(26) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", 2d ed, Wiley-Interscience, New York, N.Y., 1975.
(27) This sample of *cis*-PBD was generously provided by the Polymer Corporation Limited of Sarnia, Ontario, Canada.
(28) R. H. Becker, C. U. Yu, and J. E. Mark, *Polym. J.*, **7**, 234 (1975).
(29) We are indebted to Dr. Earl C. Gregg, Jr., of the B. F. Goodrich Co., not only for providing these materials but also for very valuable guidance with regard to curing and subsequent purification (extraction) techniques.
(30) J. E. Mark, *J. Phys. Chem.*, **68**, 1092 (1964).
(31) R. S. Jessup, *J. Res. Natl. Bur. Stand.*, **60**, 47 (1958).
(32) R. M. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972).
(33) C. U. Yu and J. E. Mark, *Macromolecules*, **6**, 751 (1973).
(34) C. U. Yu and J. E. Mark, *Polym. J.*, **7**, 101 (1975).
(35) D. Froelich, D. Crawford, T. Rozek, and W. Prins, *Macromolecules*, **5**, 100 (1972).
(36) J. Furukawa, S. Yamashita, T. Kotani, and M. Kawashima, *J. Appl. Polym. Sci.*, **13**, 2527 (1969).
(37) B. E. Eichinger, *Macromolecules*, **5**, 496 (1972).
(38) W. W. Graessley, *Macromolecules*, **8**, 186, 865 (1975).
(39) R. T. Deam and S. F. Edwards, *Phil. Trans. R. Soc. London, Ser. A*, **280**, 317 (1976).
(40) H. M. James and E. Guth, *J. Chem. Phys.*, **15**, 669 (1947).
(41) M. Cesari, L. Gargani, G. P. Giuliani, G. Perego, and A. Zazzetta, *J. Polym. Sci., Part B*, **14**, 107 (1976).
(42) P. J. Flory, *Science*, **124**, 53 (1956).
(43) J. E. Mark, *J. Am. Chem. Soc.*, **88**, 4354 (1966).

Intrachain Reactions of a Pair of Reactive Groups Attached to Polymer Ends. 3. Intrachain Charge-Transfer Complex on Polysarcosine Chains Having Terminal Electron Donor and Terminal Electron Acceptor Groups in Chloroform Solution

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ABSTRACT: Polysarcosine having a terminal *p*-dimethylaminoanilide group and a terminal 3,5-dinitrobenzoyl group was synthesized. The number-average degree of polymerization $\bar{n}$ was varied from 6 to 25. In chloroform solution this polymer showed a distinct absorption band around 455 nm, which was attributed mostly to intramolecular charge-transfer interactions. The extinction coefficient of the charge-transfer complex was determined for low molecular weight model compounds. Using the same extinction coefficient, the fraction of polymers forming intrachain charge-transfer complex was evaluated at infinite dilution. The fraction was about 0.15 for $\bar{n}$ = 6 and decreased asymptotically with increasing $\bar{n}$ finally to 0.03 for $\bar{n}$ = 25. These values are almost 20–100 times as large as those estimated from the Monte Carlo calculation and on the basis of the intramolecularly catalyzed hydrolysis on polysarcosine chain. This indicates that the cyclized conformations of polysarcosine chain are greatly stabilized by the formation of intrachain charge-transfer complex. The fraction of the cyclized polymer was decreased with increasing temperature for short chains. The thermodynamic parameters characterizing the conformational change required for cyclization in chloroform were obtained and compared with those for the same reaction in ethanol solution, as well as those for the intramolecularly catalyzed hydrolysis on polysarcosine chain in aqueous solution.

Three-dimensional structure of protein is stabilized by intramolecular secondary valence forces, such as hydrogen bonds, electrostatic forces, hydrophobic forces, and charge-transfer interactions. The nature of these forces has been subjected to considerable investigations and their total effect on the protein structure has now been clarified to some extent.[1] However, the effect of the individual force on the protein structure seems still unclear, since these secondary valence forces are operating in a protein molecule concurrently and cooperatively. In view of this situation, it is hoped to investigate the effect of the individual secondary valence force in much simpler macromolecular systems, such as X–Y-type polymers where X and Y are interacting groups.

In this series of investigations the intrachain reactions and interactions have been studied on X–Y-type polymers.[2,3] In the first paper the intrachain reaction on polysarcosine chain was studied,[2] and the experimental results were compared with the Monte Carlo calculation of the ring-closure probability of polysarcosine chain in the second paper.[3] In the above case it was assumed that the equilibrium conformations of polysarcosine chain were not greatly affected by the incorporation of the terminal reactive groups. The assumption is reasonable, as far as no interactions exist between the pair of terminal groups. In the present study electron-donating and electron-accepting groups were attached to respective ends of the polysarcosine chain and the effects of an intrachain charge-transfer force upon the conformation of polymer chain were discussed. There are several reasons to study the charge-transfer interaction as a secondary valence force in biopolymers.[4,5] (1) The formation of charge-transfer complex can be easily detected by the characteristic absorption band of the charge-transfer complex which occurs at a longer wavelength than the component species. (2) The amount of the complex is determined directly from the intensity of the charge-transfer band, provided that the extinction coefficient is given. (3) The measurement can be carried out under a variety of conditions of the polymer concentration, solvents, and temperature.

