associated with trapped alkyl radicals generated by carbon–chlorine bond scission. Post-irradiation storage at 250°K produces allyl radicals, characterized by an absorption band at 2520 Å. Allyl radicals result from dehydrochlorination of the highly reactive alkyl radicals. Further dehydrochlorination leads to polyenyl radicals. Chain transfer reactions between polyenyl radicals and PVC, probably involving abstraction of labile chlorine from the latter, produce polyenes and regenerate alkyl radicals which decay readily to allyl and polyenyl radicals. An intermediate in polyenyl radical formation, the dienyl radical was associated with ultraviolet absorption at 2900 Å. As a consequence of chain transfer reactions, allyl and dienyl radicals appear to attain steady-state concentrations, while the polyene absorption increases on post-irradiation storage. Polyenes are characterized by a series of absorption bands above 3200 Å. Polyene formation is enhanced by post-irradiation heating of PVC.

Radical and polyene portions of the absorption spectrum are distinguished by oxygen scavenging. Radical intermediates are very susceptible, whereas polyenes require prolonged exposure to oxygen for reaction. Based on these observations, absorptions at 2910 and 3300 Å are assigned to dienyl and trienyl free radicals, respectively, in irradiated PVC. From oxygen scavenging at selected stages of polyene formation, it is inferred that alkyl radicals are precursors of allyl radicals which lead ultimately to polyenes *via* intermediate polyenyl radical formation.

Acknowledgment. The experimental assistance of Misses B. E. Prescott and D. M. Dodd is acknowledged with gratitude.

Circular Dichroism Studies on Poly-L-lysine in Water–Sulfuric Acid Mixtures

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ABSTRACT: Circular dichroism (CD) measurements have been carried out on poly-L-lysine (PLL) dissolved in H_2O–H_2SO_4 mixtures of varying composition. In concentrated sulfuric acid the CD spectrum of the polymer is very similar to that recorded in water solution at acid pH's, but the intensities of the dichroic bands are much lower. In addition there is a red-shift of the negative $\pi \rightarrow \pi^*$ CD band on going from water to concentrated sulfuric acid solutions. The results are interpreted in terms of solvation and protonation of the peptide backbone. The evidence for protonation of amide groups is substantiated by intrinsic viscosity measurements of PLL in various H_2O–H_2SO_4 mixtures.

Very recently conformational studies have been carried out on polypeptides dissolved in water–strong acid mixtures.[1-4]

All examined poly(α-amino acids), including poly(γ-ethyl L-glutamate) (PELG), poly-L-phenylalanine (PLP), and poly-L-cyclohexylalanine (PCHA) in concentrated sulfuric or methanesulfonic acid, exhibit circular dichroism (CD) spectra typical of the random coil conformation except for the intensities of the dichroic bands, which are lower compared to those of polypeptides in the unordered conformation in aqueous solutions (poly-L-lysine and poly(L-glutamic acid) with charged side-chain groups[5,6]). These results were tentatively interpreted in terms of solvent effects on the CD pattern of the coiled form.

In the attempt of further investigating on this point, we have studied in the present work the behavior of poly-L-lysine (PLL) in H_2O–H_2SO_4 solvent mixtures. The polymer is soluble in the whole range of solvent composition and it should be always in the form of a random coil, owing to the electrostatic repulsions among protonated side-chain amino groups. It is therefore possible in such a case to observe directly the CD properties of a coiled form in different solvent media.

Experimental Section

Materials. Dioxane (Carlo Erba R.P.) was dried over potassium–anthracene complex as previously described[7] and distilled immediately before use. Ethyl acetate and chloroform (both Merck puriss) were dried over $CaCl_2$ and then fractionally distilled. Petroleum ether (bp 40–70°) was dried over sodium metal wires and then distilled. Acetone (Merck puriss) was used without further purification. Concentrated sulfuric acid (Merck puriss) was used directly; potentiometric titration showed an acid content of 95.2% by weight.

Polymers. Poly-N$^\epsilon$-carbobenzoxy-L-lysine (PCBL) was prepared by polymerization of N$^\epsilon$-carbobenzoxy-L-lysine, N-carboxy anhydride[8] (Z-Lys-NCA) (4 g) in dioxane (120

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ml), using sodium methoxide (in 1:1 methanol–benzene solution[9]) as the initiator.

