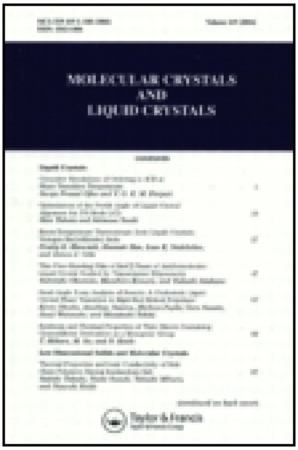

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Mesogenic Alkyl(Diammonium) Dicarboxylate Salts†

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Aliphatic α,ω-diamines have been reacted with α,ω-dicarboxylic acids to form 1:1 salts. Depending on the lengths of the alkyl segments of each moiety, the salts may be liquid crystalline. The observed mesophase is smectic A. A structural model is discussed which involves aggregation into distinct ionic and hydrocarbon regions.

INTRODUCTION

Organic ionic compounds exhibiting thermotropic liquid crystal behavior have been known since Vörlander's[1] work on alkali metal alkanoates. Ordered fluid phases were observed for butanoates and longer chain species. More recent work revealed the smectic behavior of long-chain primary ammonium metal halides,[2] and of some quaternary ammonium salts.[3] In particular, detailed x-ray diffraction measurements have enabled elucidation of the structure of long-chain primary ammonium halides in both crystal and fluid phases.[4,5] For these simple salts, $C_nH_{2n+1}NH_3^+X^-$, the solid melts to a smectic fluid when $n \geq 6$. The x-ray data show that even in the optically clear fluid, small ordered domains persist and a true isotropic melt is not obtained before the temperature of decomposition is reached. Busico and co-workers[5] propose a structural model in which layers of aligned hydrocarbon chains alternate with ionic layers. On melting, the ionic layers remain intact to minimize

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electrostatic energy, and are separated by layers containing the flexible hydrocarbon "tails." Experiments show that for very long chains, $n \geq 18$, the tendency of the chain to disorder competes with the tendency of the ionic layer to order. In such cases the layer structure is maintained but with a slightly less stable ionic layer arrangement. Similar studies have been made on a series of alkyldiammonium zinc halides[6] (1) and the analogous alkyldiamine zinc halide polymers[7] (2). X-ray diffraction data show a layered structure in the solids, similar to the previous model but with both chain ends fixed in rigid ionic layers.

$$(H_3\overset{+}{N}—(CH_2)_m—\overset{+}{N}H_3)ZnX_4^{2-} \qquad 1$$

$$(—H_2N—(CH_2)_m—NH_2—ZnX_2—)_n \qquad 2$$

In both cases smectic behavior in the fluid was only observed for the longest methylene chain studied, that is when m is 12.

Since both long-chain alkylammonium and alkanoate salts exhibit smectic liquid crystalline behavior, it was considered of interest to investigate alkyl(diammonium) dicarboxylate salts. In contrast to previously studied salts, these have hydrophobic segments covalently attached to both anionic and cationic groups. This type of nylon salt was first utilized by Carothers[8] in the preparation of high molecular weight polyamides for fiber production. Structural properties of the molten salt may be an important factor in the nature of the fibers drawn from the melt. The salts have been described as polymeric,[9] but no evidence has been given to support this conjecture. In comparison, Economy[10] showed the existence of polymeric chains of alkyldicarboxylate calcium salts. However, there has been no investigation of the thermotropic mesophase behavior of these halatopolymers nor of their long-range structural ordering.

Reported here are results of an investigation into the thermal behavior of a wide range of alkyl(diammonium) dicarboxylate salts.

EXPERIMENTAL

α,ω-Alkyldiamines and α,ω-alkyldicarboxylic acids were purchased from Aldrich Chemical Company. The salts (3) were prepared by mixing

$$H_3\overset{+}{N}—(CH_2)_n—\overset{+}{N}H_3\overset{-}{O}_2C—(CH_2)_m—C\overset{-}{O}_2 \qquad 3\ [n,m]$$

near saturated ethanol solutions containing equimolar quantities of diacid and diamine. The precipitated salts were recrystallized from ethanol or an ethanol–water mixture. Where literature data were available,[9] melting temperatures of the prepared salts showed good comparison. Confirmation of salt formation was given by FTIR spectra; ν ca. 3000 cm^{-1}, broad primary ammonium NH stretch; 2920 and 2850 cm^{-1} CH stretch; 2200 cm^{-1} primary ammonium NH stretch combination band; 1580 and 1410 cm^{-1} carboxylate ion stretch; 1530 and 1460 cm^{-1} primary ammonium NH bend.

