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Isotope Effects on Hydrophobic Interaction in Hydrophobic Polyelectrolytes

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ABSTRACT: An alternating copolymer of maleic acid and perdeuteriostyrene was prepared, and the pH-induced conformational transition from the compact to extended coil form was observed by pH, optical, viscometric, and ^{1}H NMR titrations in 0.01–0.27 mol/L aqueous NaCl at 5–45 °C. The transition curves were calculated from the pH and optical data in terms of the coil fraction in the molecule vs. degree of ionization of the carboxyl groups. Also, thermodynamic parameters of the conformational transition were determined from the pH-titration curves and their temperature dependence, taking into consideration dissociation of the secondary carboxyl groups. The transition curve, transition free energy, and difference of specific heats between the compact and coil forms at 0.03 M NaCl were compared with those for the maleic acid–nondeuterated styrene copolymer. All results are consistent with a more enhanced hydrophobic stabilization of the compact form in the deuterated copolymer than in the nondeuterated copolymer. Possible reasons for the enhancement of the hydrophobic interaction between the aromatic substances by deuteration are discussed.

Introduction

The hydrophobic poly(carboxylic acids) have been shown to undergo a conformational transition from a compact to an extended coil form upon ionization of the carboxyl groups. The pH-induced conformational transitions of poly(methacrylic acid),[1-7] poly(ethacrylic acid),[8-10] and alternating copolymers of maleic acid and alkyl vinyl ethers[11-15] in aqueous salts or in salt-free solutions have been studied with various physicochemical methods. The compact form has been indicated to be stabilized by hydrophobic interaction between the hydrophobic side chains in the polymers, although Davenport and Wright[16,17] suggested that hydrophobic interaction between the methyl groups in syndiotactic poly(methacrylic acid) is not required to account for the conformational transition.

We have found the compact-to-coil transition in an alternating copolymer of maleic acid and styrene, $(\text{MA–St})_n$, in aqueous solutions.[18-22] This copolymer made application of optical methods to study the transition possible. The optical data and other physicochemical results showed that (1) in the compact form the phenyl groups are buried in the interior of the molecule and (2) hydrophobic interaction between the phenyl groups plays an important role in stabilizing the compact form. We compared the transition data of $(\text{MA–St})_n$ with those of another aromatic copolymer, maleic acid–α-methylstyrene copolymer, $(\text{MA–MSt})_n$, which includes two groups of hydrophobic residues, α-methyl and phenyl.[23] However, the compact form of $(\text{MA–MSt})_n$ was more unstable than that of $(\text{MA–St})_n$. the groups do not cooperatively stabilize the compact form. However, such a result does not always mean that hydrophobic interactions between the side chains in the maleic acid copolymers are not important for stabilization of the compact form.

Chemical modification of the phenyl groups in $(\text{MA–St})_n$ can change the hydrophobicity of the side chain without affecting the character of the backbone structure. Introduction of aliphatic groups in the phenyl residues at the para, ortho, or meta position enhances the hydrophobicity of the side chain, and both alkyl and phenyl groups seem to stabilize cooperatively the compact form. However, such copolymers of maleic acid do considerably aggregate in aqueous salts at acidic pH.[24]

On the other hand, substitution of hydrogens in the phenyl groups by heavy hydrogens is an example of subtle chemical modification in the extreme. Deuteration of benzene or toluene has been reported to change their hydrophobic characters in aqueous media, and deuteration of the phenyl groups is suggested to enhance hydrophobic interaction between the phenyl groups, as shown later. We prepared an alternating copolymer of maleic acid with perdeuteriostyrene (C_8D_8), $(\text{MA–DSt})_n$. The conformational transition of the copolymer was investigated by various methods, and the data are compared with results for $(\text{MA–St})_n$ to study the role of the hydrophobic residues in the side chains in stabilizing the compact form.

Experimental Section

Materials. Perdeuteriostyrene (C_8D_8) (Sigma) was refined by distillation at 23.5 mmHg and 48–49 °C. An alternating copolymer of maleic anhydride and perdeuteriostyrene $(\text{MAn–DSt})_n$ was prepared by the same method as in the previous study of $(\text{MA–St})_n$,[18] where α,α′-azobis(isobutyronitrile) (AIBN) was used as an initiator. The molecular weight (MW) of the $(\text{MAn–DSt})_n$ prepared here was estimated to be 2.9×10^5 (DP = 1300) from its intrinsic viscosity in tetrahydrofuran (THF) at 30 °C, where a MW–intrinsic viscosity relationship for $(\text{MAn–St})_n$ in THF at 30 °C was used. Elemental analysis of $(\text{MAn–DSt})_n$ was in good agreement with theoretically predicted results. $(\text{MAn–DSt})_n$ was hydrolyzed in water at 80 °C to obtain $(\text{MA–DSt})_n$. The phenyl groups were determined by 500-MHz ^{1}H NMR to be almost completely deuterated, although the methylene protons were not completely deuterated. Aqueous NaCl solutions of $(\text{MA–DSt})_n$ were prepared by the method described previously.[18-23] Other chemicals were reagent grade (Nakarai or Wako Chemicals Co., Ltd.).

