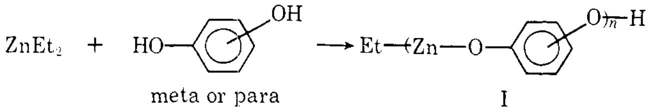
ization. In particular, the $ZnEt_2$–resorcinol (1:1) system gave a higher copolymer yield than the $ZnEt_2$–water (1:1) system, which we had found to be the most effective system among those previously examined. On the other hand, the $ZnEt_2$–monohydric phenol and –catechol systems showed almost no activity in alternating copolymerization.

Figure 1 shows the yield of the product obtained *vs.* the molar ratio of resorcinol–$ZnEt_2$. The results show the copolymer yield to be highly dependent on the resorcinol–$ZnEt_2$ ratio, with a clear optimum point at 1:1.

The infrared spectrum and the decomposition temperature of the copolymer obtained with the $ZnEt_2$–resorcinol or –hydroquinone systems were similar to those of the copolymer obtained with the $ZnEt_2$–water (1:1) system.[2] The ir spectrum of a solid film is shown in Figure 2 together with that of poly(propylene oxide).

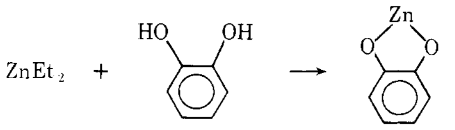
The $ZnEt_2$–resorcinol (1:1) or –hydroquinone (1:1) system may give species such as I, as shown in eq 1. On the other hand, the $ZnEt_2$–catechol system would give II (eq 2) and the $ZnEt_2$–monohydric phenol system might give III and IV (eq 3 and 4).

The difference in activities toward the copolymerization among these systems may be attributed to the presence or absence of the repeated $\text{+Zn–O–C}_6\text{H}_4\text{–O+}$ group.



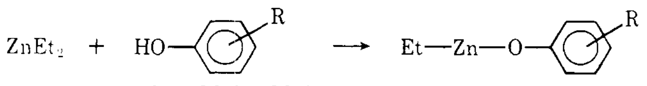
I

(1)



II

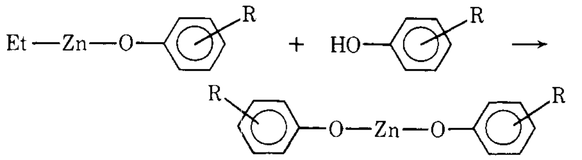
(2)



R = H, *m*-MeO, *p*-MeO

III

(3)



(4)

IV

Further studies on the copolymerization and on the nature of the catalyst systems are now in progress.

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Polarized Vacuum-Ultraviolet Absorption of Poly(L-alanine)

Assignments of spectral features in the vacuum-uv region from 1300 to 1800 Å are, generally speaking, to higher energy excitons, interband transitions, or plasmons. Assignments are made within some theoretical framework and experimental data in this region can be a guide in developing the description of electronic structure in polymers. Beyond this, and in light of the increasing simplicity of instrumentation, vacuum-uv spectroscopy will most likely begin to play an increasing role in polymer conformational analysis. We have previously used it to demonstrate that poly(L-hydroxyproline) films take up a conformation strongly resembling poly(L-proline) I when prepared by evaporation to dryness in a dc electric field.[1]

We reported earlier the unpolarized transmission spectra of polypeptide films from 1300 to 2500 Å.[2] We and others[3–5] observed a band near 1650 Å in α-helical poly(L-alanine). Polyalanine spectra are not complicated by the presence of absorbing chromophores in the side chain, which indicates a peptide group origin for the band. Here we report the linear dichroism of partially oriented poly(L-alanine) films and summarize the evidence now available which is relevant to the assignment of the 1650-Å band.

High molecular weight poly(L-alanine) was obtained from Pilot Chemical Inc., Watertown, Mass. Samples were cast on 1-mm calcium fluoride (Harshaw Chemical) by repeated evaporation from trifluoroethanol (Aldrich Chemical Co.). Orientation was sought through needle shearing during evaporation. Spectra were taken with a McPherson Model 225 double-beam spectrophotometer using a biotite polarizer (McPherson Co.). The polarization ratio of the biotite was approximately 15:1 in the region of 1650 Å.

Films were selected for low scattering background as judged by the optical density in the nonabsorbing region from 2500 to 3800 Å. Polyalanine does not make well-oriented films, and the spectra reported here were obtained only after a number of trials which resulted in varying degrees of chain orientation. An estimated correction for scattering in the spectra of the best samples was made using Onari's suggestion[5] of a λ^{-1} dependence. Additional experimental details are given in ref 6.

