$$\epsilon_s - \epsilon_\infty = \left[\frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty}\right]\left[\frac{\epsilon_\infty + 2}{3}\right]^2 \frac{4\pi\tilde{N}}{3RT}\langle\mu^2\rangle \qquad (4)$$

where ϵ_s and ϵ_∞ are the static and high frequency dielectric constants and $\tilde{N}$ is the number of molecules per cubic centimeter. The average square molecular dipole moment, $\langle\mu^2\rangle$, can be decomposed for a high molecular weight polymer into

$$f = \langle\mu^2\rangle/(n\mu_0^2) = 1 + \frac{2}{n}\sum_{j=1}^{n}(n - j)\langle\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_{1+j}\rangle/\mu_0^2 \qquad (5)$$

where μ_0 is the chain bond moment, n is the number of chain dipoles per molecule, and $\boldsymbol{\mu}_i$ is a chain dipole vector. For a model of polyoxymethylene in which the C–O bonds are individually assigned moments, the molecular dipole moment is then made up of alternating bond moments along the chain bonds. The evaluation of the right-hand side of eq 5 is then very similar to the evaluation of the average square radius of a polymer chain. For our alternating dipole case, a formula due to Lifson[11] may be modified by changes in sign to read

$$\mu^2/(n\mu_0^2) = 1 - 2\mathbf{a}_3(\mathbf{T}^* + \mathbf{U}/\lambda)^{-1}\mathbf{a}_3^* \qquad (6)$$

where $\mathbf{T}^*$ is the transpose of the 9 × 9 bond transformation matrix and $\mathbf{U}$ is the 9 × 9 statistical weight matrix both as defined by Lifson.[11] The $\mathbf{a}_3$ and $\mathbf{a}_3^*$ matrices are nine element row and column matrices with zero elements except for the last three positions which contain the eigenvectors of the largest eigenvalue, λ, of the 3 × 3 statistical weight matrix

$$U = \begin{bmatrix} g^+(g^+) & g^+(T) & g^-(g^-) \\ T(g^-) & T(T) & T(g^-) \\ g^-(g^+) & g^-(T) & g^-(g^-) \end{bmatrix} \qquad (7)$$

where $g^-(g^+)$, $T(g^+)$, etc., indicate the Boltzmann factors assigned to pair sequences of bond conformations, $g^+(g^+)$ = *gauche* conformation (followed by *gauche* of the same sense), $T(g^+)$ = *trans* conformation (followed by *gauche*), etc. We have assigned the following values[12] to these elements

$$g^+(g^+) = g^-(g^-) = g^-(T) = g^-(T) = 1$$

$$g^+(g^-) = g^-(g^+) = 0$$

$$T(g^+) = T(T) = T(g^-) = T = \exp(-\epsilon/kT)$$

$$\epsilon = 1740 \text{ cal/mol}^{13}$$

The largest eigenvalue is given by

$$\lambda = ((T + 1) + \sqrt{(T + 1)^2 + 4T})/2 \qquad (8)$$

and its eigenvector by

$$a = (1, \lambda - 1, 1)/\sqrt{2 + (\lambda - 1)^2} \qquad (9)$$

In computing the elements of T we have used ϕ = 77° for the *gauche* state[14] and ϕ = 180° for the *trans*. The bond angle was taken to be the same[14] for O–C–O and C–O–C as 109.5°. Values of ϵ_∞ = 2.27 at 190° with a temperature coefficient of −1% per 10° and melt density of 1.20 g/cm³ at 190° with a temperature coefficient of −1% per 10° temperature were used. The value of the C–O bond moment in polyoxymethylene was taken from the work of Uchida, *et al.*,[14] as 1.31 D.

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Absorption Spectroscopy of Irradiated Poly(vinyl chloride)

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ABSTRACT: Radiolysis of poly(vinyl chloride) (PVC) was studied by ultraviolet and visible spectroscopy following post-irradiation storage at selected temperatures in a cryostatic cell. A sequence of alkyl, allyl, and polyenyl radicals followed by chain transfer to PVC leads to polyene formation. Allyl, dienyl, and trienyl radicals were associated with absorption bands at 2520, 2910, and 3300 Å, respectively. Radical intermediates react readily with oxygen.

