ratio = 6:1) were degassed at 10 mmHg by cooling at −60 °C. The stirred solutions were exposed at room temperature to white light. The time of exposure was between 3 and 30 h; if the reaction proceeded to completion, a discoloring of the solutions took place. The solutions were filtered to eliminate the inorganic salts insoluble in the reaction solvent, and the polymers were precipitated by methanol and dried under vacuum.

Characterization of Products. VPC was carried out on a Perkin-Elmer F30 A instrument equipped with 200 × 0.29 cm dual columns packed with 20% silicone gum rubber (SE-30) on 80–100-mesh Chromosorb W. ^{1}H NMR spectra were recorded on a Varian 60-MHz instrument. ^{13}C NMR monomer and model compound spectra were recorded at 30 °C in $CDCl_3$ on a Varian XL-100 instrument. ^{13}C NMR polymer spectra were registered at 140 °C on approximately 10 wt % solutions (2% for isotactic polmers) in 1,2-dichlorobenzene (126.8 ppm) and converted to the tetramethylsilane scale.

Registry No. 1, 98-51-1; 2, 1075-38-3; 3, 7397-06-0; 4, 104807-56-9; 5, 104807-57-0; 6, 60070-04-4; 2-$H_3CC_6H_4CH_3$, 95-47-6; atactic-poly(3-MSt), 25037-62-1; isotactic-poly(3-MSt), 54190-45-3; atactic-poly(4-MSt), 24936-41-2; isotactic-poly(4-MSt), 54190-46-4; atactic-poly(3,4-DMSt), 61420-50-6; isotactic-poly(3,4-DMSt), 104807-58-1.

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Helical Conformations in a Polyamide of the Nylon-3 Family

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ABSTRACT: We have studied the conformation of poly(α-isobutyl L-aspartate), which is a nylon-3 derivative with a side chain attached to each monomer unit. Alternatively it can be considered as a polypeptide in which an additional CH_2 group has been included in the main chain of each residue. The polymer conformation is thus characterized by the usual torsional angles (ϕ,ψ), plus a ξ angle for the additional carbon atom. Analysis of fiber X-ray diffraction patterns reveals two helical conformations for this polymer, which bear structural similarity to the ubiquitous α-helix in proteins. They respectively have 3.25 and 4 residues per turn of helix. We have determined the coordinates of each helix and studied the helix–coil transition in this polymer by NMR.

Introduction

Bragg et al.[1] investigated with molecular models the various helices that can be made from polypeptide chains, which contain two carbon atoms in the polymeric backbone and therefore may be considered as derivatives of nylon-2. Some of these postulated helical structures have been experimentally observed, as reviewed, for example, by Lotz and Brack,[2] although it appears that the α-helix is the structure most frequently observed in polypeptides and proteins.

With the same hydrogen-bonding schemes used by Bragg et al.[1] it is possible to build helical structures that contain a different number of carbon atoms in the main polymer chain. In our laboratory we are investigating several polymers of this type. In this paper we report our studies on the structure of poly (α-isobutyl L-aspartate) (PAIBLA), which contains three carbon atoms in its main polymer chain, i.e., one carbon more per monomer unit than in polypeptides. We have found two different helical structures in this polymer, one of which was preliminarily described elsewhere.[3] It was the first time that helical conformations of this type were described. Yuki et al.[4] had already studied this polymer, but they suggested that it had the extended β-conformation.

Materials and Methods

The polymer was prepared by a slight modification of the method described by Yuki et al.[4]. The reactions were carried out as shown in Scheme I, where the following abbreviations have been used: Z = benzyloxycarbonyl, DCCI = dicyclohexylcarbodiimide, Pcp = pentachlorophenyl, *i*-Bu = $CH_2CH(CH_3)_2$, and PAIBLA = poly(α-isobutyl L-aspartate).

All intermediates were recrystallized and their structures

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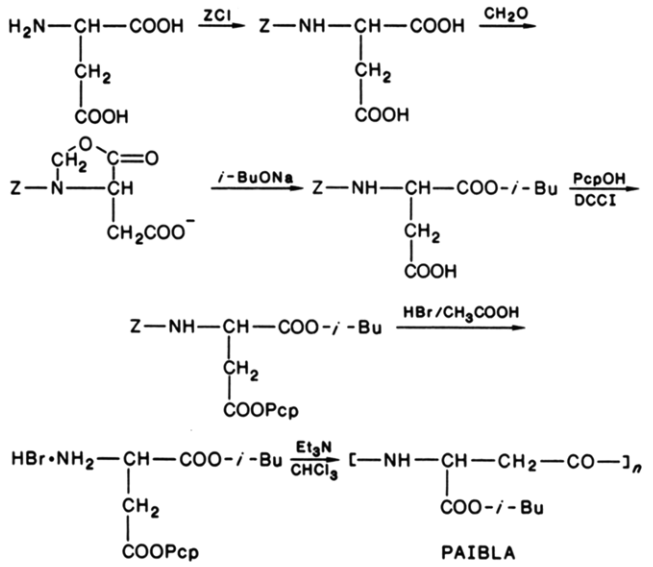
Scheme I



