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Effects of Hydrocarbon Chain Length of Cationic Surfactants on the Induction of the Secondary Structures of Anionic Polypeptides

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Received August 18, 1987

ABSTRACT: In their fully ionized state, the α-helix of poly(L-glutamic acid) (PGA) and the β-structure of poly(*S*-carboxymethyl-L-cysteine) (poly[Cys(CH_2COOH)]) were induced on addition of *n*-alkylammonium chlorides carrying a hydrocarbon chain longer than C_6. Hexylammonium chloride (C_6) induced the α-helix of PGA, while it did not induce the β-structure of poly[Cys(CH_2COOH)]. Inducing power measured as the concentration corresponding to half-induction, $C_{1/2}$, showed a linear dependence on chain length when plotted in a logarithmic way in the case of the α-helix for a range C_6–C_{12}, while a nonlinear dependence was found in the case of the β-structure induction for a range C_6–C_{14}. Different characters of hydrophobic interaction among hydrocarbon tails of surfactants bound to the polypeptides were also confirmed from fluorescence study of a hydrophobic probe; the hydrophobic region developed linearly with helical content while it exhibited a complex dependence on the β-content.

Introduction

We have been studying the effect of head groups of surfactants carrying a common hydrocarbon tail (dodecyl group) on the induction of the α-helix of poly(L-glutamic acid) (PGA)[1,2] and the β-structure of poly(*S*-carboxymethyl-L-cysteine) (poly[Cys(CH_2COOH)]).[3] These two polypeptides carry similar sidechains. The only difference is the sulfur atom present between the two methylene groups in the side chain of poly[Cys(CH_2COOH)], while it is absent in the side chains of PGA. In spite of carrying a long hydrocarbon tail, dodecyltrimethylammonium counterions were hardly effective in inducing the α-helix of PGA and completely ineffective in the induction of the β-structure of poly[Cys(CH_2COOH)].[2,3] In contrast, dodecylammonium ions effectively induced the secondary structures of both polypeptides.[1-3] Consequently, a question has arisen whether a long hydrocarbon chain is essential for the induction. In the present study, effects of chain length of hydrocarbon chains on the induction are hence examined by using hydrochlorides of primary amines, ranging from hexyl (C_6) to tetradecyl (C_{14}) groups.

Effects of chain length of surfactants have been extensively studied on their interactions with poly(L-lysine) and its side-chain homologues.[4] However, few studies on anionic polypeptides have been carried out to date.

Experimental Section

Molecular weights (degrees of polymerization) of PGA and poly[Cys(CH_2COOH)] were 1.1×10^5 (730) and 4.8×10^4 (300), respectively. *n*-Alkylamine (hexyl, octyl, decyl, dodecyl, and tetradecyl) was distilled under reduced pressure. The purity of distilled amines was more than 99% as checked with gas chromatography. Hydrochlorides of these amines (C_6–C_{14}) were prepared by passing hydrochloric acid gas through ethanol solutions of each amine followed by recrystallization from hot ethanol–acetone. *N*-phenyl-1-naphthylamine (NPN) (Nakarai Chemicals) was recrystallized 3 times from methanol–water.

Circular dichroism (CD) spectra were taken with a Jasco J-40A spectropolarimeter by using a cell of 1-cm light path. Fluorescence was measured with a Hitachi 650-10S spectrofluorimeter. These measurements were carried out at 25 °C. Concentrations of polypeptide C_p, surfactant C_D, salt C_s, and fluorescent dye C_{NPN} were expressed in molarity or monomolarity. Mixing ratios C_D/C_p were also used to specify compositions of solutions.

In the present study, aqueous solutions of polypeptides ($C_p = 1 \times 10^{-4}$ M) with no added salt were used unless otherwise stated. Dilute and unbuffered polypeptide solutions were carefully prepared under nitrogen atmosphere to prevent from contamination of carbon dioxide. A small amount of surfactant stock solution was added to the polypeptide solution under mixing.

