Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Poly(L-lysine) containing azobenzene units in the side chains: influence of the degree of substitution on liquid crystalline structure and thermotropic behaviour

Bernard Gallot; Marc Fafiotte

Online publication date: 06 August 2010

To cite this Article Gallot, Bernard and Fafiotte, Marc(1997) 'Poly(L-lysine) containing azobenzene units in the side chains: influence of the degree of substitution on liquid crystalline structure and thermotropic behaviour', Liquid Crystals, 23: 1, 137 — 146
To link to this Article: DOI: 10.1080/026782997208749
URL: http://dx.doi.org/10.1080/026782997208749

LIQUID CRYSTALS, 1997, VOL. 23, NO. 1, 137–146

Poly(L-lysine) containing azobenzene units in the side chains: influence of the degree of substitution on liquid crystalline structure and thermotropic behaviour

by BERNARD GALLOT,* MARC FAFIOTTE
Organiques à Propriétés Spécifiques, CNRS, BP 24, 69390 Vernaison, France

ADRIANO FISSI
Istituto di Biofisica, CNR, Via S.Lorenzo 26, 56127 Pisa, Italy

and OSVALDO PIERONI
Istituto di Biofisica, CNR, Via S.Lorenzo 26,
and Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
56100 Pisa, Italy

(*Received 12 November 1996; accepted 19 February 1997*)

The structure of poly(L-lysine)s containing between 20% and 100% of azobenzene units in the side chains has been studied by X-ray diffraction, between room temperature and 250°C. Except for samples having very low contents of azobenzene, the polymers are found to exhibit mesomorphic structures of the smectic A_1 type deriving from the β-structure of polypeptides. For polymers in which all lysine residues were substituted, the polypeptide main chains are arranged in layers corresponding to the sheets of a polypeptide 'antiparallel' β-structure, and the side chains are perpendicular to the smectic layers. For polymers containing both substituted and free lysine side chains, each smectic layer results from the superposition of two layers: one layer contains the free lysine side chains; the other contains the azobenzene-modified lysine side chains and the polypeptide main chains that are arranged in 'antiparallel' β-structures. All polymers exhibit only one smectic A mesophase as a function of temperature. The thickness of the smectic layers increases with increasing temperature until a thickness is reached that corresponds to the maximum interaction between the azobenzene mesogens in their *trans*-configuration.

1. Introduction

The existence of liquid crystalline properties for solutions of polypeptides was discovered in 1956 in the case of poly(γ-benzyl-L-glutamate) [1]. Then a range of studies showed that in the mesophases the polypeptide main chains exhibit a helical conformation [2–5]. Later two directions were followed to modify the polypeptide behaviour, namely the synthesis of copolymers and the modification of the polypeptide side chains. Various copolymers have been prepared, including statistical copolymers, AB and ABA block copolymers of different α-amino acids, AB and ABA block copolymers containing polypeptide and polyvinyl blocks or polypeptide and carbohydrate blocks [6]. Investigation of their liquid crystalline properties showed the existence of phase-separated lamellar structures in which the polypeptide main chains exhibited the α-helical conformation [6]. More recently, the modification of the benzyl residues in poly(γ-benzyl-L-glutamate) was undertaken [7–11]. A series of poly(γ-alkyl-L-glutamates) with 5, 6, 8, 10, 12, 14, 16 and 18 methylene groups [7–9], a poly(4-butoxy-4′-hexyloxybiphenyl-L-glutamate) [10], and poly(*n*-(4-((4-hexylphenyl)azo)phenoxy)alkyl-L-glutamates) with $n=2$, 4 and 6 [11] were synthesized. The study of their behaviour, as a function of temperature, confirmed the high tendency of poly(L-glutamate) polypeptide chains to adopt the α-helical conformation [7–11].

Among polypeptide polymers, poly(L-lysine)s are especially attractive as they can adopt both the typical protein structures, α-helix and β-structure. So, in principle, different kinds of mesophases can be formed in poly(L-lysine)s bearing mesogenic groups. In fact, we have recently described the liquid crystalline behaviour

*Author for correspondence.

0267–8292/97 $12·00

of a poly(L-lysine) containing 44 mol % of azobenzene, and reported the first observation of a lamellar structure of the smectic A_1 type with the polypeptide chains in a β-conformation [12]. In the present paper, the investigation is extended to a series of poly(L-lysine)s containing between 20% and 100% of azobenzene units in the side chains: their liquid crystalline structures are described and the influence of azobenzene content, as well as temperature, on the thermotropic behaviour of the polymers is shown.

2. Experimental

2.1. *Synthesis of the polymers*

2.1.1. *Poly(L-lysine)*

This was obtained by polymerization of *N*ε-benzyloxycarbonyl-L-lysine *N*-carboxy-anhydride, followed by removal of the side chain protecting groups with anhydrous HCl and HBr, according to the literature [13]. The polypeptide was thoroughly dialysed against 0·01M HCl or 0·01M acetic acid, and then against distilled water, to replace the bromide with chloride or acetate ions. The dialysed polymer solution was finally lyophilized to give poly(L-lysine hydrochloride) or poly(L-lysine acetate) as a white material. The corresponding poly(L-lysine hydrobromide) showed a viscosity value $\eta_{sp}/c =$ 0·60 ($c = 1\,g\,dl^{-1}$, 1M NaCl, pH 3, 25°C), relating to an average molecular weight $M_w = 150\,000$, evaluated on the basis of the equation of Yaron and Berger [14].

2.1.2. *Azo-modification of poly(L-lysine)*

Some typical experiments, carried out in the presence of different azo-containing reagents, are described (see the table).

