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Smectic liquid crystalline character of *n*-alkylammonium pyroglutamates

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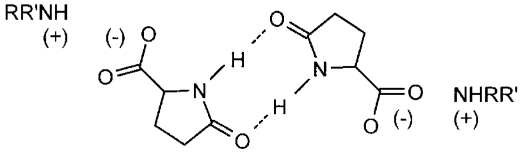
A series of *n*-alkylammonium and *n*-dialkylammonium pyroglutamates were synthesized and characterized. Their thermotropic liquid crystal behaviour was investigated using differential scanning calorimetry and optical microscopy. The structures of their crystal and smectic A phases were studied by X-ray diffraction.

1. Introduction

A facile method of obtaining smectic liquid crystals is to neutralize long chain *n*-alkylamines with halogen acids to form *n*-alkylammonium halides [1–3]. Upon interaction with halides of divalent metals, these in turn produce salts, of the general formula $(RNH_3)_2MX_4$, which also exhibit liquid crystalline behaviour [4, 5]. Smectic A phases are obtained as well with alkylammonium alkanesulphonates [6] prepared by interaction of long chain alkylamines with short chain alkanesulphonic acids (C_1 to C_4) in equimolar proportions. Incidentally, *N*-alkylammonium salts of polyacrylic or polymaleic acids owe their liquid crystalline character [7, 8] to the polymeric nature of the counterion, as supported by the fact that their monomeric analogues (for instance, propanoates) are not mesomorphic [7]. The present paper investigates the case of *n*-alkylammonium salts of pyroglutamic acid, in which the pyroglutamate anion is not only bulky, but furthermore is susceptible to dimerization through hydrogen bonding.



R = C_{12} - C_{18}

R' = H, C_{12}, C_{18}

2. Experimental

2.1. *Preparation of n-alkyl- and n-dialkyl-ammonium pyroglutamates*

L-Pyroglutamic acid [(*S*)-(-)-2-pyrrolidone-5-carboxylic acid], obtained from Aldrich, was recrystallized twice from ethanol. The salts of pyroglutamic acid with normal dodecyl, tetradecyl, hexadecyl, octadecyl, didodecyl and dioctadecyl amines were prepared by dissolving in ethanol equimolar quantities of the acid and the corresponding alkylamine and allowing them to react at room temperature. The precipitated salts were filtered off and recrystallized from ethyl acetate. The formation of salts was confirmed by FTIR (protonated NH group at 2800–2500 and 2200 cm^{-1} for the primary amines, carboxylate group at 1586 and 1390 cm^{-1}), NMR and elemental analysis. $C_{17}H_{34}O_3N_2$: calc. C 64.93, H 10.90, N 8.91; found C 65.04, H 10.96, N 8.87%. $C_{19}H_{38}O_3N_2$: calc. C 66.63, H 11.18, N 8.18; found C 65.94, H 11.45, N 8.05%. $C_{21}H_{42}N_2$: calc. C 68.06, H 11.42, N 7.56; found C 67.96, H 11.58, N 7.52%. $C_{23}H_{46}O_3N_2$: calc. C 69.30, H 11.63, N 7.03; found C 69.30, H 11.80, N 6.92%. $C_{29}H_{58}O_3N_2$: calc. C 72.15, H 12.11, N 5.80; found C 72.27, H 12.22, N 5.72%. $C_{41}H_{82}O_3N_2$: calc. C 75.63, H 12.69, N 4.30; found C 75.77, H 12.76, N 4.22%.

2.2. *Characterization*

The liquid crystalline character of the salts was studied using a LEITZ WETZLAR polarizing microscope equipped with a hot stage and a Linkam TMS 91 controller. The polymorphic behaviour was investigated

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Figure 1. Fan-shaped smectic texture of *n*-hexadecylammonium pyroglutamate observed on cooling from the isotropic melt (×200).

using a TA DSC-10 instrument with heating and cooling rates of 10°C min^{-1}. Thermogravimetric analysis was performed with a TA TGA-2050 instrument. The liquid crystalline structures were established by X-ray diffraction. Powder samples in Lindemann capillaries were analysed using a Guinier focusing camera equipped with a bent-quartz monochromator ($\mathrm{CuK}_{\alpha 1}$ radiation from an INEL X-ray generator) and an INSTEC hot stage. Diffraction patterns were registered using an INEL CPS-120 curved position-sensitive detector.

3. Results and discussion

3.1. *Thermal stability*

The salts, heated dynamically at a rate of 10°C min^{-1}, exhibited satisfactory thermal stability at temperatures below 140°C. At that particular temperature, the least stable C_{12} derivative was found to have lost less than 0.2% of its weight. Isothermal heating at 100°C for three hours did result in a weight loss of about 7%. Prolonged heating at high temperature must therefore be avoided.

