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Intrachain Charge-Transfer Complex in Ethanol Solution on a Polysarcosine Chain Having a Terminal Electron Donor and a Terminal Electron Acceptor Groups*

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Polysarcosine having a terminal electron donating group (*p*-dimethylaminoanilide group) and a terminal electron accepting group (3,5-dinitrobenzoyl group) was synthesized. An ethanol solution of the polymer showed a distinct charge-transfer absorption band around 435 nm. With use of the extinction coefficient determined for the low-molecular-weight model compounds, the fraction of polymers forming an intrachain complex was evaluated to be about 0.08 for $\bar{n}=6$ ($\bar{n}$ is the degree of polymerization of the polysarcosine chain). The fraction decreased with rise in temperature and increase in chain length. The fraction experimentally observed was considerably larger than that estimated from the Monte Carlo calculation on polysarcosine chain, indicating that the cyclic conformations are greatly stabilized by the intrachain charge-transfer interaction. Thermodynamic parameters were determined for the intrachain complex. The chain length dependence of the parameters in ethanol was the opposite of that obtained previously in a chloroform solution. The difference was explained in terms of the difference of the conformations of polysarcosine chain in chloroform and in ethanol solutions. This was evidenced by the NMR spectra recorded in the solvents.

The intrachain reaction between a pair of terminal groups (X and Y) attached on a polymer chain is affected by the conformational properties of the connecting polymer chain in solution.[1-9] For the reaction with a moderately high activation energy, the intrachain reaction is determined by the equilibrium conformational property, *i.e.*, the probability that a pair of reactive groups approach within a short distance capable of the reaction.[2,5,8,10] The conformational equilibrium would depend not only on external factors such as temperature, solvent, *etc.*, but also on internal factors such as intrachain interactions. If a stabilizing force operates between X and Y, the fraction of cyclic conformations would increase considerably, strongly enhancing the intrachain reaction or intrachain interaction. In this respect, protein molecules are regarded as a limiting case, in which various types of intramolecular interactions operate to stabilize the three-dimensional structures in solution.

The results of a study on the hydrolysis of a *p*-nitrophenoxycarbonyl group catalyzed intramolecularly by a pyridyl group attached to the same polysarcosine chain were found to be in line with the ring-closure probability calculated by the Monte Carlo method taking no intrachain force into account.[2] This indicates that intrachain force virtually does not participate in the above system. On the other hand, when electron-donating and electron-accepting groups are attached to respective ends of a polysarcosine chain, a relatively weak intrachain charge-transfer interaction greatly increases the fraction of cyclic conformations in a chloroform solution.[3] This prompted us to investigate the above system in more detail, the present experiment being carried out with an ethanol solution. Since the conformation of polysarcosine has been found to show a marked solvent dependence,[11-13] it was expected to clarify the effct of polymer conformation upon the intrachain interaction.

Experimental

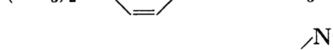
Polymer samples were synthesized by the polymerization of sarcosine *N*-carboxyanhydride (NCA) with sarcosine *p*-dimethylaminoanilide as an initiator. After complete polymerization, 3,5-dinitrobenzoyl chloride was added to incorporate an electron-accepting group into the other end of the polymer chain. The average degree of polymerization $\bar{n}$ was calculated by Eq. 1,[14] the results agreeing with those determined by vapor pressure osmometry.

$$\bar{n} = [\mathrm{NCA}]/[\mathrm{initiator}] + 1 \tag{1}$$

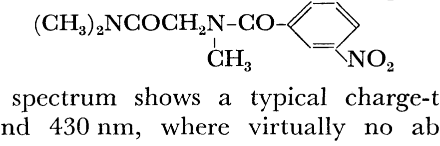
A Poisson type distribution of the degree of polymerization was expected.[14] This was confirmed with polysarcosines obtained with use of sarcosine dimethylamide as an initiator.[15] Details of the synthesis of other compounds and the characterization of polymer samples have been reported.[3] Ethanol used for the optical measurement was fractionally distilled from magnesium metal. 220-MHz NMR spectra were obtained with a Varian HR-220 instrument.

