Helix Initiation and Propagation by Isolated Arginine Residues in Aqueous Sodium Dodecyl Sulfate

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ABSTRACT: Circular dichroism spectra have been recorded in aqueous sodium dodecyl sulfate ($NaDodSO_4$) for fractions of a random copolymer of L-arginine and (hydroxybutyl)-L-glutamine. The mole fraction of Arg is 0.11. The helix content at low temperatures is reduced upon interaction with $NaDodSO_4$, and there is a small increase in helix content at high temperature. Analysis in terms of the customary Zimm–Bragg parameters shows that $NaDodSO_4$ produces a decrease in s and an increase in σ, for the Arg residue. The increase in σ is the more important effect if helices must be short and the helix content is low, as is the case with small peptides. The decrease in s is the dominant effect at high helix content.

Introduction

Neither the α helix nor the β sheet is a tenable conformation for fully ionized poly(L-arginine), poly(L-histidine), poly(L-lysine), or poly(L-ornithine) in dilute aqueous solution because of the repulsive interaction of the charged side chains. The conformational properties experience a dramatic change upon the addition of sodium dodecyl sulfate ($NaDodSO_4$). Circular dichroism (CD) in aqueous $NaDodSO_4$ unequivocally demonstrates formation of an α helix by poly(L-arginine)[1] and poly(L-ornithine)[2,3] and formation of β sheet by poly(L-lysine).[3-6] A conformational transition produced by $NaDodSO_4$ can also be detected in poly(L-histidine).[1] The ordered structure formed is probably a β sheet, but the assignment is made difficult because the side chains contribute to the CD. Presumably, the negative $DodSO_4^-$ ions interact with the positive charges in a manner that reduces the electrostatic stress in the ordered structures, thereby increasing the stability of the α helix and β sheet.

The behavior of members of the poly[(hydroxyalkyl)-L-glutamine] series is much different from that seen with the cationic poly(amino acids). The thermally induced helix–coil transitions of the nonionic poly(amino acids) are affected very little by $NaDodSO_4$,[7,8] which is in marked contrast to the dramatic effect on order–disorder transitions in the cationic polymers. These neutral polymers contain no charged groups that can interact strongly with $DodSO_4^-$, which presumably accounts for the small effect on the helix–coil transition. One means of accounting for the small size of the changes in the helix–coil equilibrium at 5 °C is to attribute them entirely to an alteration in the Zimm–Bragg[9] propagation parameter, s. The increase in s is only 0.003 for the (hydroxypropyl)-L-glutaminyl residue and 0.012 for the (hydroxyamyl)-L-glutaminyl residue.[8] An excellent first approximation is that the values of σ and s deduced for a poly[(hydroxyalkyl)-L-glutamine] in water are also appropriate in aqueous solutions of $NaDodSO_4$.

Studies by Yang et al. of the effect of $NaDodSO_4$ on the CD of copoly(amino acids) that contain Lys provide convincing evidence that the type of ordered structure produced may depend on the amino acid sequence.[10,11] The only sequences studied that form a stable β sheet in $NaDodSO_4$ are $(Lys\text{-}Xxx)_n$, where Xxx = Ala, Leu, Lys, or Ser, and $(Lys\text{-}Lys\text{-}Lys\text{-}Ser)_n$. Stable α helices were formed by $(Lys\text{-}Lys\text{-}Leu\text{-}Leu)_n$ and by "random" $(Lys^x\text{–}Leu^{100-x})_n$ and $(Lys^y\text{–}Ala^{100-y})_n$, where $x < 75$ and $y < 65$.

CD studies of a variety of small peptides of biological importance that contain Arg, Lys, or His show that order is often produced upon interaction with $NaDodSO_4$, and the ordered structure formed is frequently an α helix.[12,13] It is of considerable interest to determine the relationship between the elevation in helix content in the peptides and the dramatic conformational changes seen in the cationic homopoly(amino acids). Since thermally induced helix–coil transitions of the poly[(hydroxyalkyl)-L-glutamines] are insensitive to $NaDodSO_4$, the values of σ and s for isolated cationic residues surrounded by nonionic residues should be readily accessible by the "host–guest" approach.[14,15] That approach is implemented here for copolymers of (hydroxybutyl)-L-glutamine (HGB) and L-arginine.[16] The values of σ and s for Arg are determined as functions of temperature for $NaDodSO_4$ concentrations above and below the critical micelle concentration (cmc).