Methods. The pH, viscometric, optical, and ^{1}H NMR titrations of the copolymer in aqueous NaCl were performed by the same methods as in our previous studies on the conformational transitions of the hydrophobic polyelectrolytes.[10,18-23]

To analyze the potentiometric behavior, we take into consideration dissociation of the secondary carboxyl groups in maleic acid. The maleic acid copolymers have two carboxyl sites with different dissociation constants ($K_1°$ and $K_2°$) for protons. By introducing a differential change in the electrostatic and conformational free energy per monomole, dG, which accompanies a differential change in the dissociation degree of the carboxyl groups, $d\alpha$, we may express α as

$$\alpha = \sum_{i=1}^{2} \frac{K_i° \exp\left(-\dfrac{1}{RT}\dfrac{dG}{d\alpha}\right) \Big/ a_{H^+}}{1 + K_i° \exp\left(-\dfrac{1}{RT}\dfrac{dG}{d\alpha}\right) \Big/ a_{H^+}} \qquad (1)$$

where a_{H^+} shows activity of H$^+$. The potentiometric formula of poly(diprotonic acids) can be derived from eq 1 in terms of $K_1°/K_2°$ as

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$$\mathrm{pH} - 0.434\frac{1}{RT}\,\frac{\mathrm{d}G}{\mathrm{d}\alpha} = \log\left[\frac{1}{2}\left\{\left(\left(\frac{K_1° + K_2°}{K_1°K_2°}\right)^2\left(\frac{1-\alpha}{2-\alpha}\right)^2 + \frac{\alpha}{K_1°K_2°}\left(\frac{1}{2-\alpha}\right)\right)^{1/2} - \left(\frac{K_1° + K_2°}{K_1°K_2°}\right)\left(\frac{1-\alpha}{2-\alpha}\right)\right\}\right] \quad (2)$$

If $K_2° = 0$, eq 1 expresses a well-known potentiometric formula for poly(monoprotonic acids):

$$\mathrm{pH} - 0.434\frac{1}{RT}\,\frac{\mathrm{d}G}{\mathrm{d}\alpha} = \mathrm{p}K_1° + \log\frac{\alpha}{1-\alpha} \quad (3)$$

Also, if $K_2° \ll K_1°$, we can derive eq 4 from eq 1. For the maleic acid copolymers, eq 4 is useful. Equation 4 shows that $K_1°$ can be determined from extrapolation of a plot of pH − log $\{\alpha/(1-\alpha)\}$ against α to $\alpha \rightarrow 0$ and $K_2°$ from eq 5, which was derived from eq 2.

$$\mathrm{pH} - 0.434\frac{1}{RT}\,\frac{\mathrm{d}G}{\mathrm{d}\alpha} = \mathrm{p}K_1° + \log\frac{\alpha}{1-\alpha} + \log\left(1 - 2\alpha\frac{K_2°}{K_1°}\,\frac{2-\alpha}{(1-\alpha)^2}\right) \quad (4)$$

$$\left(\mathrm{pH} - 0.434\frac{1}{RT}\,\frac{\mathrm{d}G}{\mathrm{d}\alpha}\right)_{\alpha=1} = \frac{1}{2}(\mathrm{p}K_1° + \mathrm{p}K_2°) \quad (5)$$

First we plotted pH − log $\{(\alpha/(1-\alpha)\}$ against α at $\alpha < 0.95$, and the $K_1°$ value and the second term of the left side in eq 4 or 5 at $\alpha = 1$ were determined by extrapolating the plotted curve to $\alpha \rightarrow 0$ and 1, respectively. The $K_2°$ value was initially estimated with the pH value at $\alpha = 1$. Next we calculated the correction term (the third term of the right side in eq 4) by using the $K_1°/K_2°$ value and replotted the left side in eq 4 against α, from which the $K_2°$ value was reestimated by extrapolating the plotted curve to $\alpha \rightarrow 1$. For both $(\mathrm{MA{-}St})_n$ and $(\mathrm{MA{-}DSt})_n$ in aqueous NaCl, the difference between the initial and reestimated values of p$K_2°$ was within ±0.1–0.2, and we used an average of the two $K_2°$ values. Furthermore, in both cases, $K_2°/K_1°$ was less than 10^{-4}, and it was found to be unnecessary to consider dissociation of the secondary carboxyl groups in the analysis of the pH-titration figures at $\alpha < 0.90$.