Results

Dependence of the Induction on Hydrocarbon Chain Length. Conformations of the two polypeptides were determined based on their CD spectra, as shown in Figure 1. CD spectra of the α-helix of PGA are characterized by the "double minima" feature, i.e., negative bands at 208 nm and 222 nm, while induction of the β-structure of poly[Cys(CH_2COOH)] is accompanied by the development of a positive band around 200 nm. Residual ellip-

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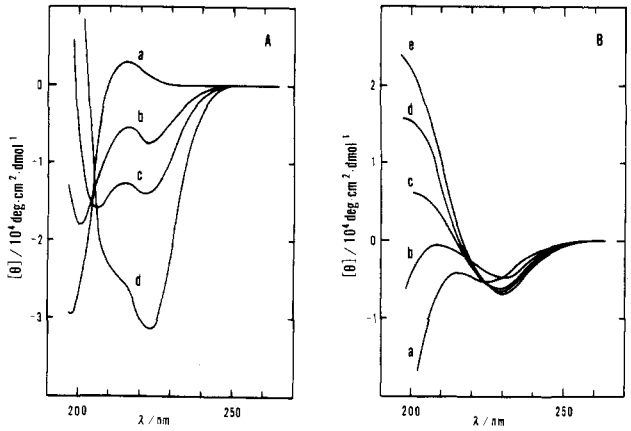

Figure 1. CD spectra of PGA (A) and poly[Cys(CH_2COOH)] (B) in the presence of decylammonium chloride. Mixing ratios: (A) (a) 0, (b) 1.6, (c) 7.1, and (d) 44.6; (B) (a) 0, (b) 5, (c) 10, (d) 15, and (e) 25.

ticity at 222 nm, $[\theta]_{222}$, was used as a measure of the helix content f_h of PGA, while that at 205 nm, $[\theta]_{205}$, was used for the β-content, f_β, of poly[Cys(CH_2COOH)]. Fractions of the secondary structures were calculated according to eq 1 and 2.

$$f_h = (2000 - [\theta]_{222})/4.2 \times 10^4 \quad (1)$$

$$f_\beta = ([\theta]_{205} + 1.1 \times 10^4)/3.9 \times 10^4 \quad (2)$$

In Figure 2, values of $[\theta]_{222}$ are plotted against mixing ratios C_D/C_P for four different surfactants (C_6–C_{12}) in the case of PGA. The maximum induction was found at mixing ratios of 5500 for C_6, 350 for C_8, 45 for C_{10}, and 3 for C_{12}. Precipitation took place in each case when the mixing ratio exceeded the highest value shown in Figure 2. The extent of maximum induction ($f_{h,max}$) also depended on chain length of surfactants in the following order: $C_8(1) > C_{10}(0.75) \sim C_{12}(0.75) > C_6(0.5)$. This order clearly indicates the aggregation tendency of polymer–surfactant complexes which increases with hydrocarbon chain length, except for C_6. Probably, hydrophobic complexes were readily salted-out at high ionic strengths of about 0.6 M in the case of C_6. Precipitation occurred about 2 or 3 h after the preparation of the solutions at the compositions of the maximum induction for C_8 and C_{10}, respectively.

In Figure 2B–D, dependence of $[\theta]_{222}$ on the mixing ratio is sigmoidal. This dependence resembles that of binding of surfactant ions by random coil polyions without any discrete conformational change.[5,6] Hence, f_h is expected to change linearly with bound amount of each surfactant. In Figure 2A, the sigmoidal behavior is not clearly seen. As shown in Figure 4A, however, the data on C_6 are consistent with those obtained on other chain lengths. We expect hence that interactions with PGA are qualitatively similar for these four surfactants.

