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Mesomorphic-like character of long-chain amine salts formed by template neutralization on polyacids

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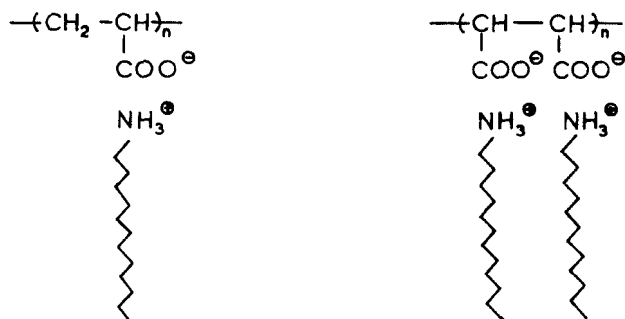
Several examples of monomeric and polymerized surfactants exhibiting liquid-crystalline behaviour have recently been reported. In the present investigation a novel process for the formation of liquid crystals is introduced, according to which certain functionalized polymers induce mesomorphism when they react with appropriate amines. For instance, neutralization of polyacrylic or polymaleic acid with long-chain amines forms alkylammonium salt surfactants which exhibit mesomorphic-like character. In this type of experiment, however, the known lamellar structure of alkylammonium salts was modified by this so-called template neutralization. The carboxylate groups, due to their location on the polymeric chain, appear to exert a topochemical effect on alkylammonium moieties which in turn affect the mesomorphic behaviour compared with that of common surfactants. The mesomorphic behaviour of these materials was established by optical microscopy and differential scanning calorimetry.

1. Introduction

In several recent reports it has been shown that long-chain aliphatic amine salts [1-5], quaternaries [6-10], carboxylates [11-16], *n*-alkyl functionalized carbohydrates [17-19] and various other salts [20-22] exhibit smectic-like character in the melt in addition to their well-known property of forming molecular organizes (micelles or vesicles) in water. This type of mesomorphism is attributed to the presence of distinct molecular portions that form layer structures consisting of polar and lipophilic sublayers. In principle this liquid-crystalline character can also be exhibited by polymers consisting of segregated polar and lipophilic moieties, as for instance *N*-alkyl or *N,N*-dialkyl polymaleamic derivatives [23]. Thus, in a recent study it has been found that *N,N*-didodecyl polymaleamic acid exhibits mesomorphic character, whereas there were ambiguities as far as the liquid-crystalline behaviour of mono-alkyl, dodecyl and octadecyl polymaleamic acid derivatives were concerned. In conjunction with this investigation mesomorphic phases were also observed when dodecylamine was reacted with polymaleic anhydride which was accidentally partially hydrolysed, or when polymaleic anhydride has reacted with an excess of the same amine. In both cases an *n*-alkylammonium salt was formed. It becomes evident, therefore, that the crucial parameter for the exhibition of this type of mesomorphism is the formation of long-chain alkylammonium salts by a 'template' neutralization of the carboxylic group of polymaleamic acid with these amines.

This observation triggered our interest for a more systematic study of the liquid crystallinity of materials resulting from template neutralization of long-chain amines with polyacids such as polyacrylic or polymaleic acid (Scheme 1). To our knowledge

this is the first time that the formation has been reported of a liquid-crystalline phase by such a template mode, in analogy to the template mechanism for the preparation of polymers [24, 25].



Scheme

2. Experimental

2.1. Formation of *n*-alkylammonium polyacrylates

Polyacrylic acid (Adrich; molecular weight 5000) was dissolved in ethanol and dodecyl- or octadecylamine was added to this solution in a 1:1 molar ratio. The immediately precipitating materials were filtered and extracted with acetone or methanol. The remaining salts were extensively dried. When didodecylamine was used for the neutralization of polyacrylic acid the procedure was modified; the amine was dissolved in chloroform and added to alcoholic polyacrylic acid solution. Solvents were distilled off and the remaining material was redissolved in alcohol and precipitated twice with acetone. The material was further purified by dissolving it in chloroform and reprecipitating with acetone.

2.2. Formation of *n*-alkylammonium polymaleates

Polymaleic anhydride [23] of molecular weight 7000, obtained by γ -radiation of maleic anhydride, was hydrolysed and subsequently neutralized with dodecylamine or octadecylamine. The precipitate of dodecyl derivative was purified by extraction with ethanol and the remaining material was extensively dried. The octadecyl derivative was dissolved in carbon tetrachloride and reprecipitated with ethanol.