Results and Discussion

Intermolecualr Charge-Transfer Complex between Model Compounds. First, the nature of charge-transfer complex in an ethanol solution was examined with model compounds for the terminal electron-donating and electron-accepting groups. The absorption spectrum of the mixture of *N*-acetyl-*N′*,*N′*-dimethyl-*p*-phenylenediamine (I) and *N*-(3,5-dinitrobenzoyl)-sarcosine dimethylamide (II) in ethanol is shown in Fig. 1.



(I)



(II)

The spectrum shows a typical charge-transfer band around 430 nm, where virtually no absorption was observed for the component species. No spectral change was detected at least for five days, indicating the chemical stability of the charge-transfer complex in the ethanol solution. The plots of the absorbance

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[*] Intrachain Reaction of a Pair Reactive Groups Attached to Polymer Ends. Part IV.

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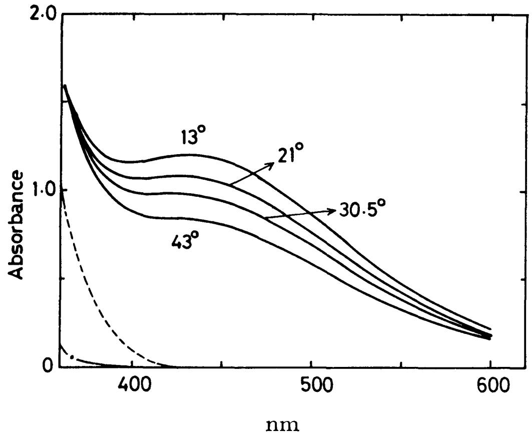


Fig. 1. Absorption spectra of a mixture of the model compounds I and II in ethanol solution at four different temperatures. $[I]=7.3\times10^{-3}$, $[II]=3.7\times10^{-1}$ M. (—·—): The spectrum of I, $[I]=7.3\times10^{-3}$ M, (----): The spectrum of II, $[II]=3.7\times10^{-1}$ M, cell length = 1.0 cm.

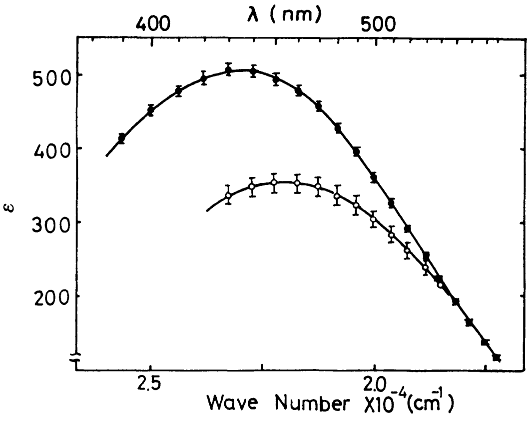


Fig. 2. Extinction coefficient for the charge-transfer complex between I and II in ethanol solution at 13 °C (-●-) and in chloroform solution at 10 °C (-O-) Vertical bars represent the standard errors in non-linear least squares calculation.

TABLE 1. ASSOCIATION CONSTANT AND EXTINCTION COEFFICIENT FOR THE CHARGE-TRANSFER COMPLEX BETWEEN MODEL COMPOUNDS I AND II IN ETHANOL SOLUTION

Temp (°C)	K_2 (M^{-1})	ε_{450}
13.0	1.14±0.01[a]	494±8[a]
21.0	1.01±0.02	494±7
30.5	0.89±0.02	496±6
43.0	0.73±0.04	497±6

$\Delta H_2 = -11.3$ kJ mol^{-1}, $\Delta S_2 = -38.4$ J mol^{-1} K^{-1}

a) Standard errors obtained in non-linear least squares calculation.