In Figure 3, values of $[\theta]_{205}$ are plotted against mixing ratios for five different surfactants (C_6–C_{14}) in the case of poly[Cys(CH_2COOH)]. Formation of the β-structure accompanying aggregation generally follows a long time course extending over several hours. Data shown in Figure 3 were taken from the constant CD spectra, which were obtained 10–12 h after the preparation of the solution. On addition of C_6, the β-structure was not induced in solution up to 0.4 M. Precipitation occurred at concentrations beyond this value, which implied that the β-structure, if induced at all, was immediately salted-out at such a high ionic strength. Maximum induction of the β-structure was found at mixing ratios of about 200 for C_8, 35 for C_{10}, 5 for C_{12}, and 1.1 for C_{14}. Extent of the maximum induction

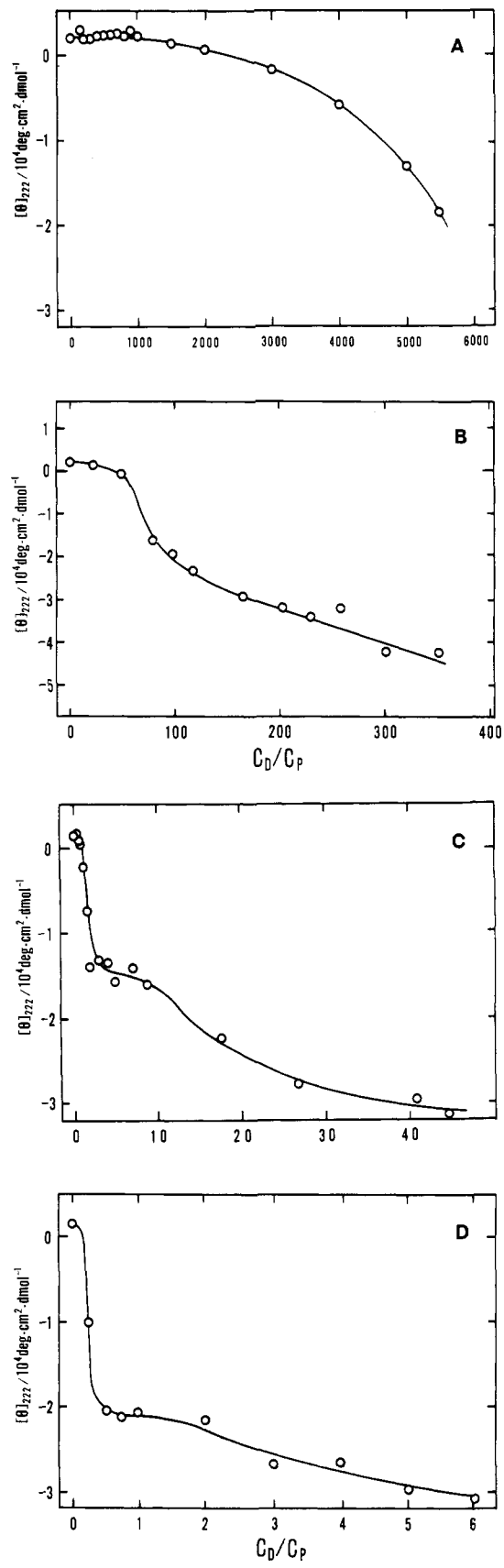

Figure 2. Dependence of $[\theta]_{222}$ of PGA on mixing ratio C_D/C_P: (A) hexylammonium chloride, (B) octylammonium chloride, (C) decylammonium chloride, and (D) dodecylammonium chloride.

($f_{\beta,max}$) depended on chain length in the following order: $C_8(1) > C_{10}(0.79) > C_{12}(0.67) > C_{14}(0.56)$. As in the case of the α-helix, precipitation took place in those mixing ratios higher than the maximum one shown in Figure 3. Solubilization took place, however, only in the case of the