Optical observations were made using a Reichert Thermovar polarizing light microscope fitted with a Mettler FP5/52 hot stage. Differential scanning calorimetry (DSC) was carried out using a Du Pont 910 DSC with a 990 thermal analyzer. X-ray diffraction measurements were made on a General Electric XRD-700 x-ray diffractometer. Samples were packed in quartz capillary tubes by repeated dropping onto a bench top through a 1 meter long glass tube. No heat treatment of the samples was possible due to their instability at elevated temperatures.

RESULTS AND DISCUSSION

Studies of the molten salts were complicated by the instability of the melt. Above the melting temperature a chemical reaction occurs with the evolution of gas. After an initial DSC heating run, subsequent scans show different but reproducible thermal behavior. Comparison with the DSC of the corresponding polyamide, prepared independently, confirm that decomposition is due to polyamide formation.

Optical observations were made at rapid heating and cooling rates to minimize sample decomposition. In certain instances, for example 3 [9,1] and 3 [10,0], conversion to polyamide was so rapid in the melt that accurate observation of transition temperatures was not possible. Those salts exhibiting enantiotropic liquid crystallinity gave shear opalescence of the melt on heating from the solid, and smectic fans typical of the smectic A phase were observed on cooling the isotropic liquid. Table I shows the range of salts synthesized and indicates those having a S_A phase. Only those salts containing one long and one relatively short alkyl chain are liquid crystalline. Interchange of the diammonium and dicarboxylate alkyl segments does not necessarily produce another mesogenic salt, for example compare 3 [4,10] and 3 [10,4]. Therefore mesogenic behavior cannot be solely dependent on the ratio of alkyl chain lengths. Transition temperatures for mesogenic and some nonmes-

TABLE I

Occurrence of liquid crystallinity in synthesized salts

$H_3\overset{+}{N}$—$(CH_2)_n$—$\overset{+}{N}H_3\bar{O}_2C$—$(CH_2)_m$—$C\bar{O}_2$ 3 [n,m]

m	0	1	2	3	4	8	10	14
n								
3		x				x		LC
4		x	x			x	LC	LC
5						x	x	LC
6	x				x	x	x	x
7	x					x	x	x
8	x	x	x	x	x	x		
9	x	LC	x	x				
10	LC	LC	x	x		x		
12	LC	LC	LC	x	x	x		x

x = not liquid crystalline
LC = S_A phase observed

ogenic salts were confirmed by DSC, and are given in Table II. In general, salts containing long alkyl chains exhibit one or two small endotherms due to solid–solid transitions. Melting and clearing transitions are sharp but may overlap with the broad endotherm observed above ca. 170°C due to decomposition to polyamide. Figure 1 shows a typical DSC trace for a liquid crystalline salt, 3 [12,0].

X-ray diffraction measurements were also hampered by the thermal instability of the salts. High temperature studies of the melt were not possible and attempts to rapidly quench the melt structure into a solid phase were unsuccessful. Data have been obtained for a series of salts in their room temperature solid form. For a salt with both alkyl chains relatively short, 3 [6,4], the x-ray diffraction pattern shows the solid to have a highly ordered crystalline structure. For those salts studied which have one, or both, long alkyl chains, the rings in the diffraction patterns suggest a lamellar structure. The number and the intensity of the rings observed vary for different salts. The measured spacings from these data are given in Table III. It is seen that even for a series of salts with one invariant long chain component, that is 3 [*x*,14], a consistent spacing is not found as *x* varies. In this series, the longest observed spacing decreases with the length of the shorter alkyldiamine chain. Also, there is no significant difference between the diffraction patterns of the salts which do exhibit a smectic phase on melting and those which do not.

As was described in the Introduction, previous structural models for long-chain alkylammonium and alkanoate salts involve aggregation into ionic and hydrocarbon layers. Analogous models were considered for the salts studied here. Both the

TABLE II

Transition temperatures of selected salts.

3 [n,m]	K → I or K → S_A (°C)	S_A → I(°C)
3,14	165	182
4,14	160	184
5,14	123	164
6,14	156	—
7,14	157	—
12,14	165	—
4,10	156	(140–146)[a]
5,10	108	—
9,0	234	—
9,1	ca. 180	(—)[a,b]
10,0	239	(—)[b]
10,1	149	160
12,0	ca. 180	190
12,1	146	168
12,2	188	(153–157)[a]
12,8	165 (157)[c]	—
6,4	196 (183)[c]	
	—	—

[a] Monotropic S_A formed on cooling isotropic melt.

