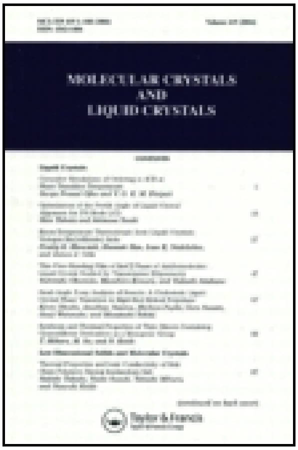

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Thermotropic Liquid Crystals of n-Alkylammonium Poly(α, L-Glutamates)

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Thermotropic Liquid Crystals of n-Alkylammonium Poly(α, L-Glutamates)

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The interaction of poly(α, L-glutamic) acid of varying molecular weights with long chain primary or secondary amines leads to the formation of salts which exhibit smectic B, E or A liquid crystalline phases as established by optical microscopy, DSC and X-ray diffraction studies. The type of ordering observed depends on temperature and also on the chemical nature of the amine used. Upon salt formation, the polyglutamic acid, partially in a β_2-sheet conformation, is transformed completely into α-helices. The structure and structural parameters of the observed phases are determined.

Keywords: synthetic polypeptides; polyeletrolyte-surfactant complexes; smectic phases; poly(α, L-glutamic acid)

INTRODUCTION

The interaction of polyacids with long-chain amines induces the formation of liquid crystalline phases. The first examples of such liquid crystalline phases, characterized as "template induced" liquid crystals,[1] were obtained with polyacrylic acid[1-7]. The n-alkyl ammonium polyacrylates were found to produce a diversity of liquid crystals, including A, B and E smectic phases[2-7], depending on the amine employed. The n-alkyl and quaternary n-alkyl ammonium poly(vinylsulfonates) were found to have a similar behavior[8].

We thought it of interest to investigate whether n-alkylammonium polyglutamates, resulting from the interaction of polyglutamic acid with long-chain primary and secondary amines, exhibit a similar liquid crystalline behavior. Polyglutamic acid can adopt in the solid state at room temperature both α-helical or β-sheet conformations[9]. Ester derivatives of polyglutamic acid exhibit[10, 11] thermotropic liquid crystals when the alkyl chains are longer than decyl[11]. Specifically, a hexagonal packing of α-helices surrounded by melted aliphatic chains was observed for poly(n-dodecyl glutamates)[10]. Due to prospected practical applications and interesting physical characteristics, the subject of long-chain polyglutamate esters was recently reviewed[12].

EXPERIMENTAL

Poly(α, L-glutamic acids) of molecular weights 2,000-15,000, 15,000-50,000 and 50,000-100,000 (Fluka) were reacted with equimolar quantities of n-hexadecyl amine or di-n-hexadecylamine in DMF. The precipitated polymers were filtered-off and extensively dried in vacuum over phosphorous pentoxide. The formation of salts was established by ^{1}H-NMR and FT-IR spectroscopy. From the ratio of peak intensities of the polyglutamic α-CH (δ = 4.0 ppm) and the alkylammonium (δ = 0.83 (CH_3, 3H), 1.19-1.26 (CH_2, 26H)) protons, it was estimated that more than 98% of the acid units were neutralized. FT-IR spectroscopy confirmed this result, the carbonyl band of polyglutamic acid at 1733 cm^{-1} being totally absent in the spectra of the salts.

Liquid crystal textures were observed using a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot-stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA Instruments). Liquid crystal structures were studied by X-ray diffraction using either a Guinier focusing camera (Cu K_{α_1} radiation from an INEL X-ray generator, powder samples in Lindemann capillaries, INSTEC hot-stage) and an INEL CPS-120 curved position-sensitive detector, or else a Rigaku rotating anode (operating at 50 kV, 100 mA) and a R-AXIS IV image plate. FT-IR spectra at various temperatures were obtained with a Nicolet Magna-550 spectrometer equipped with a VLT-2 heating sample-holder (Research & Industrial Instruments Company).