verified by standard procedures. In particular, before polymerization, the monomer was recrystallized in acetic acid. The elemental analysis and IR and NMR spectral results were as anticipated and did not indicate the presence of any impurity. The polymerization reaction was carried out during 8 days at room temperature, starting with a paste containing 1.7 g of monomer/mL of chloroform. Triethylamine (1.8 mol/mol of monomer) was added in order to liberate the amino groups and to neutralize the acidic substances (HBr and pentachlorophenol) generated during polymerization. The polymer was precipitated with ethanol. Any low molecular weight oligomers were removed with ethanol at 60 °C. No transesterification reaction on the polymer was observed at this point. The yield of polymer was 58%. We found that shorter times and lower amounts of triethylamine resulted in lower yields and lower molecular weights.

The chemical structure of the polymer was ascertained by ^{1}H NMR with a Bruker AM 300 WB spectrometer operating at a frequency of 300 MHz. A Perkin-Elmer Model 783 spectrophotometer was used for IR. No traces of either imido rings or peptide groups in the α-position could be detected. The degree of racemization was determined both by measuring the optical rotation of a hydrolyzed sample and by separation of diastereoisomers.[5] By both methods we found between 0 and 5% of the D-amino acid after correction of the blank value. These values are not very accurate due to the expected racemization in the hydrolysis step required in these analytical methods. We conclude therefore that the degree of racemization in the polymer is negligible.

In order to obtain an approximate value for the molecular weight, we determined the intrinsic viscosity of the polymer in dichloroacetic acid at 25 °C, which was measured to be 0.57 dL/g. This value corresponds to a molecular weight of 90 000 if the equation for poly(γ-benzyl glutamate) in the same solvent[6] is applied. The flexibility of both polymers should be similar, since the peptide groups have a rather high conformational freedom in solution.[7] Since the molecular weight of the monomeric unit is lower in our polymer (171) than in poly(γ-benzyl glutamate) (219), we would expect a molecular weight in the 60 000–80 000 range for our sample. About twice this value is obtained when the equation for poly(*N*-benzyl-β-alanine) is used, as suggested by Yuki et al.[4] In any case it is evident that we are dealing with a polymer and not with a low molecular weight oligomer.

For X-ray diffraction the samples were placed in a vacuum to remove air scatter, and the diffraction pattern was recorded on film using pinhole collimation and nickel-filtered Cu Kα radiation of wavelength 1.542 Å.

Results

The Two Conformations Found in the Solid State. Two different types of X-ray diffraction patterns have been observed depending on the conditions used to prepare the sample. When fibers were pulled from a concentrated solution in chloroform, we obtained oriented patterns such as those shown in Figure 1. An indexing of the observed diffraction signals is presented in Figure 2, and the observed and calculated interplanar spacings are given in Table I. A layer line spacing of c = 19.9 Å is measured, whereas the equatorial diffraction signals can be indexed

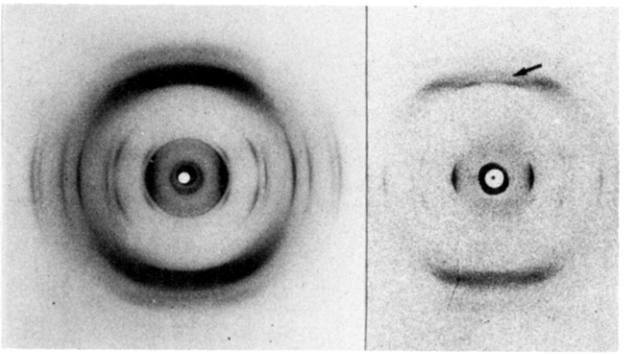


Figure 1. X-ray diffraction patterns with different exposures of an oriented fiber of poly(α-isobutyl L-aspartate) in the hexagonal conformation. The arrow points to the quasi-meridional reflection on the fourth layer line.

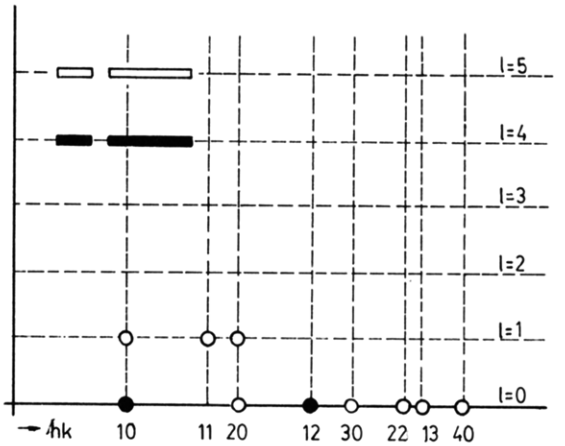


Figure 2. An interpretation of the patterns shown in Figure 1. Diffraction on the fourth and fifth layer lines is not well defined and is indicated by dashes. Empty symbols correspond to weaker reflections. The *hk* indices correspond to a simple hexagonal cell with one molecule per unit cell. In fact a larger unit cell should be used, as discussed in the text.

