Though the relaxation mechanisms are not clear in this stage, relaxation behavior should bear some relation to the molecular packing state, as far, instance, the loosening of interchain hydrogen bonding.

#### Tensile Properties

The tensile properties of block copolymer membranes are dependent on copolymer composition, block molecular weights, molecular conformations of block components, and microheterophase structures. The tensile stress-strain parameters obtained experimentally for MBM-DL and MBM-L block copolymers, in addition to the corresponding homopolymer

membranes are summarized in Table II. Young's modulus  $E$  at a strain of 1% and the strength  $\sigma_B$  at the breaking point of block copolymer membranes are generally less than those of corresponding homopolymer membranes. The values of the mechanical parameters,  $E$  and  $\sigma_B$  for MBM-DL and MBM-L block copolymer membranes in Table II decrease with increasing content of the polybutadiene block portion.

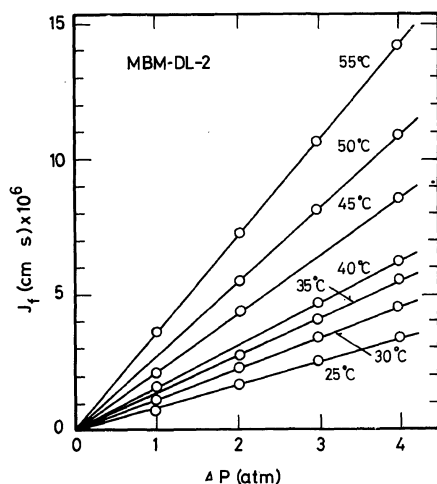
The tensile parameters on  $E$  and  $\sigma_B$ , for the PMDLG membrane cast from the same solvent system, and consequently that for MBM-DL membrane, is higher than that for the MBM-L membrane. Since these D,L-copolymer membranes contain some molecular chains with interchain hydrogen bonds as well as  $\alpha$ -helical chains, the interchain interaction affects the tensile properties. Thus, it is concluded that the secondary structure of the main chain of the A blocks becomes a major factor affecting the mechanical properties of membranes, and that the mechanical parameter  $E$  increases with an increase in the number of interchain hydrogen bonds in the cast membranes.

#### Water Permeability

The hydraulic permeability  $K$  of water is defined<sup>16-19</sup> by

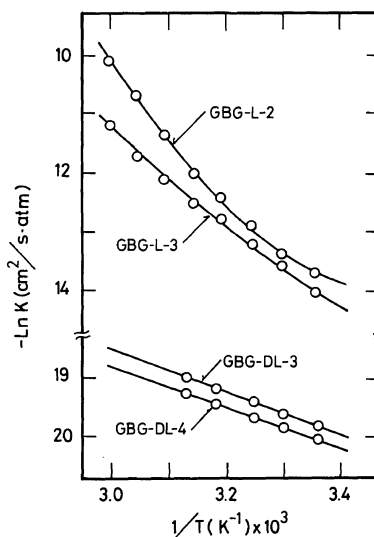
**Table III.** Water permeability coefficient  $K$  and activation energy  $E_a$  for membranes

Code	A	Case solvent	K	$E_a$
	mol%		$\text{cm}^2 \text{s}^{-1} \text{atm}$	$\text{kcal mol}^{-1}$
GBG-DL-1	51.9	CF	$4.39 \times 10^{-9}$	
GBG-DL-2	68.7	CF	$3.20 \times 10^{-9}$	
GBG-DL-3	81.1	CF	$2.54 \times 10^{-9}$	7.6
GBG-DL-4	87.5	CF	$2.01 \times 10^{-9}$	7.5
PBDLG-1	100.0	CF	$1.00 \times 10^{-9}$	
GBG-L-1	69.5	CF	$2.32 \times 10^{-6}$	22.5
GBG-L-2	81.6	CF	$1.01 \times 10^{-6}$	18.1
GBG-L-3	87.7	CF	$8.65 \times 10^{-7}$	15.6
PBLG-1	100.0	CF	$1.11 \times 10^{-9}$	9.3
MBM-DL-1	70.0	CF-TFE (2:1)	$4.01 \times 10^{-9}$	
MBM-DL-2	86.0	CF-TFE (2:1)	$2.94 \times 10^{-9}$	8.0
PMDLG-1	100.0	CF-TFE (2:1)	$1.19 \times 10^{-9}$	
MBM-L-1	67.8	CF-TFE (2:1)	$4.43 \times 10^{-9}$	
MBM-L-3	91.9	CF-TFE (2:1)	$3.53 \times 10^{-9}$	9.4
PMLG-1	100.0	CF-TFE (2:1)	$3.36 \times 10^{-9}$	9.3