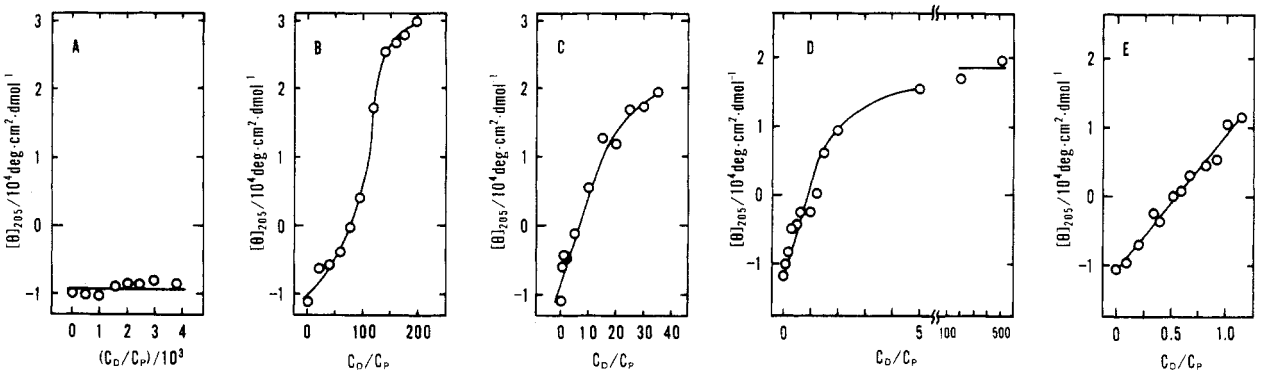

Figure 3. Dependence of $[\theta]_{205}$ of poly[Cys(CH_2COOH)] on mixing ratio C_D/C_P: (A) hexylammonium chloride, (B) octylammonium chloride, (C) decylammonium chloride, (D) dodecylammonium chloride, and (E) tetradecylammonium chloride.

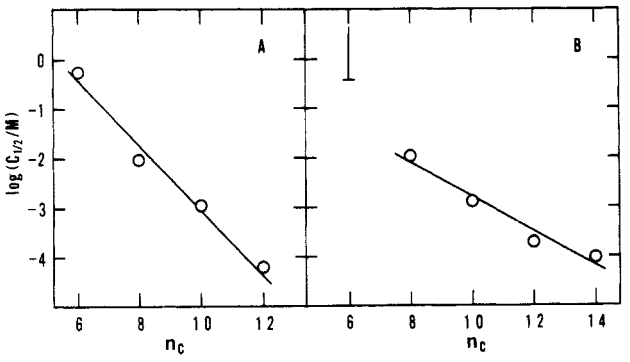

Figure 4. Dependence of inducing power on the number of carbon atoms n_c of hydrocarbon tails: $C_{1/2}$, concentrations required for the half-induction; (A) PGA and (B) poly[Cys(CH_2COOH)].

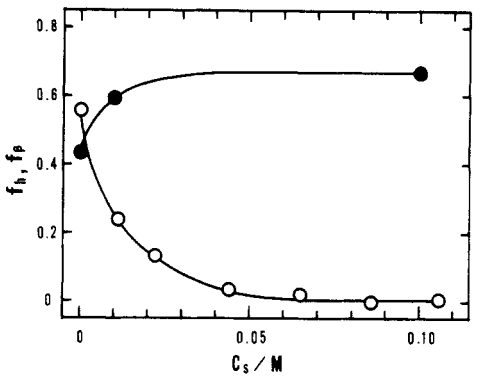

Figure 5. Effect of NaCl concentration (C_s) on the induction of the α-helix and the β-structure by dodecylammonium chloride: (○) f_h of PGA,[2] C_D/C_p = 1; (●) f_β of poly[Cys(CH_2COOH)], C_D/C_p = 1.5.

C_{12}–poly[Cys(CH_2COOH)] complex in the range of mixing ratios 200–400, as shown in Figure 3D. The β-structure was found in the solubilized solutions.

Sigmoidal behavior is seen for C_8 (Figure 3B) just as found in the α-helix induction. For C_{10}–C_{14}, however, dependence on the mixing ratio is not sigmoidal but linear. In this way, induction of the β-structure by C_8 differs not only quantitatively but also qualitatively from that by any one of its higher homologues.

