intrinsic viscosity as a function of the solubility parameter of the solvent. However, a most significant difference in this case is that information is being obtained on the molecular in contrast to the bulk level.

It is quite clear that the excimer probe is sensitive to the host matrix. However, before we may proceed with an analysis of the molecular morphology in these blends, we must determine which type of excimer site is displaying the host sensitivity.

The intramolecular site depends upon the population of suitable local conformational states of the chain, i.e., rotational dyads. The intermolecular site, on the other hand, is independent of local conformational structure and is sensitive solely to aggregation of guest aromatic vinyl polymers. At this stage of the study it is not clear whether any differences in spectral parameters between intermolecular and intramolecular excimer sites should be expected. Thus, direct experimental measurement is not yet possible. Nevertheless, a distinction may be made if what is known about the effect of solvent on chain conformational structure in fluid solutions is applied to these solid state blends. It is generally accepted that increasing the solvent quality will lead to expansion of the coiled polymer chain. However, only the long-range conformational structure of the chain is affected; the local conformational distribution is insensitive to the solvent medium. Thus we would not expect the intramolecular excimer site distribution in the solid blends to depend upon the host matrix.

The situation is quite different for the intermolecular sites. These arise entirely from clustering of the guest polymer chains or the chain bending back upon itself. In a good host medium there will be extensive interpenetration of the guest and host chains causing the local concentration of aromatic rings to drop. In addition, expansion of the chain will reduce the likelihood of chain "back-bending". Both effects will lead to reduction in I_D/I_M as is observed in Figure 2 for $|\Delta\delta| = 0$. As the host matrix becomes a thermodynamically poorer solvent for the P2VN guest, chain expansion will decrease and the extent of mutual interpenetration of the guest and host will also decrease causing the local concentration of aromatic rings to rise. These effects will lead to an increase in the number of intermolecular excimer sites and I_D/I_M will increase. As an alternative explanation,[18] it is also possible that the higher molecular weight components of our unfractionated P2VN sample which initially are compatible with the host matrix become incompatible as the host polymer becomes a poorer solvent.

A more complete study is in progress.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. DMR 77-09372), the Stanford School of Engineering, the NSF-MRL Program through the Center for Materials Research at Stanford University, and the Research Corporation. The authors wish to thank Herbert Morawetz for very helpful comments on the manuscript.

References and Notes

(1) S. Krause, *J. Macromol. Sci., Rev. Macromol. Chem.*, 7 (2), 251 (1972).
(2) T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, 7, 667 (1974).
(3) T. Nishi and T. K. Kwei, *Polymer*, 16, 285 (1975).
(4) T. Nishi, T. T. Wang, and T. K. Kwei, *Macromolecules*, 8, 227 (1975).
(5) P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *Polymer*, 18, 1022 (1977).
(6) N. E. Weeks, F. E. Karasz, and W. J. MacKnight, *J. Appl. Phys.*, 48, 4068 (1977).
(7) W. M. Prest, Jr., and R. S. Porter, *J. Polymer Sci.*, Part *A-2*, **10**, 1639 (1972).
(8) R. G. Kirste, W. A. Kruse, and K. Ibel, *Polymer*, **16**, 120 (1975).
(9) H. Morawetz and F. Amrami, *Macromolecules*, 11, 281 (1978).
(10) J. B. Birks *Prog. React. Kinet.*, **5**, 181 (1970).
(11) C. W. Frank and L. A. Harrah, *J. Chem. Phys.*, **61**, 1526 (1974).
(12) C. W. Frank, *J. Chem. Phys.*, **61**, 2015 (1974).
(13) C. W. Frank, *Macromolecules*, **8**, 305 (1975).
(14) P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
(15) K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
(16) G. Natta, *Makromol. Chem.*, **35**, 93 (1960).
(17) F. A. Bovey and G. V. Tiers, *J. Polym. Sci.*, **44**, 1973 (1960).
(18) H. Morawetz, personal communication.

