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Effect of Alkyl Group Size on the Cooperativity in Conformational Transitions of Hydrophobic Polyacids

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ABSTRACT: The effect of alkyl group size on the cooperativity of the conformational transition of hydrolyzed copolymers of maleic anhydride and alkyl vinyl ethers, observed by potentiometric titration, has been studied. An improved method for estimating the cooperative unit size yielded values of 19 and 13 for the butyl and pentyl copolymers, respectively, in 0.2 M LiCl. Two other, more qualitative, treatments of the data confirmed this inverse relationship between the cooperativity and the alkyl group size. The apparent contrast with the direct relationship between micelle and hydrocarbon size usually found for ordinary amphiphiles is attributed to differences in the ionization ranges in which the transitions of the copolymers occur.

Introduction

The hydrolyzed 1-1 copolymer of maleic anhydride and butyl vinyl ether undergoes a conformational transition upon ionization.[1] We have recently shown that this transition can be described in terms of a cooperative breakup of uniformly sized small micelles formed from adjacent chain elements and have developed a method for estimating the size of these micelles from potentiometric titration data for the case where the micelles are much smaller than the polymer.[2]

During the study to be reported in this paper we were surprised to find that the micelle size characterizing the conformational transition of the corresponding pentyl copolymer was smaller than that of the butyl copolymer. In the course of our investigation we developed an improved method for estimating micelle sizes. We shall begin with a brief description of this refined method.

Modified Method for Evaluating Cooperative Unit Size

For a large polymer chain in which noninteracting micelles (each containing n adjacent repeat units) and random coil portions of any size alternate, the negative standard molar free energy of forming a micelle from n adjacent residues obeys the equation[2]

$$\frac{\Delta G^\circ_{\mathrm{mic}}}{RT} = \ln \frac{1-\theta}{n\theta + (1-\theta)} - n \ln \frac{n\theta}{n\theta + (1-\theta)} \qquad (1)$$

The quantity θ is the fraction of residues in the random coil form, obtained from the relation[1,3]

$$\theta = (\alpha - \alpha_{\mathrm{m}})/(\alpha_{\mathrm{r}} - \alpha_{\mathrm{m}}) \qquad (2)$$

where α, α_{m}, and α_{r} are the degrees of deprotonation of the actual polyacid and its hypothetical micellar and random

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coil forms, respectively, at a given pH. Since the repeat units of our copolymers contain dicarboxylic acid groups whose intrinsic first and second pK's differ significantly (by 3 units), it has been found convenient to define α to be unity at half-deprotonation.[1]

Alternatively, the standard free energy of transition per monomole of polyacid from micellar to random coil form, $\Delta g°$, at any pH, is given by the identity

$$\frac{\Delta g°}{RT} = \frac{\Delta g°(\alpha = 0)}{RT} - (\ln 10) \int_{-\infty}^{\mathrm{pH}} (\alpha_{\mathrm{r}} - \alpha_{\mathrm{m}})\, \mathrm{dpH} \quad (3)$$

This equation is derived by means of a stepwise process in which the micellar form is discharged ($\Delta G = RT \ln 10 \int_{-\infty}^{\mathrm{pH}} \alpha_{\mathrm{m}}\, \mathrm{dpH}$),[4] the transition is carried out at zero charge ($\Delta G = \Delta g°(\alpha = 0)$), and the random coil form is charged ($\Delta G = -RT \ln 10 \int_{-\infty}^{\mathrm{pH}} \alpha_{\mathrm{r}}\, \mathrm{dpH}$).[4]

Since $\Delta G°_{\mathrm{mic}}$ given by eq 1 and $\Delta g°$ given by eq 3 apply to the same process, the first for n residues and the second for one residue, we have

$$\ln \frac{1 - \theta}{n\theta + (1 - \theta)} - n \ln \frac{n\theta}{n\theta + (1 - \theta)} = \frac{n\Delta g°(\alpha = 0)}{RT} - nf(\mathrm{pH}) \quad (4)$$

where

$$f(\mathrm{pH}) = (\ln 10) \int_{-\infty}^{\mathrm{pH}} (\alpha_{\mathrm{r}} - \alpha_{\mathrm{m}})\, \mathrm{dpH} \quad (5)$$

