Microheterophase Structure of the A–B–A Type Block Copolymer Consisting of α-Helical Poly(γ-benzyl L-glutamate) as the A Component and Polybutadiene as the B Component

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ABSTRACT: The microheterophase separation produced by a novel A–B–A type block copolymer of γ-benzyl L-glutamate (A) and butadiene (B) in helicogenic solvent was thermodynamically investigated by taking into account conformational parameters of the component block chains, A block as a rod-like chain and B block as a Gaussian chain. The microheterophase structure resulting therefrom was analyzed based on three well-defined types of micelle model, i.e., sphere, cylinder, and lamella. For determining the micelle dimensions, the interfacial free energy of the A/B interface was evaluated from surface tensions of both block component polymers estimated from contact angles of various liquids on the component polymers. The shape and size of the micelles, i.e., the microphase domains, calculated were in accord with the observation by electron microscopy.

Since Sadron's model proposal[1-4] of "organized structure" produced by block copolymers, investigations on the microphase separation of block copolymers such as A–B type and A–B–A type and the microheterophase structure resulting therefrom have been extensively advanced. In particular, the formation mechanism and the structure of regular and periodic microheterophase produced by solvent casting from solutions of block and graft copolymers were quantitatively investigated by Kawai,[5-7] Meier,[8,9] Krause,[10,11] and Bianchi.[12] For these studies, mainly A–B type or A–B–A type block copolymers were used in which both block component chains are nonionic and exist in random coil conformation in solution.

One of the authors (A.N.) has reported[13] elsewhere a new type of membrane cast from A–B–A type block copolymer solution in which the A component was quaternized poly(vinylpyridine), i.e., an ionic species.

In recent years, synthetic block copolymer materials exhibiting the microheterophase structure have been examined in the biomedical field, owing to their expected antithrombogenic action.[14,15] Biomembranes also exhibit the microheterophase structure composed of both hydrophilic and lipophilic domains.

In this study, our concern is with A–B–A type block copolymer consisting of poly(γ-benzyl L-glutamate) as the A component and poly(*trans*-1,4-butadiene) as the B component. As is well known, the former exists in an α-helical conformation in helicogenic solvent, and the latter is in random coil conformation in any solvent. Domain formation for such "rod–coil–rod" type block copolymers, in connection with the microheterophase structure, will be quantitatively investigated in this study. Such a study may afford not only basic information on domain formation of such a novel block copolymer but also possible applications in some fields of biological interest.

Domain Formation of the A–B–A Type Block Copolymer Consisting of an α-Helical A Component and a Random Coil B Component

The molecular chain conformation of a polypeptide–polydiene–polypeptide block copolymer, of which the degrees of polymerization of the A block chain and the B block chain are P_A and P_B, respectively, in a helicogenic solvent, is represented by a model indicated in Figure 1, where a is the radius of cross-section of the A rod and h is the residue translation in the α-helix. Further, a B chain is divided into two unit chains connected at the midpoint M of the chain, and the root mean square end-to-end distance and the root mean square radius of gyration of the unit chain having a degree of polymerization of $P_B/2$ are denoted by $\langle r^2_{B/2}\rangle^{1/2}$ and $\langle s^2_{B/2}\rangle^{1/2}$, respectively.

Now we define the volume fraction of the domain occupied by B blocks relative to the total volume occupied by the copolymer, both in solution, by φ_B.

$$\varphi_B = \frac{\frac{4}{3}\pi\langle s^2_{B/2}\rangle^{3/2}}{\frac{4}{3}\pi\langle s^2_{B/2}\rangle^{3/2} + \pi a^2 P_A h} \tag{1}$$

In a helicogenic solvent, a copolymer chain may be dispersed in such a shape as that arranged side-by-side between two helical blocks (see Figure 2a). At the critical micelle concentration, each of the A and B blocks undergoes microphase separation and aggregates into characteristic micelles such as spherical, cylindrical, and lamella-like micelles, as illustrated in Figure 2b, in accordance with the copolymer composition, dimensions of blocks in the copolymer, and environmental conditions.