RESULTS AND DISCUSSION

Investigated by optical microscopy, the polyglutamic acid complexes with n-hexadecylamine showed to melt at about 50 °C into a birefringent fluid with oily-streak textures similar to those observed for the smectic A phases of n-alkylammonium polyacrylates[1, 3] or polysulfonates[8]. On heating above 120 °C, thermal degradation was found to occur, the smectic textures of the samples persisting, however, up to 200 °C. The di-n-hexadecylamine salts showed to transform at about 65 °C into smectic phases with blurred schlieren textures (Fig. 1) and to melt reversibly into an isotropic liquid at *ca.* 100 °C.

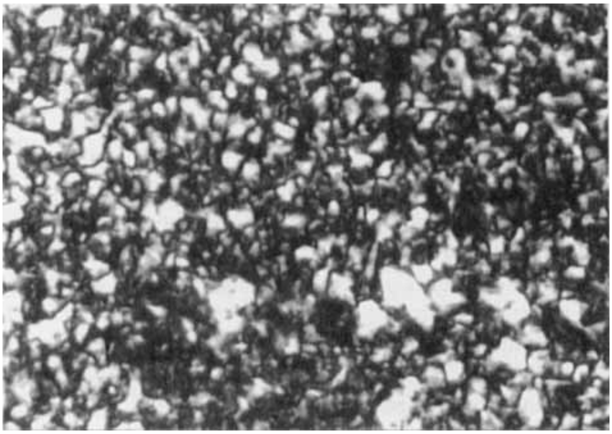

FIGURE 1 Optical texture of di-n-hexadecylammonium polyglutamate obtained on cooling at 87 °C.

The polymorphic behavior of the complexes was then studied by DSC. For the n-hexadecylamine derivatives, the melting of the alkyl chains (at 48, 50, and 51 °C for the low, intermediate and high molecular weight polymers, respectively) was found to increase slightly with the molecular weight of the polyglutamic counterion. The corresponding melting enthalpies measured (22, 28, and 30 kJ/mol) allow a rough estimate of the crystallinity of the alkyl chains[11]: depending on the length of the polymer, about 5.5 to 7 methylene groups are crystallized, in good agreement with previously reported results of long n-alkyl polyglutamic esters[11], whereas about 10 methylene groups are in a disordered state.

As for the dihexadecyl derivatives, they present two transitions, one at 64-65 °C for the melting into a smectic phase and one other at 100 °C for the clearing into an isotropic liquid. The enthalpy change at the first transition (80-83 kJ/mol) is consistent with the melting of 19-20 methylene groups, indicating a more pronounced ordering of the alkyl chains in the dialkyl as compared to the monoalkyl complexes. The enthalpy change at the second transition (1-2 kJ/mol) is very small, as expected.

The conformation of the polypeptide backbone and of the alkyl chains was investigated, at different temperatures, by FTIR. The amide I, amide II and amide III bands at 1653, 1545 and 1295 cm^{-1} respectively, indicate that polyglutamic main chains adopt predominantly an α-helical form[13, 14]. This result is in agreement with previous reports on polyglutamic acid - alkyltrimethylammonium surfactant complexes[9] and poly(n-alkyl glutamates)[11]. It is of interest to note that the parent polyglutamic acids used appeared as mixtures of α-helical and β_2-sheet forms, as evidenced by an extra peak at 1604 cm^{-1} assigned to the amide I band of a β_2-sheet[15]. Therefore, upon salt formation, the densely-packed antiparallel chains of the pleated β_2-sheet form are transformed into α-helices. On heating the amine complexes of polyglutamic acid up to 100 °C, only minor changes were observed in the IR absorption bands of the α form, indicating that the helical structure remained substantially the same in the smectic phase.

The vibrational bands of the aliphatic chains in the region between 1480 and 700 cm^{-1}, which are sensitive to conformational motions, provide information on the packing of the alkyl chains. Thus, for the dihexadecyl derivatives, the doubling of the methylene rocking-mode band at 719 and 729 cm^{-1} and of the methylene scissoring-mode band at 1462 and 1471 cm^{-1} indicate an all-trans conformation of the aliphatic chains crystallized in an orthorhombic unit cell[16]. On heating from about 40 °C up to the first transition at 65 °C, a gradual change in the methylene rocking progression[16b] was observed, indicating a gradual deformation of the all-trans conformation of the alkyl chains, in agreement with DSC results. On the other hand, for the n-hexadecylamine derivatives, the presence of a methylene scissoring-mode band at 1467 cm^{-1} and of methylene rocking-mode band at 721 cm^{-1} suggests a less constrained packing of the alkyl chains, similar to the hexagonal one observed for the high-temperature crystal form of linear paraffins[16a].

