NOTES

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Properties of Polysarcosine Dodecylamide of Low Molecular Weight

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Properties of polysarcosine dodecylamide (*N*-dodecylpolysarcosineamide) in aqueous solution vary systematically with the degree of polymerization of the polymer, since the hydrophilic part of this amphiphilic polymer is proportional to the degree of polymerization.[1] However, unexpected properties were observed with polysarcosine dodecylamide of low molecular weight, which was synthesized (degree of polymerization: 5) and its properties examined. *N,N'*-dimethyldiketopiperazine was prepared and its properties were compared with that of polysarcosine dodecylamide of low molecular weight synthesized by Izumi *et al.*[1] From the results, it is concluded that the abnormal properties of polysarcosine dodecylamide of low molecular weight reported previously are caused by the presence of *N,N'*-dimethyldiketopiperazine in the products of polymerization.

Experimental

Polysarcosine dodecylamide was prepared by polymerization of *N*-carboxy-sarcosine anhydride in dioxane with dodecylamine as initiator.[1] *N*-carboxy-sarcosine anhydride was made from sarcosine by the phosgene method.[2] A solution of 0.483 g of dodecylamine in dioxane (59 m*l*) was added with vigorous stirring to a solution of 1.5 g of *N*-carboxy-sarcosine anhydride in dioxane (100 m*l*) at room temperature. The molar ratio of anhydride to initiator, [A]/[I], was chosen to be 5. The reaction mixture was put to stand overnight at room temperature. The polymer was precipitated by pouring the reaction mixture into ethyl ether. A white waxy solid was obtained. This polymer is denoted by PSD-5S.

Found: C, 54.64; H, 9.39; N, 15.44%. Calcd for $C_{27}H_{52}N_6O_5$: C, 59.97; H, 9.69; N, 15.54%.

N,N'-dimethyldiketopiperazine was obtained by heating sarcosine at 215°C for about 3 hr.[3] The product was recrystallized 3 times from ethanol and obtained as clear needles, mp 144°C, molecular weight 142 (by mass spectrum).

Needle-like crystals were extracted from the materials denoted by PSDA-5[1] with ethanol. 0.637 g of PSDA-5 was dissolved in 12 m*l* of ethanol. A trace amount of white powder was removed from the solution by filtration. The filtrate was evaporated to about 2 m*l* under reduced pressure, and needle-like crystals, mp 144°C, molecular weight 142 (by mass spectrum), were obtained at about −15°C. The crystals showed no melting point depression (144°C) on being mixed with *N,N'*-dimethyldiketopiperazine.

Found: C, 50.42; H, 7.09; N, 19.70%. Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71%.

Surface tension was measured by the drop-weight method. Measurements of electric conductance were performed with an AC-bridge (Yokogawa, 4225A). The cell constant was 0.535, as calibrated with 0.01 M potassium chloride. All measurements were carried out at 25°C. NMR spectra were recorded with a Varian A-60 apparatus. Polymers were dissolved in D_2O at a concentration of 10 wt%. IR spectra were determined in KBr pellet with a Yamaco ISG-25 spectrometer. Mass spectra were measured with a Hitachi RMU-6E operating at 70 eV.

Results and Discussion

The surface tension (γ) *vs.* concentration (c) curve for PSD-5S in aqueous solution is shown in Fig. 1. The results obtained by Izumi *et al.*[1] are also shown in Fig. 1. The critical micelle concentration (CMC) of PSD-5S was found to be 0.033 g/d*l*. The present preparation gave a much clearer CMC and a much smaller surface tension than those calculated from the γ-c curve obtained by Izumi *et al.*[1] The specific conductance (κ) *vs.* concentration (c) curve for PSD-5S is shown in Fig. 2. The value of κ_0 obtained by extrapolating the concentration to zero is in accord with the value of water. The CMC value at the bend in

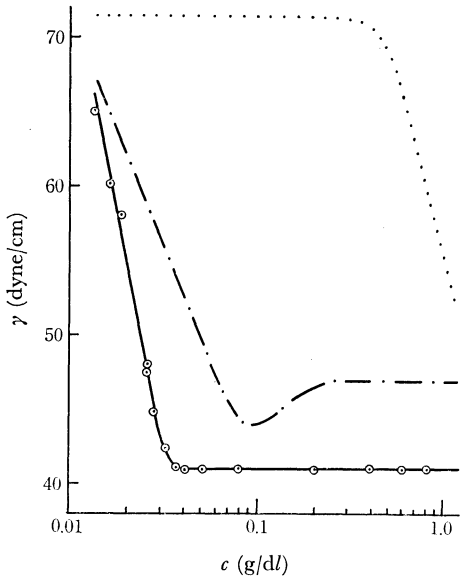

Fig. 1. Surface tension (γ) *vs.* concentration (c) curve for PSD-5S (-⊙-⊙-) at 25°C
(PSDA-5; ·····, PSDA-10; -·-·-, reported by Izumi *et al.*)

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1) T. Izumi, A. Suzuki, and T. Isemura, presented at the 21st Symposium on Colloid and Surface Chemistry, Chemical Society of Japan, Kyoto, 1968.