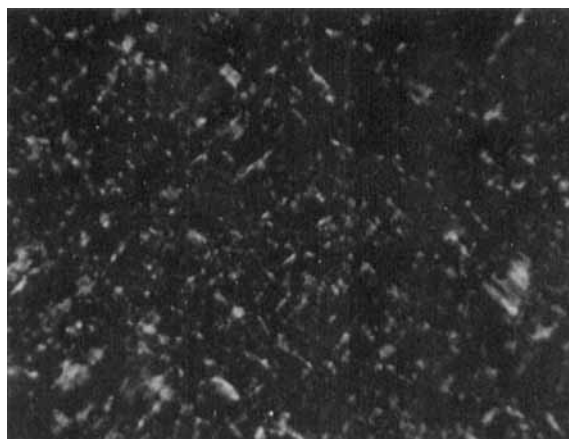
Neutralization of polyacrylic and polymaleic acid with the above amines was established by 1H -N.M.R. spectroscopy in deuterated chloroform ($CDCl_3$)- d_6 solutions using a Varian FT 80A spectrometer operating at 80 MHz.

2.3. Liquid crystalline characterization

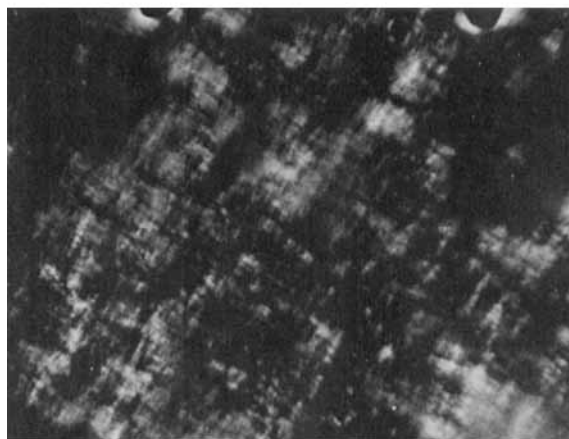
Optical microscopy studies were performed using a Reichert Thermopan microscope with crossed polarizers. Differential scanning calorimetry (D.S.C.) diagrams were obtained with a Du Pont 910 differential scanning calorimeter modulated with a R90 programmer at a scanning rate $1^\circ C \text{ min}^{-1}$.

3. Results and discussion

The striated textures of polyacrylic acid neutralized with dodecyl-, octadecyl- and didodecylamine are shown in figure 1 and were obtained on heating at about $140^\circ C$ (I), $150^\circ C$ (II) and $80^\circ C$ (III), respectively. It was not possible to obtain textures from



(I)



(II)

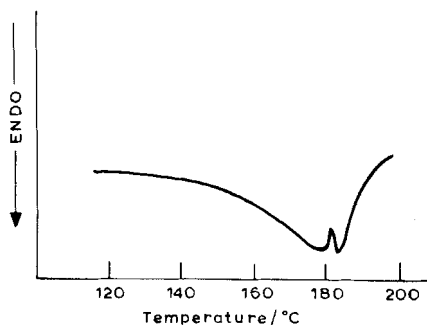


(III)

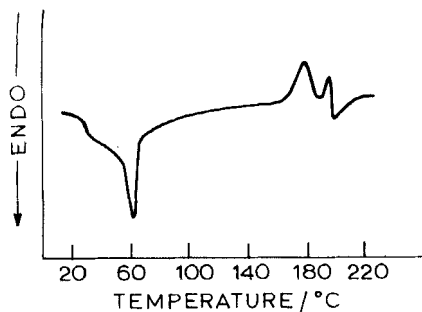
Figure 1. Optical microscopy textures of dodecylammonium (I), octadecylammonium (II) and didodecylammonium (III) polyacrylates.

the isotropic melt, since there was decomposition of the materials. These textures are not the typical mesomorphic-like textures of surfactants [1–22] since the lamellar structure of alkyl ammonium salts, established in general for surfactants, is formed and affected, in this case, by the presence of polycarboxylate counter ion. Carboxylates do not function as free counter ions, halides for instance, of monomeric ionic surfactants, since they are part of the polymeric chain. The formation of these textures was induced by pressing on the glass covers during microscopic observation, at temperatures exceeding the conformational melting of the chains, as determined by D.S.C. This finding is in agreement with the property of simple *n*-alkylammonium chloride surfactants [2] and also of quaternary ammonium surfactants [6, 7] in which ionic layers are stable up to temperatures well above the conformational disorder of alkyl chains. A monomeric counterpart of polyacrylic template, dodecyl ammonium propanoate, was also prepared and tested for the exhibition of liquid crystallinity. This salt does not show mesomorphic character, in contrast to the behaviour exhibited by analogous alkylammonium halides [1–5]. It is thus clear that the phenomenon of liquid crystallinity in surfactants is determined by the nature of the counter ion, monomeric or polymeric.