Run 1 (in presence of 4-phenylazobenzenesulphonyl chloride). Poly(Lys HCl) (0·35 g, 2·13 mmol Lys residues) was dissolved in a small amount of water (15 ml) and diluted with dimethylformamide (DMF) (80 ml). The apparent pH was adjusted to about pH 8 by addition of triethylamine; then a second solution containing 4-phenylazobenzenesulphonyl chloride (1·20 g, 4·5 mmol) in DMF (50 ml) was slowly added. The reaction mixture was kept with stirring at room temperature in the dark for 1 week, during which time triethylamine was occasionally added in order to keep the apparent pH at a slightly alkaline value. At the end of the reaction, the polymer was recovered by precipitation with ether. Any unreacted azo-reagent and water soluble materials were removed by repeated dissolution in DMF and precipitation with ethanol and water, alternately. Finally the polymer was dried to give 0·45 g of poly(*N*ε-4-phenylazobenzenesulphonyl-L-lysine) as a yellow material. Sulphur elemental analysis: calculated for 100% Lys modification, 8·6%; found, 8·7%. ^{1}H NMR (300 MHz, CF_3COOD), δ ppm: 1·7 (m, 2H, Cα–CH_2), 2·2 (m, 4H, CH_2–CH_2), 3·2 (m, 2H, N–CH_2), 4·4 (m, 1H, CαH), 7·4–8·8 (m, 9H, aromatic). UV absorption spectrum ($c = 0{\cdot}01522\,g\,l^{-1}$, in HFP): $\lambda_{max} = 320$ nm; $\varepsilon_{max} = 24\,000\,mol^{-1}\,cm^{-1}$. All methods indicated a modification extent of about 100%.

Run 2 (mixed anhydride method). Pivaloyl chloride (0·93 ml, 7·5 mmol) was added to a cooled solution of 4-phenylazobenzoic acid (1·65 g, 7·0 mmol) and triethylamine (1·04 ml, 7·0 mmol) in anhydrous DMF (130 ml). After 15 min the solution was treated with a second precooled solution of poly(Lys HCl) (0·60 g, 3·7 mmol Lys residues) and triethylamine (1·00 ml, 7·0 mmol) in 10 ml of water and 100 ml of DMF. The reaction mixture was left with stirring at 0°C for 1 h, and at room temperature overnight. The solvent was then partially evaporated and the polymer recovered by precipitation with ether. Any unreacted azo-reagent was removed by repeated dissolution and precipitation. Finally the yellow material was dried to give 0·7 g of modified polymer. ^{1}H NMR (300 MHz, CF_3COOD), δ ppm: 1·0 (s, CO–C(CH3)3), 1·7 (m, 2H, Cα–CH_2), 2·2 (m, 4H, CH_2–CH_2), 3·2 (m, 2H, N–CH_2), 4·5 (m, 1H, CαH), 7·5–8·5 (m, aromatic). On the basis of the peak areas of CαH, C(CH3)3 and aromatic protons, the chemical composition of the polymer corresponded to a modified poly(L-lysine) containing 70 mol % of azobenzene groups and 30 mol % of pivaloyl groups in the side chains.

Run 3 (in the presence of 4-phenylazobenzoyl chloride). Poly(L-lysine acetate) (0·09 g, 0·05 mmol Lys residues) was dissolved in a small amount of water (8 ml) and the solution diluted with DMF (40 ml). An excess of MgO (0·5 g) was added to the polymer solution and the mixture was treated with 4-phenylazobenzoyl chloride with stirring, at room temperature for 24 h. The modified polymer became insoluble in the reaction solvent, so the precipitate was filtered off, washed with 1M HCl to remove the magnesium salt, then with saturated aqueous $NaHCO_3$ and finally with DMF to remove any unreacted azo-reagent. The dried polymer (0·45 g) was soluble in trifluoroacetic acid and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). ^{1}H NMR (300 MHz, CF_3COOD), δ ppm: 1·7 (m, 2H, Cα–CH_2), 2·2 (m, 4H, CH_2–CH_2), 3·2 (m, 2H, N–CH_2), 4·4 (m, 1H, CαH), 7·5–8·6 (m, aromatic). NMR analysis and comparison of the UV absorption spectrum with that of the model compound 4-phenylazobenzoylglycine methyl ester ($\lambda_{max} = 324$ nm, $\varepsilon_{max} = 24\,000\,mol^{-1}\,cm^{-1}$, in HFP) indicated that the polymer contained 44 mol % of azobenzene units.

Run 5 (active ester method). 4-phenylazobenzoic acid *N*-hydroxysuccinimide ester (0·74 g, 2·3 mmol) in 50 ml of DMF was added to a solution of poly(Lys acetate) (0·30 g, 2·3 mmol Lys residues) in 20 ml of water and 30 ml of DMF, and the mixture was left stirring at room temperature for 1 h. The polymer was then recovered by

repeated dissolution in DMF and precipitation in ether and water alternately to remove any unreacted azo-reagent and water soluble materials. The water-insoluble modified polymer contained 31 mol% of azobenzene groups, as determined by 1H NMR and by comparing the absorption spectrum with that of 4-phenyl-azobenzoylglycine methyl ester in DMF.

2.2. *X-ray diffraction*

X-ray diffraction experiments were performed on powder samples with two types of camera: a Guinier-type camera and a pin-hole camera. The Guinier-type focusing camera was equipped with a bent quartz monochromator (reflection 1 0 1) giving a linear collimation of strictly monochromatic X-rays ($\lambda = 1{\cdot}54$ Å). The pin-hole camera was a laboratory-made camera using Ni filtered Cu radiation ($\lambda = 1{\cdot}54$ Å). Both cameras operated under vacuum and were equipped with an electric heating device operating between 20 and 300°C and controlling the temperature within less than 1°C.

Several exposures were made in order to measure the strongest and the weakest reflections. Intensities of the different diffraction orders were measured with a laboratory-made densitometer specially designed and built for that purpose. Experimental amplitudes of diffraction of the different orders of reflections from the smectic layers were corrected for the Lorentz and polarization factors [15] and normalized so that the strongest reflection had an amplitude of one. For instance in the case of **Azo-Lys-41**, the following corrected amplitudes were: $a_1 = 1$, $a_2 = 0$ and $a_3 = 0{\cdot}55$.