A study of the irradiation behavior of poly(vinyl chloride) (PVC) is of importance in elucidating the effects of ionizing radiation, the properties of irradiated PVC, and the relation between radiolytic and thermal stability. Unlike most polymers in which either cross-linking or chain scission predominates following energetic irradiation, the major reaction in PVC is dehydrochlorination.[2] Color formation associated with long sequences of conjugated unsaturation (polyenes) ensues.[3] In order to determine radiation behavior intrinsic to pure PVC, incipient changes must be studied.[4a] Fortunately, sensitive thermogravimetric[4b]

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and spectroscopic[5] techniques permit measurement of very small extents of reaction. Mixtures of free radicals and polyenes were sensitively detected by ultraviolet absorption. A radiolytic mechanism involving allyl and polyenyl free radicals was postulated.[4b] Although allyl radicals,[6] polyenyl radicals,[7] and polyenes are identified, their simultaneous occurrence obscured simple interpretation of their role in PVC radiolysis. Recently, a cryostatic cell[8] was designed to facilitate low-temperature irradiation of PVC films under vacuum and their study by ultraviolet spectroscopy on post-irradiation storage at selected temperatures. Oxygen scavenging of radical intermediates at controlled temperatures was also examined. The isolation of intermediates at low temperatures in the irradiation of PVC and their identification by ultraviolet and visible spectroscopy are reported.

Experimental Section

PVC films, 0.003–0.004 in. thick, were molded from Opalon 660 powder (Monsanto Chemical Co.) at 121–126°. Films were mounted in a sample holder (A, Figure 1) consisting of a copper frame with three slits. The sample holder is hinged to a hollow copper base (B) which is connected to a stainless steel dewar through tube C. Addition of liquid nitrogen to the dewar fills C and B, cooling the sample holder through flexible copper braids (D). Thermocouples were prepared using 0.005-in. copper and constantan wires and were wound around C and mounted on the sample holder and the lower center of each film. The lengths of thermocouple wire between the point of thermal contact at C and the junctions attached to films were carefully adjusted to achieve thermal equilibrium in the junctions. It was observed that erroneously low temperatures were recorded unless the thermocouple wires exceed a minimum length; lengths in the range 3–4.5 in. yielded nearly constant temperatures.[8] Thermocouple calibration tables were checked between 77 and 278°K, using seven constant-temperature baths, five consisting of freezing mixtures of pure liquids, prepared by adding liquid nitrogen and stirring reagent liquids until fine ice–liquid slurries resulted. Potential differences were recorded on a millivolt potentiometer (Leeds and Northrup Co.). Temperatures attained on filling the dewar with liquid nitrogen are 80°K for sample holder and 160°K for films. Mounting the thermocouple in several positions on the films indicated that film temperatures were approximately uniform. Successively filling the dewar with various baths permits control at a series of temperatures.

The assembly illustrated in Figure 1 is contained within a cell and evacuated to 10^{-5} mm. The sample holder is placed in a horizontal position using a mechanical probe and films are exposed to a beam of 1 MeV electrons (Van de Graaff generator) which penetrates the cell in the direction of arrow E through a 0.003-in. aluminum window. During irradiation the cell dewar is filled with liquid nitrogen. The dose rate approximates 5 Mrad/min and the dose deposited is 5–10 Mrad.[9] Film and frame temperatures are continuously monitored during irradiation with a millivolt chart recorder (Moseley Co.). Film temperatures increase about 30° during irradiation and cool rapidly thereafter. The sample holder is then rotated (using the probe) to a vertical position for spectrophotometric measurements. The entire cell is placed in a spectrometer (Cary 14) and scanned from 7000 to 2000 Å, with the spectral beam in the direction of arrow S. Coupled magnets are used to secure the sample holder in horizontal and vertical positions. Ultraviolet and visible absorption measurements were conducted at several temperatures, using a series of baths. Isothermal post-irradiation storage was long compared to warmups. Oxygen scavenging of free radical intermediates was accomplished by opening the cell to pure oxygen.

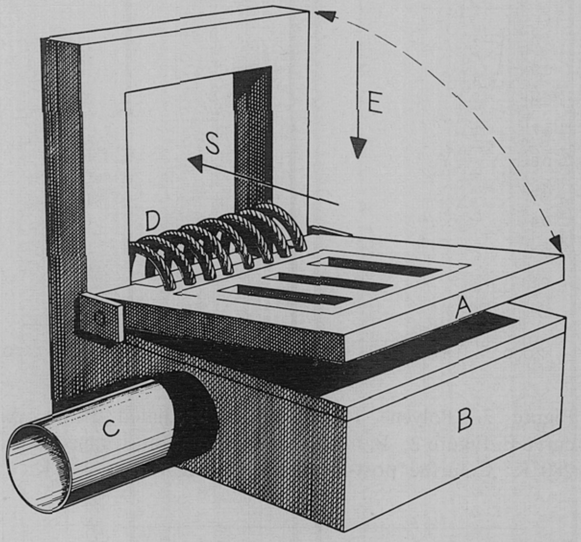

Figure 1. Sample holder and support: A, sample holder; B, base; C, tube to dewar; D, flexible copper braid; E, electron beam direction; S, spectral beam direction.

