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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Table I
Equilibrium Swelling of Nylon 6 in Different Liquids

Solvent	Mol Wt	Temp (°C)	Min Time (Days) for Equil	% Absorption (w/w)	Moles of Solvent/113 g (Mole Unit) Nylon or per Amide Group	% Absorption (w/w) at Room Temp (Ref 2)
Methanol	32	30	1	10.8 ± 2.0	0.38	19
Ethanol	46	30	2	12.0 ± 2.0	0.29	17
1-Propanol	60	30	2	13.3 ± 1.5	0.25	18
1-Butanol	74	30	5	10.9 ± 1.0	0.17	16
1-Pentanol	88	30	15	7.9 ± 0.5	0.10	
		70	7	9.4 ± 0.3	0.12	
Cyclohexanol	100	30	28	3.9 ± 1.7	0.04	
		70	28	18.4 ± 1.0	0.21	
Benzyl alcohol	108	30	3	60.8 ± 1.7	0.64	55
		70	4	61.2 ± 2.6	0.64	
Ethylene glycol	62	30	4	18.9 ± 0.6	0.34	13
Diethylene glycol	106	30	6	15.7 ± 0.8	0.17	
Glycerol	92	30	3	11.6 ± 1.2	0.14	3
0.25 *M* Phenol in CCl_4	94	30	2	68.4 ± 1.7	0.78	
		70	3	51.8 ± 1.4	0.59	

Table II
Calculated Enthalpy Change for Equilibrium Absorption

Solvent	Temp (°C)	K	ΔH° (cal mole^{-1})
1-Pentanol	30	0.101	940
	70	0.121	
Cyclohexanol	30	0.044	8010
	70	0.208	
Benzyl alcohol	30	0.636	40
	70	0.640	

though not strictly comparable to our own data, since the measurements were made at room temperature on 1-mm thick injection-molded disks, his values are shown for reference in the last column of Table I.

It is known that solvent treatment of semicrystalline polymers can induce crystallization, and in some cases produce a modification of crystal form, in the case of polymorphic polymers such as nylon.[3] However, major morphological changes are usually produced only with high degrees of swelling or extreme treatment conditions. It is probable that some morphological changes were associated with the absorption of benzyl alcohol and phenol, but any such changes were probably minor in the case of the other hydroxylic compounds. Since phenol was used in CCl_4 solution, the equilibrium absorption of pure CCl_4 was also measured; this was found to be about 2%, and thus insignificant in comparison to the phenol.

In analyzing the data at different temperatures, we have assumed for maximum simplicity that the absorption equilibrium can be described by an equilibrium constant expression of the form

$$K = [\text{concn absorbed (moles/mole)}] = e^{-\Delta G^\circ/RT} = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R} \quad (1)$$

from which a value of ΔH° can be obtained from data at different temperatures by a simple Van't Hoff calculation. Equilibrium absorption was measured at two temperatures (30 and 70°) for 1-pentanol, cyclohexanol, benzyl alcohol, and phenol-CCl_4 solution. The results for the first three liquids are listed in Table II. In these three cases, the absorption is always greater at the higher temperature (unlike the behavior observed for phenol in Table I, where absorption appeared to decrease with increasing temperature). From a thermodynamic standpoint, the results in Table II would indicate an endothermic absorption process, which would point to stronger bonding in the liquid than in the polymer. The higher value of ΔH° for cyclohexanol may reflect steric effects related to the hydrogen-bonding accessibility of the hydroxyl group. The low values of ΔH° for 1-pentanol and benzyl alcohol could indicate a relatively athermal absorption process; alternatively, the equilibrium absorption might represent a "saturation" state, in which all available absorption sites are occupied. This seems particularly likely in the case of the benzyl alcohol, where a high absolute level of absorption is observed (of a similar magnitude to that shown by phenol). The polymer-phenol bonding would appear to be exothermic; however, we did not attempt to calculate a ΔH° value for this system because there was evidence of some dissolving of the polymer.

Infrared evidence has indicated that the amide groups in nylons are essentially 100% hydrogen bonded, in both the crystalline and amorphous regions.[4] In the absorption of homologous aliphatic alcohols, one simple possibility would be that a constant absorption on a molar basis would be observed, assuming that the accessible amide groups would be the same fraction of the total in all cases. It is seen from Table I that this is not the behavior found; the equilibrium absorption on a molar basis decreases systematically with increasing size of the alcohol molecule. This result could still be compatible with saturation absorption at "accessible" amide groups if it is assumed that the number of accessible amide groups decreases progressively with molecular size of the penetrant. This would explain also the significant drop in absorption going from 1-pentanol to cyclohexanol.

An additional result evident from Table I is that although diols and triols show enhanced absorption over monohydric alcohols on a weight basis, the values on a mole basis fall within the same range as the other aliphatic alcohols, and are not simply proportional to the hydroxyl group content. It is not surprising that equilibrium absorption is not solely related to the hydroxylic content of the swelling liquid in view of the complex polymer–solvent interactions that are involved.

The final point of interest in Table I is the very strong absorption of aromatic alcohols (benzyl alcohol, phenol),

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in contrast to aliphatic alcohols (either monohydric or polyhydric). This is obviously not due to the presence of a ring structure in itself, as can be seen by comparison with cyclohexanol; evidently the aromaticity of the ring is necessary. Phenol is so strongly absorbed that it can only be used in dilute solution. A phenol solution of 0.25 *M* in CCl_4 is only about 2.5 wt %; concentrations double this or higher will totally dissolve nylon 6, indicating a total penetration of the crystalline phase. A more detailed study of the absorption behavior of substituted phenols of various types in nylon 6 is also being carried out and will be reported separately.