As a measure of inducing power, we tentatively adopt a surfactant concentration $C_{1/2}$ corresponding to the half-induction point, i.e., $f_h = f_\beta = {}^1/_2$ at $C_D = C_{1/2}$. Values of $C_{1/2}$ for the α-helix were 0.55, 9.1×10^{-3}, 1.1×10^{-3}, and 5.0×10^{-5} M, for C_6, C_8, C_{10}, and C_{12}, respectively. Values of $C_{1/2}$ for the β-structure were 1.1×10^{-2}, 1.3×10^{-3}, 1.9×10^{-4}, and 9.7×10^{-5} M for C_8, C_{10}, C_{12}, and C_{14}, respectively. In Figure 4, values of log $C_{1/2}$ are plotted against n_c, carbon number of hydrocarbon chain of surfactants. In the case of the α-helix (Figure 4A), a linear relation approximately holds for C_6–C_{12}. The slope determined by the least-squares method was 0.65. If we extrapolate the line to $n_c = 4$, then we obtain $C_{1/2} \sim 10$ M, which is beyond the solubility and hence we can conclude that no induction occurs under the condition in the present study (no salt, $C_p = 1 \times 10^{-4}$ M) for butylammonium chloride and lower homologues.

In the case of poly[Cys(CH_2COOH)], a slightly concave curve is seen in Figure 4B for a range of C_8–C_{14} surfactants, reflecting the qualitatively different nature of the interaction in the case of C_8. The least-squares slope (Figure 4B) equals 0.35. The data on C_6 in Figure 3A only indicate that $C_{1/2}$ is greater than 0.4 M. This lower bound for $C_{1/2}$ is shown in Figure 4B at $n_c = 6$, which is much greater than the extrapolated value according to the straight line. Hence, inducing power exhibits a nonlinear dependence on chain length in the case of the β-structure. This indicates that C_6 interacts with the polypeptide differently from C_8 and other members. Induction of the β-structure can thus discriminate difference in hydrophobic interaction among surfactants of different chain lengths, contrary to the case of the α-helix induction.

From the results shown in Figure 4, we can conclude that hydrophobic interaction also plays an important role in the induction of both the α-helix of PGA and the β-structure of poly[Cys(CH_2COOH)] by cationic surfactants.

It is to be noted that values of $C_{1/2}$ are similar between the two conformations for C_8 and C_{10}.

Values of the slopes of Figure 4 differ greatly for the two polypeptides. However, at least two different factors contribute to the slope: effect of ionic strength and of chain length. In Figure 5, the effect of NaCl concentration on the induction by C_{12} is compared between the α-helix and the β-structure. As reported previously,[1-3] induction of the α-helix is inhibited in the presence of excess salt while that of the β-structure is not inhibited but slightly enhanced. When the effects of ionic strength shown in Figure 5 are taken into account, the slope in Figure 4B (for the β-structure) is expected to represent correctly the effect of chain length on hydrophobic interaction, while that in Figure 4A (for the α-helix) is contributed from the effect of ionic strength in addition to that of chain length.

Fluorescence Study Using a Hydrophobic Probe. The results in the preceding section indicate that hydrophobic interaction among hydrocarbon chains of bound surfactants certainly differs between PGA and poly[Cys(CH_2COOH)]. To obtain more information in this respect, fluorescence of a hydrophobic probe, *N*-phenyl-1-naphthylamine (NPN) was measured. This dye has been used in studying the phase transition of lipids.[7] As shown in the inset in Figure 6, fluorescence of NPN excited at

