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Structural Study of Liquid Crystalline Long-Chain *n*-Alkylammonium Polyacrylates

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ABSTRACT: A series of alkyl and dialkylammonium polyacrylates were synthesized by neutralizing a 5000 molecular weight poly(acrylic acid) with alkyl- and dialkylamines. Their thermal stability was investigated using thermogravimetry. Their thermotropic liquid crystal behavior was analyzed using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The dodecyl, didodecyl, and tetradecyl derivatives exhibited a smectic A phase in the whole range of temperatures explored, from ambient to thermal degradation. The hexadecyl, octadecyl, and dioctadecyl derivatives exhibited a smectic A phase at high temperatures and an ordered smectic B or E phase at low temperatures. Structures and structural parameters are briefly discussed.

Introduction

The thermotropic liquid crystalline behavior of ionic and nonionic amphiphiles is generally attributed to the segregation of the lipophilic and hydrophilic parts of the molecules. It has been widely studied in the past and is still actively investigated in many laboratories. As summarized in two recent review articles,[1,2] the principal classes of amphiphiles explored up to now are soaps, protonated and quaternary long-chain ammonium salts, amphiphilic and bolaamphiphilic carbohydrates, and polyols. Ionic amphiphiles containing polymeric counterions, such as polyacrylates or polysulfonates, have also been considered in the last few years.[3−6]

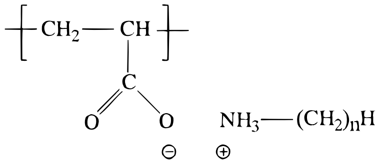
Regarding specifically the protonated and quaternary long-chain ammonium salts that show liquid crystalline behavior, investigations have up to a recent date been dealing essentially with the synthesis and characterization of compounds containing low molecular weight (monomeric) counterions. Ammonium salts containing high molecular weight (polymeric) counterions were reported only very recently.[7] Their preparation was achieved thanks to reactions between long-chain amines and poly(acrylic acids) or poly(maleic acids). Their liquid crystalline phases were initially considered to be "template induced", for they were obtained by neutralizing polyacids with amines in a way reminiscent of what is known as "template polymerization".[8]

In the present paper, our previous work on polymeric ammonium salts[7] is taken up again and completed by a detailed characterization of liquid crystalline structures obtained from a series of polyacrylic salts of both primary and secondary amines.

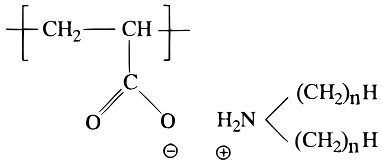
Experimental Section

Synthesis. The alkylammonium polyacrylates (noted in the following as PA-C_n for primary amines and PA-2C_n for secondary amines) were prepared according to a method described previously,[7] by neutralizing a 5000 molecular weight poly(acrylic acid) (Aldrich) dissolved in alcohol with long-chain primary (dodecyl, tetradecyl, hexadecyl, octadecyl) and secondary (didodecyl, dioctadecyl) amines. The salts of secondary amines were purified by dissolving in $CHCl_3$ and precipitating in acetone. Chemical structures and purity were checked by elemental analysis [PA-C_{12} Calc: C, 71.0; H, 12.1; N, 5.4. Found: C, 69.4; H, 11.8; N, 5.1. PA-C_{14} Calc: C, 71.5; H, 12.4; N, 4.9. Found: C, 70.9; H, 12.4; N, 4.7. PA-C_{16} Calc: C, 72.8; H, 12.5; N, 4.5. Found: C, 72.2; H, 12.6; N, 4.2. PA-C_{18} Calc: C, 73.8; H, 12.7; N, 4.1. Found: C, 73.0; H, 12.4; N, 3.9. PA-2C_{12} Calc: C, 76.2; H, 13.0; N, 3.3. Found: C, 75.6; H, 12.7; N, 3.0. PA-2C_{18} Calc: C, 78.9; H, 13.4; N, 2.4. Found: C, 78.1; H, 13.2; N, 2.3. Poly(acrylic acid) Calc: C, 50.0; H, 5.6. Found: C, 49.2; H, 6.0]. The degrees of neutralization deduced from the N content of each compound [PA-C_{12}, 0.94; PA-C_{14}, 0.96; PA-C_{16}, 0.93; PA-C_{18}, 0.95; PA-2C_{12}, 0.91; PA-2C_{18}, 0.96] were found to be close to unity, their small divergence from unity being very likely due to the presence of end groups on the (low molecular weight) polymer chains [see chemical composition of the poly(acrylic acid) used in the experiments]. This result was confirmed by FT-IR spectroscopy, which could not detect the presence of unreacted carboxylic acid groups in the final compounds, even with accumulations of 120 scans.