Curtis W. Frank* and Muhammed Amin Gashgari
Department of Chemical Engineering,
Stanford University, Stanford, California 94305

Received July 19, 1978

Effect of D_2O on the Thermal Stability of the β Conformation of Poly[*S*-((3-hydroxypropyl)-carbamoylmethyl)-L-cysteine]

Poly(*S*-(carboxymethyl)-L-cysteine) is known to undergo a pH-induced β-coil transition in aqueous solution,[1,2] and we have recently published a paper concerning its circular dichroism and β-coil transition in detail.[3] In order to avoid the complication arising from the electrostatic effect of ionized groups, we have prepared a water-soluble, nonionizable polypeptide, poly[*S*-((3-hydroxypropyl)carbamoylmethyl)-L-cysteine] (poly[Cys(CamPrOH)], and investigated its conformation in aqueous solutions by measurement of circular dichroism. In this communication we report the characteristic temperature dependence of its conformation in D_2O.

Poly[Cys(CamPrOH)] was synthesized by a method similar to that for preparing poly[N^5-(3-hydroxypropyl)-L-glutamine].[4] Poly(*S*-(carbobenzoxymethyl)-L-cysteine)[5] was amidated by a large excess of 3-aminopropanol at 60 °C for a few days, and the reaction mixture was poured into a 3% acetic acid solution. After the solution was dialyzed against distilled water, poly[Cys(CamPrOH)] was isolated by lyophilization. Poly[Cys(CamPrOH)] is soluble in dichloroacetic acid (DCA) but is sparingly soluble in water. Sample code, TX-4071: $\bar{M}_n$ 12 000 in 0.1% CH_3COOH solution, [η] 0.31 dL g^{-1} in DCA at 25 °C.

The infrared spectra of solid film cast from an aqueous solution shows an amide I band at 1625 cm^{-1} and an amide II band at 1528 cm^{-1}. Then poly[Cys(CamPrOH)] is in the β structure in the solid state.

Figure 1 shows the circular dichroism of poly[Cys(CamPrOH)] in H_2O at 25 °C and in D_2O at different temperatures, the concentrations of which are about 0.02 g dL^{-1} or 10^{-3} N. Circular dichroism of an H_2O solution does not change appreciably with temperature; it has two negative bands around 198 and 225 nm. This spectrum is similar to that of poly(*S*-(carboxymethyl)-L-cysteine) in the fully ionized state,[3] and the conformation of poly[Cys(CamPrOH)] in H_2O is, therefore, assigned to the random coil. On the other hand, circular dichroism of a D_2O solution is strongly dependent on temperature. At 1.5 °C the spectrum has a strong positive band at 198 nm and a negative band at 227 nm and is similar to that of poly(*S*-(carboxymethyl)-L-cysteine) at low degrees of ionization.[3] Then poly[Cys(CamPrOH)] is in the β conformation in D_2O solution at low temperature. With increasing temperature, the circular dichroism changes markedly, both positive and negative bands becoming

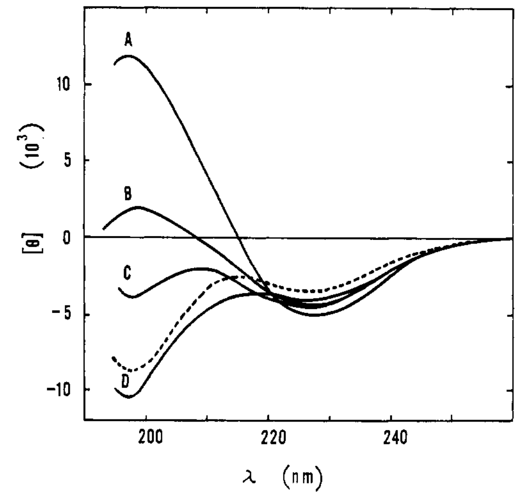


Figure 1. Circular dichroism of poly[Cys(CamPrOH)] in D_2O at different temperatures. Each solution was freshly prepared: A, 1.5 °C; B, 20 °C; C, 30 °C; D, 60 °C (- - -, in H_2O at 25 °C).

