The asymmetric membrane is thus seen to be related to the structure of the freshly cast polymer solution. The various procedures devised to prepare a high flux membrane appear to have been optimized to retain the solution structure in the solid phase. One may consider this trapped solution morphology as a functional definition of the asymmetric membrane of the type first described by Loeb and Sourirajan. This viewpoint clearly differentiates such membranes which have yielded the highest reverse osmosis fluxes from those fabricated with a thin dense layer of normal solid morphology.

The question of whether the micelles in the casting solution exist at room temperature, or form during the rapid freezing to a glass, requires comment. In the latter case, the freezing process must be considered to produce changes analogous to those occurring during precipitation,[9] and the discussion above would refer to an undescribed solution orientation which leads to the micellar structures on freezing. The prior existence of the micelles is, however, suggested by the constancy of their sizes when a solution is frozen either very slowly or extremely rapidly in the form of a capillary film.

The micelles in the polyamide–hydrazide solution are not apparent in small-angle X-ray scattering experiments, possibly because of insufficient density variation between the swollen polymer and the solvent. It is, of course, conceivable that experiments based on density differences (X-ray) or refractive index difference (light scattering) may measure dimensions of the basic micellar morphology which differ from those determined by the techniques of this paper.

Acknowledgment. The authors acknowledge the excellent technical assistance of Mr. Arthur Strickland and to thank Dr. N. L. Cox and Dr. P. Manos for some of the membranes studied.

(9) R. E. Kesting, "Synthetic Polymeric Membranes," McGraw-Hill, New York, N. Y., 1971.

Infrared Studies of the Side-Chain Orientation in Solid Films of Esters of Poly(L-glutamic acid)

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ABSTRACT: Five polymers of substituted benzyl L-glutamates have been studied by infrared spectrophotometry: poly(L-glutamates) of *o*-, *m*-, and *p*-nitrobenzyl, poly(L-glutamate) of *p*-methylbenzyl, and poly(L-glutamate) of 2,4,6-trimethylbenzyl. Two polymers exhibit a significant linear dichroism in the absorption bands of the side-chain chromophores. These are the poly(L-glutamate) of *p*-nitrobenzyl and the poly(L-glutamate) of 2,4,6-trimethylbenzyl. For both of these polymers, the axial rise per residue is slightly different from that of an α helix. But these interactions between side chains do not give a stabilization of the helical structure. Indeed, only the *p*-nitrobenzyl poly(L-glutamates) exhibit a linear dichroism in the absorption bands of the side-chain chromophores, yet the more stable helical structure is obtained with the ortho derivative. Therefore, the interactions of side groups with one another do not play the main role in the stability of the helical form.

In two previous papers[1,2] from this laboratory, several esters of poly(L-glutamic acid) have been studied by circular dichroism (CD) and optical rotatory dispersion (ORD), in order to determine the influence of the side chains on the secondary structure of polypeptides. Five polymers have been synthetized and studied by these methods: the *o*-, *m*-, and *p*-nitrobenzyl poly(L-glutamates),[1] and the *p*-methylbenzyl and 2,4,6-trimethylbenzyl poly(L-glutamates).[2]

It is further known that there is a frequency-conformation correlation for polypeptides in different secondary structures.[3] In addition, dichroic effects in oriented films of polypeptides give an indication of secondary structure and of orientation of side chains.[4]

In the present paper, we report an investigation by infrared spectrophotometry of these polymers. The poly(benzyl L-glutamate) has been studied also as a reference[3] standard for a right-handed α helix.

(1) P. Le Barny and M. H. Loucheux, *10th Prague IUPAC Microsym.*, in press, 1972.
(2) M. Delporte-Leroy and M. H. Loucheux, *Bull. Soc. Chim. Fr.*, 1529 (1972).
(3) E. J. Ambrose and A. Elliott, *Proc. Roy. Soc., Ser. A*, **205**, 47 (1951).
(4) E. M. Bradbury, B. G. Carpenter, and R. M. Stephens, *Macromolecules*, **5**, 8 (1972).

Experimental Section

Materials. The polymers were prepared by polymerization of *N*-carboxyanhydrides of the corresponding L-glutamates.[5] The molecular weights were determined by viscosimetry by using the relation known for poly(benzyl L-glutamate).[6] We have verified this relation for one polymer by using the light-scattering technique. The molecular weights obtained are as follows.