Figure 1 shows the spectra of our most oriented low-scattering sample. The two curves are labeled according to whether the plane of polarization of the radiation was parallel (‖) or perpendicular (⊥) to the direction in which the needle shearing was applied. The sum of the two curves gives a spectrum identical with that of the same film using unpolarized radiation.

The spectra from 1900 to 2400 Å should be comparable to the earlier results of Gratzer, Holzwarth, and Doty.[7] The differences can be explained on the basis of our films being less oriented than the films studied by Gratzer, *et al.* Thus, their maximum in parallel polarization at 2060 Å appears as a shoulder in our spectrum, and the maximum at 1950 Å in our parallel polarization has considerable contribution from the perpendicular component of unoriented chains. The high background absorbance in our spectrum near 1800 Å is most likely due to an inadequate correction for scattering. The accepted assignments in this low-energy region attribute the 2200-Å band to an n–π^* transition polarized perpendicular to the helix and the bands at 2060 and 1910 Å to exciton components of the π–π^* monomer transition.

Figure 1 shows that the polarization of the absorption band near 1650 Å is dominantly parallel to the direction of shear-induced orientation.

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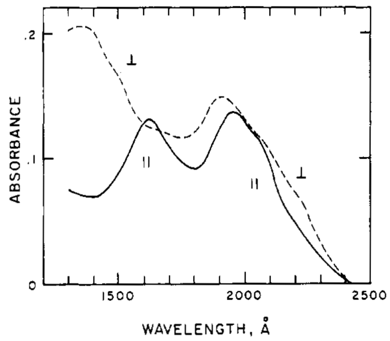

Figure 1. Polarized absorption spectrum of poly(L-alanine) film. Indicated polarizations are relative to the direction of shear orientation.

The assignment of the 1650-Å band to bound solvent is counterindicated by the following observations. (a) The band remains after 12 hr under vacuum in the monochromator. (b) The band is at the same position whether the samples were evaporated from trifluoroethanol, trifluoroacetic acid,[3] or dichloroacetic acid.[5] This evidence indicates an origin in the polymer chain. The saturated nature of the side chain further indicates an origin in the amide chromophore.

Parallel-polarized bands are also observed near 1650 Å in poly(γ-methyl L-glutamate) films[3,6] and poly(L-hydroxyproline) films.[6] Nonpeptide chromophores in those films make those data difficult to interpret, but our present observation of such a band in poly(L-alanine) makes it more likely that all of these bands have a common origin. In insulators, by far the most natural assignment is to an exciton with parentage in the monomeric amide states, and the past success in describing insulator spectra in terms of excitons is a strong argument in favor of such an assignment in this case. In the α helix, the amide groups are oriented with the C=O bond very nearly parallel to the helix axis. Therefore, monomer transitions polarized either perpendicular to the amide plane or in plane but perpendicular to the C=O bond cannot account for the parallel polarization of Figure 1, if an oriented-gas model is even approximately correct.

Several amide bands have been observed to the blue of the well-documented $\pi-\pi^*$ transition. Simpson[8] has assigned one of these to an $n'-\pi^*$ transition polarized perpendicular to the amide plane, which can be ruled out as the origin of the polymer band. Even if the monomer states are perturbed in the polymer, so that an oriented-gas model is not strictly correct, a valence-shell $n'-\pi^*$ transition would not be distorted sufficiently to account for the parallel polarization of the polymer band.

There is also evidence, both experimental[8,9] and theoretical,[9] for a Rydberg $n-\sigma^*$ transition in this region of model amide spectra. The polarization of such a transition, in the monomer, would be in plane and perpendicular to the C=O bond, which is not consistent with the observed polymer polarization in an oriented-gas model. For this transition, however, in which the terminal orbital is spatially delocalized, the oriented-gas model may break down completely so that the polymer band may have mixed polarization. That is, Figure 1 does not preclude some perpendicular polarization for the 1650-Å band.

Another possible origin for the polymer band is the second $\pi-\pi^*$ transition,[8,9] denoted also as NV$_2$ or $\pi_+-\pi^*$. Its location in the monomer spectrum has not been determined, but on the basis of a low-level molecular orbital calculation[10] it is expected to have a mixed polarization in the polymer, similar to the first $\pi-\pi^*$ transition.

An alternative approach to the assignment, based on the random-phase calculation of Barnes and Rhodes,[11] would be to a collective excitation. The observed polarization is consistent with that assignment, but the observed intensity is several times smaller than the calculated. This objection can be accommodated with the *ad hoc* explanation that in the actual physical situation the resonance is strongly damped in a way not incorporated by the calculation. The band could nevertheless be essentially a plasmon, as modified calculations would show. Yet, random-phase calculations are, generally speaking, subject to artifactual collective excitations that do not correspond to the physical situation. Little is known about the possibility of observing plasmons in insulators, and we tend to prefer an exciton assignment until the question of collective excitations in insulators is clarified.

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