Experimental Section

Materials. The chemical structures of compounds used in this study are illustrated in Figure 1.

Synthesis of *N*-Acetyl-*N'*,*N'*-dimethyl-*p*-phenylenediamine (I). To an ice-cooled solution of acetic anhydride (5 g) in ether (30 ml) with a small amount of pyridine (1 g) was added the ethereal solution of freshly distilled *N*,*N*-dimethyl-*p*-phenylenediamine (3.5 g/20 ml). After 1 h the precipitated product was collected, washed with ether, and recrystallized repeatedly from benzene and ethylacetate giving colorless plates of I (2.7 g): mp 133–134 °C (lit.[13] 134–135 °C). Anal. Calcd: C, 67.4; H, 7.9; N, 15.7. Found: C, 67.7; H, 8.1; N, 15.8.

Synthesis of *N*-(3,5-dinitrobenzoyl)sarcosine Dimethylamide (II). To an ice-cooled solution of sarcosine dimethylamide (1.2 g) in benzene (15 ml) was added the benzene solution of 3,5-dinitrobenzoyl chloride (2 g/55 ml) with a catalytic amount of pyridine. After 1 h the

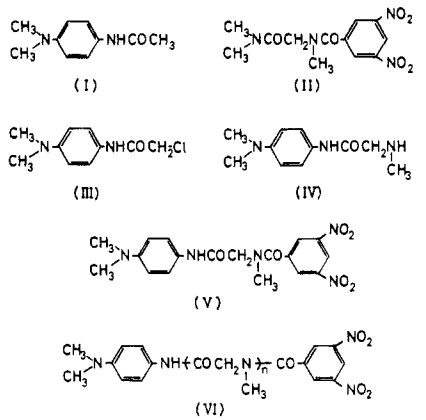

Figure 1. Structures of compounds used in this study.

precipitate was filtered off and the filtrate was evaporated. The residual oil was crystallized after standing overnight (crude yield: 2.6 g). Repeated recrystallizations from ethanol yielded a colorless product of II: mp 134–135 °C. Anal. Calcd: C, 46.5; H, 4.6; N, 18.1. Found: C, 46.4; H, 4.4; N, 17.9.

Synthesis of *N*-Chloroacetyl-*N'*,*N'*-dimethyl-*p*-phenylenediamine (III).[6] A freshly distilled *N*,*N*-dimethyl-*p*-phenylenediamine (13.6 g) was dissolved in water (100 ml) containing sodium hydroxide (5 g). To the ice-cooled aqueous solution, chloroacetyl chloride (11.3 g) in ether (50 ml) was added dropwise under vigorous stirring. After standing at room temperature for about 20 min, the precipitated product was collected and washed repeatedly with water and ether. The crude product (16.7 g) was reprecipitated from ethanol repeatedly to colorless needles of III: mp 144–145 °C (lit.[14] 140.0–140.5 °C). Anal. Calcd: C, 56.5; H, 6.2; N, 13.2; Cl, 16.7. Found: C, 56.3; H, 6.3; N, 13.1; Cl, 16.6.

Synthesis of Sarcosine (*p*-Dimethylamino)anilide (IV). Ethanol solution (25 ml) containing 30% methylamine was cooled by ice and III (3.4 g) in chloroform (70 ml) was slowly added. After standing for 4 days the solvents were evaporated and benzene (50 ml) was added to the residual oil. NaOH solution (2 N) (5 ml) was then added with shaking and the benzene layer was dried over anhydrous potassium carbonate. Evaporation of the benzene gave an oily product which was crystallized after standing overnight at room temperature. The crude crystal (3.0 g) was recrystallized repeatedly from benzene/petroleum ether giving colorless product of IV: mp 55.8–56.8 °C. Anal. Calcd: C, 63.7; H, 8.3; N, 20.3. Found: C, 63.5; H, 8.4; N, 19.7.

Synthesis of *N*-(3,5-Dinitrobenzoyl)sarcosine (*p*-Dimethylamino)anilide(V). Compound IV (1 g) was dissolved in benzene (30 ml) containing a small amount of pyridine. A solution of 3,5-dinitrobenzoyl chloride (1.2 g) in benzene (30 ml) was then added dropwise to the ice-cooled solution under stirring. After 2 h the mixture was shaken with dilute NaOH solution and the benzene layer was dried and evaporated to dryness. The crude crystal was dissolved in ethanol containing a small amount of hydrochloric acid and poured into aqueous sodium bicarbonate solution. The reprecipitation was repeated giving a reddish crystal of V: mp 218.5–220 °C.