Poly(L-glutamate) of	Mol Wt
o-Nitrobenzyl	180,000
m-Nitrobenzyl	77,000
p-Nitrobenzyl	30,000
p-Methylbenzyl	75,000
2,4,6-Trimethylbenzyl	45,000
Benzyl	220,000

Infrared Spectroscopy. The infrared spectra were recorded on a Perkin-Elmer 257 double-beam spectrometer and on a Perkin-Elmer 225 double-beam spectrometer when polarized radiation was used.

The films of macromolecules were obtained by evaporation of the viscous solutions until dry. The solvents used were chloroform

(5) R. Ledger and F. H. C. Stewart, *Aust. J. Chem.*, **18**, 1477 (1965); *ibid.*, **19**, 1729 (1966). M. H. Loucheux and J. Parrod, *C. R. Acad. Sci.*, **267**, 614 (1968).
(6) P. Doty, J. H. Bradbury, and A. M. Holtzer, *J. Amer. Chem. Soc.*, **78**, 947 (1956).

for poly(benzyl L-glutamate), poly(*p*-methylbenzyl L-glutamate), and poly(2,4,6-trimethylbenzyl L-glutamate); and hexafluoro-2-propanol (HFIP) for the three poly(nitrobenzyl L-glutamates).

The orientation was produced by unidirectional shearing of viscous solutions by the following process. A few drops of the solution were put on a glass cylinder rotating at 60 rpm. Then a glass plate was put on the film to obtain a film around the cylinder. This film was removed by using a razor blade and dropped on a sodium chloride plate. The best films were chosen after examination under a polarizing microscope.

For the Perkin-Elmer 257 spectrometer the accuracy of the position of the bands was within 5 cm^{-1} for 1500–1200 cm^{-1} and within 3 cm^{-1} for frequencies shorter than 1200 cm^{-1}; for the amide A region, the accuracy was within 15 cm^{-1}. For the Perkin-Elmer 225 spectrometer this accuracy was respectively 2, 1, and 5 cm^{-1}.

To record the spectrum, the film had an inclination of 45° with respect to the direction of polarized radiation.

Determination of the Dichroic Ratios. The experimentally determined dichroic ratio R of a particular mode of vibration is equal to $A_{\parallel}/A_{\perp}$, where A is equal to the absorbance at the band maximum with electric vector parallel and perpendicular to the orientation direction, and is equal to log (P_0/P), P_0 being the incident radiant intensity and P the transmitted radiant intensity. It is difficult to measure absolute values of incident and transmitted radiation; for these determinations, the base-line method was used. It consists in drawing a base line for the absorbance band from the shoulders on each side of the peak. The per cent transmission corresponding to the base line gives P_0. P is the per cent transmission at the band maximum. Thus, at the band maximum, the film's contribution to the absorption is the difference between P_0 and P. Using a base-line method in this manner eliminates some of the errors encountered in attempting to correct measured P_0 and P for stray and scattering radiation losses.

The base line is drawn for each band and for both parallel and perpendicular absorption curves.

Results

Unpolarized Infrared Study. Table I gives the frequency values obtained for three poly(nitrobenzyl L-glutamates) and for poly(*p*-methylbenzyl L-glutamate), poly(2,4,6-trimethylbenzyl L-glutamate), and poly(benzyl L-glutamate). The amide frequencies of 1655 cm^{-1} for the amide I and 1550 cm^{-1} for the amide II for poly(benzyl L-glutamate) are characteristic of a polypeptide in right-handed α-helix form. The five substituted benzyl poly(L-glutamates) show about the same frequencies for these bands. But the amide A and the amide B respectively at 3295 and 3065 cm^{-1} for poly(benzyl L-glutamate) do not appear at these frequencies for the substituted poly(benzyl L-glutamates).

From the values of amide A, B, and II vibrations, ν_A, ν_B, and ν_{II}, it is possible to estimate the variation in the hydrogen-bond lengths between the substituted poly(benzyl L-glutamates) and poly(benzyl L-glutamate). The unperturbed NH stretching frequency ν_{NH} can be estimated from the formula[7,8]

$$\nu_{NH} = \nu_A + \nu_B - 2\nu_{II}$$

Differences $\Delta\nu_{NH}$ between the value of NH in poly(benzyl L-glutamate) and the other polymers studied can be used to determine the difference in hydrogen-bond lengths ΔR from the expression[9]

$$\Delta R = \Delta\nu_{NH}/548$$

The results so obtained are given in Table I.