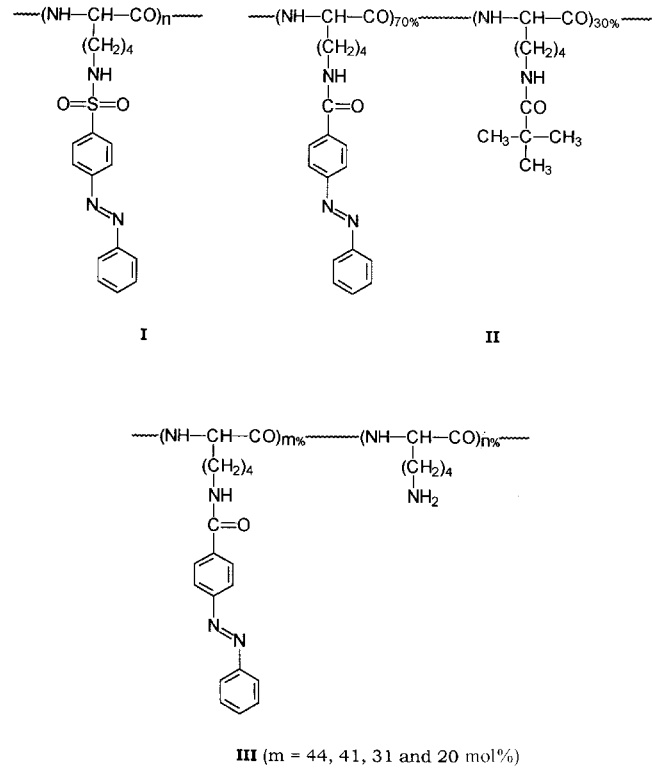
2.3. *Infra-red spectroscopy*

Infrared measurements were performed with an FTIR spectrometer Nicolet 20SX using KBr samples.

3. Results

3.1. *Synthesis of the polymers*

High molecular weight poly(L-lysine) was reacted with various azo-reagents in order to link azobenzene units to the side chains of the poly(L-lysine). Various polymers, having the structures illustrated in the scheme, were obtained using different reaction conditions (see § 2·1).



Scheme 1. Chemical structures of the investigated series of L-lysine polymers containing azobenzene units in the side chains. **I**: Poly(4-phenylazobenzensulphonyl-L-lysine) (**AzoS-Lys-100**); **II**: Poly(L-lysine) containing both 4-phenylazobenzoyl (70 mol%) and pivaloyl (30 mol%) substituents in the side chains (**Azo-Piv-Lys-70**); **III**: Partially modified poly(L-lysine)s having various azobenzene contents: $m = 44$ mol% (**Azo-Lys-44**); $m = 41$ mol% (**Azo-Lys-41**); $m = 31$ mol% (**Azo-Lys-31**); $m = 20$ mol% (**Azo-Lys-20**).

The reaction of poly(L-lysine) with 4-phenylazobenzenesulphonyl chloride gave poly(4-phenylazobenzensulphonyl-L-lysine) (**AzoS-Lys-100**). The modification extent was determined by ^{1}H NMR, by sulphur elemental analysis, and by comparing the absorbance of the polymer with the molar extinction coefficient of low molecular weight compounds containing the same chromophore: all methods indicated that the side chains

Table. L-Lysine polymers having various azobenzene contents in the side chains: geometrical parameters of the liquid crystalline structures at room temperature.

Run	Polymer	Azo units/mol %	L_1/Å	d/Å	b/Å	a/Å
1	**AzoS-Lys-100**	100	24	25·0	7·3	5·1
2	**Azo-Piv-Lys-70**	70	23	23·6	7·6	5·1
3	**Azo-Lys-44**	44	23	32·0	7·6	5·0
4	**Azo-Lys-41**	41	23	31·8	7·5	5·0
5	**Azo-Lys-31**	31	23	33·3	7·4	4·8
6	**Azo-Lys-20**	20				

of poly(L-lysine) were quantitatively modified and the azo-lysine residues were found to be substantially 100% [16].

In another procedure, poly(L-lysine) was treated with 4-phenylazobenzoic acid in the presence of pivaloyl chloride according to the mixed anhydride method. This procedure led to a modified polymer whose chemical composition corresponded to a poly(L-lysine) containing both azobenzoyl (70 mol %) and pivaloyl (30 mol %) groups in the side chains (**Azo-Piv-Lys-70**).

In other experiments, poly(L-lysine) was reacted with 4-phenylazobenzoyl chloride or with 4-phenylazobenzoic *N*-hydroxysuccinimide ester (active ester method). These modification reactions gave partially modified L-lysine polymers containing 44 mol % (**Azo-Lys-44**), 41 mol % (**Azo-Lys-41**), 31 mol % (**Azo-Lys-31**) and 20 mol % (**Azo-Lys-20**) azobenzene units [17]. For the latter polymers the modification extent was determined spectroscopically, by comparing the maximum absorbances of the polymers with the molar extinction coefficient of a low molecular weight compound containing the same chromophore. The determination of polymer composition by comparing the integrated areas of the proton resonances of the NMR spectra led to different values depending on which set of signals was considered. The average discordance was about 5% with respect to the values estimated from the absorption spectra. The sequence distribution of azo units is not known, but it may be assumed to be substantially random.

3.2. *Liquid crystalline structures*

3.2.1. *General*

The azobenzene-containing polypeptides were studied by X-ray diffraction between room temperature and 240°C, since the commencement of decomposition was observed at MDNM250°C.

The X-ray diagrams exhibited 2–4 sharp reflections and a diffuse band (figures 1–3), except for the polymer containing 20 mol % of azobenzene that does not exhibit mesophases.

The sharp reflections can be divided into two groups depending on whether their position varies or does not vary with temperature. The reflections observed at the lowest angles, and with Bragg spacings varying with temperature, can be indexed as the 0 0 1 reflections of a lamellar structure of thickness d, with d increasing with temperature. The sharp reflection observed at higher angles and corresponding to a repeat distance b between 7·3 and 7·6 Å, depending on the composition of the polymer, is independent of temperature. The wide angle band corresponding to a distance $a=4{\cdot}8$ to 5·1 Å, depending on the polymer, is also independent of temperature and the value of a is similar to the distance between