**Figure 6.** Water flux  $J_f$  plotted against pressure  $\Delta P$  at various temperatures for the MBM-DL-2 membrane cast from a CF-TFE mixture ( $33 \mu\text{m}$  in thickness).

$$J_f = K(\Delta P / \Delta X) \quad (4)$$

where  $J_f$  is the flux of water per unit area of membrane subjected to a hydraulic pressure difference  $\Delta P$  across the membrane whose thickness is  $\Delta X$ . Figure 6 shows the relation between the water flux  $J_f$  ( $\text{cm s}^{-1}$ ) and applied pressure  $\Delta P$  (atm) at various temperatures for the MBM-DL-2 block copolymer membrane

**Figure 7.** Temperature dependence of the hydraulic permeability  $K$  of water for GBG-DL and GBG-L block copolymer membranes.

( $33 \mu\text{m}$  in thickness) cast from a CF-TFE (2:1, v/v) mixture. In the pressure range examined, the relation between  $J_f$  and  $\Delta P$  was linear, indicating the effect of compression on the membrane to be negligible. The water flux increases with increasing temperature and applied pressure. From Figure 6, the  $K$  value at

each temperature was calculated using eq 4.

Figure 7 shows the Arrhenius plots of  $\log K$  for the GBG-DL and GBG-L block copolymer membranes cast from CF. The activation energy  $E_a$  was calculated from the slopes of these curves. The magnitude of  $K$  and the activation energy  $E_a$  at 25°C are given in Table III. The numerical values of  $E_a$  shown in Table III are larger than the activation energy of 4 kcal mol<sup>-1</sup> (at 25°C) for the viscous flow of water.<sup>20</sup> Thus, water flow in the membrane is considered to be different from the viscous flow of pure water. The nature of the microheterophase structure in the membrane should play an important role in the permeability of water through the membrane. The most remarkable characteristic of the GBG-L membranes compared to GBG-DL membranes is that the values of  $K$  and  $E_a$  for the GBG-L membranes are remarkably higher than those for GBG-DL membranes in which the molar content of the B portion is of the same order; the  $K$  values for GBG-L is 500 to 2000 times that for GBG-DL, while the  $K$  value for GBG-DL membranes is only a few times larger than that for PBDLG or PBLG membranes.

The  $K$  values for the block copolymer membranes vary widely according to the casting solvent used in contrast to the corresponding homopolymer membranes, as shown in Table IV. The  $K$  value for the MBM-DL-1 membrane cast from a CF-TFA (8:1, v/v) mixture is about 35 times that for the MBM-DL-1 membrane cast from TFE. In the case of the MBM-L-1 membrane, the  $K$  value when casting from a CF-TFA (8:1, v/v) mixture is 100 times as much as that when casting from a CF-TFE (2:1, v/v) mixture. The values for PMDLG and PMLG membranes are almost independent of the casting solvents. Such a drastic increase in  $K$  values and the remarkable dependency on casting conditions for block copolymer membranes should be attributed mainly to the specific feature of the interfacial zone between the A and B domains in the A-B-A block copolymer and the high sensi-

Table IV. Casting solvent dependence on membrane  $K$  values

Code	A mol%	TFE	$K \times 10^9$ cm <sup>2</sup> s <sup>-1</sup> atm Casting solvent system			
			CF-TFE		CF-TFA	
			2:1	4:1	8:1	4:1
MBM-DL-1	70.0	3.38	4.01	4.43	118.0	
MBM-DL-2	86.0		2.94		47.5	
PMDLG-1	100.0		1.19		1.10	
MBM-L-1	67.8		4.43			518.0
MBM-L-3	91.9		3.53			321.0
PMLG-1	100.0		3.36		3.23	