Synthesis of Polysarcosine Having a Terminal *p*-Dimethylaminoanilide Group and a Terminal 3,5-Dinitrobenzoyl Group (VI). Sarcosine *N*-carboxyanhydride (NCA) was polymerized in DMF solution with IV as initiator. After the polymerization was completed (overnight), a threefold excess of 3,5-dinitrobenzoyl chloride was added to the solution. After 1 day the polymer was precipitated in ether–acetone mixture and washed repeatedly with ethyl acetate and acetone. To make the terminal dimethylamino group free from hydrogen chloride, the polymer was dissolved in methanol and passed through the anion-exchange column (Amberlite IR-45). The solution was then poured into ether and the precipitated polymer (VI) was collected, washed, and dried thoroughly under vacuum. No impurity was detected by the gel chromatography with the use of Sephadex LH-20 column in methanol solution. The number-average degree of polymerization $\bar{n}$ was calculated according to eq 1.[7]

$$\bar{n} = [\mathrm{NCA}]/[\mathrm{IV}] + 1 \qquad (1)$$

The calculated values were compared with the experimental values measured by vapor pressure osmometry.

A polymer sample having a terminal *p*-dimethylaminoanilide group and a terminal acetyl group was also synthesized and treated with dinitrobenzoyl chloride by the same procedure as the synthesis of polymer VI. The absorption spectrum of this polymer was virtually equivalent to the spectrum of a polymer sample before treating with the acid chloride, indicating that *p*-dimethylaminoanilide group suffered no chemical modification during the dinitrobenzoylation.

Purification of Solvents. DMF used as a polymerization solvent was distilled twice under reduced pressure from calcium hydride. Chloroform used for the optical measurements was shaken with concentrated H_2SO_4, water, dilute NaOH, and finally water. After the chloroform was dried with anhydrous potassium carbonate, it was fractionally distilled immediately before use.

Table I
Characterization of Polymer Samples

$\bar{n}$[a]	$\bar{M}_n \times 10^{-2}$ Calcd[a]	$\bar{M}_n \times 10^{-2}$ Obsd[b]	Fraction of polymer carrying terminal group: Acceptor[c]	Fraction of polymer carrying terminal group: Donor[d]
6	7.5	7.6	0.90	0.86
11	11.6	11.1	0.92	0.89
16	14.2	14.5	0.96	0.85
21	17.6	17.9	0.93	
25	20.2	21.4	0.94	
32	25.6	25.6	0.87	

[a] Calculated value according to eq 1. [b] Experimental value with vapor pressure osmometry. [c] Measured by the absorption at 330 nm. [d] Measured by the NMR method.

Methods

The number-average molecular weight of polymer samples was determined in ethanol solution with a Hitachi-117 vapor pressure osmometer using II as the reference substance. The molecular weight was calculated by averaging the values obtained in triplicate experiments at different polymer concentrations.

UV and visible spectra were measured by a Shimadzu UV-210 instrument with a thermostatted cell holder. Quartz cells with 10-, 50-, and 100-mm path lengths were used.

Least-squares calculations of the association constant and the extinction coefficients for the charge-transfer complex were made according to the method of Wentworth et al.[8] The program coded by us was computed at the Data Processing Center of Kyoto University.

Results and Discussion

Characterization of Polymer. The number-average molecular weight of the functionalized polysarcosine was measured by vapor pressure osmometry. The results were compared with the values calculated from eq 1, assuming a quantitative incorporation of the 3,5-dinitrobenzoyl group to an end. The observed and the calculated values are listed in Table I. The agreement between them is quite good. In the following discussion the calculated value was used as the molecular weight of a polymer sample. The good applicability of eq 1 suggests that the Poisson-type molecular weight distribution was obtained for the polymer.[7] This has been confirmed for the polymer samples obtained with sarcosine dimethylamide as initiator.[9] The amount of 3,5-dinitrobenzoyl end group of the polymer was determined on the basis of the absorbance of the dinitrobenzoyl group at 330 nm in ethanol solution. The obstruction which arose from the absorption of the *p*-dimethylamino anilide end group was eliminated by adding a small amount of hydrochloric acid to the solution. The hydrochloride of the *p*-dimethylamino anilide group shows virtually no absorption at 330 nm. The extinction coefficient of the dinitrobenzoyl end group was taken equal to that of the model compound II. The fraction of dinitrobenzoyl end group in a polymer as determined by the ratio of the observed value to the theoretical value of the absorbance

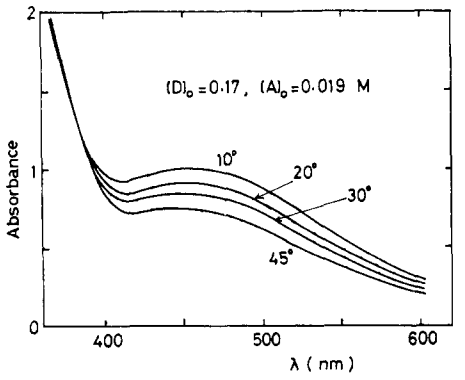

Figure 2. Absorption spectra of the mixture of model compounds I and II in chloroform solution: [I] = 0.17 M, [II] = 0.019 M, cell length = 10 mm. The temperature is indicated in the figure.