3.2. *Thermal and optical studies*

The mesomorphic character of the salts was investigated by polarizing optical microscopy. On heating, the materials exhibited a phase transition from the crystal into a liquid crystal phase, followed by a second transition from the liquid crystal into the isotropic melt. Upon cooling from the melt, well-developed fan-shaped smectic textures were obtained as shown in figure 1. When observed between glass plates treated with octadecyltrichlorosilane to achieve homeotropic alignment, the liquid crystalline samples showed no birefringence, suggesting the presence of a uniaxial phase, probably smectic A. Among the compounds studied, the dioctadecyl derivative exhibited monotropic smectic textures appearing only upon cooling from the isotropic melt.

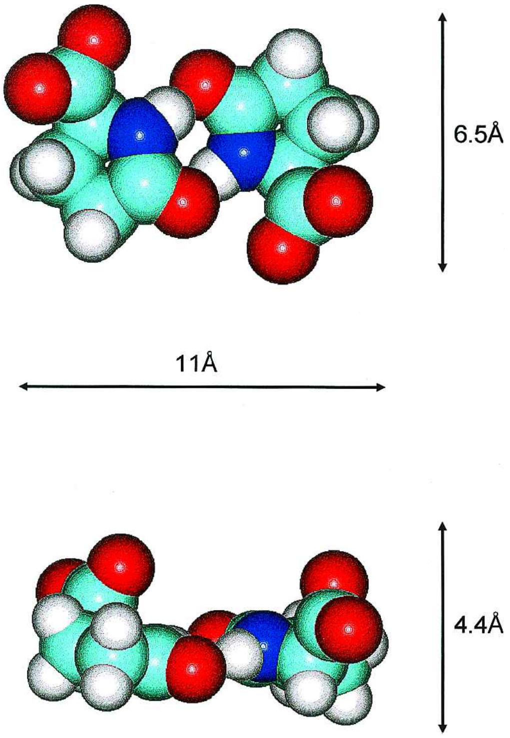

Figure 4. Dimerized pyroglutamic head groups: top and side view of the Hyperchem molecular model (nitrogen in dark blue, carbon in light blue, hydrogen in grey and oxygen in red) with dimensions shown. The carboxylate groups of the dimer are pointing to the same side with respect to the average plane of the pyrrolidone moiety. The volume of two polar heads ($4.4 \times 6.5 \times 11 = 314.6$ Å^3) is in fair agreement with that (295.7 Å^3) deduced from the known density of L-pyroglutamic acid: 1.45 g cm^{-3} [10].

The DSC experiments were in agreement with the optical observations. From measurements summarized in the table it emerges that the transition temperatures

Table. Transition temperatures (onset) and enthalpies of mono- and di-alkylammonium pyroglutamates, measured by DSC upon heating. Subscripts s and i refer to the crystal–smectic and smectic–isotropic phase transitions, respectively.

R	R'	T_s/°C	T_i/°C	ΔH_s/kJ mol^{-1}	ΔH_i/kJ mol^{-1}
C_{12}	H	72.5	113.0	41.5	0.8
C_{14}	H	81.0	145.5	50.0	1.0
C_{16}	H	86.5	158.0	59.0	1.1
C_{18}	H	91.0	162.0	68.5	1.2
C_{12}	C_{12}	57.5	76.5	63.5	4.8

as well as the width of the mesomorphic ranges increase for the monoalkyl and decrease for the dialkyl derivatives as a function of increasing alkyl chain length. For the monoalkyl derivatives, the molar enthalpy of the crystal-to-smectic phase transition is a linear function of the number of carbon atoms in the alkyl chains (figure 2), according to the equation ΔH (kJ mol^{-1}) $= -2.8_{\pm 1.2} + 4.5_{\pm 0.1}\, n$. The slope of the straight line corresponds to a melting enthalpy of 4.5 ± 0.1 kJ per methylene group, slightly larger than but still consistent with that (≈ 4.1 kJ) usually found for *n*-paraffins. The negative value of the enthalpy extrapolated to $n = 0$ suggests that the ordering of the polar head groups is stabilized at the transition from the crystal to the liquid crystal phase. The corresponding entropy (11.3 ± 0.2 J K^{-1} per methylene group) is identical to that (≈ 11.1 J K^{-1}) of *n*-paraffins. As for the transition enthalpy from the smectic to the isotropic liquid, it is small and independent of the chain length, as expected.