Results and Discussion

Results of these experiments are summarized in a series of ultraviolet-visible spectra (Figures 2–6) which were recorded between 2000 and 7000 Å for selected film temperatures and thermal treatments. Optical densities of control films at low temperatures increase with decreasing wavelength, exceeding unity at 2130 Å (curve A, Figure 2). Intense absorption below 1600 Å

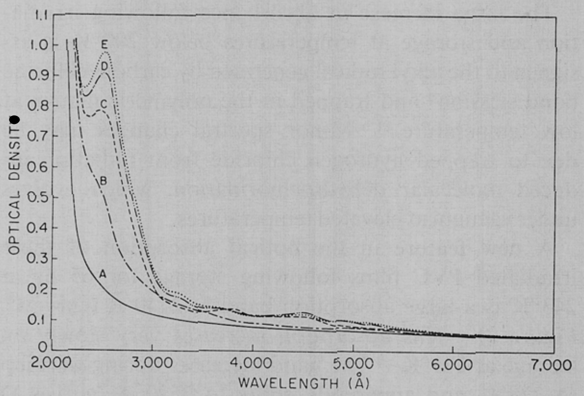

Figure 2. Allyl radical formation in irradiated PVC: A, control, 153°K; B, irradiated, 5.9 Mrad; 159°K; C, post-irradiation storage, 65 hr, 243°K; D,E, intermediate stages during warmup between 243 and 278°K.

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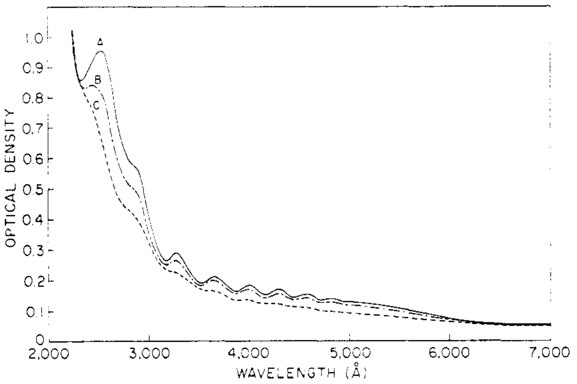

Figure 3. Polyene formation in irradiated PVC: A, curve E, Figure 2; B, further post-irradiation storage, 18 hr, 280°K; C, further post-irradiation storage, 6 days, 286°K.

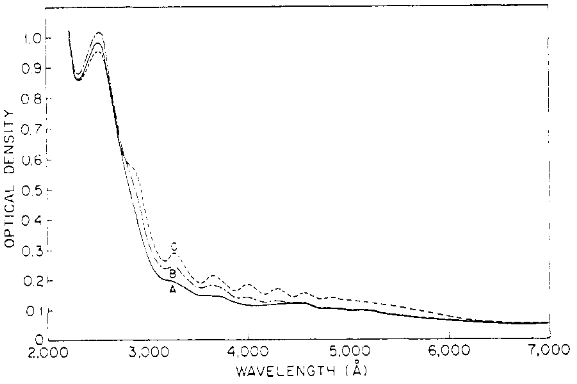

Figure 4. Effect of oxygen on irradiated PVC: A, curve C, Figure 3; B, after 200 min exposure to oxygen, 286°K; C, additional 18 hr exposure to oxygen, 286°K.

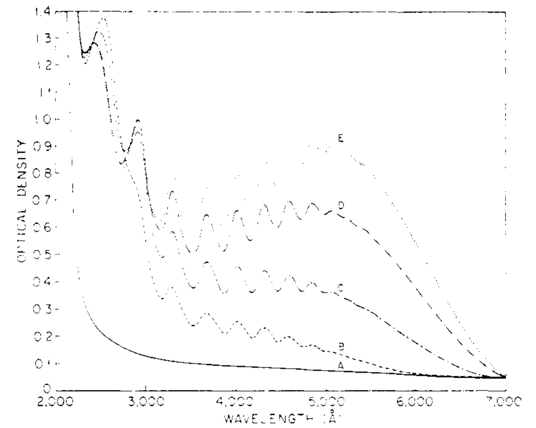

Figure 5. Polyene formation in irradiated PVC: A, control; B, irradiated, 5.9 Mrads; warmed to 334°K; C, post-irradiation storage, 17.5 hr, 334°K; D, after warmup to 373°K; E, post-irradiation storage, 1.5 hr, 363°K.