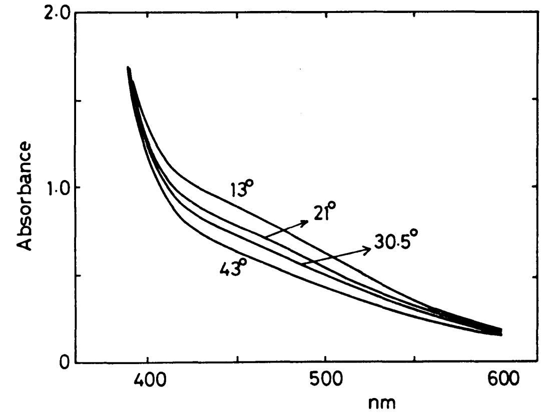


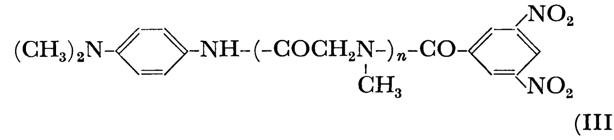
Fig. 3. Absorption spectra of the polymer sample III in ethanol solution at four different temperatures, $c_0=6.5\times1^{-3}$ M, $\bar{n}=16$, Cell length = 5.0 cm.

at 450, 500, and 550 nm were made as functions of the mole fraction of I, the total concentration of I and II being kept constant. The intensity was strongest at an equimolar concentration of I and II, showing that the composition of the charge-transfer complex was 1 : 1.

The association constant K_2 and the extinction coefficient ε_i at each wavelength for the complex were calculated by the non-linear least squares method.[16] 210 absorption values for 10 different pairs of concentrations and 21 different wavelengths in the range 380—580 nm were used for the calculation. The measurements were made at four temperatures and the least squares calculations were carried out independently at each temperature. The initial set of K_2 and ε_i's for the iterative calculation was obtained from the Benesi-Hildebrand plot.[17] The results are given in Table 1 and the extinction coefficients are plotted in Fig. 2 as a function of the wave number. The extinction coefficient showed virtually no temperature dependence in the range 13—43 °C. Figure 2 also shows the extinction coefficients in a chloroform solution. The absorption maximum lies at about 435 nm and at 455 nm in ethanol and chloroform solutions, respectively. The hypsochromic shift of the charge-transfer band caused by a strongly solvating solvent, such as alcohol, has been explained in terms of the specific solvation in the ground state of the component species.[19] The association constant determined in an ethanol solution was nearly equal to that in a chloroform solution.[3]

The plot of log K_2 against $1/T$ gave a straight line. The thermodynamic parameters ΔH_2 and ΔS_2 were evaluated (Table 1). Although the values of K_2 were almost the same in both solvents, the thermodynamic parameters in the ethanol solution were substantially different from those in the chloroform solution ($\Delta H_2 = -5.86$ kJ mol^{-1}, $\Delta S_2 = -20.4$ J mol^{-1}K^{-1}).[3]

Intrachain Charge-Transfer Complex on Polysarcosine Chain. Figure 3 shows the absorption spectrum of polysarcosine having a terminal *p*-dimethylaminoanilide group and a terminal 3,5-dinitrobenzoyl group (III). Although



(III)

the polymer concentration is too low to form a measurable amount of *inter*-molecular charge-transfer complex, the spectrum of III shows a considerable intensity

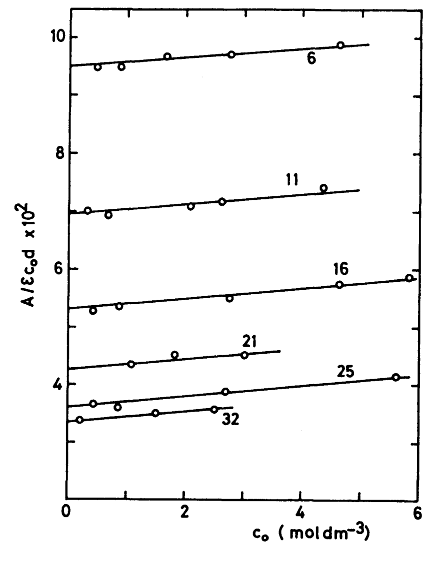


Fig. 4. Plots of $A/\varepsilon c_0 d$ against c_0 for six different degrees of polymerization at 13 °C. Solid lines were drawn with a theoretical slope evaluated according to Eq. 2.