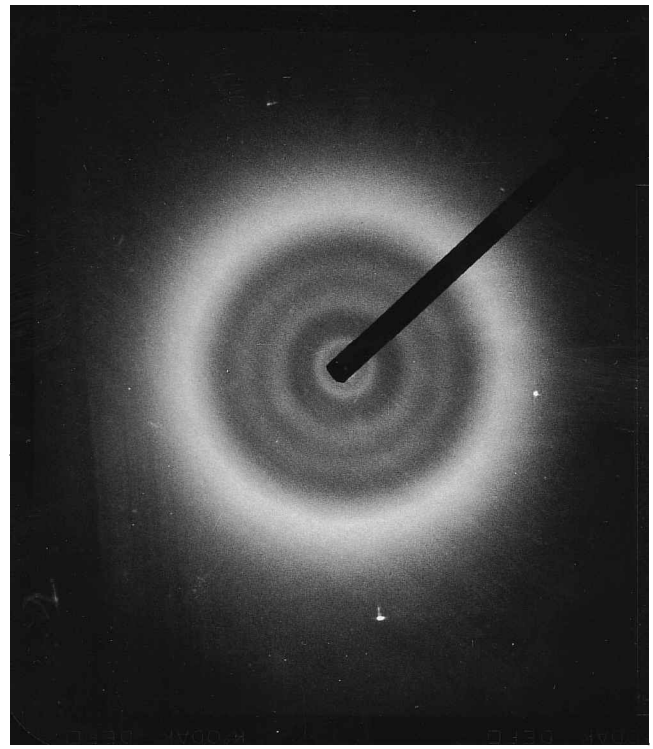


Figure 1. Example of a pin-hole camera powder X-ray diagram of the azo-substituted poly(L-lysine) **Azo-Lys-41** containing 41 mol % of azobenzene units and showing the three sharp reflections and the diffuse band.

mesogenic groups in disordered smectic structures of side chain liquid crystal polymers [18, 19].

Such X-ray diagrams suggest a lamellar structure of the smectic A type deriving from the β-pleated-sheet structure classical for polypeptides and proteins [20]. The antiparallel β-structure is illustrated in figure 4. It is characterized by polypeptide chains having opposite orientations linked by a pattern of hydrogen bonds, thus generating sheets. The R side chains are perpendicular to the plane of the sheet and point alternately above and below the sheet. The distance between two consecutive side chains along the same polypeptide chain is reported to be 7·00 Å [21], while the average distance between two parallel R side chains belonging to adjacent macromolecules is about 5 Å (it varies between 4·5 and 5·5 Å depending upon whether they point above or below the plane).

The diffuse band observed at $a=4{\cdot}8$ to 5·1 Å, depending upon the composition of the polymer, is in agreement with the average distance between side chains belonging to adjacent molecules (backbone spacings). The sharp reflection at 7·3 to 7·6 Å is in good agreement with the repeat distance of pleated polypeptide chains (figure 4); the slightly higher value with respect to theoretical may be due to the bulky groups present in the

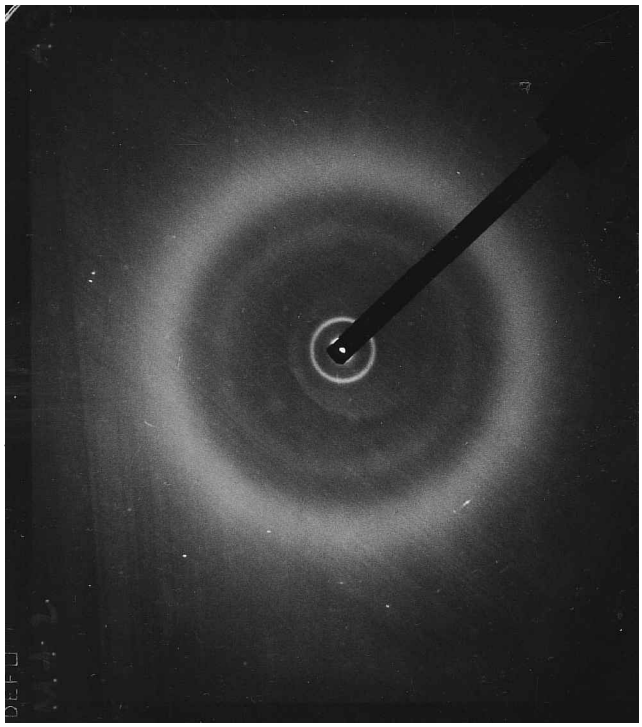


Figure 2. Example of a pin-hole camera powder X-ray diagram of the completely azo-substituted poly(L-lysine) **AzoS-Lys-100**, showing two sharp reflections and a diffuse band.

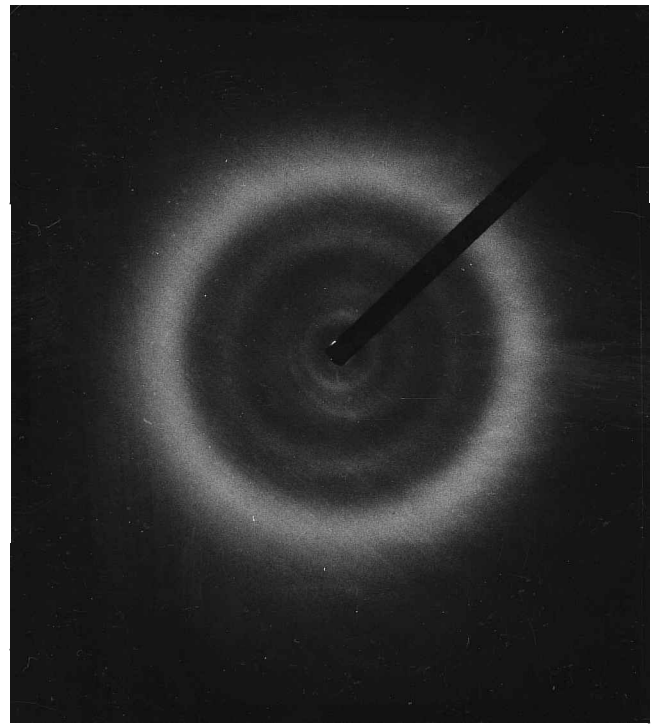


Figure 3. Example of a pin-hole camera powder X-ray diagram of the poly(L-lysine) **Azo-Piv-Lys-70** having azobenzene and pivaloyl substituents, showing two sharp reflections and a diffuse band.

side chains. Infrared spectroscopy measurements performed on the powder samples used for X-ray studies showed the presence of Amide A, Amide I and Amide II bands at 3279, 1629 and 1540 cm^{-1}, respectively, thus confirming the presence of an antiparallel β-structure [21]. A similar pleated sheet structure was found for dry oriented fibres of sodium poly(L-glutamate) [22].