Table I
Composition, Sedimentation Coefficients, and Molecular Weights

HBG:Arg ratio	$S^0_{20,w} \times 10^{13}$, s	M_w	HBG:Arg ratio	$S^0_{20,w} \times 10^{13}$, s	M_w
9.0:1.0	2.3	17 000	8.9:1.1	3.7	45 000
8.8:1.2	3.0	32 000	8.9:1.1	3.9	57 000
8.9:1.1	3.2	36 600	8.9:1.1	4.1	78 000
8.9:1.1	3.5	37 300			

Experimental Section

Fractionation. The preparation and fractionation procedures were similar to those described previously.[16] The poly(HBG–Arg) copolymer was dissolved in a 0.9 M NaCl solution, mixed with methanol (volume ratio 1:9), and fractionally precipitated with ethyl ether. The precipitate obtained after each addition of ether was isolated by centrifugation, redissolved in water, and dialyzed against water. The polymer was removed by lyophilization when the conductivity of the dialyzate became constant. All lyophilized fractionated polymers were dried thoroughly under vacuum.

Amino Acid Composition Analysis. Amino acid composition analysis was performed on a PICO-TAG amino acid analyzer (Waters Assoc.) which consisted of two solvent delivery systems (Model 6000A) and a fixed-wavelength detector (254 nm) with a controller (Model 720). The procedure was that described in the PICO-TAG operator's manual. The copolymer fractions were hydrolyzed in vacuo for 24 h at 110 °C in 6 N HCl and the acid was removed by evaporation. The hydrolyzed samples and standards of free amino acids were dried down again after addition of 10–20 μL of ethanol–water–triethylamine (TEA). The samples were then derivitized by phenyl isothiocyanate (PITC). The derivatization reagent was freshly prepared ethanol–TEA–water–PITC. PITC amino acids were formed by addition of 20 μL of reagent to the dried sample and sealing after application of vacuum for 20 min at room temperature. Samples were injected in 40-μL volume by an autoinjector (Model 710B). A gradient formed from an aqueous buffer and 60% acetonitrile in water was used as the eluent.

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Only one fraction (the one with M_w = 32 000) exhibited a detectable peak in the position expected for the γ-ester of Glu and aminobutanol.[17,18] Since the composition of this fraction is not significantly different from the others reported in Table I, it is assumed that the amount of the γ-ester was not sufficient to affect the results.

Ultracentrifuge. The solvent for all ultracentrifuge measurements was 0.1 M NaCl. The molecular weight of each fraction was determined with a Spinco Model E ultracentrifuge equipped with schlieren optics and a temperature-control unit calibrated against a certified thermometer. Archibald's method[19] or the low-speed approach to equilibrium method and the modifications proposed by Klainer and Kegeles[20] were followed throughout. Archibald[19] showed that the following equations hold for the top and bottom of the ultracentrifuge cell for all times during the run:

$$M_m = \frac{RT}{(1 - \upsilon\rho)\omega^2} \frac{(dc/dx)_m}{x_m c_m} \quad (1a)$$

$$M_b = \frac{RT}{(1 - \upsilon\rho)\omega^2} \frac{(dc/dx)_b}{x_b c_b} \quad (1b)$$

In eq 1a and 1b, M and υ are the molecular weight and partial specific volume, respectively, R is the gas constant, T is the absolute temperature, ρ is the density of the solution, ω is the angular velocity, and c and dc/dx are the concentration and concentration gradient, respectively. The subscripts, m and b, refer to the meniscus and the bottom of the cell. The initial concentration at zero time, c_0, was measured in arbitrary units by the use of a synthetic boundary cell. c_m and c_b were calculated from c_0 according to the equations derived by Klainer and Kegeles[20] by integration of the concentration gradients across the boundaries at the cell meniscus and bottom. If the sample is homogeneous, then M_m and M_b are equal, and measurements of c and dc/dx at the two ends of the cell give the same value for the molecular weight. For inhomogeneous material, there is a preferred redistribution with the more massive species being concentrated toward the cell bottom. Consequently, M_b increases and M_m decreases with time. For some fractions, the weight-average molecular weight M_w was obtained through the extrapolation of the M_b versus time and M_m versus time curves to the common zero, the initial zero time of these two curves. However, for the samples with molecular weights of 37 300, 57 000, and 78 000, M_w's were obtained from the intersections of the curves because the best straight lines intersect at a time greater than zero. If the molecular weight were calculated instead from extrapolation of $(M_m + M_b)/2$ to zero time, the values would have been 36 000, 55 000, and 85 000, respectively.

The ultracentrifuge cells used for both the velocity and equilibrium runs were 12 mm long. Sample concentrations for the equilibrium runs were varied from 0.2% to 0.4% for all the fractions. The heights of solution in a cell and the rotor speeds selected for the equilibrium runs were such that the value of $M(1 - \upsilon\rho)/2RT$ was always close to 1.[21] The partial specific volumes for the polymers were calculated from amino acid compositions and the tabulated apparent specific volumes given in literature.[22] The schlieren patterns were recorded on Kodak metallographic plates with typical exposure times of 5–12 s. The angle of the schlieren diaphragm was maintained at 65° throughout the equilibrium runs.