3.3. *Structural studies*

The polymorphic behaviour observed by optical microscopy and differential scanning calorimetry was confirmed by X-ray diffraction. The X-ray patterns of the crystal phases of the monoalkylammonium pyroglutamates show four sharp equidistant reflections in the small angle region, characteristic of a lamellar arrangement of the molecules; they further show quite a few sharp reflections in the wide angle region, indicative of a three-dimensional crystal ordering. Independent of temperature, the lamellar periods *d* are close to the length of the molecules in an all-*trans*, fully extended conformation (as estimated by molecular modelling using Hyperchem software); they vary linearly with *n* (figure 3) according to the equation $d(\text{Å}) = 8.8_{\pm 0.3} + 1.21_{\pm 0.02}\, n$. The slope of *d* versus *n* (2.42 Å per ethylene unit) is almost equal to the usual lengthening of all-*trans*, fully extended alkyl chains, suggesting that the alkyl chains in the crystal are interdigitated and stand almost upright with respect to the layers. The value of the *Y*-intercept (8.8 ± 0.3 Å) is close to twice the height of the pyroglutamate polar head groups laterally dimerized through hydrogen bonding (see figure 4). Dimerization is confirmed by FTIR spectroscopy from the presence of NH stretching vibrations at 3190–3200 cm^{-1} [9]. Quite probably therefore, the polar pyroglutamate head groups are arranged in double layers as shown in figure 5. The coverage of the layers by the molecules (6.5×11 Å $\cong 72$ Å^2, see figure 4) is equal to four times the known cross-sectional area (18–19 Å^2 [11]) of paraffin chains in the crystalline state, in perfect agreement with the structural model proposed.

The X-ray patterns of the *n*-alkylammonium pyroglutamic acid salts in the liquid crystalline state contain up to three sharp, equidistant reflections in the small angle region, indicative of a smectic layering, and a broad band at 4.6 Å related to the paraffin chains in a disordered conformation. The smectic spacings measured increase linearly with the number of carbon atoms in

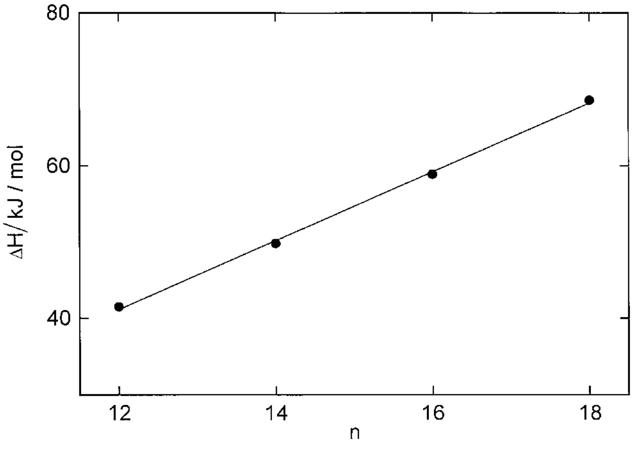

Figure 2. Crystal to smectic phase transition enthalpies for the *n*-alkylammonium pyroglutamates as a function of the number of carbon atoms (*n*) in the alkyl chains.

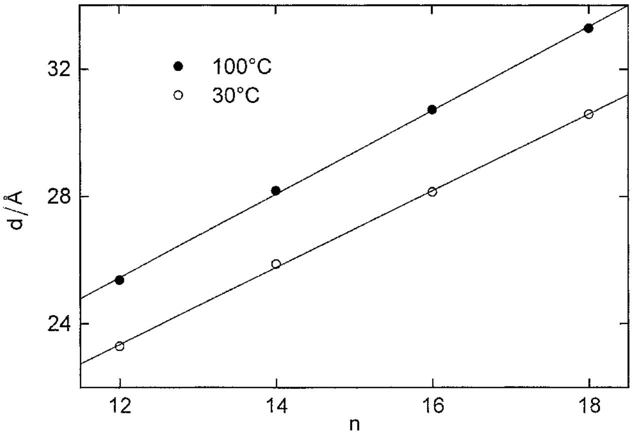

Figure 3. Chain-length dependence of the lamellar periods of the *n*-alkylammonium pyroglutamates in the crystalline state (○ at 30°C) and the smectic A state (● at 100°C).