Fraser *et al.*[10] have shown that there exists a correlation between the axial rise per residue, h, and the hydrogen-bond length. It is seen from Table I that in the case of poly(*p*-nitrobenzyl L-glutamate) a considerable change in hydrogen-bond length is detected, and this change is much less important for poly(*m*-nitrobenzyl L-glutamate); the ΔR value obtained for poly(*o*-nitrobenzyl L-glutamate) is too weak and is not significant. For these three poly(nitrobenzyl L-glutamates), the ΔR value is positive and therefore would mean an increase in h. These results are in good agreement with those of Fraser *et al.*[10] On the other hand, this ΔR value is slightly negative for poly(*p*-methylbenzyl L-glutamate) and poly(2,4,6-trimethylbenzyl L-glutamate); that is to say, for these polymers the axial rise per residue is slightly decreasing.

Polarized Infrared Studies. Figure 1 gives the dichroic spectra of three poly(nitrobenzyl L-glutamates): poly(*p*-methylbenzyl L-glutamate), poly(2,4,6-trimethylbenzyl L-glutamate), and poly(benzyl L-glutamate). In each case, amide A and I bands indicates a parallel dichroism. For both poly(benzyl L-glutamate) and poly(2,4,6-trimethylbenzyl L-glutamate), the amide II band indicates a perpendicular dichroism. For poly(*p*-methylbenzyl L-glutamate) and poly(nitrobenzyl L-glutamates) there is an overlapping of the amide II band at about 1515 cm^{-1} and the band due to the substitution of aromatic ring at about 1530 cm^{-1} when the electric vector of polarized radiation is parallel to the direction of stroking. In the case of poly(2,4,6-trimethylbenzyl L-glutamate), both bands have exactly the same frequency and are superimposed at 1515 cm^{-1}. These observations are in good agreement with the presence of a right-handed α-helical form for each studied polymer.

The main side-chain absorption bands are from the largely ester C=O stretching vibration at 1780 cm^{-1} and the ester C-O-C stretching vibration at 1160 cm^{-1}. It can be seen in Figure 1 that the dichroism of these bands is not the same for each polymer.

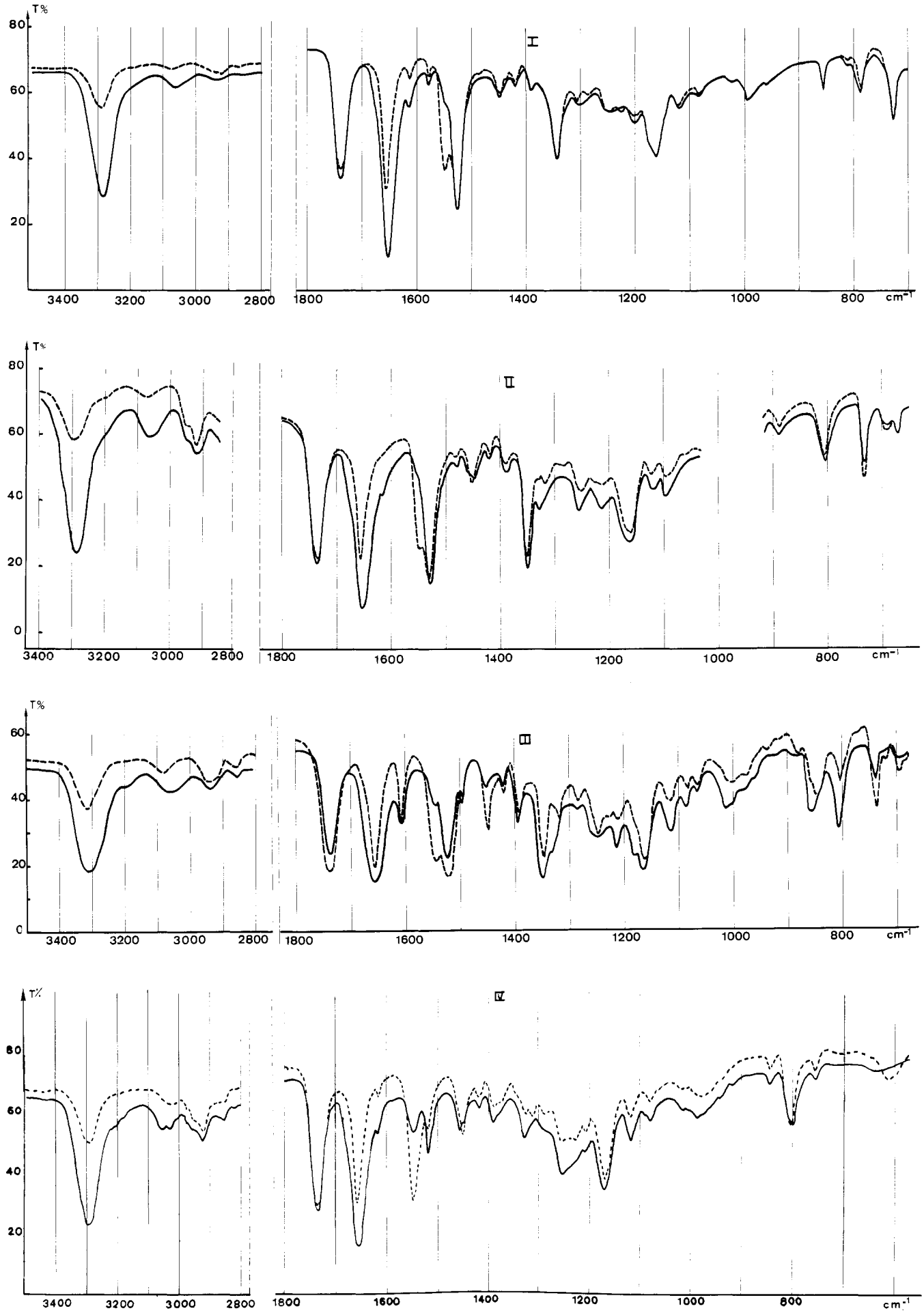
Because the aromatic band vibration and δ-CH_2 deformation band are superimposed at about 1450 cm^{-1}, it is difficult to know the origin of dichroism at this frequency; but since for poly(*p*-methylbenzyl L-glutamate), for example, side-chain bands are nondichroic, it is probable that dichroism at 1450 cm^{-1} is due to the δ-CH_2 deformation band. For poly(*p*-methylbenzyl L-glutamate) and poly(2,4,6-trimethylbenzyl L-glutamate), the aromatic substitution band at 805 and 845 nm shows a perpendicular dichroism more important for poly(2,4,6-trimethylbenzyl L-glutamate) than for poly(*p*-methylbenzyl L-glutamate). Side-chain bands of three poly(nitrobenzyl L-glutamates) due to aromatic substitution at about 850, 805, and 787 cm^{-1}, show a high dichroism only for the poly(*p*-nitrobenzyl L-glutamate). This dichroism is parallel for the bands at 850 and 805 cm^{-1} but perpendicular for the band at 787 cm^{-1}.