The measurements of the ultracentrifuge patterns were obtained from enlarged tracings, drawn from projections made by a Nikon photographic projector. Values of dc/dx were determined directly (in arbitrary units) as the ordinates of the schlieren patterns on tracing paper, and dx was the interval between tabulated dc/dx readings. Furthermore, both dc/dx and dx readings were corrected for the magnification factors of the camera lens and the projector. To obtain the most reliable values of $(dc/dx)_m$ and $(dc/dx)_b$, the values near both ends of the cell were plotted as a function of distance, and the best-fitting straight lines were drawn through the points. The integrations required for the calculations of c_m and c_b were then performed as a summation process by counting down dc/dx from the meniscus to the plateau or from the cell bottom to the plateau.

It has been reported[23] that, in high centrifugal fields, some redistribution of components of the solvent may occur, in which case it is imperative to make a correction for the contribution from the solvent to the values of dc/dx determined. A separate run under identical conditions for the solvent must be carried out. The values of dc/dx for the solvent are then subtracted from the values measured for the solution run to give corrected values of the concentration gradient due only to solute. However, in the results reported here, no base-line corrections were made because the centrifugal fields were sufficiently low that no redistribution of salts was observed. The reproducibility of runs conducted under similar experimental conditions was about 92%. Some inaccuracy could result from the drawing of straight lines near the meniscus and bottom. The typical error in evaluating the ordinates at the menisci was 0.02 mm, which would cause an error of 4% in the molecular weight determined, thereby accounting for half of the difference in the values obtained in duplicate runs.

The measured sedimentation coefficients vary linearly with the initial concentration. The sedimentation coefficient at infinite dilution, $S^0_{20,w}$, was obtained by fitting the $S_{20,w}$ versus concentration curve to a straight line.

Viscosity Measurements. Viscosity measurements in 0.1 M NaCl were carried out with a Cannon semimicrodilution viscometer at 20 °C. The intrinsic viscosity, $[\eta]$, was obtained from linear extrapolation of $(t - t_0)/t_0c$ to zero concentration. Here t and t_0 are the flow times for solution and solvent, respectively.

Circular Dichroism Measurements. CD measurements were carried out with a JASCO J-500A spectropolarimeter by using calibrated fused quartz cells with an optical path of 10 mm. Except for the sample with M = 57 000, for which the spectra were scanned from 250 to 195 nm, partial spectra from 230 to 215 nm were obtained because the CD information required in the analysis is $[\theta]$ at 222 mm. Solvent base lines were recorded for all runs. The polymer concentrations were 0.012–0.018 mg/mL. Three $NaDodSO_4$ concentrations were used. The smallest is substantially below the critical micelle concentration (cmc) determined previously,[24] and the other two are slightly above and far above the cmc. The latter two concentrations lie on either side of a transition in the micelle structure that can be detected with a fluorescent probe.[24] Cell temperature was maintained with a circulating water bath connected to a brass water jacket surrounding the cell. Sample temperature was determined with a Yellow Springs Instrument Model 42 SC telethermometer before each spectrum was recorded.

The uncertainty for $[\theta]_{222}$ was from 0.5% to about 4%. $[\theta]_{222}$ was used to calculate the helix content through the equation

$$f = ([\theta] - [\theta]_c)/([\theta]_h - [\theta]_c) \quad (2)$$

Here $[\theta]_c$ and $[\theta]_h$ are the mean residue ellipticities for the completely disordered and completely helical polypeptide, respectively. Values for $[\theta]_c$ were obtained from the interpolated results of a graph of $[\theta]_{222}$ against temperature for poly[(hydroxyethyl)-L-glutamine].[25] A value of −36 000 deg cm^2 dmol^{-1} was chosen for $[\theta]_h$.[26]

Calculations. Theoretical analysis of the CD data is achieved by a matrix treatment based on the Zimm–Bragg theory.[9] It is assumed that the amino acid sequences are completely random. The configuration partition function, Z, for a partially helical copolypeptide containing n amino acid residues in a defined sequence can be written as

$$Z = [1 \quad 0]\mathbf{U}_1\mathbf{U}_2 \ldots \mathbf{U}_n \, \mathrm{col}(1,1) \quad (3)$$

where col(1,1) denotes a column vector in which both elements are 1. The statistical weight matrix for residue i is

$$\mathbf{U}_i = \begin{bmatrix} ! & \sigma s \\ 1 & s \end{bmatrix}_i \quad (4)$$

where rows index the state of amino acid residue $i - 1$, columns index the state of amino acid residue i, and the order of indexing is c, h. The fraction of the residues that are in helix states is obtained by standard matrix techniques that rigorously evaluate $(1/n)(\partial \ln Z/\partial \ln s)$.