Ionization of the secondary carboxyl groups in the maleic acid copolymers was previously considered by Dubin and Strauss,[11] who estimated both p$K_1°$ and p$K_2°$ for the copolymer with ethyl or butyl vinyl ether by the same method as in this study. Application of $K_2°/K_1° \ll 1$ to their potentiometric expression leads to a formula very similar to eq 4 in this study. The $K_2°/K_1°$ values of the aromatic copolymers of maleic acid are less than that of the copolymer with ethyl or butyl vinyl ether, as shown later. Even at $\alpha = 0.90$–0.95, where the molecule is in the coil form, the correction term (the third term on the right side of eq 4) due to ionization of the secondary carboxyl groups is negligible. In analysis of the transition free energies of the aromatic copolymers, therefore, neglect of the $K_2°$ term is not so serious, but rather exact determination of the p$K_1°$ value and estimation of the potentiometric curve for the hypothetical coil form at low α seem to be important.

Results and Discussion

The conformational behavior of $(\mathrm{MA{-}DSt})_n$ in aqueous NaCl is very similar to that of $(\mathrm{MA{-}St})_n$ in aqueous salts. The pH-titration data for $(\mathrm{MA{-}DSt})_n$ in aqueous NaCl at 25 °C is shown in Figure 1, in which pH − log $\{\alpha/(1-\alpha)\}$ is plotted against α at $\alpha < 1$ and ionic strength I = 0.01–0.27. Figure 1 also shows results for $(\mathrm{MA{-}St})_n$[18] at $I = 0.03$ for comparison. Correction for ionization of the secondary carboxyl groups is shown at $I = 0.03$ and 0.27. At $\alpha < 0.90$, ionization of the secondary carboxyl groups scarcely affects the plots. The pH-titration results shown in Figure 1 were almost independent of polymer concentration c_p in the range 0.012–0.001 monomol/L. Values of p$K_1°$ and p$K_2°$ are listed in Table I, in which those for $(\mathrm{MA{-}St})_n$ are shown for comparison. The p$K_2°$ of $(\mathrm{MA{-}St})_n$ was calculated from previous data.[18]

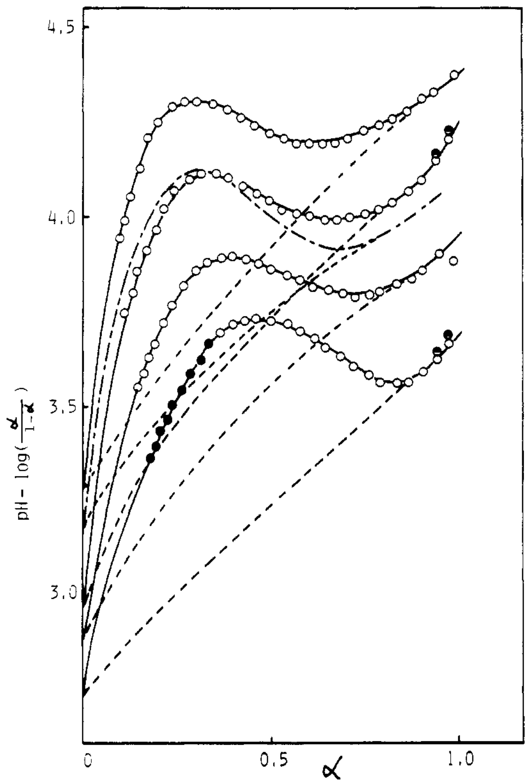

Figure 1. Potentiometric titration curves of $(\mathrm{MA{-}DSt})_n$ in aqueous NaCl at I = 0.01, 0.03, 0.10, and 0.27 (from top to bottom) and at 25 °C. Filled and half-filled circles represent existence of aggregation and the corrected results of ionization of the secondary carboxyl groups calculated by the method described in the text, respectively. Broken curves show the hypothetical potentiometric curves at low α for the coil form, which were estimated by referring to the pH-titration curve of maleic acid–ethylene copolymer in aqueous NaCl (the maleic acid–ethylene copolymer does not change conformation as pH is changed). Polymer concentration c_p was 1.21×10^{-2} monomol/L. The dot–dash curve shows the titration curve of $(\mathrm{MA{-}St})_n$ in 0.03 M aqueous NaCl at 25 °C.