Table II
Association Constant for the Charge-Transfer Complex between Compounds I and II in Chloroform Solution

Temp, °C	K_2, M^{-1}	ϵ at 460 nm
10.0	1.04 ± 0.04[a]	353 ± 14[a]
20.0	0.96 ± 0.06	347 ± 15
30.0	0.89 ± 0.06	349 ± 13
45.0	0.80 ± 0.08	344 ± 13

$\Delta H_2 = -1.40$ kcal/mol, $\Delta S_2 = -4.87$ eu

[a] Standard errors obtained in the nonlinear least-squares calculation.

is listed in the last column of Table I. The incorporation of the dinitrobenzoyl group was highly efficient and nearly quantitative. In the following optical measurements, the feed concentration multiplied by the fraction was taken as the true concentration of donor–acceptor pairs.

A quantitative incorporation of *p*-dimethylaminoanilide group is expected from the polymerization mechanism of sarcosine NCA.[7] This expectation was confirmed by the measurement of the amount of *p*-dimethylaminoanilide group by the NMR peak areas of phenyl protons in deuteriochloroform solution, the peak area of main-chain methylene protons being used as a standard. Results are listed in Table I in the form of the ratio of observed value to the theoretical one. Taking into account relatively large experimental errors involved in the NMR method, the agreement between the observed and calculated values is satisfactory.

Intermolecular Charge-Transfer Complex between Model Compounds. Absorption spectra of the mixture of compounds I and II in chloroform solution are shown in Figure 2. A new band appeared around 455 nm where the component species showed virtually no absorption. Therefore, this is assignable to the charge-transfer band. No change of the spectrum was detected at least in 24 h. The determinations of the association constant K_2 and the extinction coefficients ϵ_i at each wavelength were made by the nonlinear least-squares method[8] using 72 experimental points obtained for six different pairs of concentrations and at 12 different wavelengths. The calculation was carried out at four different temperatures independently and K_2 and ϵ_i's were varied at once in the iterative procedure. The initial set of K_2 and ϵ_i's was obtained from the Benesi–Hildebrand plot or the Scott plot.[5] The most probable values of K_2 with the standard errors are listed in Table II. The extinction coefficients are plotted as a function of wavenumber in Figure 3. The value of K_2 and the wavelength of the absorption maximum (455 nm) are reasonable

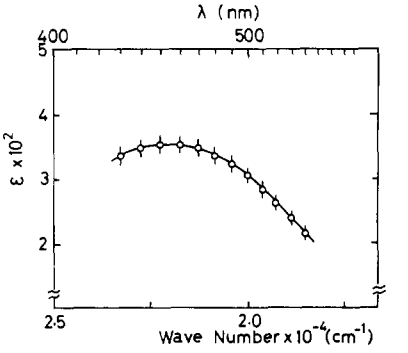

Figure 3. Extinction coefficients for the charge-transfer complex between I and II in chloroform solution at 10 °C. The vertical bars represent the standard errors.

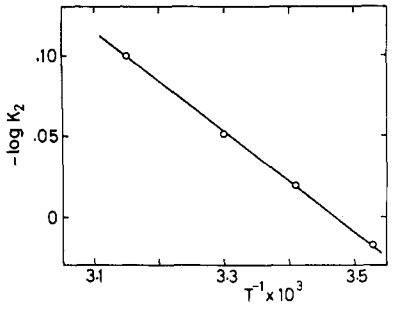

Figure 4. Temperature dependence of the association constant of the intermolecular charge-transfer complex between I and II in chloroform solution.

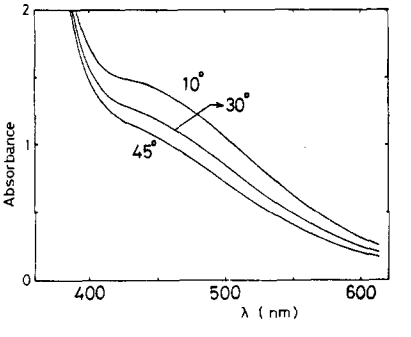

Figure 5. Absorption spectra of polymer sample VI with $\bar{n} = 6$ in chloroform solution: [VI] = 0.0047 M, cell length = 50 mm. The temperature is indicated in the figure.

in view of the other reported values.[5] The extinction coefficient was virtually constant over the temperature range of 10–45 °C. A similar result has been reported for the tetracyanoethylene (TCNE)–hexamethylbenzene complex in dichloroethane solution by Foster et al.[10]

Plot of log K_2 against $1/T$ is shown in Figure 4. From the slope and the intercept, thermodynamic parameters, ΔH_2 and ΔS_2, were calculated and are also listed in Table II.