Table I
Observed and Calculated Spacings (Å) for the Hexagonal Fiber Pattern Obtained from Poly(α-isobutyl L-aspartate)

d_{obsd}	hkl^a	hkl^b	d_{calcd}
11.72	100	020, 110	11.70
6.75[c]	110	200, 130	6.75
5.87	200	040, 220	5.85
4.41	120	240, 310	4.42
3.88	300	060, 330	3.90
3.36	220	400, 260	3.38
3.23	130	420	3.24
2.91	400	080, 440	2.92
10.18	101	021, 111	10.08
6.47	111	201, 131	6.39
5.61	201	041, 221	5.61
4.98	004	004	4.98
		014	4.87
		104	4.67
4.46–4.50	104	024, 114	4.58
		124	4.34

[a] Calculated from a hexagonal unit cell: a = 13.5 Å, c = 19.9 Å. [b] Calculated from an orthorhombic (pseudohexagonal) unit cell containing two molecules: a = 13.5 Å, b = 23.4 Å, c = 19.9 Å. [c] Measured on the first layer line.

Table II
Calculated and Observed Spacings for the Tetragonal Pattern (a = 14.0 Å, c = 4.95 Å) Obtained from Poly(α-isobutyl L-aspartate)

d_{obsd}	hkl	d_{calcd}
14.0	100	14.00
9.85	110	9.90
6.25	210	6.26
4.95	220, (001)[a]	4.95
4.63	300	4.66
	101	4.67
4.42	310, 111	4.43
4.07	201	4.04
3.87	320, 211	3.88
3.40	410	3.40
3.11	420	3.13
2.81	500	2.80
2.74	510	2.75

[a] This reflection should not be observed in perfectly helical molecules.

in a hexagonal system with $a = b$ = 13.50 Å, although the 110 spot is absent. This feature indicates that the orientation of the side chains is such that there is a minimum of the molecular transform at this point. This fact has been taken into account in the quantitative analysis of the models presented below.

Although in the equator the pattern can be indexed with $a = b$ = 13.50 Å, the presence of strong diffraction near the meridian on the fourth and fifth layer lines indicates a larger unit cell. In a weak pattern obtained from a slightly inclined fiber, shown in Figure 1 (right), it is possible to ascertain that the strong diffraction on the fourth layer line corresponds to a quasi-meridional diffraction spot at a distance from the meridian equivalent to a spacing of 20–25 Å. We therefore conclude that the true unit cell contains at least two molecules, and therefore in Table I we have also indexed the pattern using an orthorhombic unit cell with a = 13.50 Å and b = 23.40 Å (11.7 × 2). This unit cell contains two hexagonal primitive cells, such that the two chain axes run parallel but with opposite polarity with respect to the c axis. In fact we have obtained thin lamellar crystals from this polymer, in which the molecules should be folded back and forth, so that molecules running in opposite directions must be present in the crystals.

A different type of structure is observed when the sample is prepared by precipitation of the chloroform solution with ethanol. Under these conditions a powder is formed, which we have been unable to orient. The powder diffraction pattern is presented in Figure 3. As shown in Table II the diffraction rings can be indexed on a tetragonal unit cell with $a = b$ = 14.0 Å and c (chain axis) = 4.95 Å. The equatorial indexes ($hk0$) have been confirmed by electron diffraction from single crystals (not shown). The most striking difference with the hexagonal patterns described above is that the strong ring corresponding to the equatorial spacing is now found at 14.0 Å, whereas in the hexagonal samples it occurs at 11.7 Å. These two forms have also been found in single crystals which we are presently studying and which will be described in detail elsewhere.

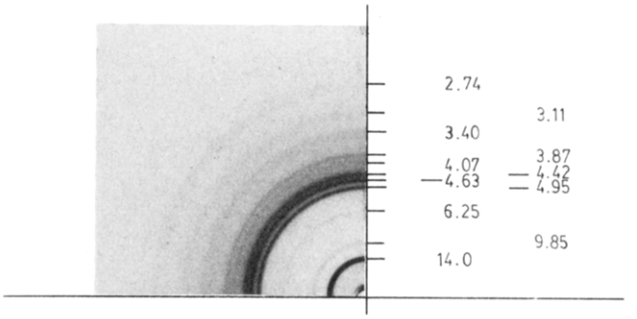


Figure 3. X-ray diffraction pattern obtained from a powder of poly(α-isobutyl L-aspartate) in the tetragonal conformation. The equivalent Bragg spacings of the diffraction rings are given in angstroms.