The Gibbs free energy ΔG per unit volume for the micelle formation is represented by the following equation

$$\Delta G = \Gamma \Delta W - T\Delta S \tag{2}$$

where Γ is the area of A/B interface per unit volume of micelle, ΔW is the interfacial free energy per unit area of A/B interface, and ΔS is the entropy change accompanied by the micelle formation. Now it is assumed[6] that all the junction points of A block and B block locate on spherical, cylindrical, and planar interface, respectively, for spherical micelle, cylindrical micelle, and lamella-like micelle, and, furthermore, the midpoint M of the B-block chain locates at the center of the micelle for spherical and cylindrical micelles, and at points in the center layer for lamella-like micelle, as illustrated in Figure 2b.

In the cases of spherical and cylindrical micelles, the packing density of the A component may be high at the interface and low at the outer surface, but this density gradient can be averaged by using N calculated from $N = 1/\{\frac{4}{3}\pi\langle s^2_{B/2}\rangle^{3/2} + \pi a^2 P_A h\}$. N is the number of junction points between A and B block per unit volume of micelle, i.e., twice the number of block copolymer per unit volume of micelle. It was assumed that the A component does not affect ΔS, though conformation of A-block side chains may differ along the radial direction for the spherical and cylindrical domains. Thus the entropy change ΔS for micelle formation is attributed only to the B-block chain.

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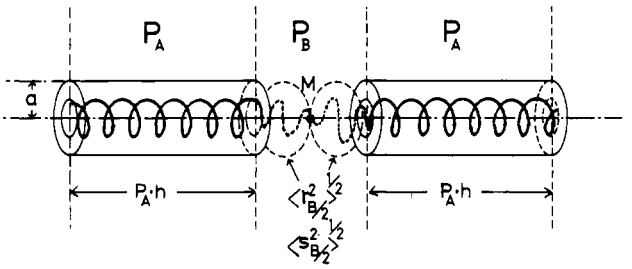

Figure 1. Molecular conformation of the A–B–A type block copolymer consisting of α-helical poly(γ-benzyl L-glutamate) as the A component and poly(*trans*-1,4-butadiene) as the B component.

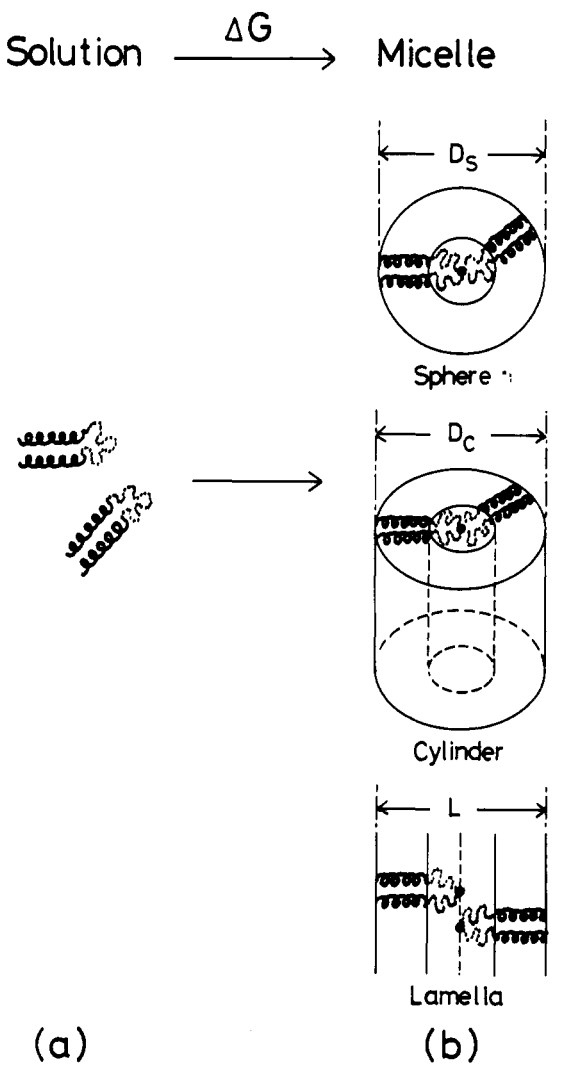

Figure 2. Model for micelle (spherical, cylindrical, and lamella-like micelle) formation of rod–coil–rod type block copolymer from solution at critical concentration.

Further, a B-block chain is assumed to be composed of two Gaussian chains connected at M point, neglecting the effect of the junction. In other words, an A–B–A block copolymer chain is regarded as a chain composed of two A–B type block copolymers connected at M, each consisting of an A block of P_A and a B block of $P_B/2$.