[b] Conversion to polyamide prohibits observation of S_A → I transition temperature.

[c] Literature values for observed melting point.[9]

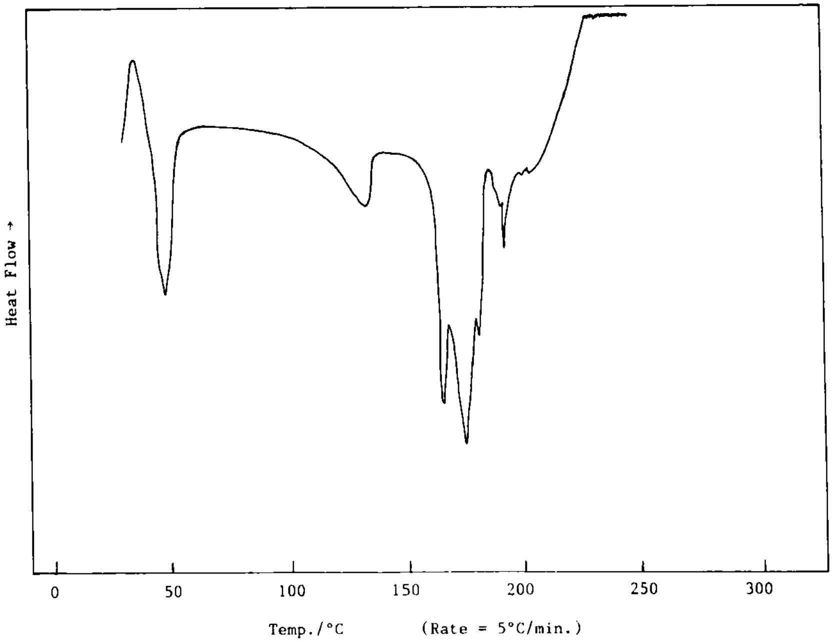

FIGURE 1 DSC trace for mesogenic salt, 3[12,0].

polymeric and lattice models of Figure 2 are highly ordered and expected to yield corresponding x-ray diffraction patterns. Constant values of a given layer spacing within a homologous series such as 3 [*x*,14] are also predicted. Obviously these models and the observed x-ray data for the solid salts are inconsistent. It is unlikely that the solid melts from a less ordered structure to give either of these structures in the smectic phase. However, some alternative lamellar structure which is maintained in the mesogenic melt is possible. A model is proposed which maintains the idea of aggregation of ionic and hydrocarbon moieties but allows disorder within the layers formed by this aggregation. Figure 3 shows how this model might apply

TABLE III

Measured spacings from x-ray diffraction ring patterns

3 [n,m]	Spacings (Å)			
3,14	20.0			
4,14	15.9			
5,14	ca. 22	17.3	11.3	7.6
6,14	11.7			
7,14	23.9	11.8[a]		
12,14	18.5			
12,1	16.1	8.1[a]		
10,1	14.7			

[a] Second order diffraction rings (weak intensity).

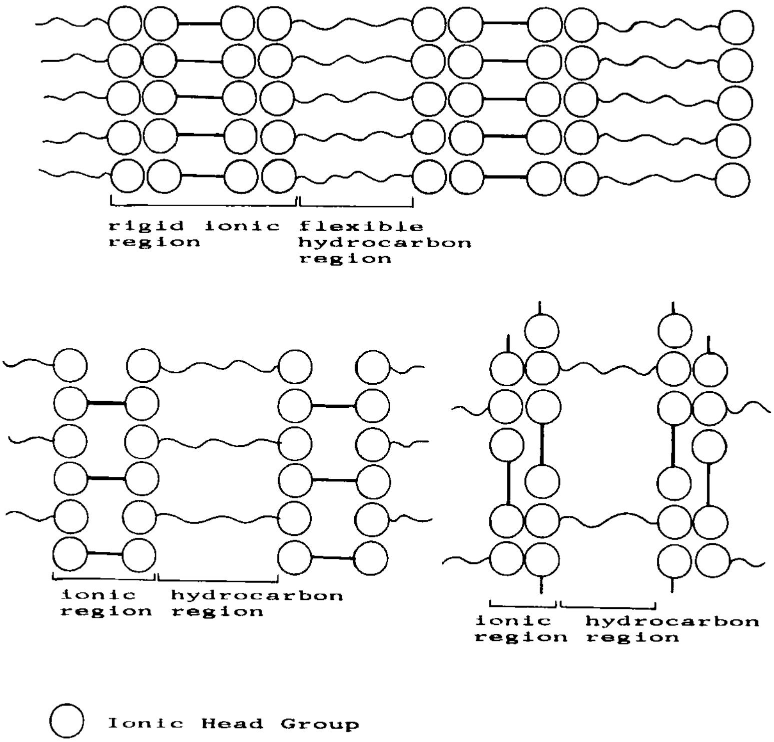

FIGURE 2 Possible lamellar structure models.