In order to determine in more detail the differences between the two structures, we obtained the infrared spectra of both samples. Table III shows that only slight differences are found. It appears that in both conformations the absorbing groups have rather similar environments. In Table III we also show that the position of the absorption maxima is similar to that found in other polypeptides. In fact only small differences can be detected among these and other related polymers. It is difficult to draw any clear conclusion from the slight changes found in some cases. We should also mention that we were unable to prepare an oriented sample suitable to obtain a polarized infrared spectrum.

Structural Analysis of the Hexagonal Conformation. The strong diffraction at about 5.0 Å observed in the meridional direction (Figure 1) is similar to that found in α-helical polypeptides. The cross-β structure, in which the polypeptide chains are oriented perpendicular to the direction of stretching,[13] yields a 4.7-Å meridonal reflection. This spacing is outside the experimental error in the observed 5.0-Å reflection, and therefore this possibility can be dismissed. The observed unit cells favor a helical conformation of the polymer chains. In fact the X-ray pattern presented in Figure 1 can only be reasonably interpreted on the basis of a helical conformation.

The pattern shown in Figure 1, which has been indexed as indicated in Table I, has strong quasi-meridional spots in the fourth and fifth layer lines, with a weaker but clear first layer line. These features can be most easily explained by a helical structure with an integral number of residues in four turns. On stereochemical grounds either 11 or 13 residues in four turns appear possible. On the other hand, an analysis of the diffraction expected from such a helix,

Table III
IR Absorption Maxima (cm^{-1}) Observed in Poly(α-isobutyl L-aspartate) and in Some Related Polypeptides

	PAIBLA		PBBLA[a]			PGBLG[b]	PGMLG[c]		nylons[d,e]	
			α							
	hexa	tetra	levo	dext	ω	α	α	β	α	γ
amide A	3260	3277	3302	3296	3296	3291	3292	3287	3290	3295
amide B	3062	3059				3064			3050	3080
CO lateral group	1729	1738	1735	1741	1731	1733				
amide I	1642	1649	1666	1675	1675	1652	1654	1628	1642	1643
amide II	1537	1537	1557	1536	1536	1550	1551	1525	1540	1560
amide V	665	666	662	658	666	614			690	715

[a] Poly(β-benzyl L-aspartate); Bradbury et al.[8] [b] Poly(γ-benzyl L-glutamate); Block.[9] [c] Poly(γ-methyl L-glutamate); Bamford et al.[10] [d] Nylon-6; Bradbury and Elliott.[11] [e] Amide V from Matsubara et al.[12]

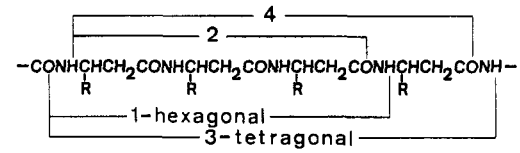


Figure 4. Hydrogen-bonding schemes compatible with the helical conformations of poly(α-isobutyl L-aspartate).

on the basis of the rules established by Cochran et al.,[14] indicates that an 11/4 helix should have a strong third layer line and a weak fifth layer line, whereas the reverse occurs for a 13/4 helix. Therefore our experimental results favor a helix with 13 residues in 4 turns, which is equivalent to 3.25 residues or 13 main chain atoms per helical turn. The calculated density for such a structure is 1.18 g/cm^3, which is in very good agreement with the experimentally determined value of 1.17 g/cm^3.

A puzzling feature of the diagrams we have obtained is that we have been unable to observe a meridional reflection in inclined fibers at a spacing of 1.53 Å (19.9/13), which should be present in a helical structure such as the one we are studying. The absence of such a reflection may indicate either a definite position of the side chains or a mutual displacement in the *c* direction of the two helices in the unit cell of about 0.76 Å. In either case the meridional reflection could be canceled as observed.

Structural Analysis of the Tetragonal Conformation. We first considered whether the tetragonal form could be a different packing arrangement of the same type of helices found in the hexagonal form. This is most unlikely since the interchain spacing is significantly larger in this case and would indicate a considerably decreased density. The larger interchain spacing is also not due to incorporation of solvent into the sample, since this form is stable up to 200 °C. We therefore conclude that the tetragonal form corresponds to a different type of helix. In fact an integral helix with four residues per turn can easily explain the observed X-ray pattern and corresponds to a density of 1.17 g/cm^3 (assuming c = 4.95 Å), which is identical with the density determined experimentally for both the hexagonal and tetragonal forms.

In this latter case, as in the hexagonal form, the unit cell should be larger, containing at least two molecular chain segments, of opposite polarity, but since we have been unable to obtain an oriented pattern, this feature cannot be directly demonstrated.