Previously n was determined from an expression obtained by differentiating eq 4 with respect to pH.[2] This procedure yielded a value of n for each data point, and these values were then averaged. An improved method for determining n, which weights the data more evenly, consists in using eq 4 directly. Since only θ and $f(\mathrm{pH})$ depend on pH, a plot of the left-hand side of eq 4, i.e., $\Delta G°_{\mathrm{mic}}/RT$, against $f(\mathrm{pH})$ should have $-n$ as its slope.[5] Since the initially unknown value of n appears on the left-hand side, one can use trial values until a fit is obtained. This is most efficiently accomplished by successive approximations where the slope of a trial line is used as the next trial value. Since the left-hand side of eq 4 varies very slowly with changing trial values of n, the convergence of this process is fast, and normally only a few trials are necessary.

Results and Discussion

The new method has been successfully applied to the butyl and pentyl copolymers (our samples B-II[1] and P). For the butyl copolymer, which had been treated previously using the original approach, the results serve as a test of the new method. As before, the α_{r} values are based on the potentiometric titration data of the propyl copolymer (our sample Pr-I[6]) which exhibits a random coil conformation over its whole ionization range. The values of α_{m} were derived from the titration data of the hexyl copolymer (our sample C[3]). This copolymer manifests a compact conformation up to approximately $\alpha = 0.5$. The values of α_{m} needed beyond this range were obtained by extrapolation of the pK_1^{a} vs. α curve of the hexyl copolymer, where pK_1^{a} is obtained by the equation

$$\mathrm{p}K_1^{\mathrm{a}} = \mathrm{pH} + \log \left\{ \frac{1}{2}\left(\frac{1-\alpha}{\alpha}\right) + \frac{1}{2}\left[\left(\frac{1-\alpha}{\alpha}\right)^2 + \left(\frac{4K_2°}{K_1°}\right)\left(\frac{2-\alpha}{\alpha}\right)\right]^{1/2} \right\} \quad (6)$$

The ratio of the intrinsic first and second ionization constants of the dicarboxylate groups, $K_2°/K_1°$, was taken to be 1.0×10^{-3} as reported previously.[1] The pK_1^{a} against α curves for the propyl, butyl, pentyl, hexyl, and "compact" copolymers are presented in Figure 1.[7] From these curves the data necessary for constructing the plots of $\Delta G°_{\mathrm{mic}}/RT$ against $f(\mathrm{pH})$ according to eq 1 and 4 are obtained. The use of various trial values of n in $\Delta G°_{\mathrm{mic}}/RT$ shows the insensitivity of the slope of these plots to the trial values. Thus, for the butyl copolymer a negative slope of 19 is obtained with trial values ranging from 15 to 23, and for the pentyl copolymer a negative slope of 13 is obtained with trial values ranging from 8 to 16. The plots with the final values of n used in $\Delta G°_{\mathrm{mic}}/RT$, i.e., 19 and 13 for the butyl and pentyl copolymers, respectively, are shown in Figure 2. It should be noted that the degrees of conversion, θ, over which these curves are linear extend from 0.17 to 0.86 for the butyl copolymer, and from 0.36 to 0.74 for the pentyl copolymer. The result for the butyl copolymer compares well with the value of 18 obtained for n by the previous method.[2]

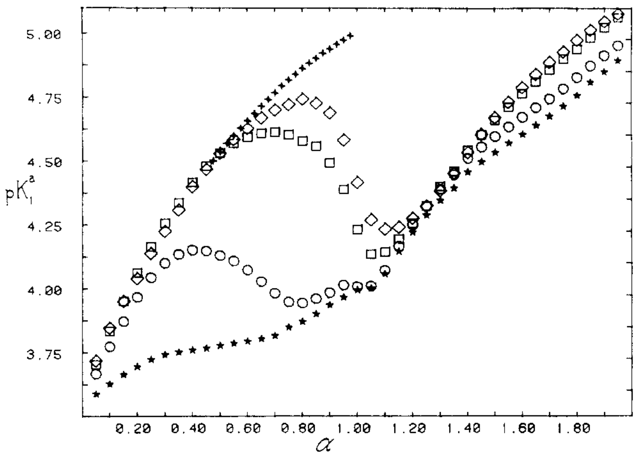

Figure 1. Plots of pK_1^{a} against α for polyacids in 0.2 M LiCl at 30 °C. The symbols are as follows: (☆) propyl copolymer; (○) butyl copolymer; (□) pentyl copolymer; (◇) hexyl copolymer; (+) hypothetical compact copolymer.