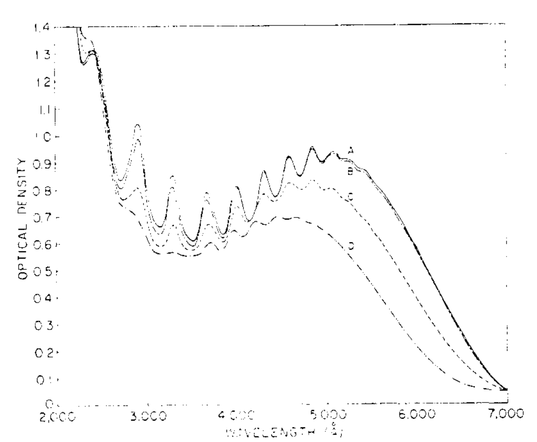

Figure 6. Effect of oxygen on irradiated PVC: A, PVC film of Figure 5, additional 65 hr storage, 298°K; B, 1 min exposure to oxygen, 298°K; C, 4 hr exposure to oxygen, 298°K; D, 23 hr exposure to oxygen, 298°K.

was reported for very thin films of PVC.[10] Following irradiation to 5.9 Mrad at 153°K, the optical density is increased throughout this range (curve B, Figure 2) and is invariant on post-irradiation storage for 22 hr at 159°K. Spectral changes are slight following rapid (1.5 hr) warmup to 243°K. A PVC film irradiated at 190°K and stored at 198°K for 22 hr yielded similar spectra; warmup to 254°K produced only slight changes, particularly a decrease in absorbance at 3300 Å.

The large increase in absorbance following irradiation and storage at temperatures below 200°K is assigned to the alkyl radical generated by carbon–chlorine bond scission[2] and trapped in the polymeric matrix at low temperature.[11] Minor spectral changes may be due to trapped hydrogen chloride from radiation induced molecular dehydrochlorination, which evolves under vacuum at elevated temperatures.

A new feature in the optical absorption of these irradiated PVC films following storage for 65 hr at 243°K is a large absorption band at 2440 Å (curve C, Figure 2). This absorption increases very slowly on storage at 243°K. The band increases during warmup to 278°K and apparently shifts to 2520 Å (curves D and E, Figure 2). The shift is a consequence of the decrease in the overlapping absorption band on the short wavelength side corresponding to a decrease in alkyl radical concentration at these temperatures.[7] Small increases in optical absorption are also noted between 3500 and 6000 Å.

The band about 2500 Å (curve C, Figure 2) is assigned to allyl radicals.[12] Allyl radical formation coincides with alkyl radical decay and presumably arises from dehydrochlorination of alkyl radicals.[6,7] This process occurs slowly under vacuum at 243°K and more rapidly at 278°K. Allyl radical formation is sensitive to the temperature of post-irradiation storage. An irradiated PVC film stored for 65 hr at 254°K indicates much larger allyl radical absorption than a similar film stored at 243°K. Increases in optical density above 3500 Å, particularly at 278°K, are due to incipient polyene (conjugated unsaturation) formation.[3] Post-irradiation storage at 243 or 254°K did not generate polyenes.

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Further storage for 18 hr at 280°K leads to an absorbance increase at 2520 Å and the development of a banded structure above 3200 Å (curve B, Figure 3). The film was then warmed to 286°K, stored at that temperature for 6 days, and the ultraviolet spectrum recorded at intervals. The spectrum shown in Figure 3 (curve C) was observed at the conclusion of that period. The banded structure above 3200 Å has been assigned to polyenes.[3] The absorption band at 2520 Å due to allyl radicals decreases on prolonged storage at 286°K (Figure 3).

Since allyl radical decay under vacuum coincides with polyene formation, it is inferred that dehydrochlorination of allyl radicals generates long chains of conjugated unsaturation forming polyenyl radicals and polyenes.[6] A small absorption band, not previously evident, is noted at 2850 Å and is assigned to the dienyl radical,[13–15] an intermediate stage in polyene formation. The dienyl absorption although small is reproduced in all similarly treated films. Experimental conditions under which this absorption may be enhanced will be discussed below.