Table I
Electrochemical Parameters of the Conformations of $(\mathrm{MA{-}St})_n$ and $(\mathrm{MA{-}DSt})_n$ in Aqueous NaCl at 25 °C

copolymer	I, mol/L	p$K_1°$	p$K_2°$
$(\mathrm{MA{-}St})_n$	0.01	3.3	7.4
	0.03	3.2	7.3
	0.10	3.1	7.2
	0.27	3.0	7.0
$(\mathrm{MA{-}DSt})_n$	0.01	3.3	7.3
	0.03	3.0	7.1
	0.10	2.9	7.0
	0.27	2.8	6.8

We analyzed the standard free energy change of the transition of $(\mathrm{MA{-}DSt})_n$, $\Delta G_2°$, from the compact to the extended form in the uncharged state by the same method as in the previous studies[18,20] on $(\mathrm{MA{-}St})_n$, and so the conformational free energy changes of these aromatic copolymers can be meaningfully compared. In Table II, the calculated free energy changes are shown and compared with those for $(\mathrm{MA{-}St})_n$. Irrespective of I, $(\mathrm{MA{-}DSt})_n$ is concluded to be in a more stable acidic form than $(\mathrm{MA{-}St})_n$ at acidic pH.

Virtually no temperature dependence was found for the pH-titration plot of $(\mathrm{MA{-}St})_n$ in aqueous NaCl at 5–45 °C.[21] However, $(\mathrm{MA{-}DSt})_n$ at $I = 0.03$ shows temperature-dependent pH-titration behavior, as seen in Figure 2. The conformational free energy change, $\Delta G_t°$, at $\alpha = 0$ and $I = 0.03$ was calculated at each temperature, and the conformational enthalpy and difference in specific heats,

Table II
Free Energy Change, $\Delta G_t°$, of the Conformational Transition of $(MA\text{-}St)_n$ and $(MA\text{-}DSt)_n$ in Aqueous NaCl

copolymer	T, °C	I, mol/L	$\Delta G_t°$, cal/monomol
$(Ma\text{-}St)_n$	25	0.01	370 ± 20
	35	0.03	350 ± 20
	25	0.03	350 ± 20
	18	0.03	350 ± 20
	10	0.03	350 ± 20
	25	0.10	320 ± 20
	25	0.27	280 ± 20
$(MA\text{-}DSt)_n$	25	0.01	430 ± 20
	45	0.03	430 ± 20
	35	0.03	430 ± 20
	25	0.03	410 ± 20
	15	0.03	400 ± 20
	5	0.03	380 ± 20
	25	0.10	350 ± 20
	25	0.27	*a*

[a] The value is not shown because aggregation was found in the solution.

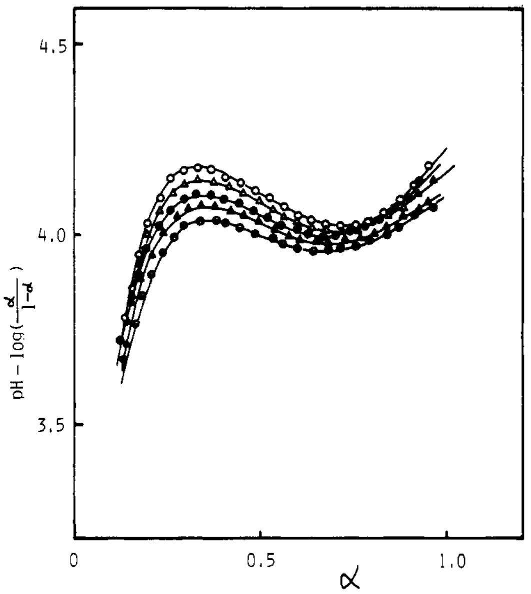

Figure 2. Temperature dependence of the potentiometric titration curve of $(MA\text{-}DSt)_n$ at the same c_p as in Figure 1 in aqueous NaCl at $I = 0.03$. Temperatures are 45, 35, 25, 15, and 5 °C from top to bottom. Polymer concentration was 1.21×10^{-2} monomol/L.

$\Delta\gamma_p$, between the compact and coil forms were calculated from the free energy changes at various temperatures by use of the following equations with the least-squares method:

$$-\Delta G_t°/T = \Delta\gamma_p \ln T + A/T + B \tag{6a}$$

and

$$\Delta H_t° = \Delta\gamma_p T - A \tag{6b}$$

where A and B are numerical constants. The calculated value of $\Delta\gamma_p$ is 12.4 (cal/monomol·deg) for $(MA\text{-}DSt)_n$ at $I = 0.03$, while it is nearly zero for $(MA\text{-}St)_n$ at $I = 0.03$ from the temperature dependence of the pH titration (the calorimetric $\Delta\gamma_p$ of $(MA\text{-}St)_n$ at $I = 0.03$ was 9 (cal/monomol·deg);[21] however, a calorimetric study has not been made for $(MA\text{-}DSt)_n$). The temperature dependence of the transition enthalpy $\Delta H_t°$ of $(MA\text{-}DSt)_n$ is compared with that of $(MA\text{-}St)_n$ at $I = 0.03$ in Figure 3. A larger $\Delta\gamma_p$ of $(MA\text{-}DSt)_n$ than of $(MA\text{-}St)_n$ may be due to enhanced hydrophobic interaction by deuteration of the phenyl groups.