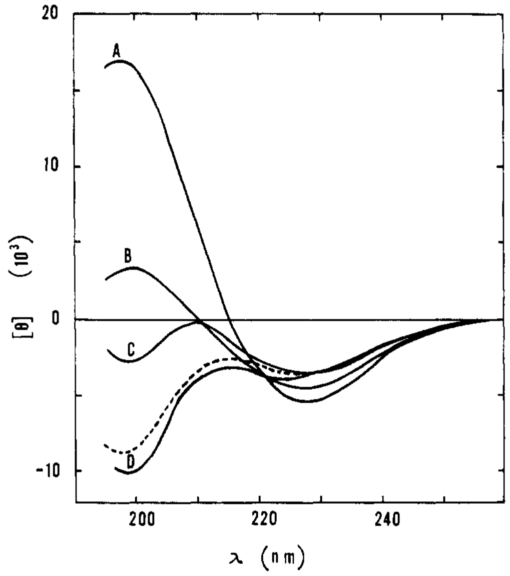


Figure 2. Circular dichroism of poly[Cys(CamPrOH)] in D_2O at different temperatures. Each solution was previously heated at 70 °C for 1.5 h. Temperature for measurement: A, 1.5 °C; B, 50 °C; C, 60 °C; D, 80 °C (- - -, in H_2O at 25 °C).

weaker. At 30 °C the positive band has changed its sign, and at 60 °C the circular dichroism becomes almost identical with that observed in H_2O, having two negative bands around 198 and 227 nm. Thus we may conclude that poly[Cys(CamPrOH)] undergoes a thermally induced β-coil transition in D_2O.

There is some complication concerning the reversibility of the transition as revealed in the circular dichroism. When a D_2O solution was stored at 4 °C, the circular dichroism as given in Figure 1 was reproduced. However, when a D_2O solution was heated at 70 °C for 1.5 h or left at room temperature for several days, a shift of the temperature dependence of the circular dichroic behavior was observed, as shown in Figure 2. At 1.5 °C the positive dichroic band is definitely stronger, but the heat-treated solution is still subject to a thermally induced β coil transition. The inversion of the circular dichroic band at 198 nm occurs around 50 to 60 °C, which is higher than the inversion temperature of the freshly prepared solution, 20 to 30 °C. At 80 °C the hysteresis of the solution seems to disappear, and the circular dichroism characteristic of a random-coil conformation is reproduced.

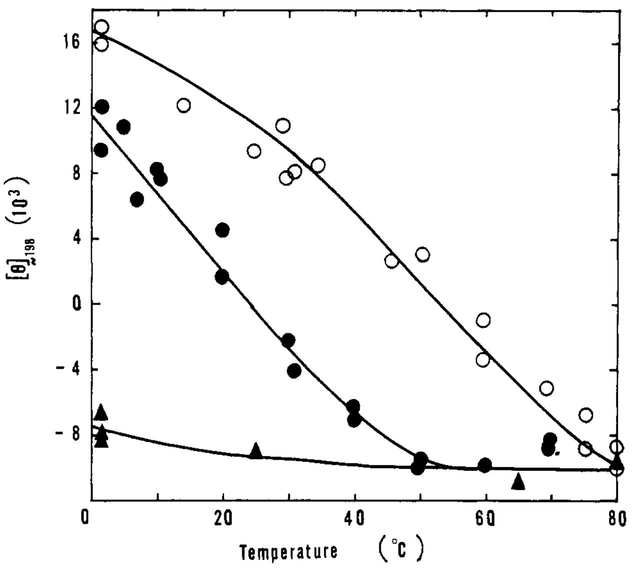


Figure 3. Residue ellipticity at 198 nm as a function of temperature: ●, freshly prepared D_2O solutions; ○, D_2O solutions after heating at 70 °C for 1.5 h; ▲, H_2O solutions.

Figure 3 shows the residue ellipticity of the band around 198 nm as a function of temperature and indicates the transition behavior for both solutions in D_2O, freshly prepared and heat treated. For comparison the residue ellipticity around 198 nm for an H_2O solution is also given, which slightly decreases with increasing temperature. It can be seen that the β conformation is completely disrupted at 60 °C in a freshly prepared D_2O solution, while it persists up to 80 °C in a heat-treated D_2O solution.

Since the sample has been dissolved at room temperature, where it is mostly in a random-coil conformation, the sample is believed to have been deuterated completely even in a freshly prepared solution. The thermal hysteresis of the D_2O solution would not be caused by different extents of deuteration but is a result of a conformational effect of D_2O.