Model Studies. There are several helical structures that can be built and appear to be compatible with the structural requirements that we have described. In this section we discuss the general features of each model. In the next section we will present a quantitative comparison of all models considered. Hydrogen-bonding schemes for all of them are represented in Figure 4. Model 1 is topologically equivalent to the helix found in polypeptides. With this hydrogen–bonding arrangement a 13/4 helix can be straightforwardly built, as already proposed by us[3] in a preliminary publication. The left-handed helix is favored since the right-handed helical version presents serious steric problems. The latter is unlikely but cannot be completely ruled out since the ester group in the side chain might interact with the peptide group in the main chain. A similar situation has been observed in poly(β-benzyl L-aspartate), which exists as an unusual left-handed α-helix.[15]

Model 2 has its peptide groups oriented in the opposite direction. It is topologically equivalent to the 3_{11} helix in polypeptides (following the nomenclature of Bragg et al.[1]) but is not feasible for stereochemical reasons. However,

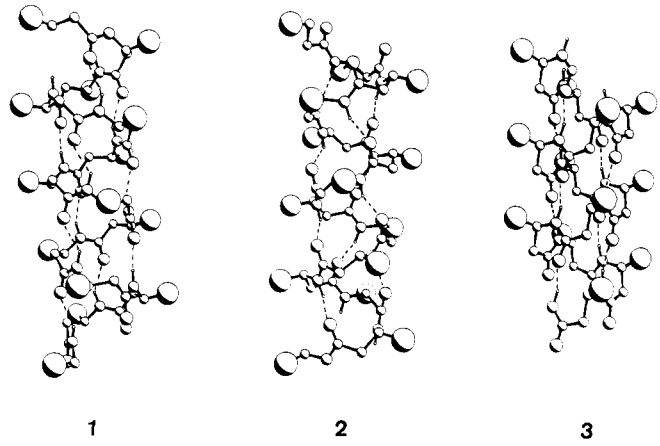


Figure 5. Projections of models obtained as described in the text following the hydrogen-bonding schemes 1–3 represented in Figure 4. Models 1 (left handed) and 3 (right handed) are respectively considered to be most likely for the hexagonal and tetragonal forms described in this paper. The N-terminal group is located at the upper end. The larger spheres indicate the $COOCH_2CH(CH_3)_2$ side chains. The smallest spheres correspond to the hydrogen atoms involved in hydrogen bonds, which are indicated as dotted lines. The rest of the hydrogen atoms are not shown.

in our case it results in a satisfactory model, since it is posible to build a right-handed 13/4 helix with negligible stereochemical problems. It appears that this model is also possible for the hexagonal form of our polymer. The left-handed form does not appear feasible on stereochemical grounds. This model had already been suggested by Kovacs et al.[16] for poly(β-L-aspartic acid) on the basis of model-building studies.

Model 3 gives a satisfactory model for the tetragonal form of PAIBLA and is shown in Figure 5. The right-handed form appears to be stereochemically favored. Finally, model 4 also results in a helix with four residues per turn, but it contains a large central hole of 3-Å diameter and we therefore consider it unlikely.

It is also possible to build a helix with four residues per turn using peptide units that are alternately oriented in opposite directions. In this case consecutive amino acid residues have different conformations, and it does not appear possible that such a structure could pack in a tetragonal unit cell. It is also unlikely that the same monomer unit could have two different conformations coexisting in a single polymer chain.

We conclude from these model studies that there are three conformations possible for the 13/4 helix, but only one for the 4/1 helix. In the following section we determine the coordinates of each model and, taking into account the circular dichroism studies of Yuki et al.,[4] we favor the left-handed conformation of model 1 for the 13/4 helix.

Quantitative Analysis of the Models. We have built precisely defined models of each of the structures considered in the previous section with the linked-atom least-squares methodology.[17] First we constructed and refined a model with one molecule per unit cell so that there were no steric contacts. In a second step we used a larger unit cell with two molecules of opposite polarity. At this stage we introduced the intensity of the diffraction spots observed on the equator and on the first layer line in order to minimize the reliability index R. We considered that all side groups had the same conformation. This is physically unreasonable, since depending on the packing environment the side chains could have different conformations. Due to the small number of diffraction spots available we did not study in detail the most likely con-

Table IV
Helix Parameters and Cylindrical Atomic Coordinates of Different Models[a]

Helix Parameters

	model			
	1-L	1-R	2	3
no. of residues per turn	3.25	3.25	3.25	4
handedness	left	right	right	right
orientation of peptide units	A	A	B	A
unit height, Å	1.53	1.53	1.53	1.245
unit twist, deg	110.8	110.8	110.8	90
pitch, Å	4.97	4.97	4.97	4.95
hydrogen bond distance (N–O), Å	3.03	2.67	2.85	2.88
hydrogen bond angle (CON), deg	151.0	143.2	150.7	168.0
torsion angle ϕ, deg	126.6	−23.2	147.7	−10.4
torsion angle ξ, deg	−102.8	−68.0	−62.1	−86.8
torsion angle ψ, deg	113.6	14.9	128.9	−2.3
R factor, %	13	not calcd	16	19