PA-C_n



PA-2C_n



Characterization. The thermal stability of the PA-C_n and PA-2C_n salts was evaluated by isothermal and dynamical thermogravimetry using a TA TGA 2050 balance. Liquid crystalline textures were observed with a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by differential scanning calorimetry with a TA DSC-10 instrument. Liquid crystal structures were studied by X-ray diffraction using a Guinier focusing camera (Cu $K_{\alpha 1}$ radiation from an INEL X-ray generator, powder samples in Lindemann capillaries, INSTEC

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hot stage, INEL CPS-120 curved position-sensitive detector). FT-IR spectroscopy was performed using a Nicolet Magna-550 spectrometer equipped with a VLT-2 heating sample-holder (Research & Industrial Instruments Co.).

Experimental Results

Thermal Behavior. The thermal stability of the salts was investigated by thermogravimetry. Upon heating under nitrogen at 10 °C/min, the monoalkyl PA-C_n compounds started to degrade at about 90 °C. Experiments performed at a constant temperature showed the rate of degradation to be slightly dependent on the length of the alkyl chains in the molecules: the shorter the chains, the faster the degradation observed. Weight losses recorded after 3 h of heating at 90 °C were 5.5, 5.3, 2.9, and 1.2% for PA-C_{12}, PA-C_{14}, PA-C_{16}, and PA-C_{18}, respectively. As confirmed by FT-IR analysis, thermal degradation is primarily due to the liberation of alkylamine (carried away in the thermogravimetry experiments by the nitrogen stream used). Much more stable, the dialkyl PA-2C_{12} and PA-2C_{18} compounds started to lose weight only above the melting temperature at about 130 °C. On isothermal heating at 90 °C for 3 h, weight losses were only 0.43 and 0.39% for PA-2C_{12} and PA-2C_{18}, respectively. FT-IR spectroscopy showed that, in the melt above 130 °C, the dialkylammonium polymers displayed an additional peak at 1725 cm^{-1}, growing with time and continuing to exist after cooling to room temperature. As previously observed in similar systems,[9] this peak suggests the formation of nonionic carboxylic groups. To sum up, the PA-C_n and PA-2C_n compounds, even though degrading readily at high temperature, are nevertheless sufficiently stable to be studied safely, provided they are carefully kept at reasonably low temperatures, e.g., below 90 °C.

The optical textures of PA-C_n and PA-2C_n turned out to be difficult to develop satisfactorily because of the high viscosity of the samples, and more importantly because of their degradation at high temperature, preventing us from proceeding by slow cooling from the isotropic melt as normally required. Nevertheless, the PA-C_n and PA-2C_n compounds proved without question to be spontaneously birefringent, which is a fair mark of liquid crystalline behavior, and occasionally showed "focal conic" textures, which is a conclusive indication of smectic structures. Directly attached to the polymer backbones, the carboxylate groups control the spatial positioning of the ammonium cations and thereby the overall structural behavior of the material. This influence shows quite clearly that the PA-C_n and PA-2C_n compounds are both smectic even though their monomeric counterparts, that is, the dodecyl- and didodecylammonium propanoates, are not liquid crystalline at all.