2) T. Isemura, S. Ikeda, F. Tokiwa, and J. Noguchi, This Bulletin, **34**, 1236 (1961); E. R. Blout and R. H. Karlson, *J. Amer. Chem. Soc.*, **78**, 941 (1956).

3) F. Mylieus, *Ber.*, **17**, 286 (1884); E. Fischer, *ibid.*, **39**, 530 (1906); *ibid.*, **65**, 1182 (1932).

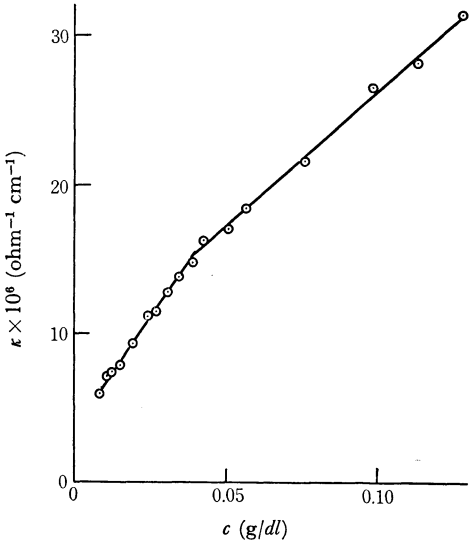

Fig. 2. Specific conductance (κ) *vs.* concentration (c) curve for PSD-5S at 25°C.

the κ-c curve was 0.04 g/dl. The NMR spectrum for PSD-5S is shown in Fig. 3. The degree of polymerization was found to be 5.2 from the ratio of the integrated signal from the dodecylamine residue and that from the sarcosine residue. This approximately corresponded to the ratio of anhydride to initiator.

With aqueous solution of *N,N'*-dimethyldiketopiperazine of concentration up to 1 g/dl, no decrease in surface tension was observed and the value of the specific conductance was $(2.5—2.8) \times 10^{-6}$ ohm^{-1}cm^{-1}, which corresponds to that of water. The NMR spectrum of *N,N'*-dimethyldiketopiperazine had two single peaks, as shown in Fig. 3. The spectrum is similar

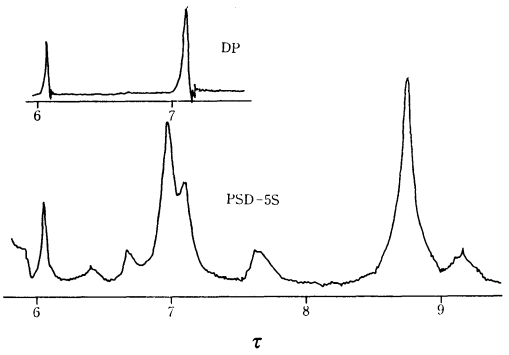

Fig. 3. NMR spectra of polysarcosine dodecylamide (PSD-5S) and *N,N'*-dimethyldiketopiperazine (DP) in D_2O at 60MHz.

to that for PSDA-5.[1)]

The fragmentation pattern in the mass spectrum of needle-like crystals extracted from PSDA-5 was in accord with that of *N,N'*-dimethyldiketopiperazine and molecular weights of these compounds were estimated to be 142. The IR spectrum of needle-like crystals was similar to that of *N,N'*-dimethyldiketopiperazine. The compound extracted from PSDA-5 was proved to be identical with *N,N'*-dimethyldiketopiperazine by the mixed melting point, elemental analysis, and studies of its IR, NMR, and mass spectra.

Thus, it is concluded that the materials reported to be polysarcosine dodecylamide, (PSDA-5) are composed mainly of *N,N'*-dimethyldiketopiperazine. The formation of *N,N'*-dimethyldiketopiperazine during polymerization of PSDA-5 might depend on the conditions for polymerization; the initiator was added to the reaction mixture in a very high concentration and at a high temperature of about 80°C.