around the charge-transfer band. This indicates the formation of an intrachain charge-transfer complex and its predominance over the intermolecular complex. The plot of the absorbance A at 450 nm against the polymer concentration c_0 shows an upward deviation from a straight line, indicating an increased contribution of the intermolecular complex at higher concentrations. In order to separate the contribution of the intrachain complex from that of the intermolecular one, $A/\varepsilon c_0 d$ was plotted against c_0, where ε is the extinction coefficient at 450 nm and d is the cell length (Fig. 4). The intercept gives the fraction of polymers forming intrachain complex at infinite dilution W_0, the slope being proportional to the association constant K_2 for the intermolecular complex between polymer ends (see Appendix).

$$A/\varepsilon c_0 d = W_0 + K_2(1-2W_0)(1-W_0)^2 c_0 + \cdots \tag{2}$$

In Eq. 2 the extinction coefficient for the intrachain complex and that for the intermolecular complex between polymer ends are assumed to be identical with that for the intermolecular complex between the model compounds (Table 1). Figure 4 shows typical plots for different chain lengths at 13 °C, The slope is in good agreement with the calculated value using the association constant between model compounds. This shows that the stability of intermolecular charge-transfer complex between polymer ends is almost the same as that between model compounds, irrespective of the chain length.

The plots was made for six different chain lengths and at four different temperatures, values for W_0 being obtained under various conditions. The results are plotted in Fig. 5 together with the data obtained in a chloroform solution.³⁾ W_0 increases with decrease in chain length and also temperature. The dependence of W_0 on the chain length is more marked in a chloroform solution, while that on temperature is more marked in an ethanol solution. The values of W_0 in either solution do not differ a great deal. They are 20—100 times as larger as those expected for "unperturbed" chains free from any interachain force. The unperturbed values have been estimated from the rate constants of intramolecularly catalyzed hydrolysis on polysarcosine chain¹⁾ and from the Monte Carlo calculation of randomly coiled polysarcosine chain.²⁾ The larger values of W_0 indicate that the cyclic conformations are greatly stabilized by the intrachain force based upon the charge-transfer interaction between a pair of terminal groups.

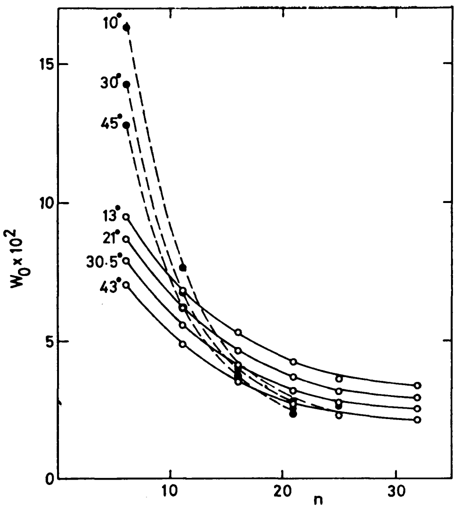


Fig. 5. Dependence of the fraction of polymers forming intraction complex upon the chain length in ethanol solution (—○—), and in chloroform solution (--●--).