For poly(*o*-nitrobenzyl L-glutamate), these aromatic substitution bands are not dichroic and for poly(*m*-nitrobenzyl L-glutamate) they show a small dichroism.

As the ester bands are clear of the absorption of other vibrations, their dichroic ratios can be used to obtain the approximate orientation with respect to the helix axis of the transition moments associated with these vibrations. This orientation can be evaluated by using a model where a fraction f of chains is considered fully ordered and $1 - f$ is considered disordered. Then, the dichroic ratio is given by the expression[11]

$$R = \frac{2\cos^2\theta + g}{\sin^2\theta + g}$$

(7) T. Miyazawa in "Polyamino Acids, Polypeptides and Proteins," M. A. Stahmann, Ed., Univ. of Wisconsin Press, Madison, Wis., 1962, p 201.
(8) T. Miyazawa, *J. Mol. Spectrosc.* 4, 168 (1960).
(9) G. C. Pimentel and C. H. Sederholm, *J. Amer. Chem. Soc.*, 24, 639 (1956).
(10) R. D. B. Fraser, B. S. Harrap, R. Ledger, T. P. MacRae, F. H. C. Stewart, and E. Suzuki, *Biopolymers*, 5, 797 (1967).
(11) R. D. B. Fraser, *J. Chem. Phys.*, 21, 1511 (1953).