The above considerations lead to ΔS shown below:

$$\Delta S = N\Delta S_{B/2} = -\frac{3}{2}kN\left[\frac{R^2_{B/2}}{\langle r^2_{B/2}\rangle} - 1\right] \quad (3)$$

where k is the Boltzmann constant, $R_{B/2}$ is the end-to-end distance of the B/2 chain in the micelle, and $r_{B/2}$ is the end-to-end distance of the B/2 chain in solution at the critical concentration.

$R_{B/2}$ is related to D_s, D_c, and L (see Figure 2b) by the following equations.

$$R^3_{B/2} = \varphi_B(D_s/2)^3 \quad (4)$$

$$R^2_{B/2} = \varphi_B(D_c/2)^2 \quad (5)$$

$$R_{B/2} = \varphi_B(L/2) \quad (6)$$

Equations 4, 5, and 6 lead to Γ's for respective micelles as shown below:

$$\Gamma_s = 6\varphi_B^{2/3}(1/D_s) \quad (7)$$

$$\Gamma_c = 4\varphi_B^{1/2}(1/D_c) \quad (8)$$

$$\Gamma_l = 2/L \quad (9)$$

Substituting these equations in eq 2, we obtain the free energy ΔG of micelle formation for each type of micelle.

$$\Delta G_s = 6\varphi_B^{2/3}(1/D_s)\Delta W + \frac{3}{2}kTN\left\{(D_s/2)^2\frac{\varphi_B^{2/3}}{\langle r^2_{B/2}\rangle} - 1\right\} \quad (10)$$

$$\Delta G_c = 4\varphi_B^{1/2}(1/D_c)\Delta W + \frac{3}{2}kTN\left\{(D_c/2)^2\frac{\varphi_B}{\langle r^2_{B/2}\rangle} - 1\right\} \quad (11)$$

$$\Delta G_l = (2/L)\Delta W + \frac{3}{2}kTN\left\{(L/2)^2\frac{\varphi_B^2}{\langle r^2_{B/2}\rangle} - 1\right\} \quad (12)$$

By differentiating eq 10, 11, and 12 with respect to D_s, D_c, and L, respectively, and equating them to zero, we obtain the equilibrium micelle dimensions as

$$D_{s,eq} = \left(\frac{8\Delta W\langle r^2_{B/2}\rangle}{kTN}\right)^{1/3} \quad (13)$$

$$D_{c,eq} = \left(\frac{16\Delta W\langle r^2_{B/2}\rangle}{3\varphi_B^{1/2}kTN}\right)^{1/3} \quad (14)$$

$$L_{eq} = \left(\frac{8\Delta W\langle r^2_{B/2}\rangle}{3\varphi_B^2kTN}\right)^{1/3} \quad (15)$$

Interfacial Free Energy between A and B Component Polymers

Interfacial free energy ΔW (erg/cm^2) is equal to the interfacial tension γ_{AB} (dyn/cm). But nothing has been reported on the interfacial tension of the poly(γ-benzyl L-glutamate)/poly(*trans*-1,4-butadiene) system. Hence, γ_{AB} for this system was evaluated in the following way.

Hata et al.,[16] by extending Fowkes equation,[17] have reported that the interfacial tension γ_{AB} is related to the surface tensions, γ_A and γ_B, of A and B components, respectively, by the following equation

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A^a\gamma_B^a)^{1/2} - 2(\gamma_A^b\gamma_B^b)^{1/2} - 2(\gamma_A^c\gamma_B^c)^{1/2} = [(\gamma_A^a)^{1/2} - (\gamma_B^a)^{1/2}]^2 + [(\gamma_A^b)^{1/2} - (\gamma_B^b)^{1/2}]^2 + [(\gamma_A^c)^{1/2} - (\gamma_B^c)^{1/2}]^2 \quad (16)$$

where the surface tension γ is assumed to be composed of

Table I
Work of Adhesion, W_a, of Various Liquids on Poly(γ-benzyl L-glutamate) Calculated from Contact Angle θ at 20 °C and γ_A^a, γ_A^b, and γ_A^c Obtained from Equation 20