Comparison of the inter-sheet spacing d with the lengths of the azobenzoyl-lysine units ($L_1 = 23$ Å), of the azobenzensulphonyl-lysine units ($L_1 = 24$ Å) and the unmodified lysine units ($L_2 = 9$ Å), measured using space filling CPK models (see the table), allows the classification of the polymers into two families: one is formed by partially modified polymers containing free lysine side chains (**Azo-Lys-31**, **-41** and **-44**), the other by polymers without free lysine side chains. (**AzoS-Lys-100** and **Azo-Piv-Lys-70**).

3.2.2. *Completely substituted poly(L-lysine)s*

For polymers **AzoS-Lys-100** and **Azo-Piv-Lys-70**, d is nearly equal to L_1 (see the table) and the lamellar structure is of the smectic A_1 type with the side chains perpendicular to the smectic layers, as schematically illustrated in figures 5 and 6. The interdigitation of the mesogenic groups favours the formation of azobenzene dimers of H type in agreement with the tendency of azobenzene to aggregate [23, 24]. Adjacent polypeptide chains are separated by an average distance $a = 5{\cdot}1$ Å. The reflection observed at 7·3 Å for the polymer **AzoS-Lys-100** and at 7·6 Å for the polymer **Azo-Piv-Lys-70**, corresponds to the periodicity b of the pleats (figure 4), as already found in the case of poly(L-lysine hydrobromide) [25].

3.2.3. *Partially substituted poly(L-lysine)s*

For polymers **Azo-Lys-31**, **Azo-Lys-41** and **Azo-Lys-44**, one observes (see the table) that d closely corresponds to the value obtained by adding the azo-Lys (23 Å) and Lys (9 Å) lengths. These values are in agreement with a lamellar structure of intersheet spacing d, resulting from the superposition of a 'hydrophilic' layer of thickness d_A containing the free lysine side chains, and a 'hydrophobic' layer of thickness d_B containing the azobenzene-modified lysine side chains and the polypeptide main chains (figure 7). Furthermore, at room temperature the unmodified lysine side chains in the 'hydrophilic' layer and azobenzene-modified lysine side chains in the 'hydrophobic' layer are completely interdigitated, and the structure is of the Smectic A_1 type with the azobenzene mesogenic groups perpendicular to the smectic layers, while adjacent polypeptide chains are separated by an average distance $a = 5{\cdot}0$ Å. In such a

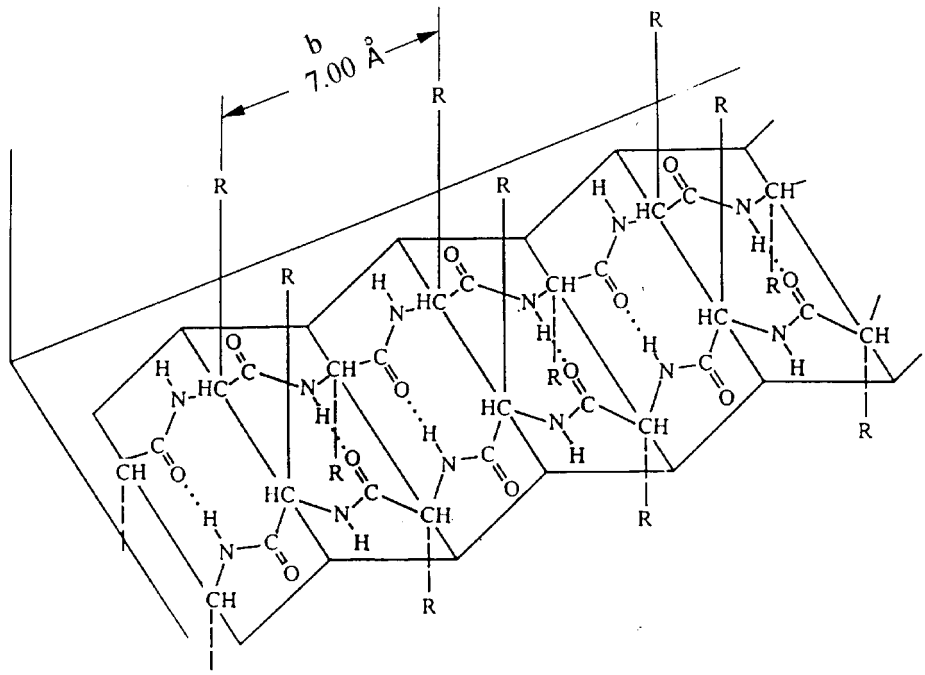


Figure 4. Schematic illustration of the antiparallel β-pleated sheet structure present in polypeptides and proteins.

structure, the unmodified lysine side chains on one side and the azobenzene-modified lysine side chains on the other side statistically point up and down out of the planes containing the polypeptide main chains (figure 7), although the polymers are not alternating copolymers. This may imply some degree of disorder for the β-structure or a non all-*trans*-conformation for some of the methylene spacers, thus allowing the azo-modified and the unmodified lysine side chains to reach the respective 'hydrophobic' or 'hydrophilic' layers [12]. The reflection observed between 7·4 and 7·6 Å corresponds to the periodicity of the pleats (figure 4).

For polymers **Azo-Lys-31**, **-41** and **-44**, we can obtain supplementary information about the structure by deducing, from the intensities of the 0 0 1 reflections, the electron density profiles along the z-axis perpendicular to the smectic layers. If we put the origin in the middle of the d_A or d_B layers, since as many mesogenic cores are pointing in the $+z$ and $-z$ directions, so that $\rho(+z)=\rho(-z)$ and $\rho(z)$ can be expressed as a Fourier series containing only the cosine terms [26] and, since we measure only the fluctuations around the average electron density ρ_0, $\rho(z)$ is given by:

$$\rho(z)=\Sigma\, a_m \cos(m2\pi z/d)$$

Experimentally we measure the intensity I_m of the orders of reflections, so we lose the phase of a_m. Due to the symmetry of the electron density distribution, the phase factor and the structure factor must be 0 or π, so a_m are real, but may be positive or negative. The phase problem then reduces to choosing the right combinations of sign for a_m ($m=1, 2, 3 \ldots$). For instance $\rho^{-}++(z)$ will correspond to the combination where a_1 is chosen negative, while a_2 and a_3 are chosen positive. As we observe two orders of diffraction, we obtain four combinations of sign for a_m, that is to say four electron density profiles $\rho(z)$ that are illustrated in the case of polymer **Azo-Lys-41** in figure 8.