Following prolonged storage under vacuum, PVC films were exposed to 1 atm of oxygen at 286°K. After 1 min exposure to oxygen the only changes noted are decreases in absorption bands at 2520 and 2850 Å. Thus, allyl and dienyl radicals are most susceptible to oxygen scavenging. Intensity changes in polyene absorption bands were much smaller. This pattern is continued on storage at 286°K in oxygen (200 min) with allyl and dienyl radical absorptions decaying and polyenes much less affected (curve B, Figure 4). An additional 18-hr storage in oxygen results in a marked decay of all banded structures yielding a broad continuum probably due to oxidation products and unsaturated structures (curve C, Figure 4).

In another experiment a PVC film was irradiated at 200°K to 5.9 Mrad and warmed rapidly to enhance polyene formation. Following warmup to 334°K a series of absorption bands between 3000 and 5000 Å indicate the presence of polyenes (spectrum B, Figure 5). Additionally, a prominent band about 2500 Å is due to allyl radicals. Further storage (17.5 hr) at 334°K (curve C, Figure 5) indicates a larger concentration of polyenes and a large additional band at 2900 Å which is assigned to the dienyl radical.[14] A similar spectrum results following prolonged (12 day) storage of irradiated PVC at 298°K. Rapid warming to 373°K produces spectrum D and storage for 1.5 hr at 363°K, curve E, Figure 5. Allyl and dienyl radicals appear to attain asymptotic concentrations, while polyene absorption increases markedly. This observation is consistent with chain transfer reactions on post-irradiation storage of PVC.[6] Chlorine abstraction by polyenyl radicals from PVC leads to formation of polyenes, transfer of the reactive site and continual formation of short chain free radicals. It is possible that labile chlorine atoms are abstracted in this process.[16] Combined with allyl and dienyl free radical decay in polyenyl formation, a steady-state concentration of short chain free radicals is observed.

An attempt was made to distinguish radical and polyene portions of the absorption spectrum by oxygen scavenging of large concentrations of these species at 298°K (Figure 6). A PVC film indicating large polyene and allyl radical absorption (spectrum A) was exposed to 1 atm of pure oxygen for 1 min (spectrum B, Figure 6). Above 4000 Å, the absorption spectrum was hardly affected. However, measureable reductions were recorded at 2910, 3300, and 3690 Å. Further exposure to oxygen for 4 hr (curve C, Figure 6) and 23 hr (curve D, Figure 6) confirms that absorptions at 2910 and 3300 Å are reduced more than higher wavelength absorptions. Ultraviolet absorption bands at 2580, 2850, 3230, and 3590 Å had been assigned to free radicals, allyl, dienyl, trienyl, and tetraenyl, respectively, in irradiated polyethylene.[14] Absorption bands in irradiated PVC that decay most readily in oxygen are likely also due to discrete free radicals. Although some absorption bands disappear in oxygen, ultraviolet absorption below 3000 Å would be enhanced on oxidation by the absorption of oxidation products. The allyl radical absorption at 2420 Å is apparently shifted to lower wavelengths. In analogy with earlier results, this is due to an increasing absorption at low wavelengths, because of unsaturation (Figure 5) and oxidation products (Figure 6). The absorption spectrum is apparently decomposed into radical and polyene components with the former more susceptible to oxygen scavenging.

The sequential relation of intermediates in the generation of polyenes in irradiated PVC was examined by oxygen scavenging at selected stages of polyene formation. A PVC film was irradiated at ~200°K and the allyl absorption at 2500 Å allowed to increase on post-irradiation storage under vacuum at ~250°K. The film was exposed to 1 atm of oxygen for 24 hr and the allyl absorption band decayed. Subsequently, the film was stored under vacuum at 298°K (2 weeks) and spectra were recorded at intervals. No spectral evidence of polyene formation was detected. Broad ultraviolet absorption due to oxidation products was noted. These observations are consistent with allyl radicals as precursors of polyenes. Another PVC film was irradiated under vacuum at 120°K, exposed to 1 atm of oxygen and warmed rapidly to 298°K (in 3 hr). The film was then stored under vacuum for 3 days. Considerably reduced ultraviolet absorption associated with allyl radicals was noted due to partial scavenging of alkyl radical precursors. More complex oxygen scavenging could not be effected because the polymeric matrix at low temperatures is impermeable to oxygen.

Conclusions

Radiolysis of PVC may be studied by ultraviolet and visible spectroscopy following post-irradiation storage at selected temperatures in a cryostatic cell. The sequence of spectral changes is probably independent of *exact* thermal history. Irradiation and storage at temperatures below 200°K yield ultraviolet spectra

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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.

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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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