	lit. value[20,21]					calcd, dyn/cm			
	dyn/cm				deg				
liquid 1	γ_1	γ_1^a	γ_1^b	γ_1^c	θ	W_a	γ_A^a	γ_A^b	γ_A^c
hexadecane	27.7	27.7	0	0	0	55.4	27.7		
methylene iodide	50.8	46.8	4.0	0	38	90.8	27.7	22.1	
water	72.8	29.1	1.3	42.4	71	96.5	27.7	22.1	7.0
glycerol	63.4	37.4	0.2	25.8	63	92.2	27.7	22.1	6.4
formamide	58.2	35.1	1.6	21.5	63	84.6	27.7	22.1	3.1
thiodiglycol	54.0	39.2	1.4	13.4	44	92.8	27.7	22.1	8.5
ethylene glycol	47.7	30.1	0	17.6	44	82.0	27.7	22.1	8.4
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three contributions, γ^a, γ^b, and γ^c respectively from dispersion force, polar force, and hydrogen bonding force, i.e.,

$$\gamma_A = \gamma_A^a + \gamma_A^b + \gamma_A^c \quad (17)$$

$$\gamma_B = \gamma_B^a + \gamma_B^b + \gamma_B^c \quad (18)$$

Thus if we know the surface tensions and their three constituent contributions for both A and B components, then we can obtain the interfacial tension from eq 16. But such data are not available for poly(γ-benzyl L-glutamate) and poly(*trans*-1,4-butadiene).

Hence, we proceeded to obtain γ_A and γ_B from other aspects. The contact angle θ of liquid 1 on liquid 2 surface is related to three surface tensions, i.e., γ_1, the surface tension of liquid 1, γ_2, the surface tension of liquid 2, and γ_{12}, the interfacial tension of 1 and 2, by Young's equation.[18]

$$\gamma_1 \cos\theta = \gamma_2 - \gamma_{12} \quad (19)$$

On one hand, the work of adhesion, W_a, of liquids 1 and 2 is represented by Dupré's equation.[19]

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} = 2(\gamma_1^a\gamma_2^a)^{1/2} + 2(\gamma_1^b\gamma_2^b)^{1/2} + 2(\gamma_1^c\gamma_2^c)^{1/2} \quad (20)$$

Further, these equations lead to

$$W_a = \gamma_1(1 + \cos\theta) \quad (21)$$

Hence, if we have data on the contact angles for various liquid 1 of known values of γ_1, γ_1^a, γ_1^b, and γ_1^c on the surface of liquid 2, then we can calculate W_a from eq 21, from which we obtain γ_2^a, γ_2^b, and γ_2^c for component 2 from eq 20.

To obtain the surface tension of poly(γ-benzyl L-glutamate), contact angles of various liquids on poly(γ-benzyl L-glutamate) reported by Zisman et al.[20] were used. The values of γ_1, γ_1^a, γ_1^b, and γ_1^c of these liquids were cited from Hata's paper.[16] Table I shows the values W^a and γ_A^a, γ_A^b, and γ_A^c for poly(γ-benzyl L-glutamate) calculated from eq 21 and 20, together with the literature values of γ_1, γ_1^a, γ_1^b, γ_1^c, and θ. Thus we obtain $\gamma_A^a = 27.7$, $\gamma_A^b = 22.1$, and $\gamma_A^c = 6.7$ dyn/cm, which lead to $\gamma_A = 56.5$ dyn/cm for poly(γ-benzyl L-glutamate).

With respect to poly(*trans*-1,4-butadiene), data sustaining such detailed analysis as mentioned above have not been reported. Only the critical surface tension of this polymer was reported as 31 dyn/cm by Lee.[21] For this polymer, only the dispersion force is noted, and γ_B, the surface tension of this polymer, is equalized to γ_B^a. The work of adhesion, W_a, of a liquid 1 at the critical point for this polymer is obtained, from eq 21, by letting $\theta = 0$, as $W_a = 31 \times 2$ dyn/cm. If we assume that $\gamma_1 = \gamma_1^a$, then we can estimate the γ_B^a from $W_a = 2(\gamma_1^a\gamma_B^a)^{1/2}$. The value obtained was $\gamma_B = 31$ dyn/cm.

Table II
Molecular Parameters of A-B-A Type Block Copolymers

designation	M_w (whole polymer)	P_A (A block)	P_B (B block)
GBG-4	8.6×10^4	188	64
GBG-2	3.8×10^4	78	64
GBG-1	2.7×10^4	53	64

Finally, from the values of surface tension, $\gamma_A = 56.5$ dyn/cm and $\gamma_B = 31.0$ dyn/cm, the interfacial tension γ_{AB} between poly(γ-benzyl L-glutamate) and poly(*trans*-1,4-butadiene) was obtained as $\gamma_{AB} = 28.9$ dyn/cm from eq 16, in which both γ_B^b and γ_B^c were assumed to be zero.