In order to choose the physically acceptable one from amongst the four profiles, we have calculated the electron density of the different parts of the repeating unit of the polymer by dividing their number of electrons by their lengths measured using CPK models. We found: $7{\cdot}8\,e^{-}\,Å^{-1}$ for the skeleton, $6{\cdot}4\,e^{-}\,Å^{-1}$ for the paraffinic spacer and $8{\cdot}4\,e^{-}\,Å^{-1}$ for the mesogenic azobenzene groups.

In the case of an orthogonal SmA_1 smectic structure, one must observe a central maximum corresponding to the interdigitated mesogenic groups surrounded by two secondary minima corresponding to the spacers of the azobenzene-modified lysine, two secondary maxima corresponding to the polymeric skeleton and two minima corresponding to lysine side chains (figure 7).

The four electron density profiles of the disordered smectic A structure of the polymer **Azo-Lys-41** are represented in figures 8(*a*) to 8(*d*). The two electron density profiles (*c*) and (*d*) must be rejected as they exhibit minima at the position of the mesogenic cores. The electron density profile (*a*) must be rejected as it exhibits maxima at the position of the lysine side chains and a secondary minimum at the position of the mesogenic cores. On the contrary the electron density profile

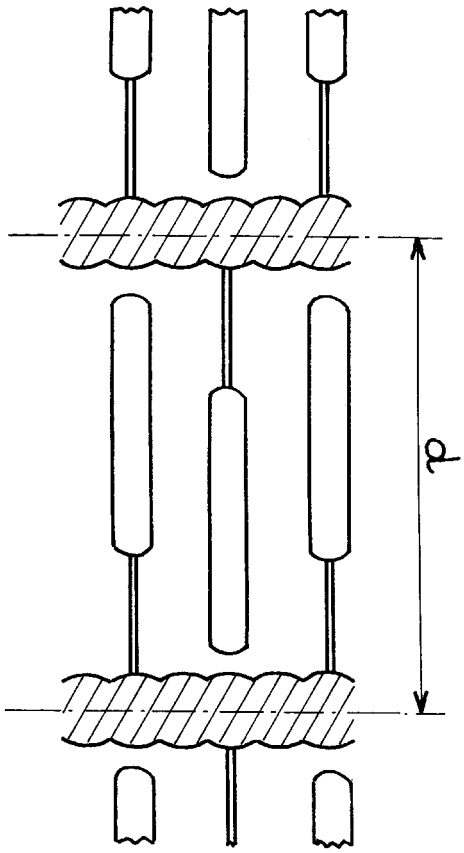


Figure 5. Schematic representations of the smectic structure of the polymer **AzoS-Lys-100** with L-lysine side chains completely substituted with azobenzene.

Main chain ;

spacer ;

mesogen .

(*b*), corresponding to the combination of signs $-+-$, exhibits a central maximum corresponding to the mesogenic azobenzene cores, two secondary minima corresponding to the spacers, two shoulders corresponding to the polypeptide main chains and two minima corresponding to the lysine side chains, in agreement with the physically acceptable profile (figure 7).

Therefore the mesomorphic structure of the polymers containing 31, 41 and 44 mol % azobenzene is of the smectic A_1 type and derives from the arrangement of the polypeptide chains in a β-pleated-sheet structure [20]. The SmA_1 structure can be described as follows: each smectic layer of thickness d results from the superposition of two layers, one of thickness d_A contains the free lysine side chains and the other of thickness d_B contains the azobenzene-modified lysine side chains and the polypeptide main chains. The periodicity b of the pleats of the sheets varies between 7·3 and 7·6 Å and is in agreement with 'antiparallel' polypeptide chains (figure 4).

3.3. *Influence of temperature*

The distance a between adjacent polypeptide chains and the periodicity b of the pleats are parameters connected to the β-structure and are independent of temperature. On the contrary, the thickness d of the smectic layers varies with temperature as shown in figures 9 to 11.

For the polymers **Azo-Lys-31**, **Azo-Lys-41**, **Azo-Lys-44** and **Azo-Piv-Lys-70**, the thickness d of the smectic layers increases with temperature until it reaches a value that corresponds to the maximum interaction between the azobenzene mesogens in their *trans*-configuration (figures 6 and 7), and then remains constant until decomposition of the polymers begins at 250°C.

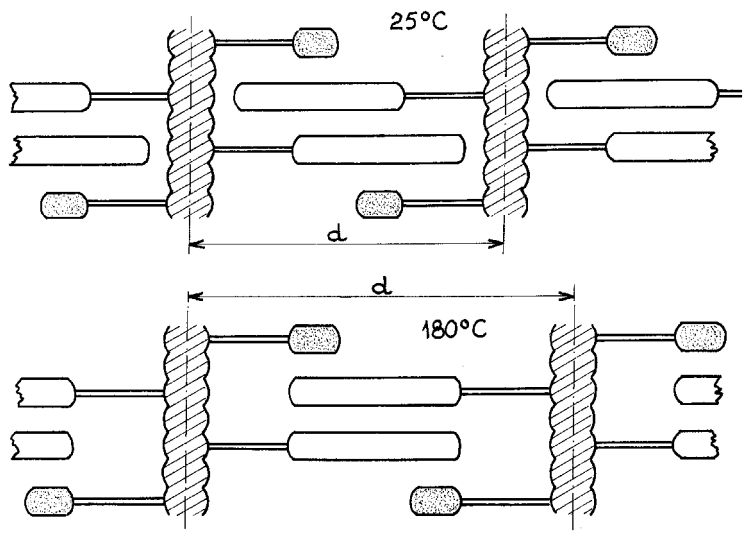


Figure 6. Schematic representation (at room temperature and at high temperature) of the respective positions of the mesogens in the smectic structure of the polymer **Azo-Piv-Lys-70**.

Main chain ;

spacer ;

mesogen ;

pivaloyl group .