Cylindrical Coordinates

	model 1-L			model 1-R			model 2			model 3		
	r, Å	ϕ, deg	Z, Å	r, Å	ϕ, deg	Z, Å	r, Å	ϕ, deg	Z, Å	r, Å	ϕ, deg	Z, Å
O	2.54	144.2	0.81	1.87	−61.5	−3.15	2.36	85.6	2.11	2.27	46.3	−0.64
C	2.28	150.4	1.99	1.48	−50.2	−2.02	2.16	96.1	0.96	2.18	54.9	0.55
N	2.14	−176.6	2.39	1.20	−91.7	−1.14	1.99	73.5	−0.06	2.04	30.9	1.53
H	2.11	−168.9	3.35	0.78	−88.5	−0.23	1.76	82.7	−0.99	1.90	38.0	2.49
Cα	2.70	−153.8	1.42	2.28	−124.5	−1.47	2.75	42.7	0.10	2.74	0.0	1.25
Cβ	2.72	−120.9	1.59	2.43	−127.6	−2.99	2.76	17.9	−0.88	2.85	−4.7	−0.27
C1(R)	4.20	−155.6	1.66	3.54	−110.7	−0.92	4.17	51.3	−0.18	4.13	6.0	1.79
O1(R)	5.07	−145.4	1.46	4.13	−95.2	−1.15	5.19	43.9	0.07	4.57	1.4	2.86
O2(R)	4.68	−170.4	2.11	4.22	−123.1	−0.16	4.36	67.2	−0.75	4.87	14.3	0.91
C2(R)	5.11	−179.9	1.02	5.17	−131.6	−0.99	5.75	69.6	−0.51	5.62	25.8	1.52
C3(R)	6.25	170.85	1.53	5.54	−146.9	−0.56	6.25	83.5	−0.45	5.35	41.2	1.11
C4(R)	7.12	177.7	2.51	5.06	−159.5	−1.45	6.51	88.1	−1.89	5.12	50.9	2.34
C5(R)	5.87	158.4	2.25	7.08	−146.9	−0.72	5.43	93.9	0.30	6.72	44.8	0.51

[a] The models have hydrogen-bonding schemes as shown in Figure 4. The orientation of peptide units corresponds to the nomenclature of Bragg et al.[1] The coordinates of only one molecule per unit cell are given.

formations for the side groups. The results obtained with this approach are given in Table IV and in Figure 5.

Model 3 is suitable for the 4/1 helix and has reasonable values for the hydrogen bond distance and angle, as shown in Table IV. In proteins these values fall in the ranges 2.8–3.3 Å and 140–170° according to Blundell et al.[18] Model 3 does not show any contacts among the atoms in different side groups of neighboring helices.

In the case of the 13/4 helix, the right-handed helix (1-R), constructed according to hydrogen-bonding scheme 1 (Figure 4), does not appear to be possible. The hydrogen bond distance is too short (2.67 Å) and the main chain presents short contacts between consecutive nitrogen atoms (2.5 Å) and between the carbonyl oxygen and the CH_2 group of the next residue (2.4 Å). These contacts could not be removed without introducing contacts among other atoms. On the other hand, the other two models (1-L and 2) both have adequate stereochemical features as shown in Table IV. In both cases we found some steric contacts among the side groups of neighboring molecules, which could be removed by allowing changes in the conformation of each individual side group. They are represented in Figure 5.

We therefore conclude that both models 1-L and 2 are stereochemically reasonable. However, the circular dichroism spectrum obtained by Yuki et al.[4] favors a left-handed conformation, and therefore we favor model 1-L. These authors also found that the circular dichroism spectra of this polymer in trifluoroethanol had a negative peak at 189 nm and a positive peak at 205 nm, whereas in the helix peaks at approximately the same positions but with opposite signs are found.[19] In the α-helix another maximum at 222 nm is found, but in PAIBLA this maximum appears to be much weaker and shows up only as a shoulder. Furthermore, Yuki et al.[4] found that the b_0 constant of the Moffitt–Yang equation was of the opposite sign to that found in the α-helix, both in chloroform and in trifluoroethanol. All these observations indicate that the 13/4 helix we are studying is left handed.

Helix–Coil Transition. In order to have additional evidence for the helical conformation of PAIBLA, we have followed its transition to the random form in solution by NMR. This method has been used very effectively with polypeptides.[20] A solution in $CDCl_3$ was prepared and either dichloroacetic acid or trifluoroacetic acid was added to it in variable amounts. Some of the spectra are presented in Figure 6 and the position of the peaks are given in Table V. The results obtained are consistent with those previously reported by Yuki et al.[4] although they used a lower magnetic field (100 MHz).