T%
80
60
40
20
3400
3200
3000
2800
1800
1600
1400
1200
1000
800
cm⁻¹
I
II
III
IV

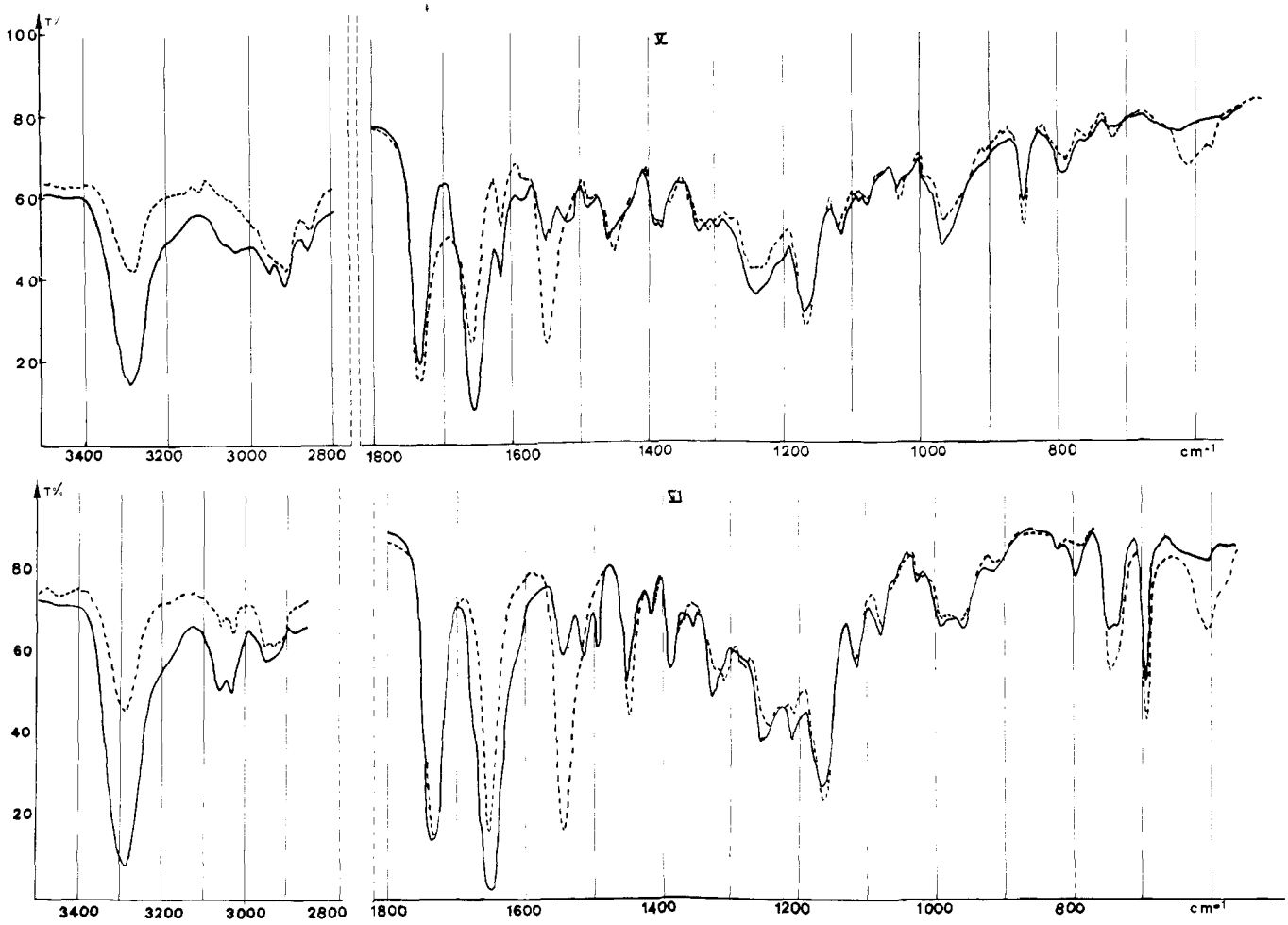


Figure 1. Polarized infrared spectra of: (1) poly(*o*-nitrobenzyl L-glutamate), (2) poly(*m*-nitrobenzyl L-glutamate), (3) poly(*p*-nitrobenzyl L-glutamate), (4) poly(*p*-methylbenzyl L-glutamate), and (5) poly(2,4,6-trimethylbenzyl L-glutamate).

Table I
Measured Frequencies of the Amide Vibrations and the Derived Values of the Unperturbed NH Stretching Frequencies ν_{NH}

Ester of Poly(L-glutamic Acid)	ν_A (cm^{-1})	ν_B (cm^{-1})	ν_I (cm^{-1})	ν_{II} (cm^{-1})	ν_{NH} (cm^{-1})	$\Delta\nu_{NH}$ (cm^{-1})	ΔR (Å)
Benzyl[a]	3291	3065	1655	1549	3258		
p-Methylbenzyl	3290	3055	1658	1550	3245	−13	−0.024
2,4,6-Trimethylbenzyl	3290	3060	1655	1549	3252	−6	−0.011
o-Nitrobenzyl	3292	3070	1660	1550	3262	+4	0.007
m-Nitrobenzyl	3292	3075	1657	1545	3277	+19	0.034
p-Nitrobenzyl	3310	3080	1657	1545	3300	42	0.076

[a] From ref 11.