Intrachain Charge-Transfer Complex on the Polysarcosine Chain. The absorption spectrum of polymer VI with $\bar{n} = 6$ is shown in Figure 5. The concentration of polymer is too low to exhibit a significant absorption due to the intermolecular charge-transfer complex, but nevertheless the spectrum shows an absorption band with a considerable intensity around the charge-transfer band. Therefore the largest part of the absorption is undoubtedly attributed to the intrachain charge-transfer complex. Since it is impossible to determine the association constant and the extinction coefficient independently for the intramolecular complex, the

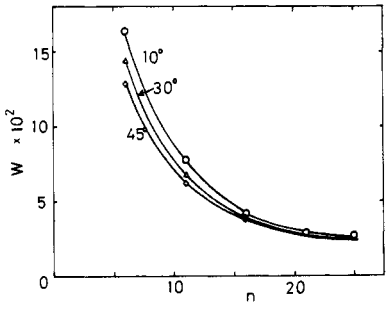

Figure 6. Fraction of polymers forming the intrachain charge-transfer complex plotted against the degree of polymerization at three different temperatures.

Table III
Association Constant K_1 of Intrachain Charge-Transfer Complex on Polysarcosine Chains in Chloroform Solution

$\bar{n}$	10 °C	$K_1 \times 10^2$ 20 °C	30 °C	45 °C	ΔH_1, kcal/mol	ΔS_1, eu
6	19.5		16.7	14.7	−1.4	−8.3
11	8.3	7.7	7.2	6.6	−1.2	−9.2
16	4.2	4.1	4.0	3.9	−0.43	−7.8
21	2.9	2.6	2.5	2.5	−0.26	−8.2
25	2.8					

extinction coefficient for the intrachain complex was assumed to be identical with that for the intermolecular complex between model compounds I and II (Table II). This was rationalized by the following considerations.

If an electron-donating group and an electron-accepting group are connected with a polymer chain long enough to assume a random orientation of the terminal groups, the geometrical structure of the intramolecular charge-transfer complex may be practically identical with that of the intermolecular complex. In fact, the shape of the charge-transfer band of intrachain complex (Figure 5) is almost identical with that of the intermolecular complex (Figure 2). A possibility of the charge transfer through the polymer chain must also be considered for short chains. However, preliminary results for sarcosine dimer and trimer (m = 2, 3) showed that the intensity of charge-transfer band for these oligomers was considerably weaker than that for the present polymer with $\bar{n}$ = 5.[11] Since the charge-transfer through polymer chain should decrease with the chain length, the above result rules out the possibility.

The limitation of the above assumption may be evident with compound V, i.e., a polymer sample VI with n = 1. This compound was insoluble in chloroform and the spectrum was measured in DMF solution. A new absorption band around 530 nm was observed which may be attributed to the intramolecular complex with a highly specific orientation or to the charge-transfer band through a sarcosine unit. Accordingly it is obvious that the extinction coefficient for the intermolecular complex cannot be applied to the intrachain complex for extremely short chains. At present, however, the possibility that the absorption band around 530 nm may be due to an impurity cannot be ruled out completely.

Estimation of the Fraction of Polymers Forming the Intrachain Charge-Transfer Complex. Using the extinction coefficient of the intermolecular complex, the fraction of polymers forming intrachain complex W was evaluated. The fraction is expressed as

$$W = \frac{[\text{complex}]}{[\text{total polymer}]} = \left(\frac{A}{\epsilon c d}\right)_{c \to 0} \qquad (2)$$

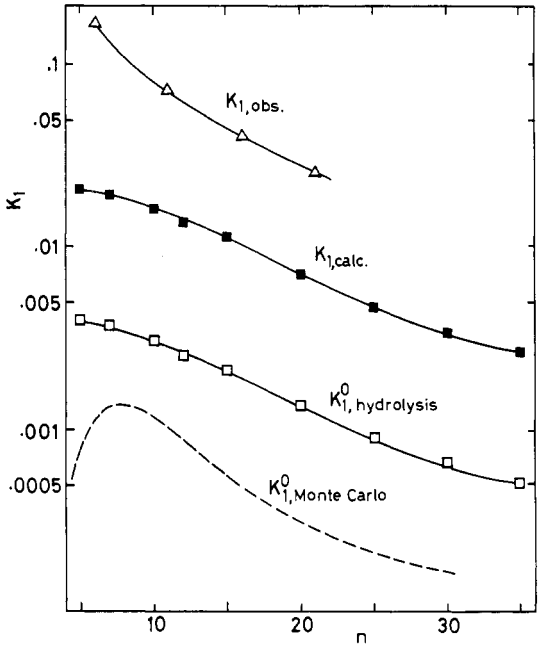

Figure 7. Comparison of the intrachain association constants estimated in four different ways: (- - -) unperturbed values evaluated in the Monte Carlo calculation;[3] (□) unperturbed values obtained in the intramolecularly catalyzed hydrolysis in aqueous solution at 35 °C;[2] (■) theoretical values calculated from eq 6 using the above experimental data; (△) the present experimental data at 30.0 °C.