The thermotropic liquid crystalline behavior of the alkyl- and dialkylammonium polyacrylates was also investigated by DSC. The thermograms recorded on heating at 10 °C/min, in the temperature range from ambient up to 90 °C, showed for PA-C_{16} and PA-C_{18} the presence of one endotherm at 54 °C (48 J/g) and 65 °C (56 J/g), respectively, indicative of a first-order phase transition. As discussed below, this transition (undetected for PA-C_{12} and PA-C_{14}) corresponds to the melting of the alkyl chains and to the occurrence of a phase transition from smectic B to smectic A. On heating at higher temperatures, no additional transitions were observed up to about 200 °C where the compounds were melting completely with severe degradation. Of the dialkylammonium compounds studied in the temperature range from ambient up to slightly above 130 °C, only PA-2C_{18} displayed a phase transition at 72 °C (90 J/g), corresponding to a phase transition from smectic E to smectic A. It is worth adding immediately that the final melting of the PA-2C_n compounds, observed at about 130 °C by optical microscopy and X-ray diffraction, could not be ascertained by DSC because of thermal degradation.

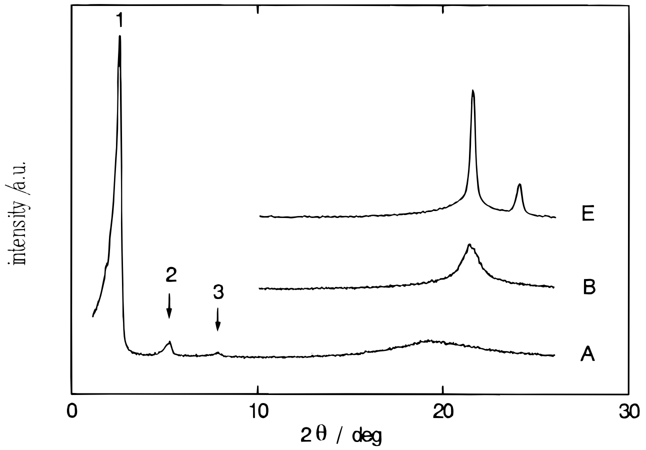

Figure 1. X-ray diffraction patterns: (A) of PA-C_{16} in the smectic A state at 70 °C, (B) of PA-C_{16} in the smectic B state at 30 °C, and (E) of PA-2C_{18} in the smectic E state at 30 °C. For clarity, small-angle smectic reflections of curves B and E have been omitted. The width of the wide angle reflections, as estimated by a Lorentzian least-squares fit method, is $\Delta(2\theta) = 5.1°$ at $2\theta = 19.6°$ for A, $\Delta(2\theta) = 1.2°$ at $2\theta = 21.4°$ for B, and $\Delta(2\theta) = 0.3°$ at $2\theta = 21.6°$ for E. The third wide-angle reflection of E at 3.0 Å is not visible on the graph.

Structure of the PA-C_n Polymers. Smectic B Structure. The exact nature of the liquid crystal phases observed was established by X-ray diffraction. The diffraction patterns of PA-C_{16} and PA-C_{18} recorded at low temperature (see Figure 1), that is, below the phase transition detected by DSC, indicated the presence of an ordered smectic B phase, similar to that described some time ago for the aqueous binary mixtures of potassium soaps[10] or for poly(*n*-octadecyl methacrylate).[11] They contain three sharp, equidistant reflections in the small-angle region, related to the smectic layering of the molecules, and a unique, rather sharp reflection in the wide-angle region, at 4.15 Å, consistent with the hexagonal packing of the alkyl chains in a fully extended conformation. Independent of temperature, the smectic periods measured, 29 Å for PA-C_{16} and 33 Å for PA-C_{18}, were nearly equal to the molecular length of the corresponding monomers (28 and 30.5 Å, as estimated by molecular modeling using Biosym software). Clearly, the alkyl chains are arranged in single layers separated from one another by the polymer backbones, as shown in Figure 2. Standing upright in a head to tail configuration, the chains inside the layers are packed according to a two-dimensional hexagonal lattice with a lateral interaxial spacing of $2 \times 4.15/\sqrt{3} \cong 4.79$ Å; their cross-sectional area, $2 \times 4.15^2/\sqrt{3} \cong 19.9$ Å^2, is identical with that (19.9 Å^2) found earlier for the linear paraffin chains in the lyotropic smectic B phases of potassium soaps.[10] The width of the wide-angle reflection suggests that the range of the hexagonal in-layer ordering of the alkyl chains is of about 70 Å, that is, smaller than usually observed (150–200 Å) for low-molecular weight smectic B phases.[12]