Experimental Section

A-B-A type block copolymers composed of poly(γ-benzyl L-glutamate) of the degree of polymerization of P_A and polybutadiene of P_B, which is high in the trans isomer, were synthesized from amine-terminated polybutadiene of P_B and γ-benzyl *N*-carboxy-L-glutamate anhydride by the reaction in dioxane–methylene dichloride mixture at room temperature in the absence of moisture. The details of preparation of polymers, molecular weight characterizations, and conformation analysis of the polypeptide block were already mentioned in the preceding paper.[22]

Microheterophase structure was investigated with electron micrographs for thin films, cast from chloroform, the butadiene domains having been stained with osmium tetroxide.

Results and Discussion

The molecular parameters of the A–B–A type block copolymers are indicated in Table II.

The molecular weight distribution of amine-terminated polybutadiene is very sharp, hence, the B-block chain is assumed to be monodisperse. Since the block copolymers were synthesized by bifunctional polymerization, the degrees of polymerization P_A on both sides of the B block are the same; furthermore, the molecular weight heterogeneity of the A block is regarded as not being large from the information on NCA polymerization by the primary amine mechanism. Thus the molecular dimensions of the copolymers are said to be well-defined. The radius of the cross-section, a, of the α-helical A rod is cited as $a = 7.5$ Å from the literature data[23] obtained from small-angle X-ray scattering for poly(γ-benzyl L-glutamate) in solution. One (A.N.) of the authors has pointed out[24] from small-angle X-ray scattering for poly(N^e-carbobenzyloxy-L-lysine) in various solvents that the value of a depends on the kind of solvent. The solvent used in this study for the analysis of the microheterophase formation is chloroform.

With respect to poly(*trans*-1,4-butadiene), the relation

$$[\langle r^2_0\rangle_f/P]^{1/2} = 5.80 \text{ Å} \quad (22)$$

was reported by Wall,[25] in which P is the degree of polymerization, and $\langle r^2_0\rangle_f$ is the unperturbed mean-square end-to-end distance for the free rotation model. Further,

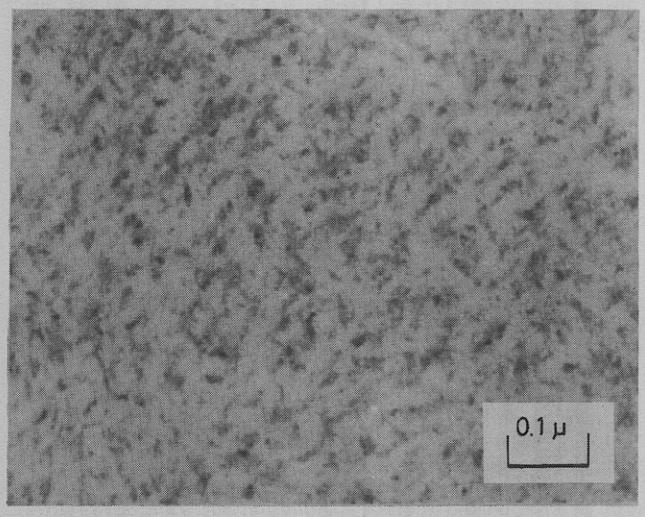

Figure 3. Electron micrograph of the GBG-4 membrane cast from chloroform at 25 °C. The dark portions correspond to B domains.

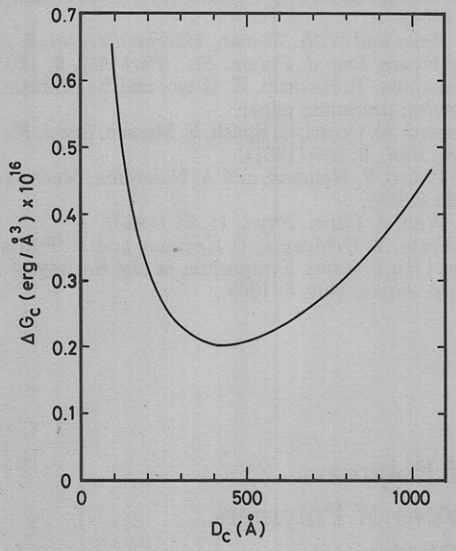

Figure 4. Gibbs free energy of micelle formation, ΔG_c, as a function of D_c for GBG-4.