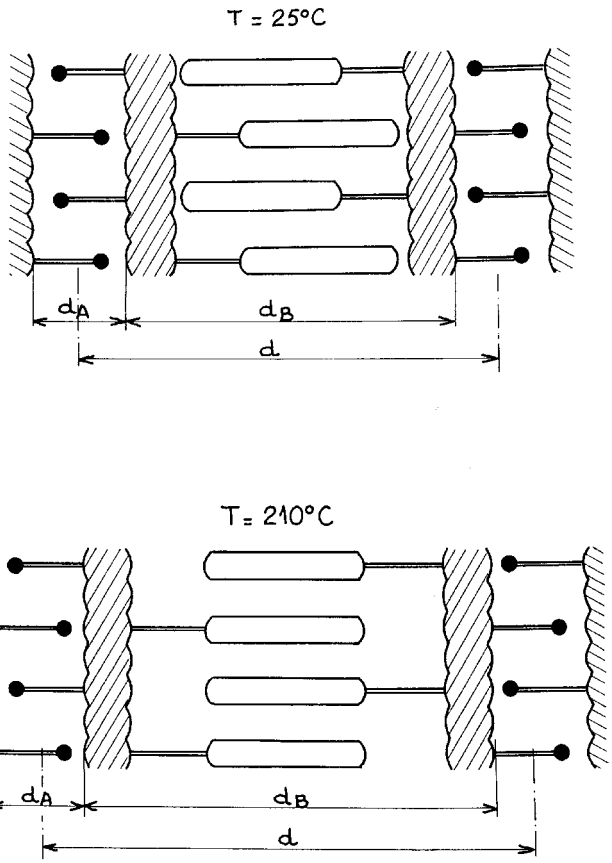


Figure 7. Schematic representations of the smectic structure of the polymers containing 31, 41 and 44 mol % of azobenzene units at room temperature and at high temperature.
Main chain ;
spacer ;
NH_2 group ●;
mesogen .

For the polymer **AzoS-Lys-100** in which all the lysine side chains are substituted by azobenzene, the variation of d as a function of temperature is smaller than that observed for the other polymers, but the thermal behaviour is more complex (figure 11). On heating, d is constant and equal to 25 Å until 70°C; then it suddenly increases to 27 Å, remains constant until 140°C, and then decreases to 25·6 Å, remaining constant until 240°C. Upon cooling or on heating again, only the higher transition can be detected. The explanation of that behaviour is presently not clear. It should not involve a modification of the β-structure and the pattern of hydrogen-bonding, because the parameters a and b do not change as a function of temperature. The first step might be attributed to a glass transition caused by the side chains. The decrease of d at temperatures higher than 140°C could be tentatively explained by a 'melting' of the methylene spacers

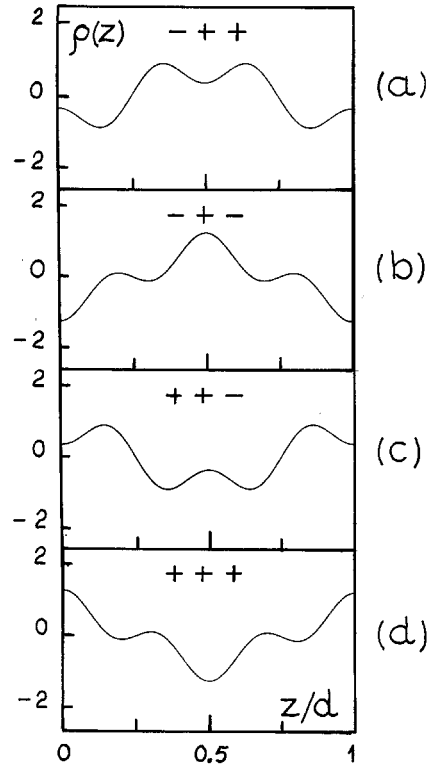


Figure 8. Projections of the electron density profiles corresponding to the different sign combinations of a_m for the polymer **Azo-Lys-41** containing 41 mol % of azobenzene units.

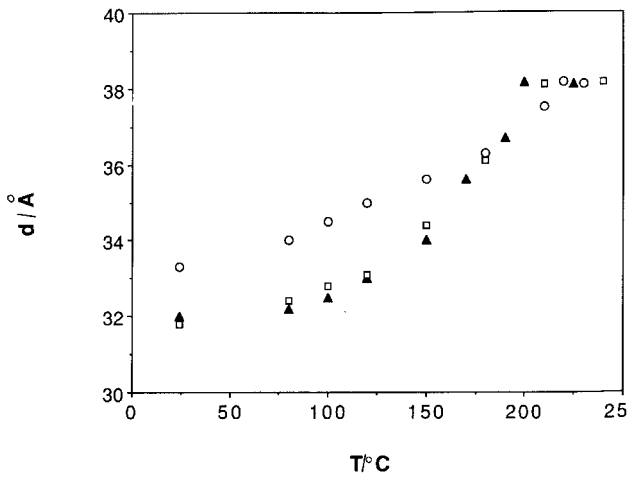


Figure 9. Variation with temperature of the layer thickness d of the smectic structure for the polymers **Azo-Lys-31** (○), **Azo-Lys-41** (□), and **Azo-Lys-44** (▲), containing, respectively, 31, 41 and 44 mol % of azobenzene units.

corresponding to the transformation of the *trans*-conformations into *gauche*-conformations.

4. Concluding remarks

In this paper we have described the structure of poly(L-lysine)s containing between 20 and 100 mol % of

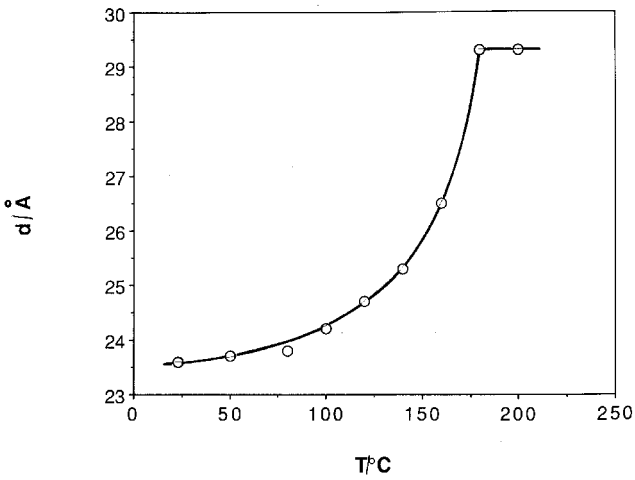


Figure 10. Variation with temperature of the layer thickness d for the smectic structure of the polymer **Azo-Piv-Lys-70** with L-lysine side chains substituted with both azobenzene and pivaloyl.