At the end of the polymerization checked by ir (disappearance of the monomeric band at 1860 cm^{-1}), the solution was directly used to prepare poly-L-lysine hydrochloride (PLL·HCl) according to the method of Fasman, *et al.*[10] Through the solution diluted with 120 ml of dioxane and with 600 ml of chloroform, dry HCl was bubbled for 0.5 hr; the solution remained perfectly clear. Anhydrous HBr was then bubbled through for 2 hr; PLL·HBr began to precipitate as a white powder a few minutes after the HBr bubbling was started. The mixture was stirred for 2 hr; after removing supernatant by decantation, the polymer was recovered by filtration and exhaustively washed with acetone. PLL·HBr so obtained was dissolved in dilute HCl and dialyzed 4 days against 0.01 *M* HCl. Finally PLL·HCl was recovered by lyophilization from the clear colorless solution, and dried under high vacuum over P_2O_5. The polymer contained 9% water as determined by chlorine, nitrogen, and carbon analysis. The intrinsic viscosity in 1 *M* NaCl was 0.40 dl/g.

Polymer Solutions in H_2SO_4–H_2O Mixtures. Sulfuric acid–water mixtures of various compositions have been prepared by mixing known amounts of acid with ice-cooled distilled water. The final composition of each solvent mixture was determined by potentiometric titration. 99.6% H_2SO_4 was prepared by the "fair and foggy" method from Merck puriss concentrated H_2SO_4 and fuming H_2SO_4 (Carlo Erba RP). PLL·HCl was dissolved in such solvent mixtures, the polymer concentration being ~0.1 g/l. for CD measurements and 0.5–1.0 g/100 cc for viscosity determinations. In all cases the measurements have been performed immediately after the preparation of the solutions in order to avoid polymer degradation (see below).

Measurements. Circular dichroism measurements have been performed with a Roussel-Jouan Model II dichrograph, which records directly the so-called dichroic absorbance ($A_L - A_R$).[11] From this quantity the molar dichroic absorption $\Delta\epsilon$ and the molar ellipticity [θ] have been calculated according to the well-known equations

$$A_L - A_R = (\Delta\epsilon)cd \quad (1)$$

$$[\theta] = 3300(\Delta\epsilon) \quad (2)$$

c being the molar concentration of amino acid residues and d being the cell path length in centimeters.

Potentiometric titrations have been performed with a Metrohm Model E 388 precision potentiometer, equipped with UX Metrohm combined glass electrodes.

Viscosity measurements have been made at 25° in a Ubbelhode viscometer with a time of solvent fluxing higher than 200 sec.

As previously mentioned PLL might undergo degradation, with consequent decrease of the degree of polymerization, in H_2O–H_2SO_4 solutions. We determined the extent of degradation by following the time dependence of the reduced viscosity (η_{sp}/C) of PLL solutions in the various H_2O–H_2SO_4 mixtures. It was found that at 25° the polymer does not show appreciable degradation when the acid content was higher than 70% (by weight) or lower than 40% (by weight). In solvent mixtures with an acid content in the range 70–40% (by weight) PLL degradates to some extent, the maximum degradation rate occurring in 50% H_2SO_4. Intrinsic viscosity measurements on PLL solutions where the polymer undergoes degradation have been performed in the following way. For each polymer concentration, in a given solvent mixture, correct η_{sp}/C values were obtained by extrapolation to 0 time of the η_{sp}/C values measured at different times from the preparation of the solution. An example of such extrapolation is shown in Figure 1. It can be observed that the semilogarithmic plot is linear, and in 1 hr there is a 15–20% decreasing of the η_{sp}/C values, in 50% H_2SO_4, where the highest degradation rate was observed.

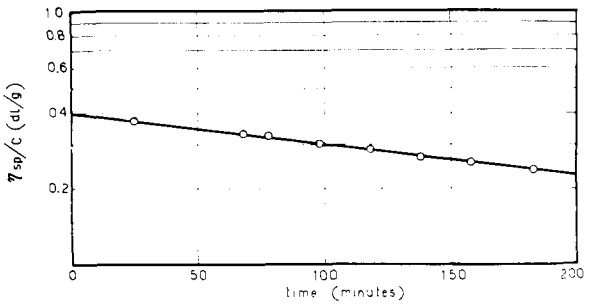

Figure 1. Reduced viscosity (η_{sp}/C) of PLL in 50.2% H_2SO_4 as a function of time.