Kurata[26] derived the following relation for poly(*trans*-1,4-butadiene)

$$[\langle r^2_0\rangle / \langle r^2_0\rangle_f]^{1/2} = 1.05 \qquad (23)$$

where $\langle r^2_0\rangle$ is the unperturbed mean-square end-to-end distance for the real chain. Accordingly, the root-mean-square end-to-end distance $\langle r^2\rangle^{1/2}$ in real solution is given by

$$\langle r^2\rangle^{1/2} = \alpha\langle r^2_0\rangle^{1/2} = \alpha 6.09 P^{1/2} \qquad (24)$$

Unfortunately, as α has not been found for chloroform, we choose $\alpha = 1.2$ as a most probable value.

As mentioned above, an A–B–A block copolymer chain is regarded as a chain composed of two A–B type block copolymers, each consisting of an A block of P_A and a B block of $P_B/2$. If we use $\alpha = 1.2$, then the end-to-end distance $\langle r^2_{B/2}\rangle^{1/2}$ for B chain having the degree of polymerization of $P_{B/2}$ is $\langle r^2_{B/2}\rangle^{1/2} = 41.34$ Å, and this value leads to $\langle s^2_{B/2}\rangle^{1/2} = 16.88$ Å.

The membranes were cast at 25 °C, so $T = 298$ K. Figure 3 reproduces the electron micrograph of the GBG-4 membrane cast from chloroform, in which the dark portions correspond to B domains. For this sample the cylindrical micelle model should be applicable.

The numberical values for GBG-4, $\varphi_B = 0.288$, $N = 1430 \times 10^{-8}$/Å^3, and $\langle r^2_{B/2}\rangle^{1/2} = 41.34$ Å, together with $\Delta W =$ 28.9 erg/cm^2, were inserted in eq 11. Thus ΔG_c as a function of D_c was shown in Figure 4. The minimum point of the curve should afford $D_{c,eq}$ given by eq 14. We obtain $D_{c,eq} = 437$ Å.

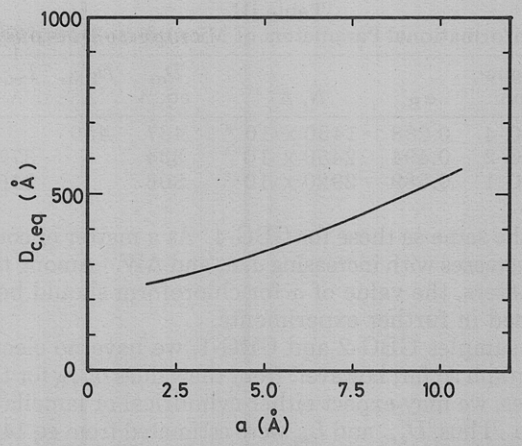

Figure 5. Dependence of the radius of cross-section of α-helix, a, on the equilibrium micelle dimension, $D_{c,eq}$, for block copolymer of $P_A = 188$, $P_B = 64$, $\varphi_B = 0.288$, $\alpha = 1.2$, and $\Delta W = 28.9$ dyn/cm.

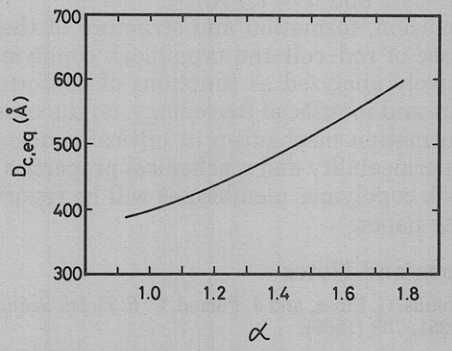

Figure 6. Dependence of the expansion factor, α, on the equilibrium micelle dimension, $D_{c,eq}$, for block copolymer of $P_A = 188$, $P_B = 64$, $\varphi_B = 0.288$, $a = 7.5$ Å, and $\Delta W = 28.9$ dyn/cm.