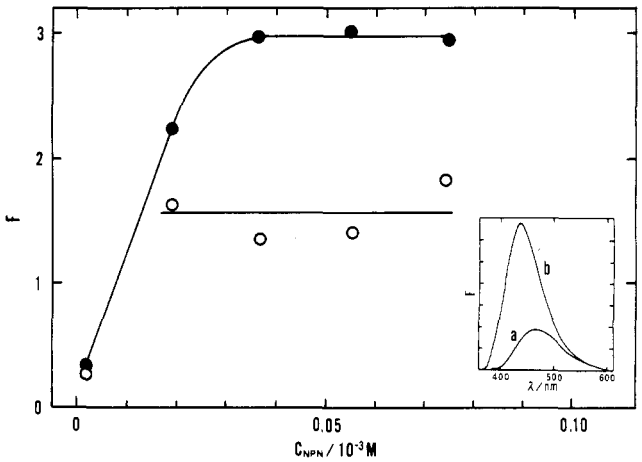

Figure 6. Concentration dependence of fluorescence F (arbitrary units) of NPN in the presence of PGA – dodecylammonium chloride complexes: C_D/C_p = 0.39 (○) and 0.77 (●). Inset: fluorescence spectra (C_{NPN} = 4 × 10^{-5} M) excited at 340 nm; (a) in water and (b) in the presence of PGA–dodecylammonium chloride complex, C_D/C_p = 0.39.

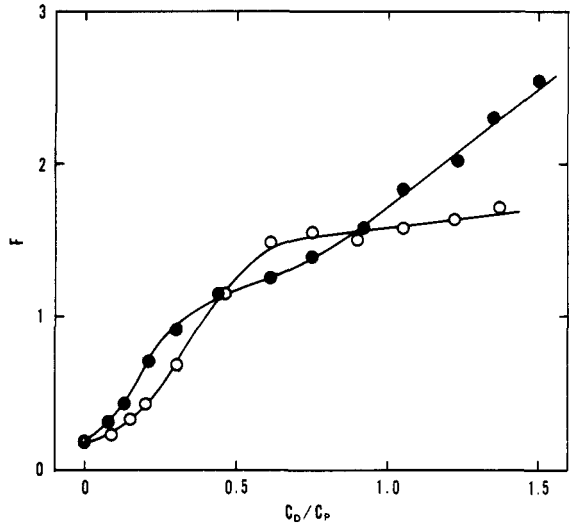

Figure 7. Dependence of the fluorescence intensity F (arbitrary unit) of NPN on the mixing ratio C_D/C_p of dodecylammonium chloride to polypeptides: C_{NPN} = 4 × 10^{-5} M; (○) PGA and (●) poly[Cys(CH_2COOH)].

340 nm increases accompanying a blue shift of emission maximum when surfactant–polypeptide complex is present. Enhancement of fluorescence was not observed when either of the two components (surfactant and polypeptides) was missing. Also, it was confirmed that the presence of NPN did not perturb the CD spectra of the polypeptides. Figure 6 indicates the dependence of fluorescence intensity on the dye concentration C_{NPN} at two different mixing ratios 0.39 and 0.77 of C_{12} to PGA at C_p = 1 × 10^{-4} M.

From Figure 6, it is concluded that results are independent of dye concentration if the latter is greater than 4 × 10^{-5} M. Dependence of fluorescence intensity on the mixing ratio was examined at this dye concentration as shown in Figure 7 for both PGA and poly[Cys(CH_2COOH)]. When the data are replotted in Figure 8 as functions of the fraction of the secondary structures, f_h and f_β, the difference between the two secondary structures shows up with respect to the hydrophobic regions of their complexes with surfactants. In the case of the α-helix, fluorescence increases linearly with f_h, indicating that the hydrophobic region develops linearly with helical amount. This is consistent with the dependence of f_h on C_D/C_p (Figure 2) showing that f_h is proportional