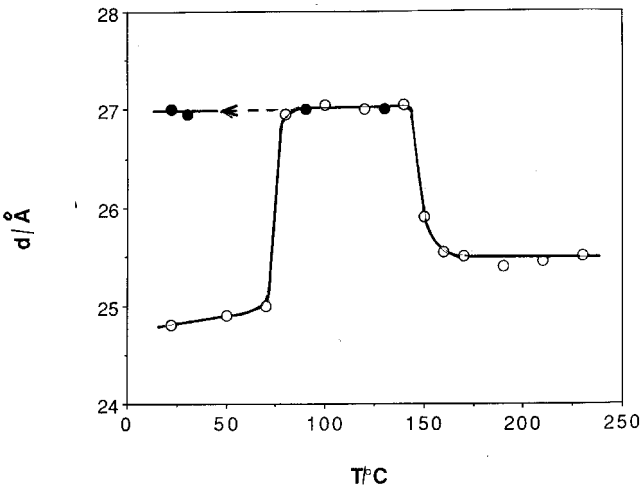


Figure 11. Variation with temperature of the layer thickness d for the smectic structure of the polymer **AzoS-Lys-100** with L-lysine side chains completely substituted with azobenzene units.

azobenzene units in the side chains. We have shown that, except for very low contents of azobenzene, the polymers exhibit mesomorphic structures of the smectic A_1 type deriving from the β-structure of polypeptides. For polymers where all the lysines have been substituted (by azobenzene or by pivaloyl groups that are both hydrophobic), the polypeptide main chains are arranged in their planes as in the 'antiparallel' β-structure, thus forming sheets, and the side chains are perpendicular to the smectic layers. For polymers containing free lysine side chains, each smectic layer results from the superposition of two layers: one contains the free lysine side chains, the other contains the azobenzene-modified lysine side chains and the polypeptide main chains which are arranged in their planes as in the 'antiparallel' β-structure.

All polymers exhibit only one mesophase as a function of temperature, and in that smectic A mesophase the thickness of the smectic layers increases with temperature until it reaches the thickness corresponding to a maximum in the interactions between the azobenzene mesogens in their *trans*-configuration. Such an increase of d allows better interactions between the azobenzene mesogenic cores in the *trans*-configuration and a stabilization of the smectic structure, balancing successfully the effect of thermal agitation and allowing the smectic structure to be stable at very high temperatures. The mesomorphic smectic structure prevents the *trans* to *cis* thermal isomerization of the azobenzene units.

The results confirm that polypeptides are quite special polymers because of their ability to exist in ordered structures. The ordered structure of the macromolecular main chains in fact produces the opportunity for the orientation of the side chains to a greater extent than in other synthetic polymers. This is a very important requirement for thermotropic self-organization of the macromolecules and for obtaining new liquid crystalline materials.

The study of poly(L-ornithine) and poly(L-glutamic acid) containing different amounts of azobenzene units in their side chains is now in progress, in order to establish the influence of the nature of the amino acid on the thermotropic behaviour of photochromic polypeptides.

References

[1] Robinson, C., 1956, *Trans Faraday Soc.*, **52,** 371.
[2] Robinson, C., Ward, J. C., and Beevers, R. B., 1958, *Discuss. Faraday Soc.*, **25,** 29.
[3] Squire, J. M., and Elliott, A., 1969, *Mol. Cryst. liq. Cryst.*, **7,** 457.
[4] Luzzati, V., Cesari, M., Spach, G., Masson, F., and Vincent, J. M., 1961, *J. Mol. Biol.*, **3,** 566.
[5] Elliott, A., 1967, in *Poly-α-Amino Acids*, edited by G.D. Fasman (New York: Dekker), p. 1.
[6] Gallot, B., 1996, *Progress in Polymer Science*, 1996, **21,** 1035, and references therein.
[7] Thierry, A., Skoulios, A., Lang, G., and Forestier, S., 1978, *Mol. Cryst. liq. Cryst.*, **41,** 125.
[8] Watanabe, J., Ono, H., Uematsu, I., and Abe, A., 1985, *Macromolecules*, **18,** 2141.
[9] Watanabe, J., and Takashina, Y., 1991, *Macromolecules*, **24,** 3423.
[10] Watanabe, J., and Tominaga, T., 1993, *Macromolecules*, **26,** 4032.
[11] Stumpe, J., Fischer, Th., and Menzel, H., 1996, *Macromolecules*, **29,** 2831.
[12] Gallot, B., Fafiotte, M., Fissi, A., and Pieroni, O., 1996, *Macromol. Chem. rapid Commun.*, **17,** 493.
[13] Fasman, G. D., Idelson, M., and Blout, E. R., 1961, *J. Am. chem. Soc.*, **83,** 709.

[14] YARON, A., and BERGER, A., 1963, *Biochim. biophys. Acta*, **69,** 397.
[15] *International tables for X-ray Crystallography*, 1952 (Birmingham: Kynoch Press).
[16] FISSI, A., PIERONI, O., BALESTRERI, E., and AMATO, C., 1996, *Macromolecules*, **29,** 4680.
[17] FISSI, A., PIERONI, O., and CIARDELLI, F., 1987, *Biopolymers* , **26,** 1993.
[18] DAVIDSON, P., and LEVELUT, A. M., 1992, *Liq. Cryst*., **11,** 469.
[19] GALLOT, B., MONNET, F., and HE, S., 1995, *Liq. Cryst*., **19,** 501.
[20] SALEMME, F. R., and WEATHERFORD, D. W., 1981, *J. mol. Biol*., **146,** 101 and 119.
[21] MIYAZAWA, T., 1967, *Poly-α-Amino Acids*, edited by G.D. Fasman (New York: Dekker), p. 90.
[22] MITSUI, Y., 1973, *Biopolymers* , **12,** 1781.
[23] MENZEL, H., WEICHART, B., SCHMIDT, A., PAUL, S., KNOLL, W., STUMPE, J., and FISCHER, T., 1994, *Langmuir*, **10,** 1926.
[24] KUNITAKE, T., 1986, *Colloid Surf*., **19,** 225.
[25] SUWALSKY, M., and LLANOS, A., 1977, *Biopolymers* , **16,** 403.
[26] GUDKOV, V. A., 1984, *Soviet Phys. Crystallogr*., **29,** 316.