laurylimidazole PEI was estimated to be 0.06 min^{-1} at pH 7.3. In the present study we have found the rate constant for hydrolysis of laurylacetylimidazole PEI to acetate ion and laurylimidazole PEI under similar conditions to be 0.1–0.2 min^{-1}. In the earlier study, the hydrolysis rate was inferred by an indirect method from the turnover rate in a steady-state situation. In view of the uncertainties in the indirect method and the difference in size of the acyl group in the two cases, the approximate equality of the deacylation rate constants in gratifying.

To resolve the uncertainty due to the difference between acetate and caproate, an experiment was attempted using caproic anhydride as the substrate. The reaction could not be followed, however, presumably because of the low solubility of caproic anhydride. On the other hand, with propionic anhydride as substrate, in which case there is no solubility problem, the course of the reaction was very much the same as in the experiments with acetic anhydride. The rate constants for decomposition of propionylimidazole are also reported in the table. They are strikingly similar to those for acetylimidazole.

To summarize, we have spectrophotometrically observed an acylimidazole intermediate in a reaction analogous to that for which kinetic analysis had previously suggested such an intermediate. The kinetic parameters deduced from indirect spectrophotometry are nearly the same as those inferred from indirect measurements described in the earlier work.[1]

Acknowledgment. This investigation was supported in part by a grant from the National Science Foundation.

Vacuum Ultraviolet Circular Dichroism of Poly(L-alanine) Films

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There has been a substantial advance in the quantum mechanical description of polymer optical properties, both in the development of powerful and efficient formalisms, and in the completion of detailed spectral calculations on several polymer systems.[1] The calculations are essentially low-frequency limit applications of theory because experimental data describing the monomer electronic states are good only for those states with low excitation energy. It is therefore important to determine at what energy the polymer calculations break down from the lack of data describing the high-energy states. Calculations of the circular dichroism of polypeptide α helices, for example, are accurate to 190 nm, which is near the limit of the energy range experimentally accessible on commercial spectrometers. Our purpose here is to show that for poly(L-alanine), which contains only saturated C–H bonds in its side chain and which is therefore a good model polymer, the calculations break down just beyond 190 nm.

Our circular dichroism instrument consists of a hydrogen discharge cold-cathode light source, a 1-m vacuum ultraviolet monochromator, a biotite linear polarizer, a stressed-plate CaF_2 modulator as quarter-wave retarder,[2] and a photomultiplier with sodium salicylate coated window. The light intensity reaching the photomultiplier when there is no sample in the light path determines a dc signal which, in our instrument, is maintained at a constant level. The light intensity reaching the photomultiplier when there is an optically active sample in the path determines an ac signal which in our instrument is proportional to the circular dichroism. After a proper onetime calibration circular dichroism can be recorded directly. The voltage on the stress plate modulator is programmed by mechanical linkage to the monochromator wavelength drive to maintain quarter-wave retardation. Our instrument is limited in wavelength range only by the transmission properties of the CaF_2 of the modulator. Other details of our instrument will be reported separately. A similar instrument has been described by Johnson,[3] and Schnepp[4] has described an early version of an instrument with moderate differences.

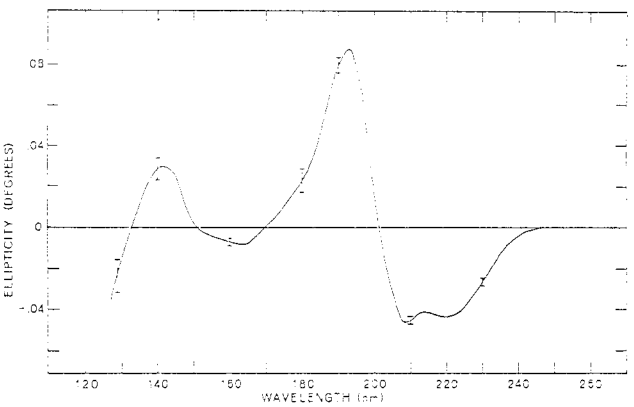

Figure 1. Circular dichroism of α-helical poly(L-alanine).

Poly(L-alanine) (Pilot Chemical Co.) was dissolved in trifluoroethanol in which it takes up the alpha helical conformation.[5] Films were prepared in a nitrogen-flushed glove box by evaporation to dryness onto calcium fluoride disks of 1 mm thickness. The total absorbance of sample plus CaF_2 was less than 1 at $\lambda > 1500$ Å; the absorbance rose below 1500 Å to approximately 2 at 1300 Å. The film thickness was estimated to be approximately 1800 Å. Spectra were recorded with a spectral slitwidth of 1.6 nm using a time constant of 10 sec. and a scan rate of 1 nm/min.

It is known that the circular dichroism of some polymer films show birefringence effects, in that the signal obtained with such films is observed to depend on the orientation of the film in the light path. We observed such an effect on some of our films. Figure 1 shows the circular dichroism obtained with a film which exhibited no orientation dependence. In this work our instrument was calibrated by measuring the circular dichroism of the same film using a Cary 60-6001 spectropolarimeter in the range 190–240 nm.