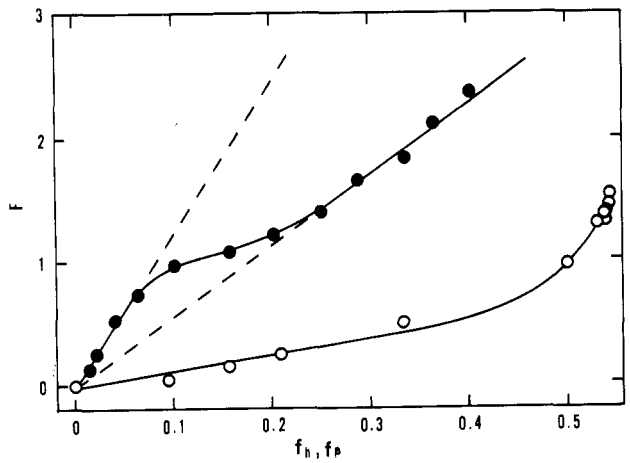

Figure 8. Fluorescence F (arbitrary unit) of NPN as functions of the content of the secondary structure: C_{NPN} = 4 × 10^{-5} M; (○) f_h of PGA and (●) f_β of poly[Cys(CH_2COOH)].

to the amount of bound surfactants. When f_h exceeds about 0.5, however, fluorescence increases sharply, which corresponds to the aggregation of the α-helices as suggested[1] and proved[2] previously.

On the other hand, dependence of the fluorescence on f_β is complex. There appears to be a transition from one region (f_β < 0.05) to another (f_β > 0.25). In each region, fluorescence increases linearly with f_β.

In the region f_β > 0.25, the slope of the straight line is about 3 times bigger than that for the α-helix. The difference can be explained as follows. Bound surfactants are expected to form a two-dimensional lattice (ca. 4.5 × 6.8 Å) on a β-sheet. Most of the hydrocarbon chains are accordingly surrounded by other chains and hence effectively shielded from the aqueous environment. On the other hand, in the case of PGA bound surfactants are scattered on a rod surface. Shielding of these hydrocarbon chains from the aqueous environment takes place effectively only through the aggregation of α-helices. Another possibility to explain the above difference in the slopes is to assume that more bound surfactants are required to induce the β-structure than the α-helix if compared at the same fraction of the two conformations.

Our results show a different behavior of the two conformations, i.e., the α-helix and the β-structure, with respect to hydrophobic interaction of bound surfactant hydrocarbon chains, in addition to the differences previously reported on the effects of head groups[1-3] and on the ionic strength.

Discussion

Dependence on hydrocarbon chain length of the hydrophobic interaction has been systematically examined. For instance, the logarithm of the critical micelle concentration (cmc) decreases linearly with the number of carbon atom n_c[8] for various series of surfactants. Values of slopes ∂ log (cmc)/∂n_c are −0.49 for hexaethylene glycol alkyl monoether, −0.5 for alkyl betaines and alkyltrimethylammonium bromide in 0.5 M NaBr, and −0.44 for alkyl sulfates in water.[8] Surface tension of aqueous solutions decreases with surfactant concentration. The concentration giving a specified value of surface tension also depends on n_c. From the famous Szyszkowski relation,[9] we have ∂ log (cmc)/∂n_c = −0.49 for fatty acids of C_1–C_6.

In the present study, log $C_{1/2}$ for the α-helix formation follows this general linear dependence on n_c for a range C_6–C_{12}. In contrast, the β-structure induction exhibits a nonlinear dependence on n_c, since the data for C_6 are not consistent with the straight line drawn through four points

(C_8–C_{14}) based on the least-squares method. In the present study, hydrophobic interaction among bound surfactants was monitored through the conformational change of polypeptide chains as a result of their interaction with surfactants. A slight difference in the interaction can be largely amplified by the cooperative nature of conformational change of the polypeptide. Hence observed nonlinear dependence most likely originates from the present sensitively detecting device, which makes use of characteristic property of the β-structure.