where $g = (2/3)[(1 - f)/f]$ and θ is the angle between the transition moment and the stroking direction. If chains were fully ordered, that is to say if $f = 1$

$$R_0 = \frac{2}{tg^2\theta}$$

But generally f is unknown and must be determined. The absorption bands at *ca.* 3300, 1650, and 1550 cm^{-1}, *i.e.*, amide A, I, and II, respectively, which present a dichroism, can be used to measure f. The amide II band dichroism has been used to determine f for poly(γ-benzyl L-glutamate).[12a] But poly(γ-substituted benzyl L-glutamates) exhibit a vibration band due to the substituted aromatic ring at about 1515 cm^{-1} which is overlapping with the amide II band. Therefore, it is impossible to use the amide II band for the determination of f for these polymers. Moreover, the amide I band cannot be used for the determination of f; it has been shown that a discrepancy exists between the values obtained for dichroic ratios of this band for poly(γ-benzyl L-glutamate) and other synthetic polypeptides[12b] because the transition moment directions are not invariant from compound to compound.[12c]

Therefore, it is the dichroic ratio of the amide A band which is generally used to determine f.[13] The direction of the transition moment of the amide A vibration in the α helix has been estimated by Tsuboi[12a] to be about 28° with respect to the helix axis. Therefore, in this case R_0 =

(12) (a) M. Tsuboi, *J. Polym. Sci.*, **59**, 139 (1962); (b) A. Elliott, *Proc. Roy. Soc., Ser. A*, **221**, 104 (1953); (c) A. Elliott, *Nature (London)* **172**, 359 (1953).

(13) E. M. Bradbury, B. G. Carpenter, and R. M. Stephens, *Macromolecules*, **5**, 8 (1972).

Table II
Measured Frequencies of the Amide Vibrations When Polarized Radiation Is Used and Transition Moment Directions with Respect to Helix Axis

Ester of Poly(L-glutamic acid)	Frequencies (cm^{-1}) of Amide Bond								Dichroic Ratios			Angle θ (deg)		
	Amide A		Amide I		Amide II		Amide III							
	a	b	a	b	a	b	a	b	Amide A	Amide I	Amide II	Amide I	Amide V	f
Benzyl	3291	3289	1651	1651	1515	1545	1325	1310	4.34	2.46	0.22	53[c]	80[c]	0.78
p-Methylbenzyl	3292	3295	1655	1658			1328	1312	3.41	1.60		54	72	0.66
2,4,6-Trimethylbenzyl	3290	3285	1653	1658	1515	1548	1322	1312	3.63	2.08	1.56	54	76	0.73
o-Nitrobenzyl	3287	3285	1652	1656					3.99	2.41		52		0.74
m-Nitrobenzyl	3285	3295	1655	1657			1330	1318	4.32	2.23		54		0.78
p-Nitrobenzyl	3310	3310	1658	1657					2.90	1.18		61		0.58

[a] Electric vector is parallel to the direction of stroking. [b] Electric vector is perpendicular to the direction of stroking. [c] Values from ref 12.

Table III
Measured Frequencies of the Side-Chain Vibrations When Polarized Radiation Is Used and Transitions with Respect to Helix Axis

Ester of Poly(L-glutamic acid)	Frequencies (cm^{-1})								Dichroic Ratios				Angle θ (deg)	
	C=O Ester		C-O-C		δ-CH_2 Arom C-C		Substitut on Arom Ring							
	a	b	a	b	a	b	a	b	C=O	C-O-C	δ-CH_2 + Arom. C-C	Substitute on Arom Ring	C=O	C-O-C
Benzyl	1734	1731	1165	1165	1450	1450			1.03	0.87	0.72		53[c]	54[c]
p-Methylbenzyl	1735	1735	1170	1170	1458	1452	804	805	1.00	0.97	0.69	0.85	54	55
2,4,6-Trimethylbenzyl	1732	1730	1170	1170	1459	1450	850	850	1.00	0.75	0.83	0.69	54	60
o-Nitrobenzyl	1740	1738	1160	1162	1449	1449	728	729	1.16	1.00	0.81	1.00	52	55
m-Nitrobenzyl	1737	1735	1161	1160			805	805	1.06	1.03	0.96	1.00	54	54
p-Nitrobenzyl	1738	1739	1165	1162			806	804	0.75	0.95	0.29	2.09	61	56

[a] Electric vector parallel to the direction of stroking. [b] Electric vector perpendicular to the direction of stroking. [c] From ref 12.

7. From the observed dichroic ratio R of the amide A band, f can be found from[14]

$$f = \frac{(R - 1)(R_0 + 2)}{(R_0 - 1)(R + 2)}$$

For poly(γ-benzyl L-glutamate), that is to say, for a polymer which does not possess a band overlapping with the amide II band, f can be determined from both the amide A and the amide II bands. The two f values obtained from these different bands are in good agreement.