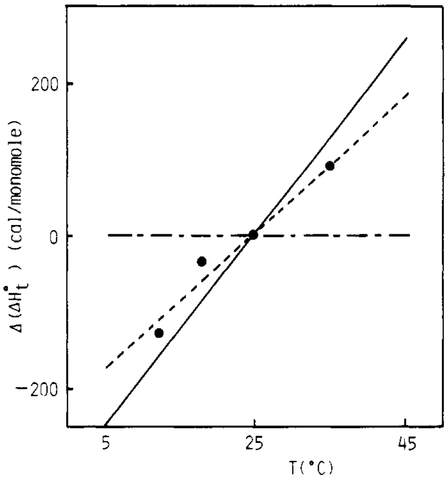

Figure 3. Plots of the transition enthalpy of $(MA\text{-}DSt)_n$ (—) and $(MA\text{-}St)_n$ (- - -) in 0.03 M aqueous NaCl, determined from temperature dependence of the pH-titration curves, against temperature. $\Delta(\Delta H_t°)$ expresses the difference in the $\Delta H_t°$, where the value at 25 °C is used as a reference. Circles represent the calorimetric data of $(MA\text{-}St)_n$ at $I = 0.03$ and the dotted line shows the result of the least-squares calculation.

The viscometric titration is shown in Figure 4a at two I's. At acidic pH, the reduced viscosity η_{sp}/c_p was almost independent of c_p at 0.004–0.013 monomol/L. In Figure 4b, intrinsic viscosity is plotted against degree of neutralization of the carboxyl groups α' at $I = 0.03$. Such viscometric results show, as in studies on $(MA\text{-}St)_n$,[18,21] that $(MA\text{-}DSt)_n$ is in a compact form at acidic pH but that it undergoes a change in conformation to the extended form as α' increases. However, the reduced viscosity clearly decreases as α' increases at $\alpha' > 1$. The change in reduced viscosity at $\alpha' > 1$ was also observed in studies on $(MA\text{-}St)_n$.[18,21]

The optical absorption spectra of $(MA\text{-}DSt)_n$ in aqueous NaCl show peaks and shoulders characteristic of the phenyl groups. The main peak at ~259 nm shifts to a shorter wavelength with a small decrease in intensity as α increases. From such a blue-shifted character of the extended form, exposure of the phenyl groups after the conformational transition can be expected. To determine quantitatively the degree of exposure of the phenyl groups, difference spectra of $(MA\text{-}DSt)_n$ at various α's were observed, with the extended form at $\alpha = 0.98$ serving as a reference. In the difference spectra eight peaks can be found between 220 and 280 nm. In Figure 5, the intensity of the peak at 269 nm is plotted against α at $I = 0.03$ and three temperatures. The peak intensity expresses the cooperative exposure of the phenyl groups, as in the previous studies on $(MA\text{-}St)_n$,[19,20] which accompanies the conformational transition.

Figure 6 shows the normalized transition curve (fraction f_c of the coil form in the molecule vs. α) at $I = 0.03$ and 25 °C calculated from the pH- and optical titration data with the same method as in the previous studies on $(MA\text{-}St)_n$,[20,21] where "a two-state model" was used. In the figure, the curve for $(MA\text{-}St)_n$ at $I = 0.03$ is shown for comparison. The midpoint of the transition in the pH-transition curve agrees well with the optical one. Also, the compact form of $(MA\text{-}DSt)_n$ is found to be more stable than that of $(MA\text{-}St)_n$.

The methine proton resonances were found at 2–3 ppm in the room-temperature 500-MHz ^1H NMR spectra of $(MA\text{-}DSt)_n$ in aqueous NaCl (sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference). Although quantitative analysis of line width of the methine proton resonance was not achieved, consid-