where A is the absorbance of a polymer sample at 460 nm, c is the concentration of the donor–acceptor pair, and d is cell length. The ratio $A/\epsilon cd$ was found to increase slightly with increasing c from 1×10^{-3} to 5×10^{-3} M. This indicates the presence of the intermolecular complex. To obtain W that is free from the intermolecular complex, the ratio was extrapolated to the infinite dilution. W values at three different temperatures are plotted as a function of degree of polymerization n in Figure 6. The fraction of intramolecularly complexed polymers increased with decreasing of the chain length. This result is consistent with the chain length dependence of the intramolecularly catalyzed hydrolysis on the polysarcosine chain.[2] The fraction also increased with decreasing the temperature. However, the temperature dependence became small at longer chain lengths. It should be noted that the fraction of intramolecularly complexed polymers is large and exceeds 10% at short chain lengths.

The association constants for intrachain complex K_1 were calculated according to eq 3 and are listed in Table III.

$$K_1 = \frac{[\text{complex}]}{[\text{total polymer}] - [\text{complex}]} = \frac{W}{1 - W} \qquad (3)$$

It should be interesting to compare the present K_1 values with the theoretical values evaluated in the Monte Carlo calculation of the polysarcosine chain[3] and with the experimental values of intramolecularly catalyzed hydrolysis in aqueous solution.[2] The comparison is made in Figure 7. In the latter two cases polymers with the end-to-end distance shorter than 4 Å were regarded as being cyclized. The Monte Carlo calculation was performed without taking intrachain forces between a pair of terminal groups into account. The Monte Carlo values agreed roughly with the experimental data of intramolecularly catalyzed hydrolysis for longer chain length. However, the intrachain charge-transfer complexation gave larger K_1 values than the other two cases by an approximate factor of 20–100. This indicates that in the present system the fraction of cyclized polymers was greatly increased by the

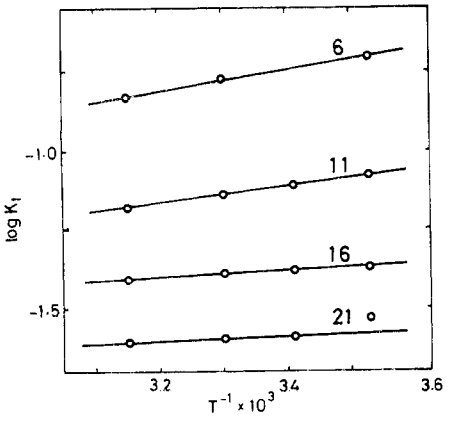

Figure 8. Temperature dependence of the association constants of the intrachain charge-transfer complex. The numbers in the figure indicate the chain lengths.

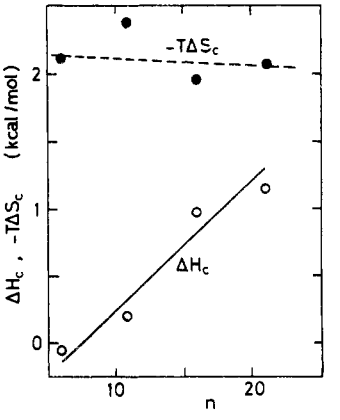

Figure 9. Thermodynamic parameters required for the conformational change for the cyclization, plotted against the degree of polymerization.

stabilization due to the charge-transfer force between a pair of end groups.

Quantitative Discussion on the Stabilization of Cyclized Conformations. In this section an evaluation of the extent of the stabilization of cyclized conformations was attempted on the basis of a thermodynamic consideration. To begin with, the free energy of the electronic stabilization in the charge-transfer complex ΔG_e was estimated from the thermodynamic parameters of model compounds (Table II). They are composed of two terms: a term concerning a bimolecular encounter (ΔH_b and ΔS_b) and an electronic term (ΔH_e and ΔS_e).

$$\Delta H_2 = \Delta H_b + \Delta H_e, \Delta S_2 = \Delta S_b + \Delta S_e \quad (4)$$

Here it was assumed that there is no interaction between a donor group and an acceptor group which are separated by more than 4 Å and the donor–acceptor pair is electronically stabilized only if the two groups came within 4 Å. From this assumption it follows that the enthalpy for the bimolecular encounter ΔH_b is zero and the entropy ΔS_b is expressed as[2]

$$\Delta S_b = R \ln \frac{4\pi r_0^3 N_a}{3000} = -3.6 \text{ eu} \quad (5)$$

where N_a is Avogadro's number and $r_0 = 4$ Å. Using the values of ΔH_2 and ΔS_2 in Table II and eq 4 and 5, the thermodynamic parameters for the electronic changes ΔH_e, ΔS_e, and ΔG_e were evaluated as $\Delta H_e = -1.40$ kcal/mol, $\Delta S_e = -1.3$ eu, and $\Delta G_e = -1.01$ kcal/mol.