Figure 1, in the region from 190 to 240 nm, shows the circular dichroism which is characteristic of a polypeptide α helix. This part of the spectrum can be reproduced correctly with detailed quantum mechanical calculations which include the coupling of the lowest two transitions of the monomeric peptide chromophores. These same calculations however give a negative circular dichroism near 180 nm, which has until recently been outside the range of experimental observations. From Figure 1 it can be concluded that this feature is not observed experimentally. Johnson and Tinoco[6] reported a similar conclusion from

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their measurements of the circular dichroism of helical poly(L-glutamic acid). Since our spectrum of poly(L-alanine) is essentially identical with that of poly(L-glutamic acid) as reported by Johnson and Tinoco,[6] the circular dichroism in this region is apparently independent of the nature of the side chain.

Cassim and Yang[7] inferred the absence of the negative feature by indirect evidence, and concluded that this absence argued against the validity of an exciton model for the optical activity of helical polypeptides. We would like to make a distinction between the theoretical formalisms describing optical properties of polymers and the application of these formalisms through detailed numerical calculations. The latter always include additional assumptions and approximations, beyond those of the formalism, which are made necessary by incomplete data on the monomer electronic states. The basic theory of the optical properties of polymers has now been derived from several different points of view, all leading to the same general equations, and it seems very unlikely that the difficulty is in the fundamental theory. On the other hand, detailed calculations suffer from lack of information on the high-energy transitions, and these transitions are either ignored completely or are described in the aggregate through the monomer polarizability. It is, for example, possible that the additional positive contribution to circular dichroism near 180 nm arises from a coupling of the π-π^* transition directly with high-energy monomer or solvent states. Such a coupling could modify the band shape of the π-π^* polymer transition in a way to give the observed circular dichroism.

Johnson and Tinoco[6] argue as we do that the absence of the negative feature is not sufficient evidence to justify rejection of the current basic theory of polymer optical activity. They argue, however, that the observed spectrum is the result of the predicted negative band being cancelled by a previously unconsidered monomer transition near 175 nm which contributes positive dichroism. As evidence for their interpretation they note an apparent shoulder in the helix circular dichroism at 175–180 nm and a negative band in that region in the circular dichroism of disordered poly(L-glutamic acid) at pH 8. Mandel and Holzwarth's[8] agreement with this interpretation is based on the appearance of the shoulder in the helix spectrum. At the present time, however, we feel that without additional experimental data it cannot be concluded that the explanation of the discrepancy is so straightforward. The apparent shoulder may be part of the π-π^* envelope perturbed as described in the preceding paragraph. The negative band observed in the disordered polymer at 175 nm may prove to be the 165-nm helix band shifted to slightly longer wavelength, and therefore may have no relation to the shoulder in the helix spectrum. We agree with the statement of Cassim and Yang[7] that all of the theoretical aspects of the optical activity of polypeptide helices cannot yet be considered completely solved, except perhaps in the low-frequency limit.

Another salient feature of the spectrum of Figure 1 is the substantial negative band near 160 nm. The circular dichroism band coincides in energy with the absorption peak observed by several workers[9-11] and shown by Bensing and Pysh[12] to be polarized parallel to the helix axis in poly(L-alanine). The positive circular dichroism below 150 nm coincides with the rising absorption observed by Bensing and Pysh[12] to be polarized perpendicular to the helix axis. These data provide additional criteria by which to judge future spectral calculations.

The conclusions of this work are twofold. First vacuum ultraviolet circular dichroism is a practical tool which can add a significant new method for characterizing polymers, including those polymers which have no chromophores in the near-ultraviolet region. Secondly, vacuum ultraviolet circular dichroism can provide new stringent criteria for future polymer spectral calculations, which include the high-energy density of monomeric states.

Acknowledgments. This research was supported by National Science Foundation Grant GP-29219.

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Hydroxylic Solvent Absorption by Nylon 6

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The tendency of nylon polymers to absorb water is well known. It seemed of interest to check the absorption of some other hydroxylic liquids to see if this absorption tendency was a general one, and how the absorption might depend on the molecular structure of the liquid involved. The tendency to absorb water is often rationalized on the basis of the hydrogen-bonding tendency of both the amide groups of the polymer and of the water.

We have examined the equilibrium absorption in nylon 6 of some homologous aliphatic alcohols, of benzyl alcohol and phenol (containing an aromatic ring), and of some molecules of the diol and triol type, in order to see if any generalizations regarding the absorption behavior could be drawn. We have also checked the swelling behavior at two temperatures in some cases, to get an indication of the temperature dependence of this type of absorption.

The nylon 6 used was a commercial 1-mil extruded film with trade name Capran 77C, furnished to us by Allied Chemical Corp. Pieces of film weighing about 0.25 g were allowed to reach equilibrium absorption by allowing them to remain immersed in the various liquids (Baker Analyzed grade or better) at a controlled temperature. Sample weight was monitored by removing from the liquid, drying with filter paper, and weighing on an analytical balance. In the case of the more volatile solvents, sample weight was followed *vs.* time, and extrapolated back to the time of removal from the liquid, in order to obtain accurate values. The data presented represent averaged values from at least three duplicate samples; these were usually, but not always, run simultaneously. The time allowed to reach equilibrium varied from 1 day to 1 month; observations were made as a function of time to ensure that equilibrium had been achieved.

The results are collected in Table I. The molecular weight of the hydroxylic compound, the time allowed for equilibration and the ratio of moles absorbed to moles of monomer units in the polymer chains (or moles of amide groups) are also tabulated. Some absorption data on alcohols in nylon 6 have also been reported by Weiske;[2] al-

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