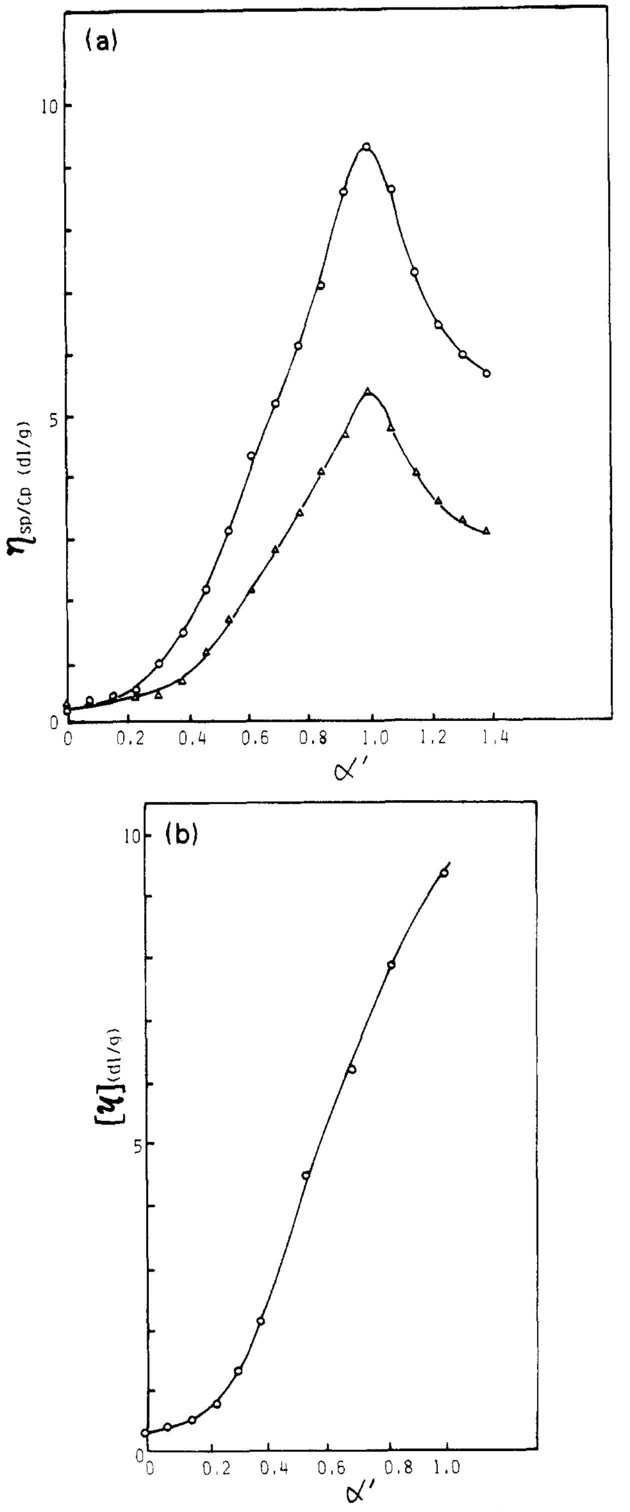

Figure 4. (a) Reduced viscosity of 1.17×10^{-2} monomol/L $(MA-DSt)_n$ in aqueous NaCl at $I = 0.03$ (○) and 0.10 (△) and at 25 °C vs. degree of neutralization of the carboxyl groups α'. (b) Plot of intrinsic viscosity of $(MA-DSt)_n$ in aqueous NaCl at $I = 0.03$ and 25 °C against α'.

erable line broadening of the resonances was found at acidic pH. It is consistent with the conclusions described above that $(MA-DSt)_n$ in aqueous NaCl is in the compact form (in which the molecule may be in a more restricted motional state than in the coil form) at acidic pH.[10]

All of the results presented here indicate enhancement of the intramolecular hydrophobic interaction when the phenyl groups in $(MA-St)_n$ are deuterated. Structures of nonpolar solutes in aqueous solutions have been extensively investigated. Stillinger has applied the scale particle

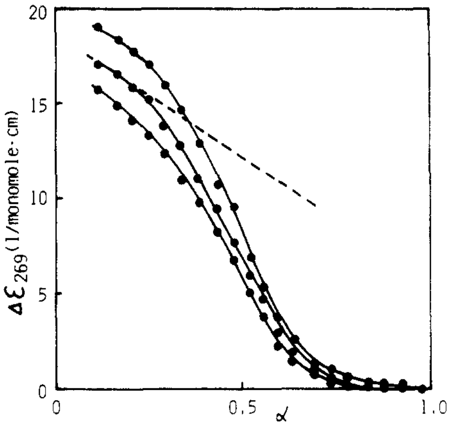

Figure 5. Difference in molar extinction coefficient at 269 nm, $\Delta\epsilon_{269}$, in the difference spectra of $(MA-DSt)_n$ in aqueous NaCl at $I = 0.03$ and 11, 25, and 38 °C (from top to bottom) vs. α. As a reference, the copolymer at $\alpha = 0.98$ was used at each temperature. A broken line shows the plot of $\Delta\epsilon_{269}$ vs. α for the hypothetical coil form. Polymer concentration was 1.16×10^{-2} monomol/L.