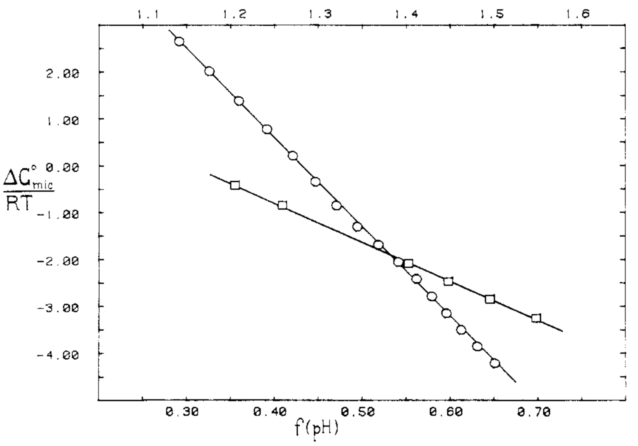

Figure 2. Plots of $\Delta G°_{\mathrm{mic}}/RT$ against $f(\mathrm{pH})$. The symbols are as follows: (○) butyl copolymer, abscissa below; (□) pentyl copolymer, abscissa above.

Equation 4 shows also that these plots allow the determination of $\Delta g°(\alpha = 0)$, the free energy of transition per monomole from the compact to the hypothetical random coil form at zero charge. The values of $\Delta g°(\alpha = 0)$ obtained in this way for the butyl and pentyl copolymers are 260 and 703 cal, respectively. Alternatively, $\Delta g°(\alpha = 0)$ can be determined from the equation[1,3]

$$\Delta g°(\alpha = 0) = (RT \ln 10) \int_0^{\alpha_{\mathrm{t}}} (\mathrm{pH} - \mathrm{pH}_{\mathrm{r}})\, \mathrm{d}\alpha \quad (7)$$

which is based on the two-step cycle: (1) compact form at $\alpha = 0$ to random coil form at $\alpha = \alpha_t$; (2) random coil form from $\alpha = \alpha_t$ to $\alpha = 0$, where α_t refers to the completion of the transition. In this way the values obtained for $\Delta g°(\alpha = 0)$ are 280 cal for the butyl copolymer and 790 cal for the pentyl copolymer. The agreement between the values obtained by the two methods, which fall well within the experimental uncertainty, estimated to be of the order of 100 cal, supports the validity of our new procedure for determining the cooperative unit size.

The surprising inverse relationship between the cooperative unit size and the size of the alkyl group can be confirmed by two additional procedures which give qualitative information concerning the sharpness of the conformational transition. These procedures are also applicable to the hexyl copolymer which we were unable to treat by the method just presented. The difficulty arises from our lack of a reliable way for obtaining the titration curve of the hypothetical micellar form above $\alpha = 1$ where a significant portion of the transition of the hexyl copolymer takes place—a portion essential for the analysis.

The first of these additional procedures involves the analysis of the data in terms of successive ionization constants, K_i, of oligomeric representative sample subunits (RSSU) containing N ionizable groups.[4,9] When this model is used, the distribution of ionization states of the RSSU's has been found to be bimodal for the butyl copolymer over the pH range of its conformational transition.[9] Table I lists the values of pK_i for the pentyl and hexyl copolymers as well as those previously reported for the butyl copolymer. It has been shown that the mole fractions, x_i, of the species with i protons dissociated at a given pH can be calculated from these data, and that the condition for a minimum in x_i, i.e., for a bimodal population distribution, is given by the inequality[4]

$$\mathrm{p}K_i > \mathrm{pH} > \mathrm{p}K_{i+1} \tag{8}$$

According to this criterion the population distribution of the butyl copolymer has a minimum at $i = 2$ at every pH between 3.47 and 4.87, i.e., over the range of its transition. The species with $i < 2$ may be associated with the micellar state and those with $i > 2$ with the random coil state. For the pentyl copolymer there appears to be a very small inversion from pK_3 to pK_4, but the difference is too small to be experimentally significant. For the hexyl copolymer there is no inversion of pK_i's and hence no bimodal distribution. One may deduce from these results that the charge distributions of the compact and random coil conformation overlap for these polymers, indicating, at least in a qualitative way, that the cooperativity of the transition is smaller for these polymers than for the butyl copolymer.