The average helix content for a random copoly(amino acid) of specified composition and degree of polymerization was calculated as follows. For each chain, the ith amino acid residue was assigned as Arg if the ith random number was less than or equal to the mole fraction of Arg residues in the copolypeptide. Otherwise

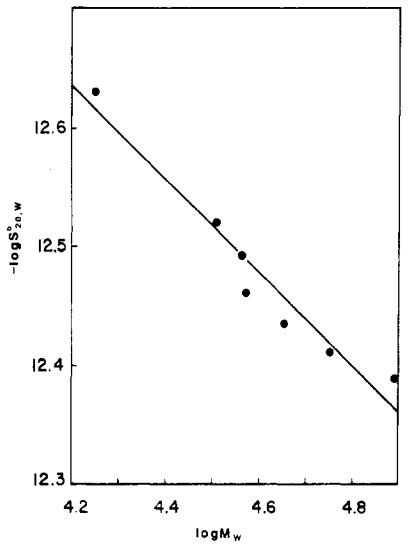

Figure 1. Molecular weight dependence of $S^0_{20,w}$. The straight line has a slope of −0.38.

the ith amino acid residue was assigned as HBG. The desired helix content is the average over a sufficiently large number of such chains. For the sake of computation time, the helix content was approximated as the average obtained from 10 independently grown chains. Trial calculations revealed no significant change in helix content when as many as 500 chains were used.

Values of σ and s for (hydroxybutyl)-L-glutaminyl residues were taken from earlier work[15] and were treated as host parameters because $NaDodSO_4$ does not affect the values. The values of σ and s for Arg were obtained from the best fit of the calculated helix content, f_{cal}, to those measured experimentally, f, as follows:

$$\tau = \sum_{i=1}^{7} (f_{cal} - f)^2 \qquad (5)$$

The summation was carried out over all seven fractions at a particular temperature in a particular solvent. A mesh composed of guest parameters was constructed, with ordinate and abscissa of the mesh being assigned to values of σ and s, respectively, of the guest. The algorithm then calculates τ at each mesh point and searches for the smallest τ. The algorithm then brings the center of the mesh to the point where τ is a minimum. A new expanded mesh is created about this point, and the point on the new mesh with the smallest τ is located. This procedure is repeated to obtain a further refinement of the values of σ and s for the guest. The CPU time per mesh point was about 1.2 s on an IBM 370 computer with a full precision of 64 bits.

Results and Discussion

Characterization of the Copolymers. The measured amino acid compositions, molecular weights, and sedimentation coefficients for the fractionated poly(HBG–Arg) are presented in Table I. For all fractions, the amino acid compositions were nearly the same despite the differences in molecular weights. This observation indicates that the amino acid sequence is indeed random in the fractionated samples.

The validity of the sedimentation studies is explored in Figure 1, in which $-\log S^0_{20,w}$ (from sedimentation velocity) is plotted against $\log M_w$ (from Archibald's method).[19] For a series of fractionated polymers that are completely disordered, the magnitude of the slope of the straight line is an indication of the goodness of the solvent in which the polymers are dissolved. For nondraining disordered polymers dissolved in a Θ solvent the slope is −0.50 while in a good solvent the value is −0.40.[27] The slope of the straight line drawn in Figure 1 is −0.38, which is close to the value expected for disordered chains in a good solvent. The difference from the value expected for nondraining

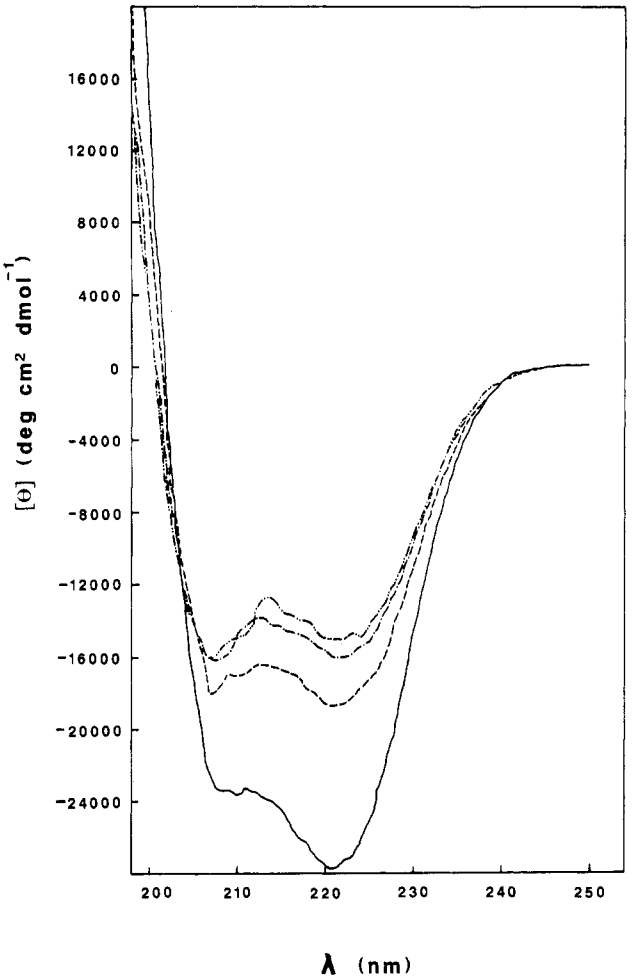

Figure 2. Circular dichroism spectra of the fraction with M = 57 000 at 5 °C in water (—), 0.005 95 M $NaDodSO_4$ (- - -), 0.0113 M $NaDodSO_4$ (· · ·), and 0.0455 M $NaDodSO_4$ (- · · -).

coils in a good solvent is in the direction expected if the coils are actually partially draining.