As temperature rises above the first transition, these bands for both series of compounds weaken in intensity and shift to 1466 and 719 cm^{-1} respectively. The absence of bands due to the crystalline state of the aliphatic chains and the concomitant presence of a new band at 1354 cm^{-1} for the dihexadecyl derivatives or the increase in intensity of this same band for the monohexadecyl derivatives (due to double gauche conformers) are clear indications of chain melting[16c].

The liquid crystal structure of the polymers was finally established by X-ray diffraction. The X-ray patterns of the n-hexadecylammonium derivatives recorded at low temperature indicate the presence of an ordered smectic B phase similar to that observed with n-alkylammonium polyacrylates[3] or polyvinylsulfonates[8]. They contain four sharp, equidistant small-angle reflections related to the smectic layering and a rather sharp wide-angle reflection at 4.10 Å consistent with a hexagonal packing of the alkyl chains, as also suggested by IR spectroscopy. The width of this latter reflection provides an estimate of the range of the hexagonal in-layer ordering of the side-chains[3], which varies from 130 Å for the low to 90 Å for the high molecular weight polymers (comparable to the correlation lengths observed respectively with low[17] and high molecular weight smectic B phases[3]), suggesting that the short (*ca.* 150 Å) α-helices disfavor less the in-layer positional ordering of the molecules than the long ones (>1000 Å). This is supported by the smectic periods measured, 33.7 Å for the low and 30.8 Å for the high molecular weight polymer, indicating a smaller molecular area and, hence, a denser packing of the molecules in the former case. Comparable to the length of the monomer units in a fully extended conformation, the smectic periods clearly suggest on the other hand that the alkyl chains, separated from one another by the polymer helices, are arranged in single layers in an interdigitated configuration (Fig. 2a). An extra weak reflection at ca. 57 Å observed with the high molecular weight polymer might tentatively be interpreted as resulting from interlayer interactions leading to a doubling of the smectic layers.

The X-ray patterns of the n-hexadecylammonium derivatives recorded at high temperature indicate the presence of a smectic A structure consisting of layers of molten alkyl chains separated by the polymer helices. They contain two sharp equidistant reflections related to the smectic stacking of the molecules and one diffuse ring at 4.5 Å related to the liquid-like conformation of the alkyl chains. The increase of the layer

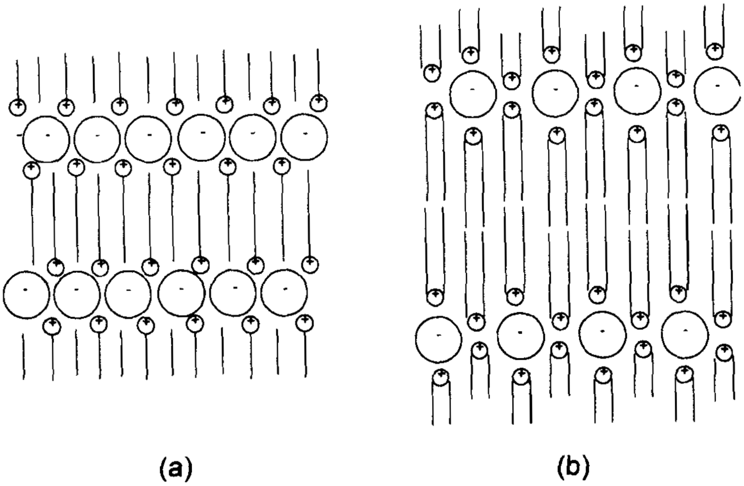

FIGURE 2 Schematic representation (a) of the smectic B structure of the n-hexadecylammonium and (b) of the smectic E structure of the di-n-hexadecylammonium polyglutamates. Large circles represent end-on views of polyglutamic acid, small circles the ammonium groups and straight lines the aliphatic chains.

thickness at the smectic B to smectic A transition (Fig. 3) suggests that the disordered alkyl chains are no longer interdigitated but rather arranged in double layers. The pronounced thinning of the smectic A layers upon heating suggests an important increase of the molecular areas, that is, of the distances between the helices, due to thermal agitation. It is useful to note in this connection that the higher the molecular weight of the polymer the thinner the smectic layers (Fig. 3), the longer polyglutamic helices (~10 times on average) leaving more free space between them to be filled by the molten aliphatic chains.