A nonlinear dependence of the hydrocarbon chain length of surfactants has been found in their binding to polyacrylate and its copolymers.[10] Attractive interaction, as monitored in terms of conductivity of salt-free solutions, decreased with decreasing chain length down to C_6, which was attributed to the decrease in the hydrophobic interaction. However, attractive interaction increased as the chain length further decreased from C_6, leading to a break around C_6. The increase was attributed to the enhancement of electric attraction due to the decrease of counterion size.[10] The trend after the break was opposite to that found in the present study. The different behavior found on short chain lengths between the two studies most likely arises from different properties employed to monitor the polyion–counterion interaction. Electrostatic interaction affects the conductivity but it alone cannot induce the β-structure, as shown in the study on dodecyltrimethylammonium counterions. Consequently, observed nonlinearity represents different things. In the present study, it represents nonlinear dependence of the hydrophobic interaction on the hydrocarbon chain length, while in the other case it occurs as a result of superposition of two interactions.

Acknowledgment. We thank Dr. S. Murata, Department of Chemistry, College of General Education, Nagoya University, for his skillful cooperation in the gas chromatography measurements. We also thank Mr. K. Fujio for helpful discussion.

Registry No. PGA (homopolymer), 25513-46-6; PGA (SRU), 24991-23-9; poly[Cys(CH_2COOH)] (homopolymer), 29433-95-2; poly[Cys(CH_2COOH)] (SRU), 31851-29-3; decylammonium chloride, 143-09-9; hexylammonium chloride, 142-81-4; octylammonium chloride, 142-95-0; dodecylammonium chloride, 929-73-7; tetradecylammonium chloride, 1838-04-6.

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Probe Molecule Diffusion in Polymer Solutions

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Received March 31, 1987; Revised Manuscript Received October 21, 1987

ABSTRACT: Translational diffusion coefficients of probe molecules have been examined as functions of polymer concentration and temperature in polystyrene and polyisoprene solutions in tetrahydrofuran (THF). The probes were azo dyes, methyl red and methyl yellow. Concentration range examined for polystyrene solution was 0–68.2 wt % while that for polyisoprene solution was for the entire range, pure solvent to pure bulk polymer. The transient optical grating technique of forced Rayleigh scattering was used to determine the diffusion coefficients. Two free volume theories, Fujita and Vrentas–Duda, were compared relative to their predictions of the concentration dependence of the probe diffusion coefficient under isothermal conditions. Both theories provide reasonable agreement with the experiment for the polyisoprene–THF system over the entire concentration range, whereas agreement is less satisfactory with the polystyrene–THF even over a narrower concentration range. In addition, temperature and concentration dependences were simultaneously examined by combining the Vrentas–Duda model with the Williams–Landel–Ferry theory.

It has long been established that one may learn about local segmental motions of polymer molecules from the study of small molecule diffusion in solutions, particularly at high polymer concentrations or in the undiluted state.[1,2] In the vast literature of small molecule diffusion in polymer systems,[1,3–12] much attention is directed toward the comparison of the frictional resistance of probe or diluent molecules undergoing translational diffusion to the resistance of segmental motion of the host polymer molecules. It is this segmental resistance which is often considered in the formulation of molecular and phenomenological theories of chain dynamics; it is often characterized by a friction coefficient ζ_0 of a monomer unit.[2] In particular, a free volume theory by Fujita[1] has been demonstrated to be rather successful in the interpretation of the concentration dependence[1,3–7] and the temperature dependence[1,3,7–9] of ζ_0 via small molecule diffusion. The free volume concept has been used to interpret the temperature dependence of steady-shear viscosity of polymeric systems via the temperature shift factor a_T; from this theory one is able to derive the Williams–Landel–Ferry (WLF) equation[13] which has proven to be widely applicable for numerous viscoelastic quantities.[2] However, it appears less clear whether the Fujita free volume theory should be applicable to the region of low polymer concentration.[1]

A more generalized approach to the free volume concept of small molecule and segmental motion has been developed by Vrentas and Duda.[14,15] In the Vrentas–Duda extension, several restrictive assumptions implicit in the Fujita treatment have been removed,[14] allowing for a possibility to extract the collisional dynamics information

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