The second procedure for characterizing the sharpness of the conformational transition involves the derivative, dα/dpH, of the titration curve. A treatment by Tanford[10] gives the second moment of the distribution of molecules having i protons removed from an N-protic polyacid as

$$\langle i^2 \rangle - \langle i \rangle^2 = \frac{1}{\ln 10} \frac{\mathrm{d}\langle i \rangle}{\mathrm{dpH}} \tag{9}$$

Since, for our case, $\langle i \rangle$ is related to α by the relation

$$\langle i \rangle = N\alpha/2 \tag{10}$$

we have

$$\frac{\mathrm{d}\alpha}{\mathrm{dpH}} = 2(\ln 10)\frac{\langle i^2 \rangle - \langle i \rangle^2}{N} \tag{11}$$

Table I
Stepwise Ionization Constants of Polyacids with N = 8

i	pK_i butyl	pK_i pentyl	pK_i hexyl
1	3.00	3.13	3.14
2	4.87	4.20	4.19
3	3.47	5.05	4.93
4	4.67	5.02	5.41
5	6.38	6.40	6.44
6	7.40	7.35	7.31
7	7.83	8.00	8.05
8	8.60	8.69	8.71

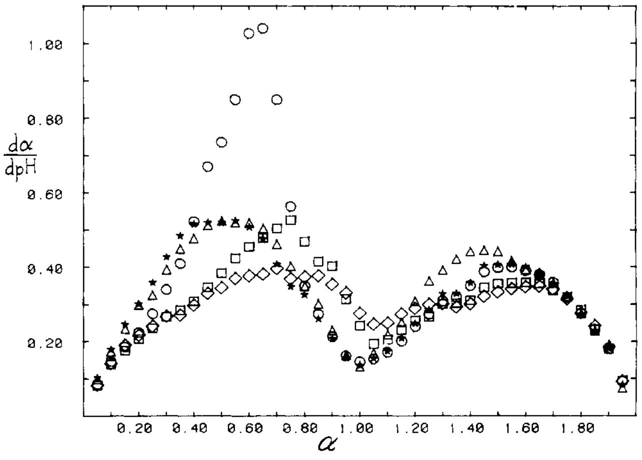

Figure 3. Plots of dα/dpH against α. The symbol for the methyl copolymer is △. The remaining symbols are the same as in Figure 1.

For a conformational transition involving at least two states with different ionization tendencies, the distribution of ionization states is expected to be broader, and therefore dα/dpH larger, than that for a single state. The use of dα/dpH for characterizing the cooperativity of conformational transitions has also been justified, from a somewhat different point of view, by Perlmann.[11] The values for dα/dpH for our methyl, propyl, butyl, pentyl, and hexyl copolymers are shown in Figure 3. The methyl and propyl curves are characteristic of random coil polydiprotic acids with widely differing first and second intrinsic pK's. The minimum at $\alpha = 1$ corresponds to the narrow distribution of ionization states to be expected and already demonstrated by the direct population distribution method.[9] It can be shown that increasing compactness of the conformation should cause a narrowing of the population distribution and thereby a lowering of the dα/dpH curve without a qualitative change in its shape. The dα/dpH curves of the initially compact butyl, pentyl, and hexyl copolymers lie, indeed, below those of the methyl and propyl copolymer curves for small α, but they rise above these curves for larger values of α. Perlmann has pointed out that for a first-order transition, i.e., one whose cooperativity is infinite, the pH vs. α curves would be horizontal and, therefore, dα/dpH would be infinite.[11] Thus the height of the maximum may be taken as a qualitative measure of the cooperativity of the transition. According to this criterion, the butyl copolymer again shows a higher cooperativity than the pentyl and hexyl copolymers.