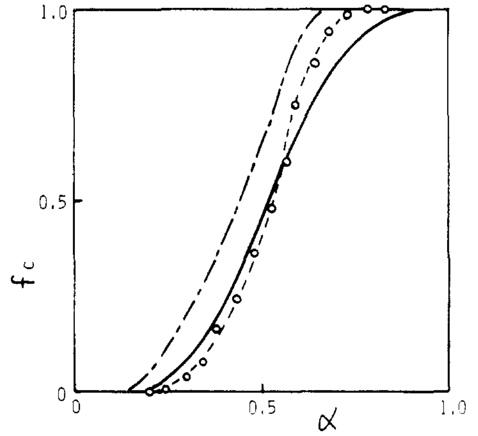

Figure 6. Normalized transition curve of $(MA-DSt)_n$ (—) determined from the pH-titration results in Figure 1 at $I = 0.03$ and 25 °C. Open circles express the calculated points from the optical data at $I = 0.03$ and 25 °C in Figure 4. The curve (- - -) refers to $(MA-St)_n$ in aqueous NaCl at $I = 0.03$ and 25 °C.

theory to the case of a rigid-sphere solute in water.[25,26] According to his model, a cage enclosing the solute consists of many water molecules arranged into regular lattices. Protons are distributed along the hydrogen bonds between the water molecules in a variety of canonical ways. Arrangement of the water molecules in the cage depends on the size of the rigid solute. Samoilov[27] has discussed in detail the hydrophobic hydration, which stabilizes the water structure around the nonpolar solutes in aqueous solutions. He has shown that the hydrophobic hydration becomes more extensive as the size of the hydrophobic solute becomes larger. On the other hand, thermodynamic properties of benzene in water and their isotope effects have recently been investigated by Choudhury et al.,[28] who used C_6H_6 and C_6D_6 in H_2O. The Henry's law constants and transfer free energies from the hydrocarbon liquid to dilute aqueous solutions were found to be sensitive to isotope label. Choudhury et al. attempted to explain theoretically the isotope effects. In their paper, it seems to be important that the apparent molar volume of C_6D_6 in H_2O (82.87 cm^3/mol) is larger than that of C_6H_6 in H_2O (82.55 cm^3/mol) at 25 °C. The hydrophobically bound water molecules are removed through the formation of clumps of the phenyl groups in the maleic acid copolymer, and the entropy of the copolymer solution increases.[29]

Therefore the entropy change of transition, from the compact to the extended coil form, of (MA–DSt)$_n$ may be more negative than that of (MA–St)$_n$ due to a more extensive hydration of (MA–DSt)$_n$ in the coil form. Also, the transition enthalpy $\Delta H_{\rm t}^\circ$ of (MA–DSt)$_n$ can be expected to be somewhat larger than that of (MA–St)$_n$, because the increase in size of the phenyl residue on deuteration results in weak van der Waals interactions in the compact form. Thus the compact form of the deuterated polymer is suggested to be more stable than that of the nondeuterated one.

The calorimetric $\Delta H_{\rm t}^\circ$ of (MA–DSt)$_n$ has not yet been determined, and the van't Hoff $\Delta H_{\rm t}^\circ$ $(=\Delta H_{\rm vH})$ of (MA–St)$_n$ could not be accurately determined. Also, the cooperative parameter σ $(=(\Delta H_{\rm cal}/\Delta H_{\rm vH})^2)$ for formation of the compact form in (MA–DSt)$_n$ has not yet been studied. Therefore, the values of $\Delta H_{\rm t}^\circ$ and $\Delta S_{\rm t}^\circ$ for the maleic acid copolymers cannot be compared here. In the future, the calorimetric $\Delta H_{\rm t}^\circ$ or the σ value of the transition of (MA–DSt)$_n$[12,30] should be determined so that comparisons of the $\Delta H_{\rm t}^\circ$ and $\Delta S_{\rm t}^\circ$ values for (MA–St)$_n$ and (MA–DSt)$_n$ may be made, which may lead to additional evidence indicating the importance of enhanced hydrophobicity due to deuteration of the phenyl groups in the maleic acid copolymer.

Although the conformational effects of deuteration of hydrogens in the hydrophobic polyelectrolytes have not yet been studied and discussed, stabilization of the compact form of (MA–St)$_n$ obtained here by deuteration of the phenyl groups may be concluded to be due to cooperative enhancement of the hydrophobic interaction between the phenyl groups.

Conclusions

A maleic acid–deuterated styrene copolymer in the compact form at acidic pH can change conformation to the extended coil form by ionization of the carboxyl groups in aqueous NaCl. The pH, optical, viscometric, and ^{1}H NMR titrations indicated behaviors very similar to that of a maleic acid–nondeuterated styrene copolymer. However, from the transition curve and the temperature dependence of the transition, the compact form of the deuterated copolymer was concluded to be more stable than that of the nondeuterated copolymer. Increase in size of the side chain in the maleic acid–styrene copolymer upon deuteration of the phenyl groups may enhance the hydrophobic hydration around the side chains and lead to a more stable compact conformation.