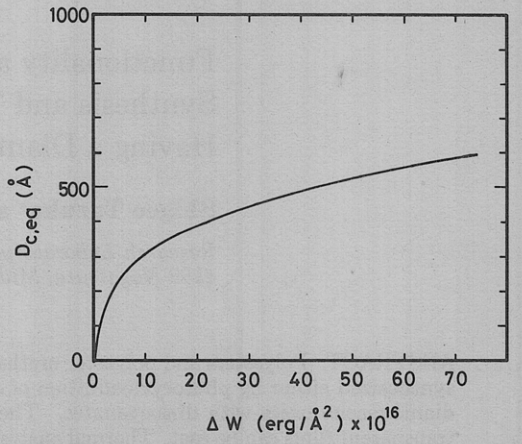

Figure 7. Dependence of the interfacial free energy, ΔW, on the equilibrium micelle dimension, $D_{c,eq}$, for block copolymer of $P_A = 188$, $P_B = 64$, $\varphi_B = 0.288$, $a = 7.5$ Å, and $\alpha = 1.2$.

If we assume that the micelle structure formed at the critical concentration is maintained as a whole at higher concentration until the solid structures are formed, we can compare the value of $D_{c,eq}$ with the dimension D_{EM} estimated from electron micrographs for cast membranes. The value estimated from Figure 3 is D_{EM} = ca. 450 Å. Agreement of both values seems to be satisfactory.

For the sake of general insight, dependences of a, α, and ΔW respectively on $D_{c,eq}$ are illustrated in Figures 4, 5, and 6, in which other parameters than the variable are assumed

Table III
Conformational Parameters of Microphase Domains

designation	α_B	N, Å^{-3}	D_c, eq, Å	D_{EM}, Å	L_{eq}, Å
GBG-4	0.288	1430×10^{-8}	437	450	
GBG-2	0.494	2450×10^{-8}	334		377
GBG-1	0.589	2920×10^{-8}	306		316

to be the same as those for GBG-4. As a matter of course, $D_{c,eq}$ increases with increasing a, α, and ΔW. Among these parameters, the value of α for chloroform should be determined in further experiments.

For samples GBG-2 and GBG-1, we have no electron micrograph so far; however, from the values of φ_B for these samples, we may expect either cylindrical or lamella-like micelle. Thus, $D_{c,eq}$ and L_{eq} were estimated from eq 14 and 15, respectively. Table III summarizes the data on microheterophase structures for GBG-4, GBG-2, and GBG-1. In Table III, all the calculations were performed by assuming $\alpha = 1.2$ and $a = 7.5$ Å.

In conclusion, formation and structure of the microheterophase of rod–coil–rod type block copolymer were quantitatively analyzed as functions of conformational parameters and interfacial free energy, on the basis of the micelle formation mechanism at critical concentration.

Water permeability and mechanical properties of such novel block copolymer membranes will be reported in a succeeding paper.

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Functionality and Structure of Polymers. 3. Synthesis and Thermal Properties of Polymers Having a Dianthracene Main Chain

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ABSTRACT: Polyesters and polyester urethanes having dianthracene units as main chain components were synthesized either by photocycloaddition of α,ω-dianthryl compounds or polyaddition of a diol containing dianthracene units with diisocyanates. These polymers are soluble in EDC or methylene chloride, and transparent films can be cast. Thermal analysis by means of torsional braid analysis (TBA) indicated distinct structural effects upon transition temperature. Polyester urethanes have higher T_g than analogous polyesters, which was attributed to hydrogen bonding in the former polymers. A temperature-dependent IR spectrum of a polyester urethane showed the participation of hydrogen bonding. The effect of hydrogen bonding is not only to affect T_g but also to control minute segment mobility above T_g which reflects on the thermal cleavage of the dianthracene main chain. Thermal decomposition of polyesters proceeded gradually above 90 °C, whereas polyester urethanes were stable up to a higher temperature probably due to restricted segment mobility caused by hydrogen bonding even above T_g. When hydrogen bonding nearly disappeared at elevated temperatures, dianthracene units in polyester urethanes were thermally cleaved rapidly. These structure–reactivity correlations were compared with the behaviors of polyesters and polyester urethanes having pendant anthryl groups presented in the previous article of this series of publication.

Anthracene and its derivatives are unique spectroscopic as well as reactive probes owing to their spectroscopic sensitivity to the state of aggregation, molecular interaction, and photochemical dimerization. We have been investigating photophysical and photochemical behaviors of various chromophores and fluorophores attached to polymers having well-defined structures.[1-5] When polyesters having pendant anthryl groups are used, the rate of photodimerization of pendant anthryl groups depends strongly on the mobility of polymer chain both in solution[2] and solid.[3] It was also found that thermal dissociation of dianthracene units in the photocross-linked polymers

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