Smectic A Structure. At high temperature, that is, above the phase transition detected by DSC, the PA-

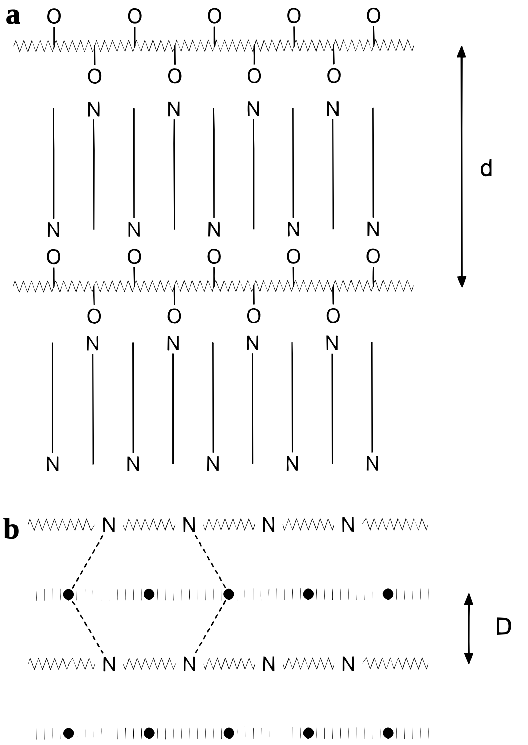

Figure 2. Schematic representation of the smectic B structure of the monoalkyl PA-C$_n$ compounds. (a) Front view of the smectic layering of period *d*. Standing upright in single layers, the alkyl chains (—) are arranged in a head to tail configuration. The polymer backbones (〰) are inserted between the alkyl sublayers with the carboxylate anions (O) pointing alternately up and down to face the ammonium cations (N). (b) Top view of one smectic layer. The alkyl chains are packed according to a hexagonal lattice of Bragg period *D*. The ammonium cations are lying in rows on the upper (N) and lower (●) surface of the alkyl sublayer. The polymer backbones are lying above (〰) and below (||) the alkyl sublayer. For the sake of simplicity, polymer backbones and rows of ammonium cations are both taken to be linear in shape.

C$_{16}$ and PA-C$_{18}$ compounds adopt a smectic A structure, consisting of layers of "molten" alkyl chains, separated by the polymer backbones. Their X-ray patterns (see Figure 1) contain three sharp, equidistant reflections in the small-angle region, related to the smectic stacking of the molecules; and one diffuse ring in the wide-angle region, at about 4.5 Å, related to the disordered, liquid-like conformation of the alkyl chains. Decreasing slightly with growing temperature ($\partial d/\partial T \sim -10^{-2}$ Å/°C), the smectic periods measured, $d = 35$ Å for PA-C$_{16}$ and 40 Å for PA-C$_{18}$ at 70 °C, exceed significantly the length of the monomer units. Although jumbled together to some extent due to their disordered conformation, the alkyl chains must therefore be arranged essentially in double layers and not in simple layers, as just described for the smectic B phase.

Upon heating, the smectic B and A phases were shown to coexist in equilibrium within a narrow temperature range enclosing the phase transition, due probably to polymer polydispersity. Upon cooling from 90 °C to room temperature, the broad wide-angle X-ray ring representative of the smectic A phase continued to exist for some time, the stable smectic B phase reforming only after annealing at 30 °C for 2 days; during this period, the narrow wide-angle ring of the smectic B phase was emerging progressively and the smectic period was continuously approaching its normal value from above. This large hysteresis effect was confirmed by FT-IR spectroscopy. The disordered conformation of the alkyl chains above 60 °C showed through the position and intensity of the rocking vibration of the CH$_2$ groups at 720 cm^{-1}, the deformation mode at 1458 cm^{-1}, and the stretching vibrations at 2925 and 2850 cm^{-1}. Upon cooling back to room temperature, the peaks characteristic of the alkyl chains in an all-trans conformation appeared again only after a period of 2 days.