The correct η_{sp}/C values were then extrapolated as usual to 0 concentration in order to get the intrinsic viscosity value [η].

On the other hand, it can be safely assumed that the polymer degradation, when present, does not affect the CD measurements. In fact it is well known from the literature that the CD patterns of synthetic polypeptides are independent of the degree of polymerization for degrees of polymerization higher than 20. In our case, during the interval of time required to run the CD spectra (usually 15–20 min) the decay of the degree of polymerization of PLL (as estimated from the decreasing of the $\eta_{sp}C$ value) was no more than 10% of the initial value.

Results and Discussion

The CD spectra of PLL·HCl in 0.1 *N* H_2SO_4 and in concentrated H_2SO_4 solutions are shown in Figure 2. In the dilute acid solution the spectrum is in quantitative agreement with that reported by many authors for charged PLL in aqueous solutions, and does correspond to the conformation of a random coil.[6] The strong negative band at 196 mμ ($\Delta\epsilon = -12.2$) has been as-

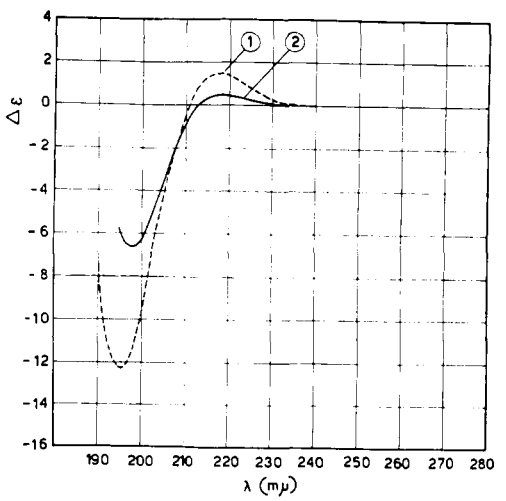

Figure 2. CD spectra of PLL in 0.1 *N* sulfuric acid (curve 1) and in concentrated sulfuric acid (curve 2).

(9) A. Berger, M. Sela, and E. Katchalski, *Anal. Chem.*, **25**, 1554 (1953).

(10) G. D. Fasman, M. Idelson, and E. R. Blout, *J. Amer. Chem. Soc.*, **83**, 709 (1961).

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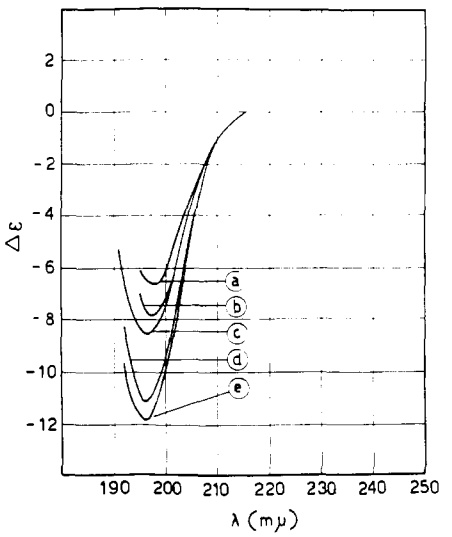

Figure 3. CD spectra of PLL in H_2SO_4–H_2O mixtures of various compositions: (a) 95.2% H_2SO_4; (b) 71.5% H_2SO_4; (c) 54.9% H_2SO_4; (d) 36.6% H_2SO_4; (e) 19.6% H_2SO_4.

signed to the $\pi \rightarrow \pi^*$ transition of the peptide chromophore.[5,12] The weak positive band at 218 mμ ($\Delta\epsilon$ = 1.47) has been assigned to the $n \rightarrow \pi^*$ peptide transition, but this assignment is still under discussion.[13] The CD pattern of the polymer dissolved in concentrated H_2SO_4 is quite different: the spectrum exhibits the same shape as that recorded in 1 *N* H_2SO_4, but the intensities of the two dichroic bands are much lower: the $\Delta\epsilon$ values are 0.49 and −6.6 for the bands at 218 and 198 mμ, respectively. Furthermore, the negative band is 2–3 mμ red-shifted with respect to the corresponding band observed in the dilute acid solution.