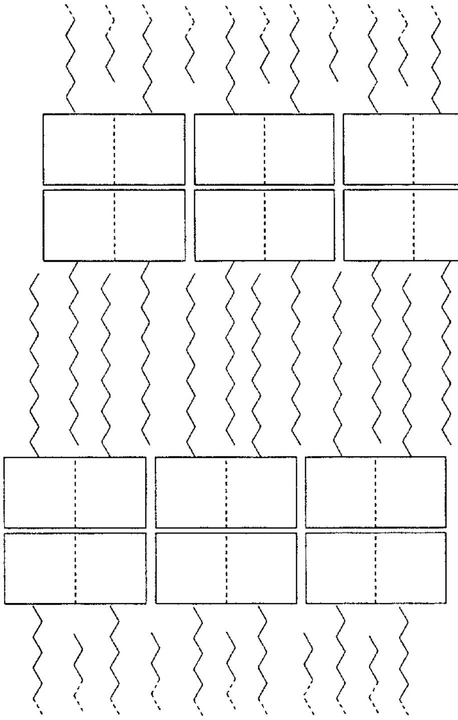

Figure 5. Schematic view of the lamellar structure of *n*-alkylammonium pyroglutamates in the crystalline state.

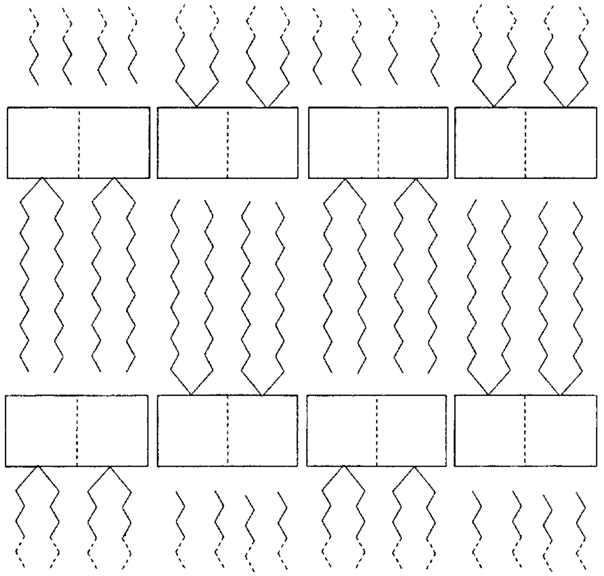

Figure 6. Schematic view of the lamellar structure of *n*-dialkylammonium pyroglutamates in the crystalline state.

the alkyl chains (figure 3) according to the equation: $d\,\text{Å} = 9.6_{\pm 0.3} + 1.32_{\pm 0.02}n$. The slope of the line, some 9% larger than that found for the crystal, reflects the volume increase of the alkyl chains upon melting at constant molecular area. The structure of the smectic phase is therefore similar to that of the crystal, the only difference being the disordered state of the alkyl chains.

The X-ray patterns of the *n*-dialkylammonium pyroglutamic acid salts in the crystalline state are similar to those of the monoalkyl derivatives, except that two of the sharp reflections in the wide angle region are particularly strong; located at 4.18 and 3.83 Å, respectively, they may easily be indexed as (1 1 0) and (2 0 0) reflections from a pseudo-centred rectangular lattice. These reflections suggest that the alkyl chains are laterally packed according to a rectangular lattice with cell parameters $a = 7.66$ and $b = 4.98$ Å at 25°C. The cross-sectional area of the alkyl chains, $a \times b/2 = 19.1$ Å^2, is again very close to that of normal paraffin chains in the crystalline state [11]. The lamellar period deduced from the small angle reflections grows linearly with n according to the equation: $d\,\text{Å} = 4.44 + 1.16n$ at 30°C. The Y-intercept of the straight line suggests that the polar heads are arranged in single layers as shown in figure 6.

In the mesomorphic state, the X-ray patterns of the dialkyl derivatives indicate the presence of a smectic A phase, with a smectic period increasing linearly with n according to the equation: $d\,(\text{Å}) = 7.21 + 1.31n$ at 80°C. From the slope of the straight line and using a value of about 28 Å^3 for the molecular volume of a methylene group at 80°C [12], one finds for the molecular area of the molten alkyl chains the reasonable value of $28/1.31 = 21.4$ Å^2.

4. Concluding remarks

The above results show that, in spite of the bulkiness of the dimerized ionic head group, the monoalkyl- and dialkyl-ammonium pyroglutamates are able to produce liquid crystalline phases in the same way as common alkylammonium halides and alkanesulphonate ammonium salts. This is probably due to the strong amphiphilic character of the molecules, originating from the added contributions of the ionic carboxylate groups and the polar pyrrolidone moieties, and also the right packing density of the head groups and alkyl chains. With this latter packing argument in mind, one may also easily understand why the head groups are arranged in single or double layers depending on the number of chains in the ammonium groups.

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