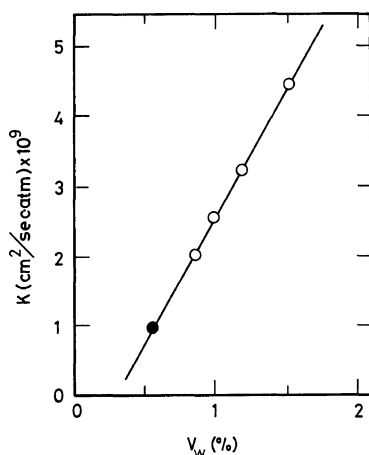
tivity of the micelle formation mechanism toward environmental conditions.<sup>7</sup> As described previously,<sup>7</sup> the interfacial zone is made up of coiled peptide residues near the end of the polypeptide chain and the terminal residues of amine-terminated polybutadiene. The NH and CO residues in this region are not incorporated into the intramolecular hydrogen bondings of  $\alpha$ -helix of polypeptide backbone, but can with bind water through hydrogen bonds. Thus, the number of the bonded water molecules should be related closely to the volume of the interfacial zone. Furthermore, such bonded water may contribute to the size reduction of water clusters. These factors may be responsible for the dramatically large  $K$ -values for A-B-A block copolymer membranes. To intensify the contribution of the interfacial region toward permeability, the  $K$ -values obtained with GBG-L block copolymers were considered a function of the interfacial area per unit volume in the preceding paper.<sup>7</sup> It is shown that the  $K$ -values increased in proportion to the interfacial area per unit volume. This supports the conclusion that the interfacial region may be responsible for the water permeability. The hydraulic permeability of water increases with increasing polybutadiene content of the GBG-L block copolymers.

The relation between the degree of swelling



**Table V.** Degree of swelling  $Q_w$  of membranes in water

Code	$\phi_B$	Cast solvent	$Q_w$ %
GBG-DL-1	0.520	CF	1.54
GBG-DL-2	0.311	CF	1.21
GBG-DL-3	0.161	CF	1.00
GBG-DL-4	0.091	CF	0.90
PBDLG-1	0	CF	0.57
MBM-DL-1	0.223	CF-TFE (2:1)	0.89
MBM-DL-1	0.223	CF-TFE (8:1)	3.67
MBM-DL-2	0.095	CF-TFE (2:1)	0.49
MBM-DL-2	0.095	CF-TFE (8:1)	1.26
MBM-L-1	0.650	CF-TFE (2:1)	1.01
MBM-L-3	0.280	CF-TFE (2:1)	0.78
PMLG-1	0	CF-TFE (2:1)	0.43

**Figure 8.** The hydraulic permeability  $K$  of water plotted against the volume fraction of water  $V_w$  in the membrane for GBG-DL (○) and PBDLG (●) membranes.

$Q_w$  and volume fraction of polybutadiene in a membrane is summarized in Table V.  $Q_w$  was measured after dipping the membranes in water for 48 h at 25°C. It is pointed out that the  $Q_w$  values obtained with GBG-DL and MBM-DL membranes are somewhat higher than those obtained with GBG-L and MBM-L membranes, comparing at the same order of the volume fraction of the polybutadiene block component, in spite of their much lower  $K$ -

values.

Figure 8 shows the relation between  $K$  and  $V_w$ , the volume fraction of water in the membrane, for the GBG-DL block copolymer and PBDLG membranes. A straight line was obtained throughout the entire range of plots. In the case of L-isomeric block copolymer membranes, a discontinuity to the corresponding homopolymer membrane was noted.<sup>21</sup> Peterlin *et al.*<sup>22</sup> suggest that permeability should increase linearly with increasing water fraction in homogeneous membrane. This may indicate that the homogeneous micelle shape and dispersion of the inclusion phase should be obtainable for GBG-DL as well as MBM-DL membranes, owing to the existence of molecular chain portions in the interrupted  $\alpha$ -helix conformation. This was confirmed by the electron microscopic observation.<sup>1</sup>

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