The dihexadecylammonium polyglutamates at low temperatures exhibit diffraction patterns (Fig. 4) that indicate the presence of an ordered smectic E structure, similar to that observed previously with dialkylammonium polyacrylates[3] or certain side-chain polymethacrylates[18]. In the small-angle region, they contain five or more equidistant sharp reflections related to the lamellar arrangement of the molecules and, in the

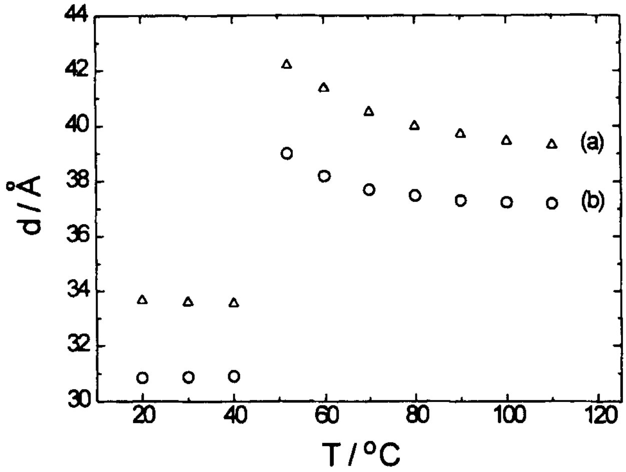

FIGURE 3 Variation of the smectic period of n-hexadecylammonium polyglutamate as a function of temperature for the low (a) and high (b) molecular weight compounds..

wide-angle region, three rather sharp peaks at 4.10, 3.69 and 2.97 Å corresponding to the (110), (200), and (210) reflections from a two-dimensional rectangular lattice with cell parameters a = 7.40 and b = 4.95 Å (with a correlation length of about 400 Å as estimated from the width of the wide (110) reflection). Independent both of molecular weight and temperature, the smectic spacing, 45.6 Å, is larger than that of the corresponding mono-hexadecyl derivative. The alkyl chains are packed in double layers according to a rectangular lattice and have a cross-sectional area of $ab/2$ = 18.3 Å^2, as usually observed with crystalline paraffin molecules[19]. It is important to add that the X-ray patterns contain two additional, rather broad, equidistant peaks in the small-angle region, similar to those reported by Safinya *et al.* for cationic liposome complexes of DNA[20]. These peaks arise from the one-dimensional ordering of the polymer helices inside the polar sublayers. The in-layer spacing of the helices, 27-29 Å, is larger than the diameter of the helices (12-17 Å [21]), suggesting that the free space between the helices is probably occupied by polar ammonium and the adjacent methylene groups (Fig. 2b).

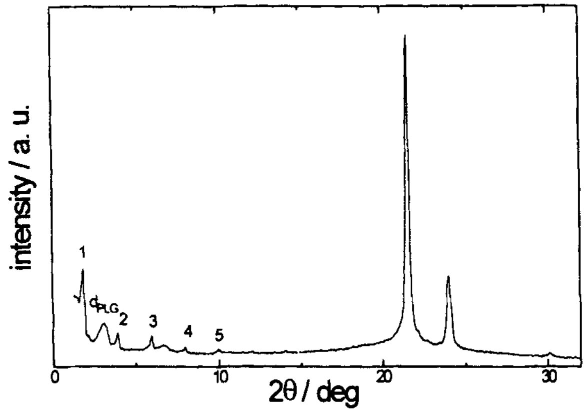

FIGURE 4 X-ray diffraction pattern of di-n-hexadecylammonium polyglutamate in the smectic E phase.

The diffraction patterns of the dihexadecylammonium polyglutamates recorded at high temperature indicate the presence of a smectic A phase similar to that of the monohexadecyl derivatives. In this case however, the layer spacing, 32.1-32.3 Å, is independent of molecular weight; its reduced value suggests that the polymer helices are drawn apart significantly, leaving more lateral space for the melted aliphatic chains.

Acknowledgments

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