Evaluation of the extent of the stabilization of cyclic conformations made previously³⁾ was applied to the present case. The free energy of the electronic stabilization in the intramolecular charge-transfer complex ΔG_e was estimated from the thermodynamic parameters of model compounds (Table 1).

$$\begin{aligned} \Delta H_e &= \Delta H_2 = -11.3\,\mathrm{kJ\,mol^{-1}}, \\ \Delta S_e &= \Delta S_2 - \Delta S_b = -38.4 - (-15.1) \\ &= -23.3\,\mathrm{J\,mol^{-1}\,K^{-1}}, \\ \Delta G_e &= \Delta H_e - T\Delta S_e = -4.23\,\mathrm{kJ\,mol^{-1}}\ (30.5\,^\circ\mathrm{C}). \end{aligned} \tag{3}$$

In the second equation the entropy for the bimolecular encounter $S_b = -15.1\ \mathrm{J\,mol^{-1}K^{-1}}$ was subtracted from the total entropy for the model compounds.¹,³⁾ The association constant for the intrachain complex K_1 is related to W_0 as

$$K_1 = W_0/(1-W_0). \tag{4}$$

K_1 should be related to the association constant K_1^0 for the cyclization of a polymer chain which is free from intrachain interaction, according to the equation

$$K_1 = K_1^0 \exp(-\Delta G_e/RT). \tag{5}$$

The "unperturbed" value of the association constant K_1^0 was evaluated from the rate constant of intramolecularly catalyzed hydrolysis on polysarcosine chain in aqueous solution¹⁾ (Table 2). The value of K_1 calculated by Eq. 5 is compared with that evaluated from the observed value of W_0 (Eq. 4, Table 2). Although the increase in the K_1 value by the electronic stabilization is definite, the calculated value of K_1 is still smaller than the observed one.

Table 2. Association constant for the intrachain interaction between a pair of terminal groups attached to polysarcosine chain

Degree of polymerization	$K_1^0 \times 10^2$ [a)]	$K_{1,\mathrm{calcd}} \times 10^2$ [b)]	$K_{1,\mathrm{obsd}} \times 10^2$ [c)]
5	0.38	2.0	
6			8.6
7	0.37	2.0	
10	0.31	1.7	
11			5.79
12	0.28	1.5	
15	0.23	1.2	
16			4.3
20	0.16	0.86	
21			3.3
25	0.11	0.60	2.9
30	0.098	0.53	
32			2.6
35	0.077	0.41	

a) The "unperturbed" value evaluated from intramolecularly catalyzed hydrolysis on polysarcosine chain in aqueous solution at 35 °C.[1)] b) Calculated by mean of Eq. 5 for 30.5 °C. c) Observed with the intrachain charge-transfer complex on polysarcosine chain in an ethanol solution at 30.5 °C.

Thermodynamic Parameters for Intrachain Complex. The plot of log K_1 against $1/T$ is linear. Thermodynamic parameters ΔH_1 and ΔS_1 were calculated from the slope and the intercept, respectively. They consist of two terms, one associated with the conformational change for the cyclization (ΔH_c or ΔS_c) and the other for the electronic change (ΔH_e or ΔS_e).

$$\Delta H_1 = \Delta H_c + \Delta H_e, \quad \Delta S_1 = \Delta S_c + \Delta S_e. \qquad (6)$$

The values of ΔH_e and ΔS_e estimated in the preceding section were used for calculating ΔH_c and $-T\Delta S_c$ (T=298 K). The results are plotted in Fig. 6 as functions of chain length. In an ethanol solution the enthalpy required for the conformational change decreases slightly and the value of $-T\Delta S_c$ increases with increasing chain length. The results are in contrast to those obtained with a chloroform solution where ΔH_c increases with increase in chain length; $-T\Delta S_c$ remaining nearly constant.[3)] The latter situation has been observed also in the activation parameters for conformational change accompanied by the intramolecularly catalyzed hydrolysis on polysarcosine chain in aqueous solution.[1)] However, the present result is consistent with the result obtained from the Monte Carlo calculation.[2)] In the Monte Carlo calculation in which no conformational energy is taken into account, the fraction of cyclic conformations decrease with increase in chain length except for very short chains. This indicates that ΔS_c decreases with increase in chain length whereas ΔH_c is zero irrespective of the chain length.

