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A. Malliaius [a], C. Christias [a], G. Margomenou-lmonidopoulou [a] & C. M. Paleos [a]

[a] N.R.C. “Demokritos”, Aghia Paraskevi Attikis, Greece

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SINGLE CHAIN QUATERNARY AMMONIUM SALTS EXHIBITING THERMOTROPIC MESOMORPHISM AND ORGANIZATION IN WATER

A. MALLIARIS*, C. CHRISTIAS, G. MARGOMENOU - LEONIDOPOULOU and C.M. PALEOS*
N.R.C. " Demokritos", Aghia Paraskevi Attikis, Greece
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ABSTRACT. In this paper the synthesis and orientational characteristics of two novel quaternary ammonium salts i.e. of dimethyl dodecyl n-propyl ammonium bromide and dimethyl dodecyl 3-hydroxypropyl ammonium bromide are reported. These salts, in addition to their ability to form organizates in water, also exhibit broad and stable smectic liquid crystalline phases.

INTRODUCTION. Recently it has been reported[1-3] that when liquid crystalline moieties are functionalized with appropiate polar heads they form lamellar and vesicular structures in water while on the other hand certain amphiphiles bearing two alkyl chains, as phospholipids[4], show thermotropic liquid crystalline character. In principle, therefore, molecules that organize in the bulk may also form organized aggregates in water. It would be in order therefore to investigate whether single chain quaternary ammonium salts widely known to form organizates in water and to induce orientation to liquid crystals[5] might also demonstrate thermotropic liquid crystalline character. Unfortunately commercially available n-alkyl trimethyl ammonium bromides such as C_9,

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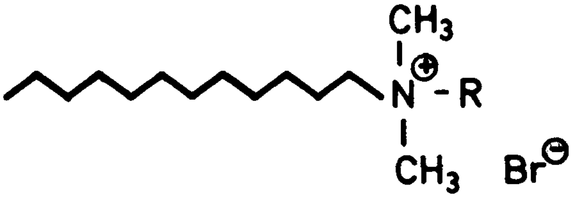
*To whom all correspondence should be addressed

C_{12},C_{14} and C_{16} are unstable and decompose before they melt. Therefore we have prepared two novel quaternary salts i.e. dimethyl dodecyl n-propyl ammonium bromide (I) and dimethyl dodecyl 3-hydroxypropyl ammonium bromide (II) and we have examined them with respect to their possible ability to organize in the bulk, forming thermotropic liquid crystals,



A

I : R, $CH_3CH_2CH_2$
II : R, $HOCH_2CH_2CH_2$

as well as in aqueous media.

<u>EXPERIMENTAL</u>. To 0.01 mole of dimethyl dodecyl amine dissolved in ethyl acetate 0,0125 mole of n-propyl bromide or 3-hydroxypropyl bromide respectively were added and the mixture was stirred for several hours. The precipitated salts were filtered, recrystallized twice from ethyl acetate and dried in vacum over phosphorus pentoxide. Analysis Calcd for I($C_{17}H_{38}NBr$): C, 60.75%; H, 11.30%; N, 4.16%. Found: C, 61.24%; H, 11.34%; N, 4.29%. Analysis Calcd for II ($C_{17}H_{38}NOBr$): C, 57.98% H, 10.79%; N, 3.97%. Found: C, 58,04%; H, 11.30% N, 4.03%.

Optical microscopy was performed with a Reichert"Thermopan" polarizing microscope whereas a Dupont 990 thermal analyser was used for differential scanning calorimetric (DSC) studies. Specific conductivity was measured with a Methohm E512 electrical conductometer in conjunction with a thermostated conductivity cell.

RESULTS AND DISCUSSION. Quaternization was performed in ethyl acetate since the reaction proceeds at relatively fast rates[5] and the salts precipitate easily due to the medium polarity of this solvent .

The thermotropic liquid crystalline behavior of these salts was established by optical microscopy. Thus on heating I on the hot-stage of the polarizing microscope with polarizer and analyzer crossed, it melted at about 57°C to a phase demonstrating almost complete optical extinction which,on further heating , was transformed to an isotropic phase at about 107°C. On displacing the cover slip,however, the partially extinct phase, occuring between 57° to 107°C, was transformed to a smectic focal conic texture which also became isotropic at 107°C. On a second heating, liquid crystalline phases were observed, i.e. by the melting of the crystals at about 57°C a smectic homogeneous phase appeared which was subsequently transformed to a focal conic and finally to an isotropic phase at 107°C. Identical behavior was observed during the third heating run indicating the thermal stability of this compound. Analogously, when II was heated on the hot-stage of the microscope it melted at about 50°C to a highly viscous fluid, of a homogenous smectic texture, which at about 82°C was transformed to a smectic focal conic structure. This phase became isotropic at about 154°C. The smectic phases were transformed to a partially homoetropic texture on pressing the cover slip. The same liquid crystalline textures were observed on second and third heating runs, a fact attributed to the thermal stability of the compound. The broader mesomorphic range and the higher mesomorphic-isotropic transition of II compared to I are apparently due to the stronger terminal forces because of the hydrogen bonding of the hydroxy group.