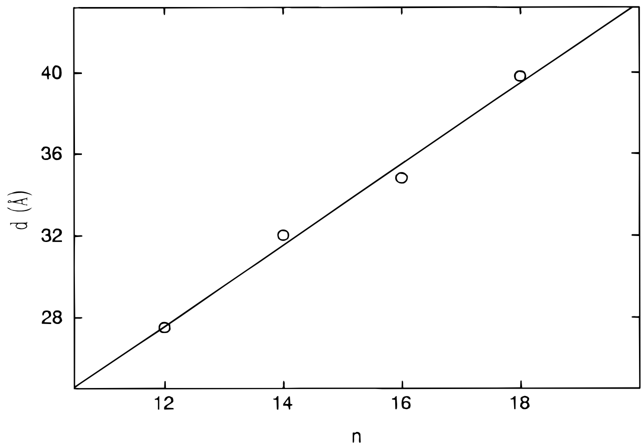

Figure 3. Smectic period of the PA-C$_n$ compounds in the smectic A state at 70 °C as a function of the number of carbon atoms in the alkyl chains.

In the case of compounds PA-C$_{12}$ and PA-C$_{14}$, the X-ray patterns indicated the presence of a smectic A phase throughout the whole range of temperatures explored, that is, from ambient up to 90 °C. It is useful to note in this connection that, at room temperature, the small-angle X-ray reflections of fresh (previously unheated) samples were rather broad, whereas they were sharp and intense above 40 °C. Rather short-ranged in fresh samples at low temperature, the smectic ordering develops therefore completely and extends over large distances only above 40 °C, owing probably to the existence (difficult to ascertain by DSC) of a glass transition just below 40 °C.

As shown in Figure 3, the smectic A period of the PA-C$_n$ compounds depends linearly on the length of the alkyl chains according to the equation d (Å) $= 5.9 + 1.82n$ (determined by a least-squares fit method; the standard errors on the Y-intercept and the slope are respectively 1.64 and 0.11 Å). Theoretically expressed by the equation $d = 2V/S = (2V_0/S) + (2V_{\mathrm{CH_2}}/S)n$, this behavior results simply from the fact that the molecular area S of the alkyl chains in the smectic double layers is the same for all the homologues, while the volume of the monomer units grows linearly with the number n of carbon atoms in the alkyl chains according to the equation $V = V_0 + nV_{\mathrm{CH_2}}$ (where $V_{\mathrm{CH_2}}$ and V_{o} represent respectively the volume of one methylene group and of one monomer unit deprived of all its methylene groups including that of the terminal methyl group). From the measured value of the slope of the straight line ($2V_{\mathrm{CH_2}}/S = 1.82 \pm 0.11$ Å) and from the known value of the volume of one methylene group ($V_{\mathrm{CH_2}} = 27.4$ Å^3 at 70 °C[13]), it is then easy to calculate the value of the molecular area of the alkyl chains: $S = 30 \pm 2$ Å^2. Much larger than in the smectic B phase (19.9 Å^2), this value merely reveals the fact that the lateral space occupied by the alkyl chains is wider when these have a disordered conformation than when they are fully stretched and laterally arranged in an orderly fashion. At the smectic B to smectic A phase transition, the alkyl chains, which are attached to the polymer backbones and so cannot move aside a long way, give up their interdigitated configuration and the smectic period grows to overstep significantly the length of the monomer repeat units.

Structure of PA-2C$_n$. Smectic A Structure. The dialkyl PA-2C$_{12}$ and PA-2C$_{18}$ compounds behave very much like their monoalkyl PA-C$_n$ counterparts. They both exhibit a smectic A structure (with periods of 28 and 39 Å at 70 °C): the former in the whole range of temperatures explored (from ambient up to the final melting point at about 130 °C) and the latter only above the phase transition detected by DSC (at 72 °C).