Some typical CD spectra recorded in H_2O–H_2SO_4 mixtures of different compositions are shown in Figure 3. In Table I the values of the $\pi \rightarrow \pi^*$ negative dichroic band in various H_2O–H_2SO_4 mixtures are collected. While the increased solvent polarity going from pure water to concentrated H_2SO_4 (the dielectric constant of which is more than 100)[14] might account for the red-shift of the $\pi \rightarrow \pi^*$ transition, an explanation for the lower intensities of both the dichroic bands in concentrated H_2SO_4, and for the no-shift of the positive band at 218 mμ is more complicated.

An interpretation of these experimental results involves, at least in part, the following points: (1) the solvation effects on the CD spectrum of a coil; (2) the protonation of peptide groups in H_2O–H_2SO_4 mixtures and its effect on the CD pattern and on the polymer conformation. It is also probable that a combination of both solvation and protonation effects is involved.

As mentioned before, the solvent medium markedly affects the position of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ peptide transitions: the higher energy $\pi \rightarrow \pi^*$ transition is

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TABLE I
$\Delta\epsilon$ VALUES OF THE NEGATIVE $\pi \rightarrow \pi^*$ CD BAND OF PLL IN VARIOUS H_2O–H_2SO_4 MIXTURES

% H_2SO_4 (by weight)	Polymer concn, g/l.	λ_{max}, mμ	$\Delta\epsilon$
95.5	0.0945	198	−6.6
76.7	0.0991	198	−7.2
71.5	0.0999	197	−7.6
66.9	0.0997	197	−7.9
61.4	0.0982	197	−8.7
54.9	0.1073	196	−9.2
52.1	0.0986	196	−9.7
47.5	0.1012	196	−11.1
45.6	0.1073	196	−11.4
38.2	0.1065	196	−11.4
33.6	0.1032	196	−11.2
28.8	0.1067	196	−11.7
23.8	0.0964	196	−11.3
19.6	0.1028	196	−11.8
0.5[a]	0.1028	196	−12.2

[a] 0.1 *N* solution of H_2SO_4.

red-shifted and the lower energy $n \rightarrow \pi^*$ transition is blue-shifted on increasing the solvent polarity.[15]

It has also been reported that the rotational strength of the $n \rightarrow \pi^*$ transition does not depend very much on the solvent polarity.[15] If the assignment of the long wavelength CD band of PLL is correct, then the observed no shift and the marked decrease of the rotational strength of such a band on increasing the solvent polarity does not follow the normal behavior of $n \rightarrow \pi^*$ transitions. This anomalous behavior has been found also by Urry[15] in the case of L-3,6-dimethyl-2,5-diketopiperazine, for which the rotational strengths of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions decrease to a large extent, and the $n \rightarrow \pi^*$ transition does not exhibit any shift on increasing the solvent polarity.[15] The Urry's explanation for the diketopiperazine could apply also to our case, that is, in polar solvents the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions tend to overlap to a greater extent than in nonpolar solvents; consequently the strong negative $\pi \rightarrow \pi^*$ band could partially mask the shift and reduce also the intensity of the weak positive $n \rightarrow \pi^*$ band.

From all these considerations it seems reasonable to assume that the observed low intensities of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ CD bands of PLL in concentrated sulfuric acid are due, at least in part, to solvation effects. However, if changes in solvation were the only phenomena involved here, one would expect the intensities of the CD bands to change gradually on varying the solvent composition. If we plot the $\Delta\epsilon$ values of the negative dichroic band as a function of solvent composition, we obtain an S-shaped graph (Figure 4); that is, the molar dichroic absorption of the $\pi \rightarrow \pi^*$ band is not a linear function of the weight per cent of sulfuric acid in the solvent mixture. An inflection point roughly located between 80 and 50% (by weight) sulfuric acid is clearly evident. It seems therefore that some other factors are involved in determining the observed CD spectra. In the particular solvent medium we used, protonation of amide groups has to be considered.

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The question of protonation of peptide groups of poly-α-amino acids in H_2O–H_2SO_4 mixtures and its effect on the CD spectrum and on the polymer conformation is a very complicated one, and very little is known on this area at the present time. In a previous investigation carried out by our group[2] it was concluded that the model N-benzoylglycyl-*n*-propylamide was roughly half-diprotonated in 74.3% H_2SO_4. Then it was assumed that an aliphatic diamide should be protonated to the same extent in 67% H_2SO_4. From these data the hypothesis was made that in poly(γ-ethyl L-glutamate) (PELG) dissolved in 70% H_2SO_4, where the polymer is almost completely in the coiled form, about 75% of amide groups are protonated. Very roughly we can assume that the same figures apply to PLL even if in this case the extent of protonation could be lower since the electrostatic repulsion of charged side-chain amino groups (which are completely protonated in the whole range of solvent composition) could make more difficult the protonation of peptide groups in the peptide backbone.