For a series of random coil polymer–solvent systems, there exists a constant that can be calculated from the sedimentation coefficient at infinite dilution, S^0, and the intrinsic viscosity measured for the solutions, $[\eta]$.[27,28]

$$\beta = \frac{S^0[\eta]^{1/3}M^{-2/3}\eta_0 L}{1 - \bar{v}\rho} \qquad (6)$$

Here η_0 is the solvent viscosity and L is Avogadro's number. If the polymer chains are nondraining coils of very high M, β should be near 2.5×10^6. The value calculated for the sample with M = 32 000 is actually 7.9×10^6. This large value is somewhat surprising; it may arise from partial draining of the chain, which has a substantial helix content.

CD Measurements. CD spectra for poly(HBG–Arg) with M = 57 000 in water and in $NaDodSO_4$ solutions at two different temperatures are depicted in Figures 2 and 3. The spectra at the lower temperature, 5 °C, show the presence of a right-handed α helix mixed with random coil, which is similar to that observed previously.[16] The spectra at 68 °C, Figure 3, exhibit a drastic change in mean residue ellipticity which shows that the copolymers undergo a thermally induced transition from α helix to random coil in water and in $NaDodSO_4$ solutions.

At 5 °C, the negative CD band at 222 nm becomes less intense upon the addition of $NaDodSO_4$. The detergent *reduces* the helix content at 5 °C, where the helix content was large before addition of $NaDodSO_4$. There is a much

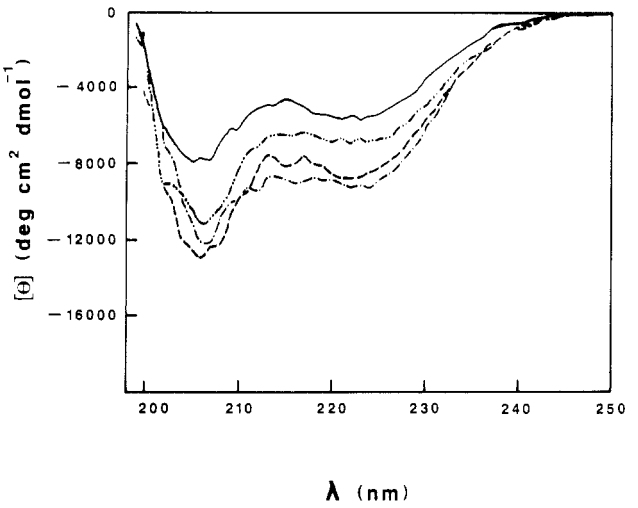

Figure 3. Circular dichroism spectra of the fraction with M = 57 000 at 68 °C in water (—), 0.00595 M $NaDodSO_4$ (- - -), 0.0113 M $NaDodSO_4$ (- · -), and 0.0455 M $NaDodSO_4$ (- · · -).

larger change upon going from 0 to 0.006 M $NaDodSO_4$ than in going from 0.006 to 0.045 M $NaDodSO_4$. This result suggests that detergent monomers are more effective than micelles in changing the helix content. At 68 °C, there is a slight *increase* in the intensity of the negative circular dichroism band when $NaDodSO_4$ is present.

Since $NaDodSO_4$ has a very small effect on the thermally induced helix–coil transition of the uncharged poly[(hydroxyalkyl)-L-glutamines],[7,8] the change in helix content of the copolymers is attributed to the interaction of $NaDodSO_4$ with the charged Arg side chain. The interaction depends on the temperature, molecular weight of the copolymer, and concentration of $NaDodSO_4$. It is fundamentally different from the interaction between $NaDodSO_4$ and the Arg homopolymer, where the detergent converts the polymer from a statistical coil to an α helix.[1] This behavior can be rationalized by a consideration of two chains with markedly different compositions. The first polymer contains a single Arg placed within a very long HBG chain. When $NaDodSO_4$ is added to the system, there is a change in the helix-forming tendency for Arg because it interacts strongly with $DodSO_4^-$. However, none of the change in helix content can be attributed to an alteration in the interaction of *pairs* of ionized residues because the chain contains only a single Arg. The second polymer to be considered is a long homopolymer of Arg. There are copious interactions of pairs of charged residues, and these interactions are modified upon interaction of the chain with $DodSO_4^-$. Therefore, $NaDodSO_4$ may have different effects on the helix content of poly(L-arginine) and a copolymer in which there is a single Arg in a chain where all other residues are HBG. The copolymers studied here contain more than one Arg, but, on the average, Arg residues are separated by ten HBG residues. Therefore, the conformational changes seen in the copolymers are more sensitive to the consequences of the interaction of $NaDodSO_4$ with an isolated Arg than is the case in poly(L-arginine) itself.[1]