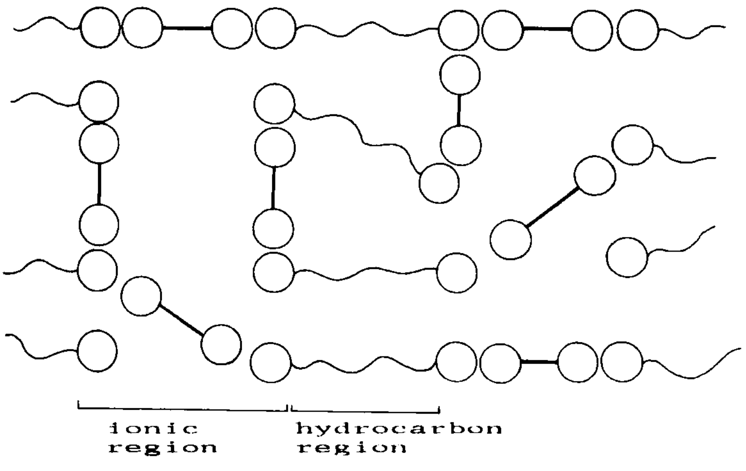

FIGURE 3 Proposed structural model for alkyl(diammonium)-dicarboxylate salts.

to one of the salts with one long and one short alkyl chain. It is expected that the amount of disorder, or variable association, allowed between chains bearing ionic end groups will vary with their length and flexibility, and also the nature of the end group. This is consistent with observed x-ray diffraction measurements giving variable layer spacings even when only one chain length is altered. Also, it may account for the difference in the number of x-ray diffraction rings seen when varying the alkyl groups. The model discounts previous assumptions of the polymeric nature of these salts. It may be assumed, following from earlier observations,[5] that some of the solid structural order is maintained in the mesogenic fluid. In this case rigid ionic layers containing a short alkyl chain, alternate with hydrocarbon regions made up of aligned alkyl chains having some flexibility. Within the ionic layer there is some disorder, as in the solid structure. It appears that a careful balance of the chain length of the two alkyl sections is required for the existence of a smectic melt. To maintain such order in the melt one of the alkyl groups must be short enough to be a rigid link between two ionic end groups, while the other must form a long hydrocarbon region. Under such conditions, the rigid ionic region and relatively flexible hydrocarbon region are significantly different such that segregation occurs and the lamellar structure is maintained.

CONCLUSION

Of the wide range of alkyl(diammonium) dicarboxylate salts synthesized and observed, a small number show mesogenic properties. The existence of a smectic A melt depends in part on the balance in lengths of the two alkyl chain segments. A structural model is proposed which involves aggregation into distinct ionic and hydrocarbon layers.

References

1. D. Vörlander, *Ber. dt. Chem. Gesell.*, **43**, 3120 (1910).
2. V. Busico *et al.*, *Mol. Cryst. Liq. Cryst.*, **78**, 221 (1981).
3. G. Margomenou-Leonidopolou, A. Malliaris and C. M. Paleos, *Thermochim. Acta*, **85**, 147 (1985).
4. V. Busico *et al.*, *J. Phys. Chem.*, **86**, 1033 (1982) and **87**, 1631 (1983).
5. V. Busico, A. Ferraro and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **128**, 243 (1985).
6. V. Busico and M. Vacatello, *Gazz. Chim. Ital.*, **111**, 13 and 235 (1981).
7. V. Busico *et al.*, *Colloid Poly. Sci.*, **261**, 224 (1983).
8. Wallace H. Carothers, U. S. Patent 2,130,947, Sept. 20, 1937.
9. D. D. Coffman *et al.*, *J. Pol. Sci.*, **2**, 306 (1947).
10. J. Economy, J. H. Mason and L. C. Wohrer, *J. Pol. Sci. Part A-1*, **8**, 2231 (1970).