It is known that for most homologous series of simple amphiphiles the micelle size increases with increasing hydrocarbon chain length.[12] It may therefore seem strange that for our copolymer series the micelle size seems to decrease with increasing alkyl group size. However, the following considerations help explain this finding. It has been established that the micelle size is controlled by the balance of the attractive forces between the hydrocarbon

Table II
Degrees of Deprotonation of Micellar and Random Coil Forms at Various Conversions

	butyl copolymer		pentyl copolymer	
θ	α_m	α_r	α_m	α_r
0.25	0.32	0.59	0.68	0.94
0.50	0.39	0.70	0.77	0.98
0.75	0.42	0.75	0.85	1.02

chains and the repulsive forces between the hydrophilic head groups.[13,14] The amphiphiles of a homologous series differ only in their hydrocarbon moieties. In contrast, because of the unequal extents of ionization over the ranges of their conformational transitions, the butyl and pentyl copolymers differ essentially also in their hydrophilic groups. To illustrate this point the degrees of ionization of these copolymers are compared at corresponding stages of their conversions in Table II. As can be seen, α_m is about twice as large for the pentyl as for the butyl copolymer. The larger repulsive forces between the residues of the pentyl copolymer arising from this difference in α_m oppose the larger attractive forces arising from its bigger hydrocarbon group. An unambiguous quantitative estimate of the relative magnitudes of these effects is not attainable at present. However, our experimental results are in accord with the effect of the repulsions exceeding that of the attractions.

It is quite possible that in the ionization range below that in which we observe the conformational transition the pentyl copolymer has larger micelles than those reported here. Some evidence for this comes from the fluorescence intensity at 520 nm of a dansylated pentyl copolymer, which was found to increase continuously with decreasing degree of ionization,[15] an indication of increasing contacts between hydrocarbon groups. The overall picture would then be that the pentyl copolymer starts out at low degrees of ionization with large micelles which gradually diminish in size with increasing ionization until a limiting size is reached at which point the micelles disintegrate with further ionization. The effect of the initial decrease in micelle size on the pH–α relation is not cooperative and therefore not pronounced enough to be deducible from the potentiometric titration data.

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(5) The negative infinity in the integral of eq 5 presents no computational problem. The integral is divided into two parts, one going from $-\infty$ to pH_0 (a pH value arbitrarily chosen from the low-α region of the titration curve), the other from pH_0 to pH. The first part can be evaluated in a number of ways. One method is to rewrite this part as $\int_0^{\alpha_0}(\alpha_r - \alpha_m)/h\,dh$, where h is the antilogarithm of the pH. The ratios α_r/h and α_m/h approach the respective intrinsic ionization constants of the r and m forms, as α_r and α_m approach zero, and thus the integrand remains finite.
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Thermodynamic Interactions in the Poly(vinyl methyl ether)–Polystyrene System

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ABSTRACT: The interaction parameters χ in the poly(vinyl methyl ether)–polystyrene (PVME–PS) system were obtained from osmotic pressure measurements for the concentrated solvent–polymer and solvent–polymer–polymer solutions. Toluene and ethylbenzene were used as solvents. The absolute values of χ thus obtained were extremely small. The modified Flory theory was applied to the present systems by extension to ternary systems. The theory reproduced well values of χ, excess volumes for binary and ternary systems with either toluene or ethylbenzene, and also heats of mixing to infinite dilution for the solvent–polymer binary systems. For the PVME–PS system, the theory gave extremely small χ values and negative excess volumes and also gave agreement with the experimental value of the heat of mixing.

Thermodynamic interactions in polymer–polymer systems have been studied experimentally and theoretically from the viewpoint of determination of polymer compatibility.[1,2] The Flory–Huggins interaction parameter χ has been experimentally evaluated mainly by gas–liquid chromatography and by vapor sorption, by using the expression extended to a ternary system by Scott[3] and Tompa.[4] In addition, recently this parameter has been determined from neutron scattering measurements[5,6] for polymer blends without a solvent and from light scattering measurements[7] for solvent–polymer–polymer ternary systems. The absolute values of χ obtained by the scattering methods appear to be very small compared with those obtained by the thermodynamic methods. Also, the

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