We attempted to obtain a completely deuterated sample in order to observe its conformation in D_2O. However, poly[Cys(CamPrOH)] is sparingly soluble in D_2O as well as in H_2O, so that the rate and extent of deuteration can be followed by infrared spectra with great difficulty. After repeating dissolution in hot D_2O and lyophilization of the sample five times, a deuterated material was isolated as a solid and its circular dichroism in D_2O solution measured at 25 °C gave a value of residue ellipticity of 8000 at 198 nm, in agreement with that for a heat-treated solution. Complete deuteration of the sample is also supported by its low concentration in the solution for circular dichroism measurements as well as by the observation that no further change in circular dichroism occurs during the storage of a freshly prepared D_2O solution at 4 °C.

Appel and Yang[6] demonstrated that the helix–coil transition of poly(L-glutamic acid) in 0.2 M NaCl occurs at pD 5.4 in D_2O, which is more alkaline than pH 4.8 in H_2O, but they attributed this shift to the weakened acidity of carboxyl groups in D_2O, since they observed that the titration behavior was explained by the shift of the p*K* values. The helix–coil transition of poly(L-lysine) in 1 M KBr also shifts from pH 10.4 to pD 11.0 and the same explanation applies to it. In contrast to these examples for helix–coil transition, we have found a large difference in intrinsic stability of the β conformation formed by poly[Cys(CamPrOH)] against H_2O and D_2O.

The large difference in the conformational effect of H_2O and D_2O observed here cannot be explained in a simple way at present. It seems likely that the effect of deuteration on the hydrogen bonding of peptide groups is generally very subtle and would be small.[7] Owing to the complicated nature of the long side chain, the effect of hydrophobic interaction, which is mainly caused by the clustering tendency of water molecules, would be strongly operative in determining the conformation of poly[Cys(CamPrOH)]. It has been argued that D_2O can form stronger hydrogen bonding or a larger number of hydrogen bonds than H_2O. Nêmethy and Scheraga[8] calculated the cluster size of D_2O to be considerably larger than that of H_2O at low temperatures, and they also found that the cluster size of D_2O falls much faster with rising temperature than that of H_2O. The cluster size of D_2O becomes almost equal to that of H_2O around 60 °C or above it. The formation of the β conformation of poly[Cys(CamPrOH)] in water is closely connected with the degree of structural order of water, and its stability is largely conferred by the hydrophobic interaction. The enhancement of the β conformation in the heat-treated D_2O solution is also related to the hydrophobic interaction, and it is, in a sense, similar to the thermally induced formation of the β conformation of poly(L-lysine).[9]

References and Notes

(1) S. Ikeda, *Biopolymers*, **5**, 359 (1967).
(2) S. Ikeda and G. D. Fasman, *J. Mol. Biol.*, **30**, 491 (1967).
(3) S. Ikeda, A. Fukutome, T. Imae, and T. Yoshida, *Biopolymers*, in press.
(4) N. Lupu-Lotan, A. Yaron, A. Berger, and M. Sela, *Biopolymers*, **3**, 625 (1965).
(5) S. Ikeda, H. Maeda, and T. Isemura, *J. Mol. Biol.*, **10**, 223 (1964).
(6) P. Appel and J. T. Yang, *Biochemistry*, **4**, 1244 (1965).
(7) F. E. Karasz and G. E. Gajnos, *Biopolymers*, **15**, 1939 (1976).
(8) G. Nêmethy and H. A. Scheraga, *J. Chem. Phys.*, **41**, 680 (1964).
(9) B. Davidson and G. D. Fasman, *Biochemistry*, **6**, 1616 (1967).

Tetsuo Tomiyama and Shoichi Ikeda*
Department of Chemistry, Faculty of Science,
Nagoya University, Nagoya, Japan

Received March 15, 1978

A Novel Synthesis of Conjugated Polymers Related to the Synthesis of Ionene Polymers[1]

Conjugated polymers are in general prepared by the polymerization of acetylenes and nitriles, elimination of small molecules from saturated polymers, polycondensations, intramolecular polymerizations, ring-opening polymerizations, and so forth.[2] In this communication we wish to disclose a novel synthetic route to conjugated polymers which is closely related to the synthesis of ionene polymers. Although cross-conjugated, the polymers obtained have some properties in common with fully conjugated polymers[3] and may be potentially useful as electrical conductors.[4]

Our reaction system consists of an α,ω-dihalide (I) and a base, and the general main reaction can be shown as follows:

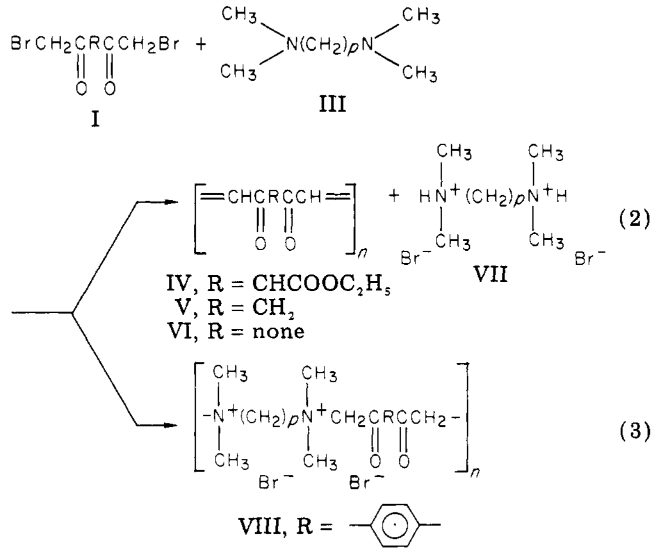
$$\underset{\text{I}}{\mathrm{XCH_2C(O)RC(O)CH_2X}} + \text{base} \rightarrow$$

$$\underset{\text{II}}{\mathrm{XCH_2C(O)RC(O)CH[{=}CHC(O)RC(O)CH{=}]_n\text{-}CHC(O)RC(O)CH_2X}} + \text{product(s) from the base and HX} \quad (1)$$

$$\text{X} = \text{halogen; R} = \text{arbitrary group}$$

Thus far, those dihalides in which group -CORCO- is conjugated within itself have been successfully polymerized by this method to obtain deeply colored polymers whose degrees of polymerization were relatively low. When an α,ω-ditertiary amine such as N,N,N',N'-tetramethyl-α,ω-diaminoalkanes (III) is used as a base, the reaction system is the same as that of the formation of an ionene oligomer or polymer[5-7] (Scheme I). Thus, the present finding in which elimination of hydrogen halide from an α,ω-dihalide predominates over quaternization also brings forward a new problem in the synthesis of polycations of ionene type.[8]

Scheme I



In a typical example, the reaction of 9.89 g (30 mmol) of ethyl γ,γ'-dibromodiacetylacetate (I, R = $CHCOOC_2H_5$; X = Br) with 3.48 g (30 mmol) of N,N,N',N'-tetramethyl-1,2-diaminoethane (III, p = 2; TMDAE) was carried out in 70 mL of acetone at -10 °C. The reaction took place instantaneously with a considerable evolution of heat. After stirring for 24 h without further cooling, the brownish yellow precipitate formed, 8.77 g, was isolated and identified as the slightly impure dihydrobromide (VII, p = 2) of TMDAE by IR and ^{1}H NMR spectroscopies as well as by elemental analyses after purification. The dark reddish brown filtrate was evaporated to dryness and the residue, 4.70 g, was purified by two reprecipitations (acetone as solvent and ether as precipitant) to give 1.80 g of a brownish yellow powder. It was easily soluble in aqueous alkaline solutions but hardly soluble in pure and acidic water. It exhibited an ability to form metal chelate compounds. Its IR spectrum (KBr disk method) showed the absorption bands due to O—H, C=O and C=C stretching vibrations at 3430, 1705, and 1605 cm^{-1}, respectively, while its electronic absorption spectrum (methanol as solvent) had absorption maxima at 219, 264, and 403 nm, the last tailing up to ca. 700 nm. In addition, the ESR spectrum of this product in the solid state consisted of a singlet with a g value of 2.0038, suggesting the presence of unpaired electrons in a delocalized state. Based on these results, we propose IV as its structure in which, however, the β-diketone structure is predominantly enolized to yield a poly-conjugated system (IX). The elemental analyses data were also in reasonably good agreement with IV, the terminal bromine content indicating that the average degree of polymerization (=n + 2) was about seven.[9]

The reaction of 1,5-dibromo-2,4-pentanedione with TMDAE yielded a similar conjugated polymer (X) but the reaction rate was remarkably smaller than that with ethyl

0024-9297/79/2212-0167$01.00/0