If it is considered that the same free energy of stabilization is applied to the intrachain complex, the association constant for the intrachain complex K_1 should be related to the association constant K_1^0 for the cyclization of a polymer chain which is free from intrachain interactions, according to eq 6.

$$K_1 = K_1^0 \exp(-\Delta G_e/RT) \quad (6)$$

The exponential factor in eq 6 represents the electronic stabilization by forming the intrachain charge-transfer complex. The "unperturbed" association constant $K_1^0 = W_0/(1 - W_0)$ was estimated from the experimental value of intramolecularly catalyzed hydrolysis on the polysarcosine chain.[2] The calculated values of K_1 are shown in Figure 7. Although the effect of intrachain stabilization energy is obvious, the calculated values are still smaller than the observed values. At the present time we cannot afford any definite explanations for the difference.

Thermodynamic Parameters for the Intrachain Charge-Transfer Complex. The association constant for intrachain complex K_1 is plotted against $1/T$ in Figure 8. From the slope and the intercept, thermodynamic parameters ΔH_1 and ΔS_1 were calculated and are listed in the last column of Table III. The thermodynamic parameters are divided into two terms as

$$\Delta H_1 = \Delta H_c + \Delta H_e, \Delta S_1 = \Delta S_c + \Delta S_e \quad (7)$$

where ΔH_c and ΔS_c are the terms associated with the conformational change for cyclization. The electronic terms, ΔH_e and ΔS_e, have been estimated in the preceding section. Using those values ΔH_c and $-T\Delta S_c$ ($T = 298$ K) were calculated and are plotted in Figure 9 as a function of the degree of polymerization. Although the points are somewhat scattered, it is clear that the enthalpy for the cyclization increases with increasing the chain length, while the entropy remains nearly constant. Although the same trend has been found in the intramolecularly catalyzed hydrolysis on the polysarcosine chain,[2] it is in contradiction to our expectation. In the Monte Carlo calculation ignoring the contribution of conformational energy, the fraction of cyclized conformation decreased with increasing chain length except for very short chains.[3] This indicates that the entropy for the cyclization decreases with chain length while enthalpy remains constant. However, these results were *not* in accordance with the present experimental results. It appears that the difference in the solvation of the polymer chain plays an important role in determining the thermodynamic parameters. Some experimental results supporting this view have been obtained in a similar experiment in ethanol solution that ΔS_c decreased with chain length and ΔH_c remained nearly constant. A more detailed discussion on this subject will be made in the next paper.[12]

To conclude, the intrachain charge-transfer force was found to make an important contribution to the conformation of the polysarcosine chain. In a more generalized expression, it was demonstrated that a relatively weak intrachain force, such as a charge-transfer force, played an important role in the determination of a polymer conformation in solution.

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References and Notes

(1) (a) D. Poland and H. A. Scheraga, "Poly-α-Amino Acids", G. D. Fasman, Ed., Marcell Dekker, New York, N.Y., 1967, Chapter 10; (b) H. A. Scheraga, "Polyamino Acids, Polypeptides, and Proteins", M. A. Stahmann,

Ed., University of Wisconsin Press, Madison, Wis., 1962, pp 241–249.
(2) M. Sisido, T. Mitamura, Y. Imanishi, and T. Higashimura, *Macromolecules*, **9**, 316 (1976).
(3) M. Sisido, Y. Imanishi, and T. Higashimura, *Macromolecules*, **9**, 320 (1976).
(4) M. A. Slifkin, "Charge Transfer Interactions of Biomolecules", Academic Press, London, 1971.
(5) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London, 1969.
(6) T. Endo, private communication.
(7) C. H. Bamford, A. Elliott, and W. E. Hanby, "Synthetic Polypeptides", Academic Press, New York, N.Y., 1956, Chapter 3.
(8) W. E. Wentworth, W. Hirsch, and E. Chen, *J. Phys. Chem.*, **71**, 218 (1967).
(9) M. Sisido, Y. Imanishi, and T. Higashimura, in preparation.
(10) R. Foster and I. B. C. Matheson, *Spectrochim. Acta, Part A*, **23**, 2037 (1967).
(11) M. Sisido, Y. Kanazawa, Y. Imanishi, and T. Higashimura, unpublished work.
(12) H. Takagi, M. Sisido, Y. Imanishi, and T. Higashimura, in preparation.
(13) R. D. Morin, J. S. Warner, and R. H. Poirer, *J. Org. Chem.*, **21**, 616 (1956).
(14) T. Mukaiyama, T. Endo, Y. Kojima, and T. Sato, *J. Am. Chem. Soc.*, **94**, 7575 (1972).