Smectic E Structure. The PA-2C$_{18}$ polymer at low temperature presents itself as an ordered smectic E phase, similar to that described earlier for the aqueous binary mixtures of rubidium soaps,[14] the thermotropic 4′-phenylbenzylidene-(4-amino-*n*-pentyl cinnamate),[15] and certain side-chain polymethacrylates bearing 4′-methoxybiphenyl mesogenic groups.[16] Its X-ray pattern (see Figure 1) contains two equidistant reflections in the small-angle region, related to the smectic layering of the molecules, and three rather sharp peaks in the wide-angle region, at 4.12, 3.7, and 3.0 Å, corresponding to the (110), (200), and (210) reflections from a two-dimensional rectangular lattice of cell parameters $a = 7.4$ Å and $b = 5.0$ Å. Though difficult to measure accurately owing to the width [of about $\Delta(2\theta) = 0.3°$ at $2\theta = 2.68°$, as estimated by a Lorentzian least-squares fit method] of the smectic reflections and to the presence of diffuse scattering in the small-angle region, the smectic period found (≅33 Å was nearly equal to that of PA-C$_{18}$ in the smectic B state. As shown in Figure 4, the alkyl chains, chemically coupled in pairs through the ammonium group, are arranged in a head to tail configuration and are standing upright in single layers separated by the polymer backbones. Laterally, they are packed according to a centered rectangular lattice, and their cross-sectional area, $a \times b/2 = 18.5$ Å^2, is very close to that of linear paraffin molecules in the crystalline state.[17]

Discussion and Conclusion

The present work shows that polymers with well-defined smectic liquid crystal structures can easily be obtained by simple neutralization of poly(acrylic acid) with linear-chain primary and secondary aliphatic amines. It shows in other words that the presence of rigid aromatic mesogenic pendant groups is not necessary for the formation of liquid crystals from poly(acrylic acid): liquid crystallinity can very well be obtained in a straightforward way by attaching simple alkyl chains onto the polymer backbones through ionic bonds. This facility obviously results from the adequate association of nonpolar chains with ionic ammonium acrylate groups, which enhances the amphiphilic character and emphasizes the tendency of the polymer to intramolecular segregation. Of course, alkylammonium polyacrylates are inclined to degrade thermally rather easily; however, as their liquid crystal phases show up at low temperatures, this weakness does not give rise to serious disadvantages.

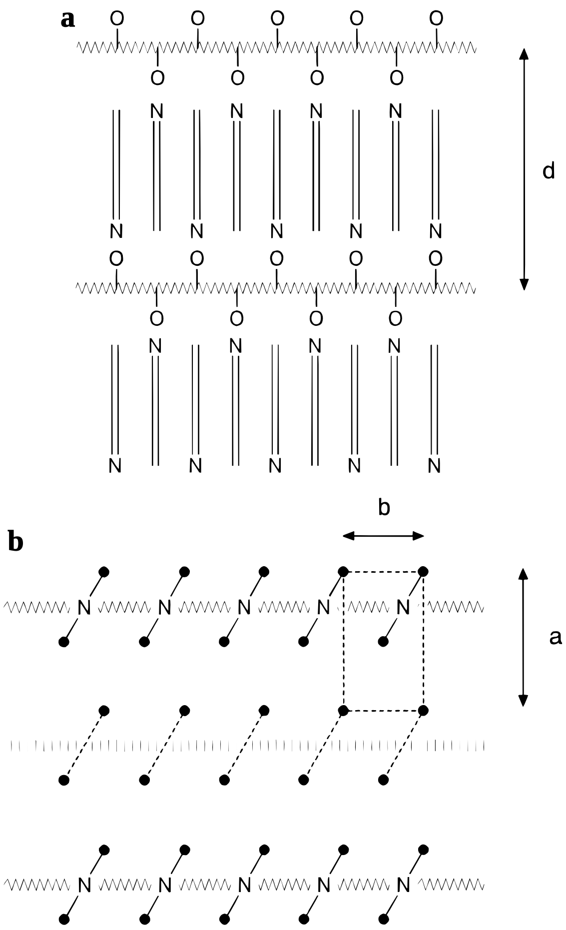

Figure 4. Schematic representation of the smectic E structure of the dialkyl PA-2C$_n$ compounds. (a) Front view of the smectic layering of period *d*. Standing upright in single layers, the alkyl chains (—) are joined in pairs and arranged in a head to tail configuration. The polymer backbones (〰) are inserted between the alkyl sublayers with the carboxylate anions (O) pointing alternately up and down to face the ammonium cations (N). (b) Top view of one smectic layer. The alkyl chains (●) are joined in pairs and packed according to a rectangular lattice of cell parameters *a* and *b*. The ammonium cations are lying in rows on the upper (N) and lower (omitted for clarity) surface of the alkyl sublayer. The polymer backbones are lying above (〰) and below (||) the alkyl sublayer. For the sake of simplicity, polymer backbones and rows of ammonium cations are both taken to be linear in shape.