A few CD spectra at 25 °C for the fraction with M = 57 000 were obtained in solutions containing 0.1 M NaCl. The dependence of f on the concentration of $NaDodSO_4$ in the presence and absence of NaCl is compared in Figure 4. In the absence of $NaDodSO_4$, there is a small increase in f upon the addition of NaCl. Addition of $NaDodSO_4$ to either solution produces a decrease in helix content. A detailed molecular interpretation is made difficult because the cmc of $NaDodSO_4$ decreases in the presence of NaCl,[29,30] as shown in Figure 4. Nevertheless, it is apparent that qualitaively similar behavior is seen in 0.0 and 0.1 M NaCl.

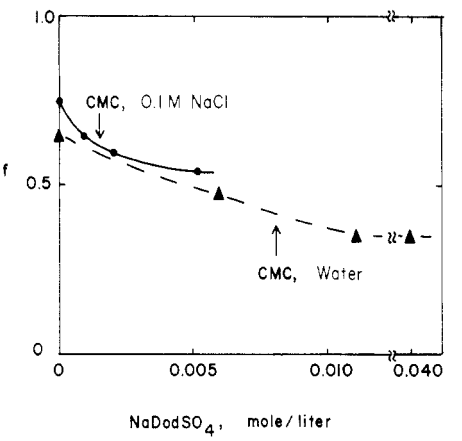

Figure 4. Helical content at 25 °C for the fraction with M = 57 000 in aqueous $NaDodSO_4$ in the presence and absence of 0.1 M NaCl. The cmc is noted for each NaCl concentration.

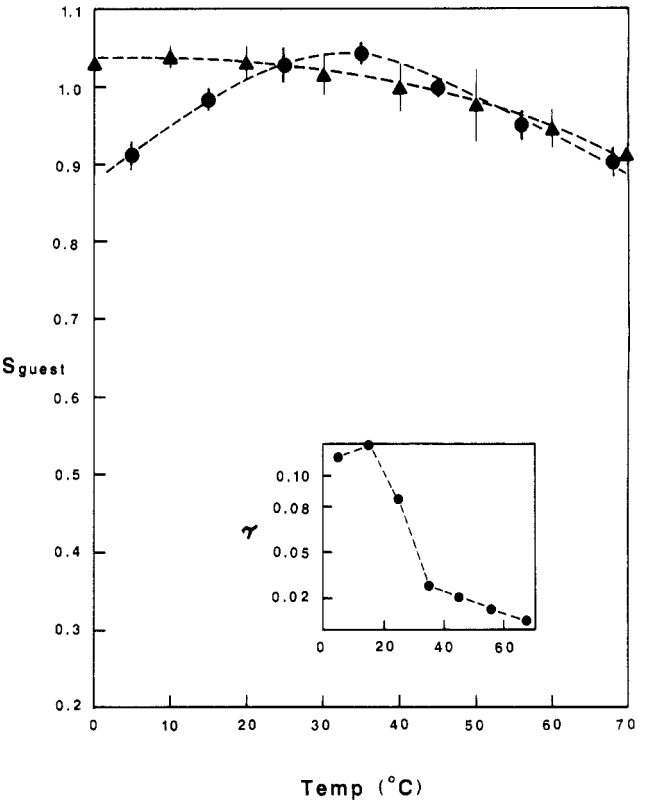

Figure 5. Helix propagation parameter, s, for Arg in water when σ is 1×10^{-5} and independent of temperature. Triangles denote the results reported previously by Konishi et al.,[16] and circles are the results obtained in the present work. The inset depicts τ for the fit to the data reported here.

Statistical Weights. Figure 5 compares the current results for the melting data of the copolymers in water with those obtained previously[16] by the LAPS (Lifson–Allegra–Poland–Scheraga) hierarchy of approximations. For temperatures above 20 °C, these two sets of results agree very well with one another. Some difference is apparent below 20 °C. The molecular weight range covered in the present study is 17 000–78 000, and previously[16] the range was 45 000–205 200. Samples are best suited for a determination of σ and s if they cover a range of M in which the helix content depends strongly on the degree of polymerization. Of course, the helix content for a copolypeptide of defined composition becomes independent of