In view of these results, the experimental finding can be interpreted as follows. In an ethanol solution ΔH_c is nearly zero irrespective of the chain length. In this case, the conformational energy can be neglected in the Monte Carlo calculation. The observed chain length dependence of ΔS_c is in reasonable accordance with the calculated one. On the other hand, ΔH_c in a chloroform solution or ΔH_c^* in aqueous solution increases considerably with increase in chain length and becomes the dominant factor to determine the chain length dependence of the intrachain association constant or intrachain rate constant. Thus the results of the Monte Carlo calculation, in which no conformational energy has been taken into account, cannot be compared with the experimental data obtained in these solvents. The difference in thermodynamic parameters may be accounted for by the difference in the polymer conformations in the three solvents.

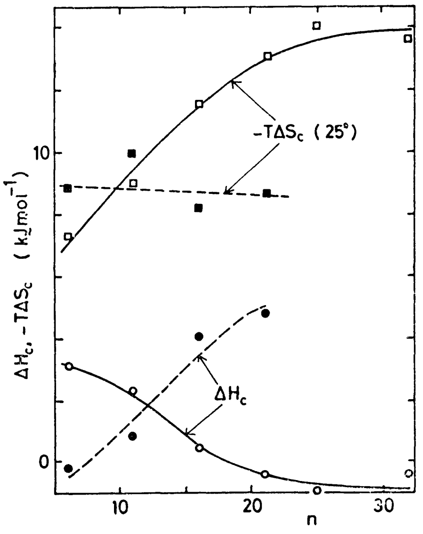


Fig. 6. Dependence of the thermodynamic parameters upon the chain length in ethanol solution (—○—, —□—) and in chloroform solution (--●--, --■--).

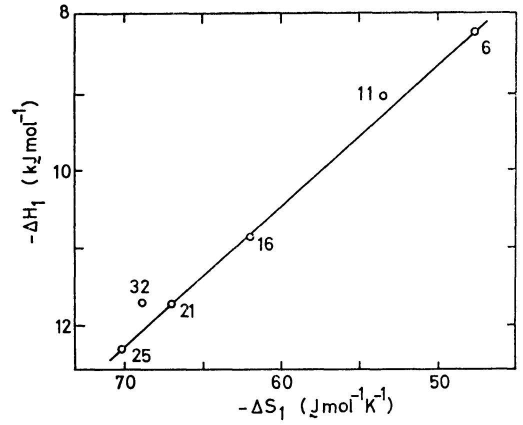


Fig. 7. Correlation between the thermodynamic parameters for the intrachain charge-transfer complex. Numbers in the Figure indicate degree of polymerization.

Figure 7 shows the plot of ΔH_1 against ΔS_1 obtained for six different chain lengths. The plot lies on a straight line with a slope of −93 °C. This suggests that the chain length dependence of K_1 vanishes at −93 °C and K_1 increases with increase in chain length below −93 °C. However, this has not been observed because of experimental difficulties.

It is interesting to compare the present result with

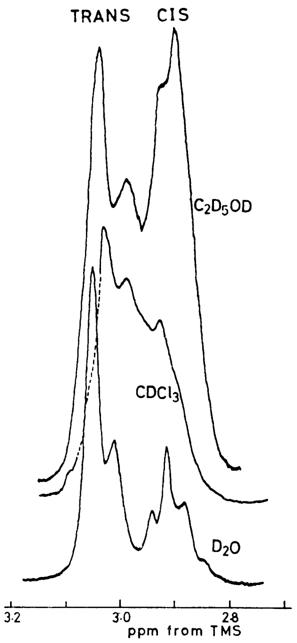


Fig. 8. Partial 220 MHz NMR spectra of polysarcosine in three different solvents. (Only the region of the main chain *N*-methyl protons is shown.) Polymer concentration=*ca.* 10 w/v%.