Protonation cannot occur without affecting markedly the CD absorption associated with the n $\rightarrow$ π^* transition.[16] Then, part of the effect observed on the long wavelength positive dichroic band of PLL on varying the H_2SO_4 content of the solvent mixture must be due to protonation of amide groups.

With regard to the $\pi \rightarrow \pi^*$ transition, very little is known at the present time on the effect of protonation on the rotational strength of the corresponding band. Bovey observed that the sign of the Cotton effect of the $\pi \rightarrow \pi^*$ transition for simple model compounds is reversed in very strong acid solvent.[17] Strong alteration of the $\pi \rightarrow \pi^*$ CD band of L-pyroglutamic acid in concentrated $HClO_4$ has been found also by Goodman and coworkers.[18] Even if in the cited examples it is difficult to distinguish solvation from protonation effects, protonation of peptide groups appear to be involved. We assume that the behavior of the curve reported in Figure 4 has to be related, at least in part, to the protonation of amide groups in the backbone. If this hypothesis is correct, one should expect PLL to possess different hydrodynamic volumes in concentrated sulfuric acid and in water for the following reasons. First, the electrostatic repulsions among positive charges in the backbone (consequent to extensive amide protonation) should act in favor of a coiled form more extended in H_2SO_4 than in water. Second, the solvation requirements of protonated amide groups are different from those of nonprotonated groups. It has in fact been concluded by Sweeting and Yates[19] that protonated amides require more hydration than free amides. Therefore protonation causes more solvent to be bound to the peptide backbone, with consequent increase of the hydrodynamic volume of PLL.

To test this hypothesis, intrinsic viscosity measurements have been carried out on PLL dissolved in

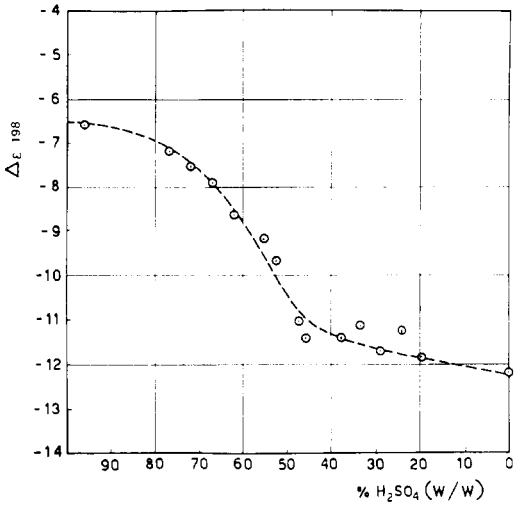

Figure 4. $\Delta\epsilon$ values of the negative $\pi \rightarrow \pi^*$ dichroic band plotted *vs.* solvent composition.

H_2O–SO_4 mixtures of various compositions. The results are shown in Figure 5.

There is a marked decrease of the intrinsic viscosity value on decreasing the sulfuric acid content from 100 to 50% (by weight) in the solvent mixture. This behavior clearly indicates that the hydrodynamic volume of the dissolved polymer molecules decreases as the acidity of the solvent medium diminishes.

A reasonable explanation for the slow and continuous increase of the intrinsic viscosity on decreasing the H_2SO_4 concentration below 50% (by weight) is more difficult. A similar effect has been found also by Bianchi, *et al.*, who reported that increasing amounts of various salts depress the intrinsic viscosity of charged PLL in aqueous solutions.[20]

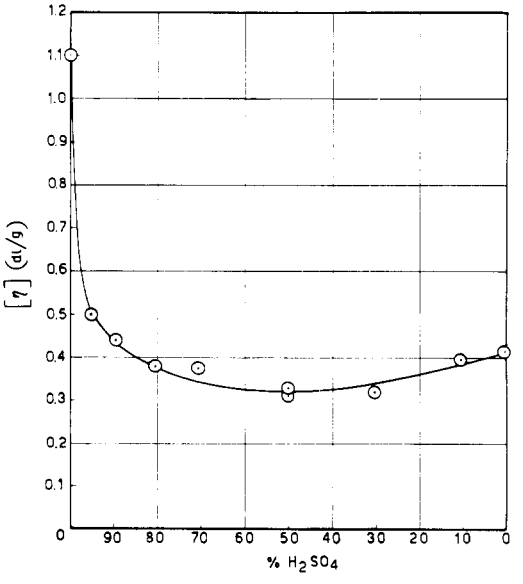

Figure 5. Intrinsic viscosity data of PLL in various H_2O–H_2SO_4 mixtures. The $[\eta]$ values in 80.5% H_2SO_4, in 70.8% H_2SO_4, and in 50.2% H_2SO_4 (where the polymer degradates to some extent), have been determined as described in the Experimental Section.