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References and Notes

(1) Mandel, M.; Leyte, J. C.; Stadhouder, M. G. *J. Phys. Chem.* **1967,** *71,* 603–612.
(2) Crescenzi, V. *Adv. Polym. Sci.* **1968,** *5,* 358–386.
(3) Crescenzi, V.; Quadrifolgio, F.; Delben, F. *J. Polym. Sci., Part A-2* **1972,** *10,* 357–368.
(4) Braud, C.; Muller, G.; Feno, J. C.; Sélègny, E. *J. Polym. Sci., Polym. Chem. Ed.* **1974,** *12,* 2767–2778.
(5) Okamoto, E.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974,** *12,* 2413–2422.
(6) Bottiglione, V.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1980,** *181,* 469–484.
(7) Morcellet-Sauvage, J.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1982,** *183,* 839–848.
(8) Fichtner, F.; Schonert, H. *Colloid Polym. Sci.* **1977,** *255,* 230–232.
(9) Joyce, D. E.; Kurucsev, T. *Polymer* **1981,** *22,* 415–417.
(10) Sugai, S.; Nitta, K.; Ohno, N.; Nakano, H. *Colloid Polym. Sci.* **1983,** *261,* 159–165.
(11) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970,** *74,* 2842–2847.
(12) Dubin, P. L.; Strauss, U. P. "Polyelectrolytes and Their Application"; Rembau, A., Sélègny, E., Eds.; Reidel: Dordrecht, 1975; pp 3–13.
(13) Strauss, U. P.; Vesnaver, G. *J. Phys. Chem.* **1975,** *79,* 1558–1561.
(14) Strauss, U. P.; Schlesinger, M. *J. Phys. Chem.* **1978,** *82,* 571–574.
(15) Martin, P. J.; Strauss, U. P. *Biophys. Chem.* **1980,** *11,* 397–402.
(16) Davenport, J. N.; Wright, P. V. *Polymer* **1980,** *21,* 287–292.
(17) Davenport, J. N.; Wright, P. V. *Polymer* **1980,** *21,* 293–302.
(18) Ohno, N.; Nitta, K.; Makino, S.; Sugai, S. *J. Polym. Sci., Polym. Phys. Ed.* **1973,** *11,* 413–425.
(19) Sugai, S.; Ohno, N.; Nitta, K. *Macromolecules* **1974,** *7,* 961–963.
(20) Okuda, T.; Ohno, N.; Nitta, K.; Sugai, S. *J. Polym. Sci., Polym. Phys. Ed.* **1977,** *15,* 749–755.
(21) Sugai, S.; Ohno, N. *Biophys. Chem.* **1980,** *11,* 387–395.
(22) Sugai, S.; Nitta, K.;f Ohno, N. *Polymer* **1982,** *23,* 238–242.
(23) Ohno, N. *Polym. J.* **1981,** *13,* 719–726.
(24) Ohno, N.; Sugai, S., unpublished.
(25) Stillinger, F. H. *J. Solution Chem.* **1973,** *2,* 141–158.
(26) Stillinger, F. H. *Science (Washington, D.C.)* **1980,** *209,* 451–457.
(27) Samoilov, O. Ya. *Zh. Fiz. Khim.* **1978,** *52,* 1857–1862.
(28) Dutta-Choudhury, M. K.; Miljevic, N.; Van Hook, W. A. *J. Phys. Chem.* **1982,** *86,* 1711–1721.
(29) Frank, F. "Water"; Frank, F., Ed.; Plenum Press: New York, 1975; Vol. 4, pp 1–94.
(30) Ohno, N.; Nitta, K.; Sugai, S. *J. Polym. Sci., Polym. Ed.* **1978,** *16,* 513–521.

Deuterium-Exchange Preparation for Small-Angle Neutron Scattering Samples of Saturated Polymers

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ABSTRACT: Deuterium–hydrogen exchange catalyzed by a suspended rhodium catalyst has been used to achieve partial deuteration of a saturated polymer, hydrogenated polybutadiene. IR and density measurements show that about 6% of the hydrogen is replaced by deuterium. Small-angle neutron scattering indicates an exchange of 60% of the hydrogens in 10% of the chains. No evidence of unwanted side reactions involving the carbon–carbon backbone of the chain was observed.

Introduction

Small-angle neutron scattering (SANS) experiments are performed on mixtures of deuterated and hydrogenated polymer chains to determine information such as single-chain conformation in the bulk state. One of the problems with these experiments is the inability to match exactly the labeled and unlabeled species in terms of molecular size and chemical microstructure. A matched set of deu-

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