At sufficiently high temperature, the liquid crystalline phases of the monoalkyl PA-C$_n$ and dialkyl PA-2C$_n$ polymers studied are all smectic A; at low temperatures, instead, they are smectic A only for the short-chain (C$_{12}$ and C$_{14}$) compounds, the others (C$_{16}$ and C$_{18}$) being smectic B or E. Quite clearly, the alkyl chains are able to arrange themselves in an orderly fashion within the smectic layers only when they are long enough and when the temperature is not too high; otherwise, they adopt a disordered conformation and arrange themselves in a random fashion. The ordered smectic phases observed are hexagonal in symmetry (smectic B) for the monoalkyl derivatives, with a cross-sectional area for the alkyl chains of 19.9 Å^2, and rectangular in symmetry (smectic E) for the dialkyl derivative, with a slightly smaller cross-sectional area of 18.5 Å^2. The pairing of the alkyl chains (*via* the ammonium group) in the dialkyl derivatives results in a denser packing, the dialkylammonium moiety taking up a hairpin configuration similar to that presented in the crystalline state by the polyethylene chains, which are folding back abruptly at the surface of their well-known lamellar single crystals through four twisted carbon−carbon covalent bonds.[18]

To discuss the smectic B and E phases observed, it is worth stressing that no three-dimensional reflections, corresponding to Miller indices all different from zero, could be detected in the X-ray patterns. As discussed recently in connection with other side-chain polymer liquid crystals,[19] this means that the smectic phases in question do not manifest long-range positional (other than stacking) correlations of the layers and cannot, therefore, be considered to be "smectic crystals". According to current views on the subject, these phases should then be declared "hexatic" in nature. But such an admission could not as yet be confirmed for polymers, owing to experimental difficulties related to the manufacture of monodomains answering to the special requirements of X-ray diffraction. In hexatic smectic liquid crystals, the positional ordering of the molecules within the layers does not extend over long distances, as opposed to the orientational ordering of the pieces of in-plane crystal lattice, which develops parallel to a common direction throughout the three-dimensional space.[12] It is only fair to add immediately that the smectic B and E phases observed might equally well be declared "disoriented" in nature, although such a description, well taken some time ago, does not seem to meet today with general acceptance. In phases of that kind, the pieces of in-plane crystal lattice would not, for some reason, be all oriented in a common direction inside the layers and consequently the smectic layers would not only glide but also rotate freely with respect to one another. In the present work, disorientation (loss of orientational ordering inside the layers) is presumably related to the presence of the polymer backbones between the layers, which disturb the long-range arrangement of the alkyl chains.

Our examination of the smectic B and smectic E phases, although successful in giving a fair description of the smectic layering and of the lateral arrangement of the alkyl chains inside the layers, has in fact been deficient in one important respect: it does not permit a detailed account of how the ammonium cations, the carboxylate anions and the polymer backbones are arranged between the layers of alkyl chains. The reason originates in the absence of three-dimensional positional correlations of the molecules, which weakens considerably the experimental investigations by X-ray diffraction. Hence our discussion of the arrangement of these species comes down to a tentative comment proceeding by analogy with what is known of the structure of other smectic side-chain liquid-crystalline polymers and standing as follows. (1) As established by neutron scattering from nonionic liquid-crystalline polyacrylates, the polymer backbones (which are rather flexible) are not only confined to the spaces between the smectic layers but are also segregated from the spacers, locating themselves in the very middle of the spacer sublayers.[20] Such must very likely be also the case of the ionic polyacrylates in the present work, especially since the polymer backbones are now connected to the side groups through ionic bonds which are more flexible, in both direction and length, than the covalent bonds of the nonionic polyacrylates and have therefore more freedom to deform and reach two-dimensional conformations. (2) As shown by a Monte Carlo simulation method, polymer chains in two-dimensional melts have a tendency to align themselves locally because entanglements are not permitted; they then have, for entropic reasons, a tendency to segregate from one another and locate themselves in juxtaposed patches statically different and dynamically varying in shape.[21] For the polymers studied in the present work (having a degree of polymerization of about 70), each patch would cover an area of about $70 \times 19.9 \cong 1400$ Å^2, that is, would have linear dimensions compatible with the experimentally observed ($\approx$70 Å) range of the in-layer positional ordering of the molecules. Quite probably, the in-layer positional correlations of the alkyl chains are not controlled by thermodynamics (describing the behavior of two-dimensional systems, and particularly their melting process through an intermediate state of hexatic ordering[22]) but rather by the presence of polymer backbones of limited length.