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A possible interpretation is that there is a progressive reduction of shielding of intramolecular electrostatic repulsions among charged side-chain amino groups on decreasing the H_2SO_4 concentration. In other words, it is possible that the large part of the polyelectrolyte effect is screened out at very low concentrations of H_2SO_4 but a residual effect persists at considerably higher H_2SO_4 concentrations. This hypothesis could explain the behavior of the curve in Figure 5, in the range of solvent composition between 0 and 50% H_2SO_4.

Conclusions

From the result presented in this paper we suggested that solvation effects and protonation of amide groups as well might account for the changes of the CD pattern of PLL in H_2SO_4–H_2O mixtures of different composition. Evidence for protonation of amide groups in the peptide backbone arises from the increased intrinsic viscosity of the polymer in concentrated H_2SO_4.

In drawing these conclusions the tacit assumption was made that the changes of the CD pattern are not a direct consequence of changes of the polymer conformation from an extended coil to a more compact one. In other words the variation of the CD spectrum of PLL on going from water to concentrated sulfuric acid solutions has been interpreted in terms of changes of protonation and solvation of the peptide groups in the different solvent media. According to our interpretation, these changes are directly responsible for the modifications of the CD pattern and not the conformational change from an extended coiled form to a more compact one. This assumption is equivalent to saying that different coiled forms in the same solvent medium should exhibit the same CD spectrum, since in the unordered state there is no possibility of coupling with the transition moments of the peptide chromophores.

In this connection we wish to comment on some recent data obtained by Tiffany and Krimm[21,22] on PLGA and PLL. According to these authors polypeptides with charged side chains are not satisfactory models for an unordered chain. They suggest that the CD spectra of charged PLGA in aqueous solutions, in the absence of added salts, indicate the presence of an "extended-helix structure with parameters close to those of the three-fold left-handed helix of polyproline II."[22] The truly unordered form of charged PLGA occurs, according to the authors, in 4.5 *M* $LiClO_4$ or in 3 *M* guanidine hydrochloride.[22] In our opinion, in these particular cases, caution must be exercised in the interpretation of changes of CD spectra in terms of changes of conformation. It is in fact quite clear that concentrated salt solutions are solvent media completely different from water in a number of features. For instance added salts might cause marked changes in the structural properties, and therefore in the solvation properties of water. It is possible that the different CD patterns of charged PLGA in water and in concentrated salt solutions reflect different solvation conditions of amidochromophores (with consequent effects on the electronic transitions) more than a conformational change of the polymer backbone. Furthermore, possible alteration of the optical rotatory properties could arise from specific binding of ions to the peptide groups.

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The Macrolattice of a Triblock Polymer

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ABSTRACT: A triblock polymer of polystyrene–polybutadiene–polystyrene, having molecular weights 21,100, 63,400, 21,100, respectively, 38.5 wt % polystyrene, was studied by small-angle X-ray scattering to determine its three-dimensional structure. A two-phase model was assumed, one phase being a pure polystyrene phase and the other phase a pure polybutadiene phase. Spherical polystyrene domains were shown to be 356 Å in diameter and assigned to an orthorhombic macrolattice of unit cell dimensions 676, 676, 566 Å. The implications of this type of macrolattice are discussed. The macrolattice is itself held in a regular array by forces due to the maximization of polymer chain entropy.

Triblock polymers, that is, polymers of $A_nB_mA_n$, where A is polystyrene and B is a diene polymer, are well known to be two-phase systems. Electron micrographs of polystyrene–polybutadiene–polystyrene do show a strong tendency to form ordered domains of styrene-rich phases imbedded in a diene-rich matrix.[2,3] Low angle X-ray studies[4] have shown the effects of

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(2) (a) J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci., Part C*, **26**, 117 (1969); (b) M. Matsuo, *Jap. Plast.*, **2**, 6 (1968).
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