The findings of the polarizing microscopy were also confirmed by DSC. Thus, for a sample of I, which in the optical examination required two heating runs for a clear observation of its phase transitions, three heating runs were needed in DSC as shown in Fig.1. Thus the peaks corresponding to the various liquid crystalline transitions were made clearly discernible only during the third heating run in DSC. The endothermic peak at about 40°C shown in the second and third heating runs should apparently be attributed to a solid-solid transition. On the other hand a sample of II clearly exhibited all its phase transition peaks during its first heating run, Fig. 2.

We have in addition examined microscopically surfactants bearing C_9,C_{12},C_{14} and C_{16} long aliphatic chains and we found that they also exhibit broad liquid crystalline phases but as it was mentioned in the introduction these compounds decompose before they melt to isotropic phases.

I and II when dissolved in water formed micelles having critical micellar concentrations (cmc) 1.2 and 1.4 x 10^{-2}M respectively at 25°C. The hydroxy derivative has higher cmc than I apparently because of its higher hydrophilicity due to hydrogen bonding of the OH group.

In conclusion it appears that compounds of the general formula A where R is propyl or 3-hydroxypropyl form stable thermotropic liquid crystals and also aggregate in water forming micelles. Further study concerning the synthesis and characterization of a series of derivatives, appropriately functionalized in order to affect their properties either in the bulk or in aqueous media, is now under way in our laboratory. The study will also elucidate the structural criteria for the formation of molecular organizates by this type of compounds.

REFERENCES

1. Y. Okahata and Kunitake, J.Am.Chem.Soc., 101, 5231 (1979).
2. Y. Okahata and T. Kunitake, Ber. Bunsenges, Phys.Chem.,

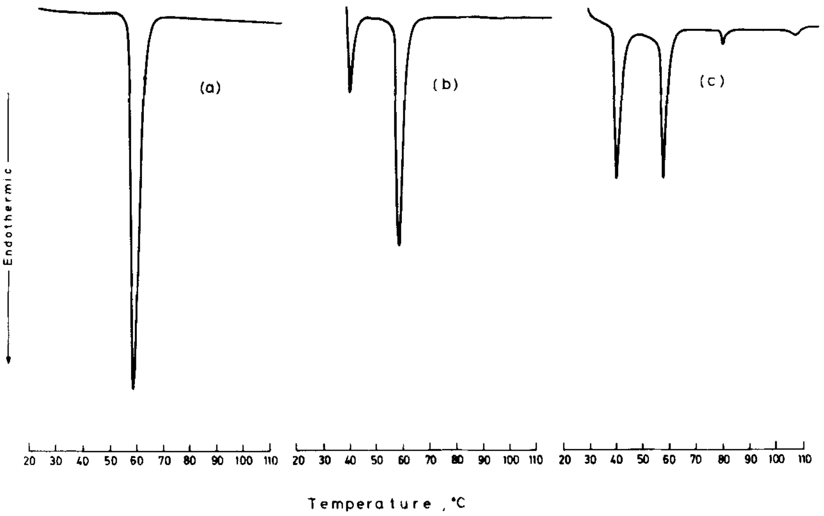


FIGURE 1. DSC trace of I: (a) first heating run; (b) second heating run; (c) third heating run.

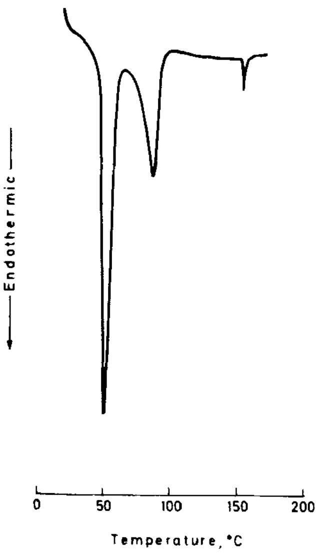


FIGURE 2. DSC trace of II.

84, 550 (1980).

3. T. Kunitake and Y.Okahata, J.Am. Chem. Soc., 102, 549 (1980).
4. D. Chapman, Pure and Appl. Chem., 50, 627 (1978) and references cited therein.
5. J. Cognard, Mol Cryst Liq. Cryst., Supplement 1, 1-78 (1982) and references cited therein.
6. J. Goerdeler in " Methoden der Organischen Chemie " (Houben-Weyl), Band XI/2, Georg Thieme Verlag, Stuttgart, 1958, p. 591.