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References and Notes

(1) Paleos, C. M. *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 159.
(2) Tschierske, C. *Prog. Polym. Sci.* **1996**, *21*, 775.
(3) Ujiie, S.; Iimura, K. *Chem. Lett.* **1991**, *411*. Ujiie, S.; Tanaka, Y.; Iimura, K. *Chem. Lett.* **1991**, 1037.
(4) Antonietti, M.; Conrad, J. *Angew. Chem., Int. Engl. Ed.* **1994**, *33*, 1869.
(5) Bazuin, C. G.; Tork, A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1996**, *37*, 776. Bazuin, C. G.; Brandys, F. A.; Eve, T. M.; Plante, M. *Macromol. Symp.* **1994**, *84*, 183. Bazuin, C. G.; Tork, A. *Macromolecules* **1995**, *28*, 8877.
(6) Tal'rose, R. V.; Kuptsov, S. A.; Sycheva, T. I.; Bezborodov, V. S.; Platé, A. *Macromolecules* **1995**, *28*, 8689.
(7) Paleos, C. M.; Tsiourvas, D.; Dais, P. *Liq. Cryst.* **1989**, *5*, 1747. Tsiourvas, D.; Arkas, M.; Paleos, C. M.; Skoulios, A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1997**, *38*, 223.
(8) Kabanov, V. A. In *Polymerization in Organized Media*; Paleos, C. M., Ed.; Gordon and Breach Publishers: Philadelphia, Paris, 1992.
(9) Tsiourvas, D.; Paleos, C. M.; Anastassopoulou, J.; Theophanides, T. *Appl. Spectrosc.* **1995**, *49*, 1311.
(10) Vincent, J. M.; Skoulios, A. *Acta Crystallogr.* **1966**, *20*, 432.
(11) Ailhaud, H.; Gallot, Y.; Skoulios, A. *Compt. Rend. Acad. Sci. Paris* **1968**, *267*, 139.
(12) De Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, U.K., 1993.
(13) Guillon, D.; Skoulios, A.; Benattar, J. J. *J. Phys. Fr.* **1986**, *47*, 133.
(14) Vincent, J. M.; Skoulios, A. *Acta Crystallogr.* **1966**, *20*, 441.
(15) Doucet, J.; Levelut, A. M.; Lambert, M.; Liébert, L.; Strzelecki, L. *J. Phys. Fr.* **1975**, *36*, C1−13.
(16) Duran, R.; Guillon, D.; Gramain, P.; Skoulios, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 181.
(17) Robertson, J. M. *Organic Crystals and Molecules*; Cornell University Press: Ithaca, NY, 1953.
(18) Davé, R. S.; Farmer, B. L. *Polymer* **1988**, *29*, 1544.
(19) Davidson, P.; Levelut, A. M. *Liq. Cryst.* **1992**, *11*, 469.
(20) Noirez, L. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 525.
(21) Carmesin, I.; Kremer, K. *J. Phys. Fr.* **1990**, *51*, 915.
(22) Kosterlitz, J. M.; Thouless, D. J. *J. Phys.* **1973**, *C 6*, 1181. Strandburg, K. J. *Rev. Mod. Phys.* **1988**, *60*, 161.

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