In pure chloroform (not shown) the peaks are broad, due to both the existence of helices and to their aggregation. The spectrum is essentially identical with that found upon addition of 2% dichloroacetic acid. The maxima corresponding to the CH_2 groups in the main and lateral chains appear split. The double signal of the main-chain CH_2 is expected, given the asymmetry of the monomer unit. On the other hand, the presence of this feature in the CH_2 of the isobutyl group suggests that its conformational freedom is restricted when the polymer has a helical conformation. Upon addition of acid, the signal of the lateral CH_2 groups becomes a single peak as the helical conformation is destroyed, whereas the main-chain CH_2 peaks do not change. It should be noted that the signals corresponding to the $CH(CH_3)_2$ group in the lateral chain do not change appreciably during this transition.

Table V
Position of NMR Peaks (ppm) in a Solution of Poly(α-isobutyl L-aspartate) in Chloroform Containing the Indicated Amounts of Acid

	NH		main-chain CH		lateral group					
	helix	coil	helix	coil	CH_2		CH_2^L		CH^L	CH_3^L
0% DCA	8.63		5.11		3.18	2.87	3.97	3.79	1.92	0.91
2% DCA	8.62	7.71	5.10	4.87	3.10	2.92	3.97	3.86	1.94	0.93
10% DCA	8.59	7.96	5.08	4.91	3.10	2.95	3.95	sh	1.95	0.92
15% DCA	8.55	7.96	5.08	4.91	3.05		3.95		1.95	0.91
20% DCA		7.98		4.90	3.03		3.94		1.93	0.90
0% TFA	8.64		5.11		3.18	2.86	3.97	3.80	1.92	0.92
1% TFA	8.59		5.09	4.90	3.07	2.93	4.00	3.89	1.95	0.93
2% TFA	8.56	7.90	5.07	4.89	3.06	2.92	4.00	3.93	1.94	0.91
10% TFA		7.94		4.88	3.05		3.95		1.92	0.88

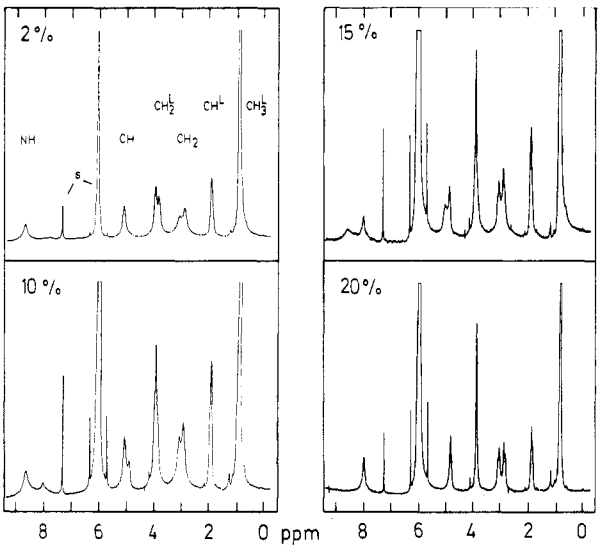


Figure 6. Proton NMR spectra of poly(α-isobutyl L-aspartate) in chloroform containing the indicated amounts of dichloroacetic acid. The different protons are identified in the first frame, where the superscript L indicates the contribution of the side chain; S indicates solvent. The helix–coil transition can be most easily followed through the main-chain CH peak.

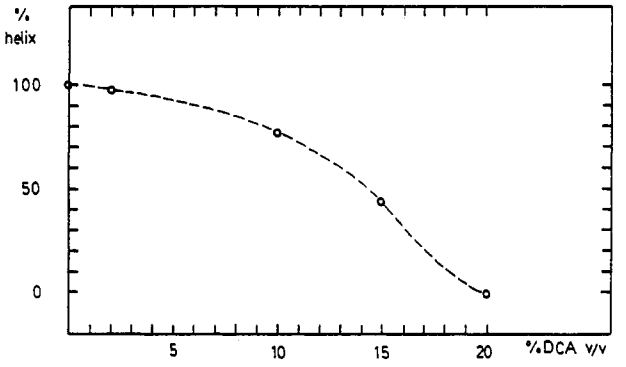


Figure 7. Helix–coil transition of poly(α-isobutyl L-aspartate) in chloroform upon addition of dichloroacetic acid. The relative amount of helix has been determined from the relative strength of the main-chain CH peaks shown in Figure 6.

The position of the NH and main-chain CH groups differs in the helical and random conformations, as indicated in Table V. From the intensity of each of the two CH peaks we have determined the relative amount of helical conformation as shown in Figure 7. The transition gradually occurs between 5 and 18% dichloroacetic acid. In trifluoroacetic acid the transition is much sharper, as can be ascertained from the values given in Table V.