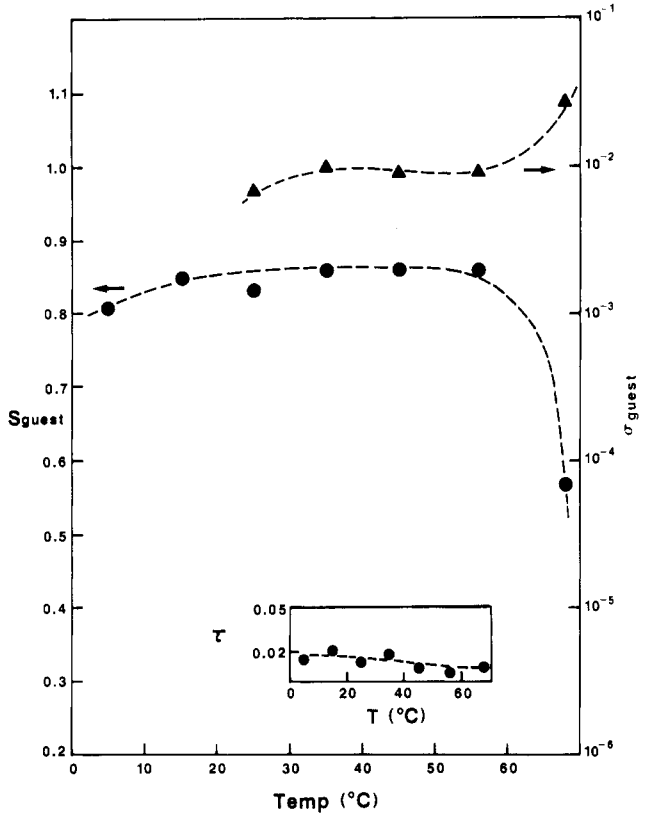

Figure 6. Behavior of σ (triangles) and s (circles) for Arg in 0.005 95 M $NaDodSO_4$ when both parameters are temperature dependent. Values are not shown for σ at temperatures of 5 and 15 °C. At these two temperatures, essentially equivalent fits were obtained with any σ so small that essentially all helix initiation is at HBG.

M as the degree of polymerization becomes infinite. The present samples cover a range of M in which f is a stronger function of the degree of polymerization than was the case in the prior study.[16]

For both sets of data, σ for Arg was fixed at 1×10^{-5} and the value of s for Arg at each temperature was obtained from the best fit of all copolymer data. The "goodness of fit" criterion is expressed in terms of the parameter τ, as defined in eq 5. It is plotted against temperature for the current data set in the insert to Figure 5. The largest values of τ are obtained at the lower temperatures. The values of τ at the lower temperatures could be made smaller if σ for Arg at these temperatures were assigned a value smaller than 10^{-5}, which means that there is essentially no helix initiation at Arg.

Figure 6 depicts the values of σ and s deduced for Arg in the presence of 0.005 92 M $NaDodSO_4$. Both σ and s were adjusted to produce the best fit to the data at each temperature. At 25–56 °C, the necessary σ is on the order of 10^{-2}, which is 3 orders of magnitude larger than the value found in water. The value of σ is not well defined at 5 and 25 °C. Here the smallest τ's are obtained with smaller σ, but neither τ nor s is much affected by changes in σ, so long as $\sigma < 10^{-3}$. In contrast, τ goes through a well-defined minimum as σ is varied if the temperature is greater than 25 °C.

The values of s in water (Figure 5) are always greater than 0.90, but none of the values of s in 0.00592 M $NaDodSO_4$ (Figure 6) exceeds 0.86. At this concentration, which is below the cmc at 25 °C, the detergent discourages helix propagation by Arg, but it also makes helix initiation less difficult.

Since σ for Arg in Figure 6 has a well-defined value on the order of 10^{-2} for temperatures between 25 and 56 °C,

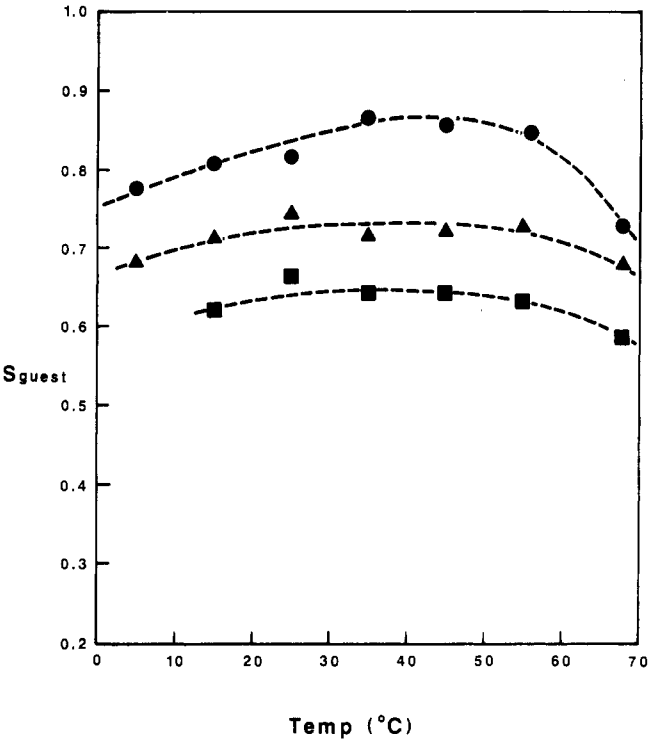

Figure 7. Behavior of s for Arg in 0.005 95 (circles), 0.0113 (triangles), and 0.0455 M (squares) $NaDodSO_4$ when σ is assigned the temperature-independent value of 0.01.