Communications to the Editor

Nuclear Magnetic Resonance Spin–Lattice Relaxation in the Lyotropic Polypeptide Liquid Crystal[1]

In this communication, we report preliminary measurements of the proton nuclear magnetic resonance (nmr) spin–lattice relaxation times of the solvent molecules in the two component lyotropic polypeptide liquid crystal dichloromethane–poly(γ-benzyl L-glutamate) solution (CH_2Cl_2–$(BzlGlu)_n$). Synthetic polypeptides, $(NHCHRCO)_n$$^-$ (for $(BzlGlu)_n$, R = $CH_2CH_2COOCH_2C_6H_5$), spontaneously form a birefringent liquid crystalline phase above a limiting concentration in various helicogenic solvents. With increasing polypeptide concentration, the solution passes from a normal isotropic fluid through a two-phase region (isotropic plus anisotropic liquid crystal) resulting in a homogeneous liquid crystal. The equilibrium *supramolecular* structure in polypeptide liquid crystals is cholesteric; the α-helical, rodlike polymer molecules assume a helicoidal arrangement in the solution.[2a] This colesteric arrangement is, however, untwisted in a magnetic field yielding a nematic *supramolecular* structure with the helical molecules aligned parallel to the field.[2b-4] This lyotropic liquid crystal is unique in that no specific interactions are required for its formation; it is a consequence of the high axial ratio of the rodlike polypeptide. An extension of the lattice theory of solutions, which incorporates the constraints involved in packing rodlike molecules with noninteracting solvent molecules, satisfactorily predicts the concentrations at which the phase boundaries occur as a function of the axial ratio.[5]

In this study, two $(BzlGlu)_n$ molecular weights were used, mol wt 550,000 and 13,000. This corresponds to axial ratios of $p = 151$ and 3.56, respectively, using a polypeptide diameter of 25 Å (obtained from a molecular model with a radially extending side chain) and a length = 1.5 (mol wt/M_w) Å, where M_w is the $(BzlGlu)_n$ peptide residue molecular weight (219) and 1.5 Å is the projection of a peptide residue along the helix axis. With these axial ratios and the above-mentioned lattice theory, we calculate the isotropic two-phase boundary to occur at N_p/N_s = 0.019 (0.355) and the two-phase liquid crystal boundary at N_p/N_s = 0.031 (0.375) for $p = 151$ (3.56); N_p/N_s is the ratio of peptide residues to solvent molecules.

Measurements of the spin–lattice relaxation, T_1, were made using a saturation-90° sequence at 8 and 30 MHz. The polymer solutions were degassed using conventional freeze-pump-thaw cycles. The large differences between the T_1 for the solvent (4–28 sec) and T_1 for the polymer ($\sim$0.5 sec) enabled us to extract CH_2Cl_2 T_1 values from the solution relaxation data. Our value for neat CH_2Cl_2, T_1 = 28 sec at 20°, is in good agreement with reported values (T_1 = 32 sec at 35°).[6] Relative rates of flow of the polypeptide solutions in the nmr sample tubes were compared with glycerine (η = 14.9 P at 20°) in order to make qualitative estimates of the viscosity.

In Figure 1a, the CH_2Cl_2 spin–lattice relaxation rate, $1/T_1$, is shown as a function of polypeptide concentration for the two values of $(BzlGlu)_n$ molecular weight. The calculated phase boundaries for the high molecular weight polymer are indicated. These boundaries are in agreement with polarizing microscope observations; *i.e.*, the sample with N_p/N_s = 0.025 is birefringent whereas the sample with N_p/N_s = 0.017 is not. In addition, the position of the isotropic-two phase boundary is consistent with the dramatic change in solution viscosity. The solid curve shown in Figure 1b is derived from previously reported studies of this phenomenon.[7] The position of the two-phase liquid crystal boundary is not easily amenable to similar experimental verification.

The gradual monotonic increase in the relaxation exhibited by the low molecular weight $(BzlGlu)_n$ solutions with increasing polymer concentration is characteristic of ordinary isotropic polymer solutions.[6,8] $1/T_1$ for the low molecular weight polypeptide solutions is independent of frequency over the concentration range investigated. Consideration of the relaxation data for the high molecular weight and low molecular weight polypeptide solutions separately, as a function of N_p/N_s, and together, at a single value of N_p/N_s, reveals a conspicuous absence of correlation between solvent relaxation rates and solution viscosities. This indicates that unlike simple liquids, macroscopic polymer solution viscosity does not reflect microscopic dynamics. There is an anomalous increase in the solvent relaxation rate at the two-phase liquid crystal boundary. Concomitantly, $1/T_1$ becomes frequency dependent. In the liquid crystalline phase, the oriented nematic solutions exhibited angular-dependent free induction decays. (The high viscosity of the polypeptide liquid crystal relative to that of thermotropic liquid crystals enables one to rotate the nematic axis away from the magnetic field direction without immediate reorientation of this axis.) When the nematic axis is at an angle of $\cos^{-1}(1/(3)^{1/2})$ with the magnetic field, dipolar interactions are removed and the free induction decay is inhomogeneity

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(1) This work was supported in part by the University of Connecticut Research Foundation.

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