The mesomorphic-like behaviour of *n*-alkylammonium polyacrylates was also studied by D.S.C., as shown in figure 2. The rationalization of D.S.C. transitions was attempted by taking into consideration the thermal behaviour of simple *n*-dodecyl- and *n*-octadecylammonium chlorides [2] showing a three melting behaviour with transitions at 64, 185, 239 and 113, 163, 193°C, respectively. Thus, it may be assumed



(I)



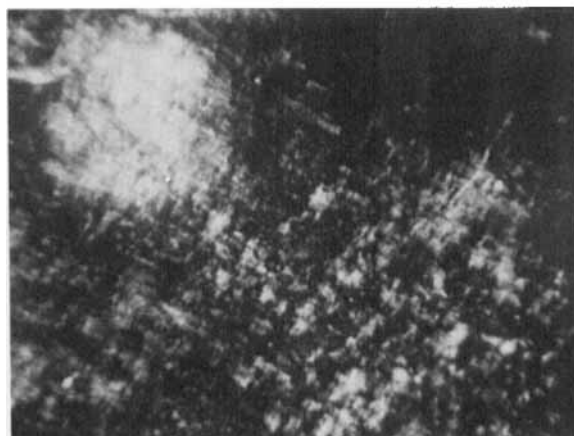
(II)

Figure 2. Differential scanning calorimetry diagrams of dodecylammonium (I) and octadecylammonium (II) polyacrylates.

that in the first thermogram of dodecyl polyacrylate the conformational melting transition of aliphatic chains is buried within the second transition (broad peak), which corresponds to the second transition of the above simple surfactant. The second transition corresponds to mesomorphic–isotropic transformation and is closely followed by the decarboxylation and/or destruction of polyacrylate. The peculiarity of the D.S.C. trace of octadecyl polyacrylate can be rationalized by the fact that poly-counter ions are solubilized, in some way, in octadecylammonium cation, and therefore their second and third transitions, in analogy with simple surfactants [2], must occur at much lower temperatures than those of dodecyl derivative. Due to the early isotropization of octadecylammonium cation, decarboxylation and/or destruction (generally favoured in isotropic media [26]) of polyacrylate occurs at lower temperatures. These latter transformations are exothermic phenomena and interfere with the endothermic phenomenon of the mesomorphic–isotropic transition. Thus, the exothermic and endothermic peaks of figure 2, observed after the first transition, result from the interference of these exothermic–endothermic phenomena. For didodecyl polyacrylate template, due to significant overlapping, distinct endothermic peaks were not observed.

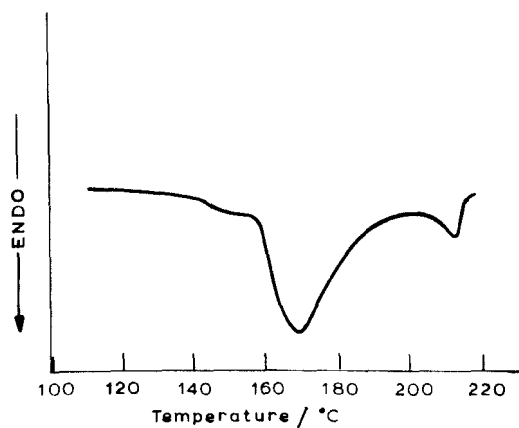


(IV)

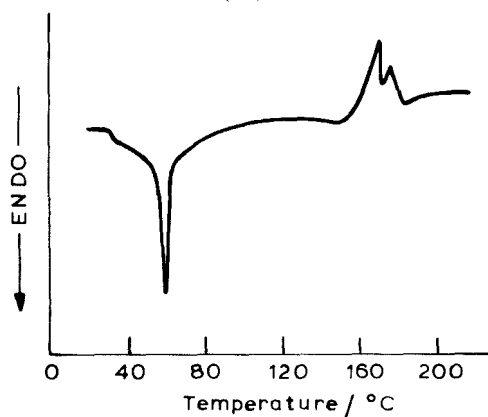


(V)

Figure 3. Textures of dodecylammonium (IV) and octadecylammonium (V) polymaleate.