Table II
Values of s at Three $NaDodSO_4$ Concentrations (σ = 0.01)

$NaDodSO_4$, mol/L	temp, °C	s	τ
0.0059	5	0.78	0.0211
	15	0.81	0.0273
	25	0.82	0.0142
	35	0.87	0.0185
	45	0.86	0.0091
	56	0.85	0.0054
	68	0.73	0.0094
0.0115	5	0.68	0.0134
	15	0.71	0.0113
	25	0.74	0.0142
	35	0.72	0.0110
	45	0.72	0.0069
	56	0.73	0.0048
	68	0.68	0.0048
0.046	15	0.62	0.0275
	25	0.66	0.0154
	35	0.64	0.0098
	45	0.64	0.0072
	56	0.63	0.0040
	68	0.58	0.0040

s for Arg was redetermined by using $\sigma = 10^{-2}$ at all temperatures. The results are presented in Figure 7 and Table II. The apparent changes in σ and s at the highest T are not significant. If the trends at 25–56 °C were followed instead, the change in the calculated f at 68 °C would be about 0.04, which does not exceed the uncertainty. At lower temperatures, the trends for s in 0.005 92 M $NaDodSO_4$ are similar in Figures 6 and 7.

Figure 7 also depicts the values of s for Arg in 0.0115 and 0.0455 M $NaDodSO_4$ when $\sigma = 0.01$. The detergent concentrations are above the cmc at 25 °C. There is no point at the lowest T for 0.0455 M $NaDodSO_4$ because that concentration exceeds the solubility of the detergent. The values of s become smaller when the detergent concentration rises above the cmc, and there is very little temperature dependence.

Table III
Calculated f for $(Ala_4ArgAla_5)_x(Ala_5ArgAla_4)_x$[a]

x	water	0.006 M $NaDodSO_4$
1	0.087	0.109
2	0.332	0.319
3	0.526	0.457

[a] 25 °C; the values of σ and s are 8×10^{-4} and 1.07 for Ala in both solvents. For Arg, they are 1×10^{-5} and 1.03 in water and 0.01 and 0.82 in $NaDodSO_4$.

Table III presents values of f calculated for copoly(amino acids) of defined sequence in which 10% of the residues are Arg and 90% are Ala. Ala is chosen here as an example of a nonionic residue with a small σ and $s > 1$. A change in the vaues of σ and s for Arg from those determined previously[16] in water to the current results in 0.006 M $NaDodSO_4$ produces a decrease in helix content if the degree of polymerization is large. The change is easily rationalized by the decrease in s for Arg. However, the same parameters predict an increase in helix content at sufficiently small degree of polymerization, as shown by the entries with $x = 1$ in Table III. Rationalization of this observation must focus on the change in σ. If helices are short (and they must be short if the degree of polymerization is small), there is no opportunity for recovery from the penalty reflected by an extremely small value of σ. Insertion of a residue with a comparatively large σ will then enhance the helix content (even if s is small), because it means that the penalty accompanying helix initiation can be overcome by an attainable number of propagation events.

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Registry No. $NaDodSO_4$, 151-21-3; (L-arginine)(hydroxybutyl L-glutamine) (copolymer), 111189-12-9.

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Catalytic Effect of HCl on the Dehydrochlorination of Poly(vinyl chloride)

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ABSTRACT: Two poly(vinyl chloride) (PVC) samples with different thermal stability were degraded in both pure nitrogen and in an atmosphere containing HCl. The degradation experiments were made in a thermogravimetric system where the weight loss was measured. The polyene sequence distributions were monitored by UV-visible spectroscopy and the increase in the number of polyene sequences during degradation was measured by ozonolysis. The PVC sample with increased thermal stability showed less severe discoloration, i.e., the polyene sequences were shorter, when degraded in pure nitrogen. On the other hand when degradation was performed in an atmosphere containing HCl both the rate of dehydrochlorination and the polyene sequence length increased. For the PVC with normal thermal stability there was no measurable difference in either the dehydrochlorination rate or the length of the polyene sequences for degradation in nitrogen compared with degradation in HCl. From these results we have suggested a mechanism for the HCl catalysis of the propagation step in the degradation of PVC, which is based on an ion-pair mechanism. Due to the presence of HCl the equilibrium is shifted to form more ion pairs and the HCl "stabilizes" the cation, thus leading to the chloride ion being nearer the end of the sequence and more able to abstract the methylene proton.

Introduction

In thermal degradation of PVC, dehydrochlorination is the dominating reaction. In earlier investigations we have been able to correlate the amount of labile chlorine to the dehydrochlorination rate.[1-3] According to these results tertiary chlorine is the most important defect, since it is much more frequent than the internal allylic chlorine. In agreement with other published reports,[4-7] we have found

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