Table II and Table III give the f and θ values obtained from the amide A dichroic ratio. One may observe that the dichroism of the main-chain bands and the angle their transition moments make with the helix axis are not the same for each polymer. The values of the dichroic ratios of the amide A and amide I vibration bands of poly(*p*-nitrobenzyl L-glutamate) are much less than for the other polymers, in which a high parallel dischroism has been shown. Perhaps this is because the fraction of chains considered as fully ordered, f = 0.58, is much less than the corresponding fraction for the poly(*p*-methylbenzyl L-glutamate), f = 0.66, and for the poly(*m*-nitrobenzyl L-glutamate), f = 0.78. The dichroic ratios of the side-chain bands and the angle their transition moments make with the helix axis are only significant for poly(*p*-nitrobenzyl L-glutamate) and poly(2,4,6-trimethylbenzyl L-glutamate). In these cases, the dichroic ratio of the ester C=O stretching band is 0.75 for the poly(*p*-nitrobenzyl L-glutamate) and the dichroic ratio of the C-O-C stretching vibration is 0.7 for poly(2,4,6-trimethylbenzyl L-glutamate).

(14) R. D. B. Fraser, *J. Chem. Phys.*, 24, 89 (1956).

Discussion

Of the three poly(nitrobenzyl L-glutamates), only poly(*p*-nitrobenzyl L-glutamate) exhibits a high dichroism for aromatic substitution bands. Therefore, there is a side-chain orientation for this polymer only. In addition, the band at about 1450 cm^{-1} due to both δ-CH_2 vibration and aromatic substitution exhibits a very high dichroism for poly(*p*-nitrobenzyl L-glutamate), and is nondichroic for the other two poly(nitrobenzyl L-glutamates). Since this band at 1450 cm^{-1} is due to two vibrations it is not possible to say if the δ-CH_2 vibration band is dichroic or not; but inasmuch as the value of the dichroic ratio is very substantial for poly(*p*-nitrobenzyl L-glutamate), we have assumed that for this polymer the δ-CH_2 vibration band is dichroic. Therefore, it is possible to take the line joining the carbon atoms of the C-O-C group as an approximate indication of the side-chain orientation with respect to the helix axis.[13] Thus, for poly(*p*-nitrobenzyl L-glutamate) this angle is 56°. This value is in qualitative agreement with the results of theoretical work of Scheraga and coworkers.[15] They predicted that the side chains of right-handed helical esters of poly(L-glutamic acid) should have a well-defined side-chain conformation. However, this polymer does not have a longitudinal orientation, as predicted, but rather a transverse orientation. It is interesting to compare these results with those obtained by optical rotatory dispersion and circular dichroism in order to emphasize the influence of the nitro substituent on the stability of the right-handed helical form of these three polymers.[1] The stability increases in the order para <

(15) J. F. Yan, G. Vanderkooi, and H. A. Scheraga, *J. Chem. Phys.*, **49**, 2713 (1968).

meta < ortho; that is to say, the interactions between side chains do not increase the stability of the helical structure. This conclusion is in good agreement with calculations of Finkelstein and Ptitsyn.[16] They determined that among local interactions affecting the helical structure of a polypeptide the interactions of side groups with one another do not play the main role in the stability of the helical form. But these interactions between side chains should play an important role in the α-helix parameters. Clearly, for poly(*p*-nitrobenzyl L-glutamate) the extension in the hydrogen-bond length, and thus in the axial rise per residue, is greatest. The influence of the substitution in the para position of an aromatic ring on the secondary structure is a well-known phenomenon for poly(p-nitrobenzyl L-aspartate).[17] In particular, an anomaly in the axial rise per residue had been shown in this case. Such a variation is more important[18] for poly(*p*-nitrobenzyl L-aspartate) than for poly(*p*-nitrobenzyl L-glutamate) but with the opposite sign. That is to say, the helix of poly(*p*-nitrobenzyl L-aspartate) is more compact than a right-handed α helix, and the helix of poly(*p*-nitrobenzyl L-glutamate) is less compact than a right-handed α helix.

It is difficult to give an explanation of the different side-chain orientations for each poly(nitrobenzyl L-glutamate). It is known that the side-chain orientations can depend on the length of the side chain.[14] But another contribution would be provided by differences, in dipole–dipole interactions. And, of course, the length of the side-chain increases and the dipole–dipole interactions change too when the nitro substituent is moved from the ortho to the para position.

An additional contribution to the greater stability of poly(2,4,6-trimethylbenzyl L-glutamate) and poly(*o*-nitrobenzyl L-glutamate) is perhaps provided by more efficient shielding of the hydrogen-bond helical backbone. Obviously, the 2,4,6-trimethylbenzyl group is bulkier than the benzyl group and the nitro substituent is nearer to the backbone when it is in the ortho position rather in the meta or para position. For both of these polymers the stability of the helical form is greater.