We should note that there has been some controversy on the interpretation of the two CH peaks we have used to derive Figure 7, as reviewed by Paolillo et al.[20] According to the interpretation favored by the latter authors, our results indicate that there is a broad distribution of molecular weights in our sample. In any case our NMR spectra show that a helix–coil transition similar to that found in polypeptides takes place in PAIBLA. In agreement with this conclusion, the intrinsic viscosity increases from 0.57 to 1.00 dL/g when dichloroacetic acid (random coil conformation) is replaced by chloroform as a solvent (helical conformation).

Discussion

Our results show that poly(α-isobutyl L-aspartate) can exist in two types of helical structure in the solid state, one of which is also stable in solution in helicogenic solvents. We have also shown that a helix–coil transition is observed in solution, similar to that found in helical polypeptides such as poly(γ-benzyl L-glutamate).[20]

When compared with the polypeptide backbone found in proteins, each monomer unit of PAIBLA contains an additional carbon atom in the main chain. This additional atom should offer greater conformational versatility to the polymer, and it is not surprising that we find two different helical conformations, whereas in most conventional polypeptides only the α-helical structure is found.

The two structures we have found have features in common with the α-helix. It is interesting to note that in this case the density of hydrogen bonds is lower than in the α-helix and therefore a higher contribution to the packing energy must be due to the van der Waals interactions among the backbone atoms in the tightly packed interior region of the helix and, eventually, to contributions from the side chains. In this respect we should note that in some related polymers that contain aliphatic side chains instead of an ester group, no helical structures were found,[21,22] so that the nature of the side group may have a strong influence on the polymer conformation. We are presently addressing this question by examining the effect of different side chains.

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Crystalline Features of 4,4′-Isopropylidenediphenylbis(phenyl carbonate) and Conformational Analysis of the Polycarbonate of 2,2-Bis(4-hydroxyphenyl)propane

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ABSTRACT: The crystal structure of a complete structural analogue of poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene) (bisphenol A polycarbonate) is reported. The crystal structure results have been used to extract valence geometry information for modeling the polymer, and a full helical parameter analysis of the polymer is reported for the first time. The helical parameter analysis has been supplemented by conformational energy calculations using molecular mechanics methods. It is found that there are only two idealized conformations that are consistent with existing fiber data on the crystalline polymer. Moreover, the calculations suggest that there are only a few conformations suitable to serve as templates for the aggregation of photoconductive pyrylium dyes.

Introduction

Poly(oxycarbonyl-1,4-phenyleneisopropylidene-1,4-phenylene) (bisphenol A polycarbonate (BPAPC)) is reported to form a cocrystalline complex with thiapyrylium salts in solvent-cast thin films.[1] These films exhibit unusually high photoconductivity, which is believed to result from an ordered arrangement of the dye molecules in the complex.[2] The optical spectrum in the region of the dye absorption displays features that are reminiscent of well-known dye aggregates in solution, which has led to the term "aggregate" in reference to the thin-film system. Similar aggregation phenomena may also occur in a number of polymer–small molecule mixtures,[3-5] but structural characterization is generally quite difficult. An unusual amount of detailed, although indirect, structural information is available for the thiapyrylium/polycarbonate aggregate, due to the preparation of single-crystal samples of a model complex in which the polycarbonate is replaced by the dicarbonate 4,4′-isopropylidenediphenylbis(phenyl carbonate) (DPBC). The resulting "model aggregate" structure has been determined by single-crystal X-ray diffraction techniques.[1] Comparison of the X-ray powder diffraction patterns of the two substances provides ample evidence that the structure of the model complex closely resembles that of the actual polymer-based system. This is also consistent with optical studies of the two complexes. Thus, these materials provide an unusual opportunity to examine various aspects of small molecule–polymer interactions at the atomic scale.

Table I
Crystal Data for 4,4′-Isopropylidenediphenylbis(phenyl carbonate)

$C_{29}O_6H_{24}$; MW = 468.5; $F(000)$ = 492 e^{-1}
a = 18.863 (3), b = 6.385 (2), c = 10.556 (2) Å
β = 110.63 (10)°, V = 1189.8 Å; $P2_1$
monoclinic
d_{obsd} = 1.31 Mg m^{-3}, d_{calcd} = 1.308 Mg m^{-3}
M(Mo Kα) = 0.85 mm^{-1}
λ(Mo Kα) = 0.7103 Å
T = 20 °C

A remarkable feature of the model aggregate structure is the extended head-to-tail arrangement of the DPBC molecules, which is analogous to the periodic propagation of a linear polymer in the crystalline phase. This observation prompted us to evaluate, through the use of helical parameter analysis, the conformational properties of polycarbonate chains from the perspective of regular periodic structures. Conformational energy calculations have also been performed to aid in assessing the relative stability of different helical structures. As a preliminary step in

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