that obtained in the intramolecularly catalyzed hydrolysis in aqueous solution.[1] In the latter case, the conformational activation enthalpy ΔH_c^* shows a linear relation to the conformational activatioon entropy ΔS_c^*, giving an isokinetic temperature of +93 °C. The temperature should coincide with that in the present experiment (−93 °C), if the conformational properties of polysarcosine chain were the same in both ethanol and aqueous solutions. It should be emphasized that in either case, a mechanism operates to compensate the loss of conformational entropy associated with the cyclization by the decrease in conformational enthalpy, or *vice versa*. If this is the case, the isokinetic or isothermodynamic temperature can be a parameter characterizing a thermodynamic property of polymer conformations in solution. By utilizing the compensation relation, it will be possible to control the intrachain reaction proceeding on a polymer chain by varying the temperature.

Conformation of Polysarcosine Chain in Ethanol, Chloroform, and Aqueous Solution. It was suggested that the conformation of polysarcosine chain in chloroform and aqueous solutions differs a great deal from that in an ethanol solution. The conformation of polysarcosine chains in these solvents was studied by 220-MHz NMR spectroscopy. Figure 8 shows the *N*-methyl region of the NMR spectra. The absorption bands split into several peaks due to the distribution of *trans* and *cis* amide links along the main chain. A peak assignment has been made.[12] The lowest-field peak is ascribed to *trans-trans* and the second lowest to *trans-cis* dyad sequence. These two peaks in lower field correspond to a *trans* conformation. The remaining peaks in higher field correspond to a *cis* conformation. It is evident that the fraction of *cis* conformation in ethanol is considerably larger than that in the other two solvents. This relation holds for other chain lengths except for very short chains.[13]

The NMR data indicate that the conformation of polysarcosine chain in an ethanol solution differs from that in chloroform and aqueous solutions. This is in line with the result of thermodynamic parameters *i.e.*, the dependence of thermodynamic perameters on the chain length in ethanol differs from that in the other two solvents. In an ethanol solution the stability of the *cis* conformation is nearly the same as that of *trans*. Hence, virtually no conformational energy is required to attain the cyclic conformations in which *cis* bond is preferred to *trans* (Fig. 6).[13] For short polysarcosine chains ($\bar{n} \leq 10$), the fraction of *cis* conformation has been found to decrease with decrease in chain length.[13] The reduced stability of *cis* conformation may explain the higher conformational enthalpy observed for shorter chains. At present, however, a correspondence between NMR data and thermodynamic parameters is not clear in chloroform and aqueous solutions.

Appendix

In a solution containing X—Y-type polymers a series of linear polymers such as X—Y, X—YX—Y, *etc.* and series of cyclic polymers such as $\underline{|\text{X—Y}|}$, $\underline{|\text{X—YX—Y}|}$, *etc.* should be relevant to present treatment. The problem is much simplified if participation of the species beyond linear "trimer" and cyclic "dimer" is neglected at a low feed concentration of the linear "monomer" X—Y. If we denote [X—Y]=c, [$\underline{|\text{X—Y}|}$]=c_1, [X—YX—Y]=c_2, and the total feed concentration of X—Y=c_0, the association constant for the intrachain complex, K_1 and that for the intermolecular complex, K_2 are expressed as

$$K_1 = c_1/c, \tag{A.1}$$

$$K_2 = c_2/c^2, \tag{A.2}$$

with

$$c_0 = c + c_1 + 2c_2. \tag{A.3}$$

The absorbance at 450 nm is expressed as

$$A = \varepsilon d(c_1 + c_2), \tag{A.4}$$

where ε is the extinction coefficient and d is the cell length. Using the above equations, A is expressed as a function of c_0 as

$$A = \varepsilon d\left\{\left(\frac{K_1}{1+K_1}\right)c_0 + K_2\left[\frac{1}{(1+K_1)^2} - \frac{2K_1}{(1+K_1)^3}\right] + \cdots\right\}, \tag{A.5}$$

where terms up to c_0^2 are retained. Equation 2 is obtained by substituting K_1 for $W_0 = K_1/(1+K_1)$.

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