The discrepancy between our results and theoretical calculations[15] for the orientation of side chains, is not surprising since theoretical calculations apply to isolated molecules *in vacuo* whereas our studies are concerned with films. In the solid state, side-chain conformations are probably modified to minimize packing energy.

(16) A. V. Finkelstein and O. B. Ptitsyn, *J. Mol. Biol.*, 62, 613 (1971).
(17) M. Goodman, A. M. Felix, C. M. Deber, A. R. Brause, and G. Schwartz, *Biopolymers*, 1, 371 (1963); M. Hashimoto and J. Aritomi, *Bull. Chem. Soc. Jap.*, 39, 2707 (1966).
(18) J. B. Aragão and M. H. Loucheux, *J. Chim. Phys.*, 1578 (1971).

Notes

Cleavage of Isotactic Poly(*tert*-butylethylene oxide) by Butyllithium

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The polymerization of *tert*-butylethylene oxide by potassium *tert*-butoxide in bulk has been found[1] to give a crystalline polymer differing in its X-ray diffraction pattern and solution nmr from the crystalline polymer prepared by typical coordination catalysts.[1,2] The latter, presumed to be isotactic, gave the expected erythro dimer glycol on butyllithium degradation.[3] The former gave equal amounts of erythro and threo dimer, supporting the view that the base-catalyzed polymer has a regularly alternating sequence of isotactic and syndiotactic placements.

Since one of the major differences between the poly(*tert*-butylethylene oxide) samples prepared by base and coordination catalysts was the very much higher molecular weight of the latter, we have felt it desirable to degrade the latter to the same molecular weight as the former in order to make a comparison of samples of approximately the same molecular weights.

(1) (a) C. C. Price and D. Carmelite, *J. Amer. Chem. Soc.*, 88, 4039 (1966); (b) C. C. Price and H. Fukutani, *J. Polym. Sci., Part A-1*, 6, 2653 (1968).
(2) G. Allen, C. Booth and S. J. Hurst, *Polymer*, 8, 385 (1967).
(3) C. C. Price, M. K. Akkapeddi, B. T. DeBona and B. Furie, *J. Amer. Chem. Soc.*, 94, 3964 (1972).

Experimental Section

Isotactic poly(*t*-BuEO)[2] was prepared by adding 10.5 ml of 16.8 wt % diethylzinc in benzene and 0.23 ml of water to 8 g of *t*-BuEO sealed under N_2 and heated to 60° for 1 week. The crude polymer was extracted several times with benzene, which gave 1.9 g of liquid polymer. After washing with 5% aqueous HCl, the benzene-insoluble polymer was dissolved in 200 ml of tetralin at 90°, filtered, and poured into 1200 ml of methanol: yield 3.1 g, mp 138–143°, $[\eta]$ = 2.14 (90° in tetralin).

"Iso-syn" poly(*t*-BuEO)[1b] was prepared from 3 g of *t*-BuEO and 0.034 g of *t*-BuOK sealed under N_2 and heated to 90° for 21 days. The crude product was dissolved in 150 ml of cyclohexane, neutralized by adding solid CO_2, washed with water thoroughly, dried, and evaporated: yield 3.0 g, mp 52.5–55.5°, $[\eta]$ = 0.057 (30° in benzene), M_n = 4700 (vapor pressure osmometer).

Polymer cleavage of 1 g of isotactic poly(*t*-BuEO) by 0.152 ml of 20.7 wt % butyllithium in hexane (Venturon Corp.) was carried out for 16 hr in 100 ml of refluxing benzene. Then 3 ml of ethanol was added followed by 20 ml of 10% aqueous HCl. After washing to neutrality with water, the insoluble polymer was collected by filtration (0.9 g). Evaporation of the benzene filtrate gave 81 mg of solid polymer: mp 113–120°, $[\eta]$ = 0.139 (30° benzene), M_n = 5000 (vpo). The process was repeated several times with similar results. Cleavage using 1.5 times as much BuLi gave 12–15% degraded polymer, mp 115–117°, $[\eta]$ = 0.101 (30° benzene, M_n = 2800 (vpo)).

The X-ray powder pattern and solution nmr for these degraded isotactic samples were identical with those reported earlier for the undegraded polymer[1b] and quite distinct from those from the base-catalyzed polymer.

Discussion

The experimental results reported here confirm the earlier conclusions that poly(*t*-BuEO) formed by base differs