(IV)



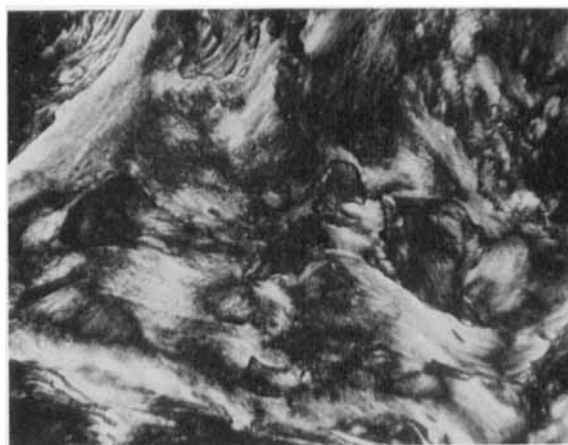
(V)

Figure 4. Differential scanning calorimetry diagrams of dodecylammonium (IV) and octadecylammonium (V) polymaleate.

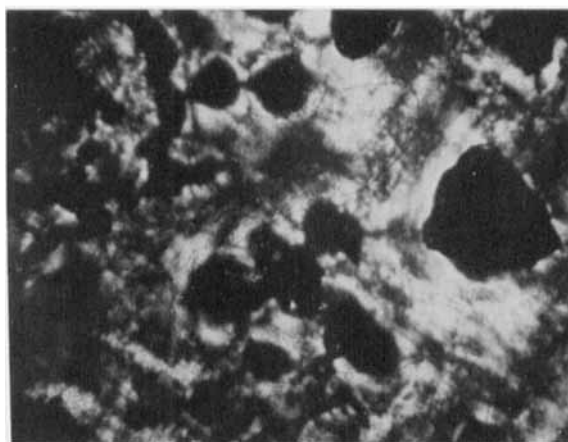
In a way similar to polyacrylic acid, polymaleic acid prepared from the hydrolysis of polymaleic anhydride [23] was neutralized with long-chain aliphatic amines such as dodecylamine or octadecylamine, and the salts were subjected to optical microscopy and D.S.C. characterization studies. The liquid-crystalline-like textures (figure 3) were similar to those of polyacrylic acid neutralized with the same amines. Also, the D.S.C. curves (figure 4) establish the thermotropic behaviour of these materials, showing striking similarity to those of polyacrylic acid salts. Dodecyl polymaleate shows a broad band at 160°C, in analogy to that of the corresponding polyacrylate derivative, and a peak at 200°C for the mesomorphic–isotropic transition. The complexity of the exothermic–endothermic peaks of octadecyl polymaleate can be rationalized in an analogous manner to octadecyl polyacrylate. It is seen that the trace of the curves are almost the same but the endothermic transitions are shifted from 58, 190 and 200°C for the polyacrylate to 55, 170 and 184°C for the polymaleate. Thus, although alkylammonium cations primarily determine the liquid-crystalline properties of these polyelectrolytes, one should not disregard the nature of polycounter ions in affecting these properties. This was exactly the case with these two polycarboxylates having similar molecular weights and very probably being amorphous.



(a)



(b)



(c)

Figure 5. Textures of octadecylammonium polyacrylate obtained at (a) 150, (b) 175 and (c) 195°C.

The differentiation in liquid-crystalline textures of this type of salt compared with simple alkylammonium salts is that carboxylate counter ions, attached on polymeric chains, have limited mobility. Thus, the organization of alkylammonium ions on polycarboxylates, in the form of liquid-crystalline phases, has to be affected by polymer structure in its broader sense (molecular weight, tacticity, linearity or branching and polymer chain mobility). In the case under investigation, the parameter that was modified was the chain conformational mobility with temperature increase. Within the mesomorphic phase the effect of temperature on this property of polymeric counter ions was exemplified by significant texture modification. Thus, in figure 5(a)–(c) are shown the textures of octadecyl polyacrylate at three different temperatures: 150, 175 and 195°C, respectively. In figure 5(c), in addition to increased thermal mobility, decarboxylation had occurred and the topochemical effect of the carboxylate group on alkylammonium ion has, at least, partially been lost.

4. Conclusion

We think that the above samples on template-induced mesomorphism established a novel method of liquid crystal formation. Further work is planned with diversified polymers coupled with appropriate reactants, in an attempt to show the potential of the method.

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