Fluorescence and Energy Transfer of Polypeptides Containing Naphthyl Groups in Their Side Chains

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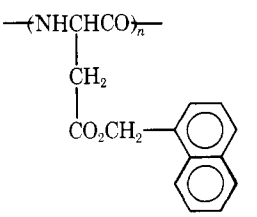
ABSTRACT: Energy transfer in the singlet state was studied in solution at 25 °C for poly(β-1-naphthylmethyl L-aspartate) and copolymers of β-1-naphthylmethyl L-aspartate and γ-benzyl L-glutamate. Transfer efficiencies, migration coefficients, migration lengths, and interaction radii were determined from the quenching studies using biacetyl as a quencher. The migration coefficient increases with increasing naphthyl groups in the copolymers. This means that singlet energy migrates among more naphthyl groups with increasing naphthyl groups in the polymer chain. Interaction radius for the fluorescence quenching by biacetyl was estimated to be in the range of 5.8 to 8.9 Å irrespective of whether energy donor is monomer or excimer. Moreover, it was shown that energy migration via excimer does not take place and energy of the excimer is localized.

Intramolecular energy transfer along the polymer chain has become a phenomenon of increasing interest and intensive study.[2-21] Functional groups situated at regular intervals along the backbone of a polymer may be compared in principle to a one-dimensional crystal and there is a possibility of energy migration from group to group along the polymer chain. Intermolecular energy transfer may also be affected by intramolecular energy transfer, since intuitively the migration of energy along the polymer chain increases the effective volume of the excited region or quenching sphere. Almost all the polymers used for such investigations are vinyl polymers. Polypeptides are well known to take some different conformations such as α-helix, β-structure and random-coil. Side chains of a helical polypeptide may be arranged along the rodlike helical main chain forming outer helix. Therefore, one can compare it to a better one-dimensional crystal than vinyl polymers because of its ordered structure and the absence of folding. One can further obtain some different arrangements of the side-chain chromophores corresponding to the difference in its secondary structure. We have been interested in studying how intra- and intermolecular energy transfer would be affected by conformational change of the polypeptides.[21,22] From this point of view, some polypeptides containing naphthyl groups in their side chain were prepared.[23-25] In the previous paper,[26] we showed evidence for singlet energy migration for poly(γ-1-naphthylmethyl L- and DL-glutamates) (PNLG and PNDLG) and copolymers of γ-1-naphthylmethyl L-glutamate and γ-benzyl L-glutamate.

We report here the results of quenching studies for poly(β-1-naphthylmethyl L-aspartate) (PNLA) and copolymers of β-1-naphthylmethyl L-aspartate and γ-benzyl L-glutamate. Their conformations have already been studied[24] and right-handed helices were assumed for all polymers except for pure PNLA only which may take a left-handed helix.



PNLA

Experimental Section

Syntheses of the polymers were described previously.[24] The degrees of polymerization of the samples were determined to be in the range of 30 to 65 by amino end-group titration. Dichloroethane (DCE) was "Dotite Spectrosol" grade. Hexafluoroisopropyl alcohol (HFIP) was Tokyo Kasei reagent grade. Naphthalene was Tokyo Kasei zone-refined grade. Biacetyl was freshly distilled before use. Solvents for fluorescence measurements are DCE and a mixed solvent of DCE and HFIP (1:1 by volume). PNLA is insolule in DCE but soluble in the mixed solvent. Therefore the mixed solvent had to be used for the polymer.

Fluorescence spectra at 290-nm excitation were measured at 25 °C with a Hitachi MPF-4 fluorescence spectrophotometer. The excitation was normal to the front surface of the cubical cell, and the fluorescence was observed through the side face at 90° to the incident light. The naphthyl molar concentration was 5×10^{-3} M for the quenching measurements. The intensities of monomer and excimer fluorescence were measured respectively at 332–333 nm (peak) and 400 nm. In the quenching experiments corrections were made for absorption of the exciting light by biacetyl. The lifetime measurements were conducted with the time-resolved attachment using the solutions 10^{-3} M in naphthyl groups. Pulsed light of the D_2 discharge lamp was triggered by the control unit. The half-value width of the sampling gate was a second or a third of the measuring lifetime. The decay curves at 320 and 400 nm were recorded on a chart-recorder. Because of the limitation of the apparatus for measurement of shorter lifetime, the lifetimes in the mixed solvent were estimated from intensity at 332 nm based on the lifetime of the copolymer containing 11% naphthyl