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Polymerization of head and tail methacrylate micelle-forming surfactants and thermotropic liquid-crystalline character of these monomers and their polymers

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The polymerization in micellar and isotropic media of a head–tail pair of surfactants, i.e. of monomers bearing the methacrylate group either at the polar head or at the end of the lipophilic chain is investigated in this study. Owing to the tailor-made structure of these monomers, any differentiations observed in their polymerization can be primarily attributed to topochemical effects resulting from the different location of the polymerizable group in the two monomers. Both monomers exhibited mesomorphic-like textures, which were examined by optical microscopy and DSC studies. Also, their respective polymers showed mesomorphic behaviour, which was found to be dependent on the position of the backbone relative to the polar head.

1. Introduction

It has been reported that certain long-chain polymerizable [1, 2] and non-polymerizable [3–6] quaternaries, as well as various other amphiphilic compounds [7–18], exhibit smectic-like character in the melt in addition to their well-known property of aggregating in water-forming micelles, vesicles or, in very concentrated solutions, liquid crystals. In the melt the lamellar structure of the solid phase, consisting of alternating lipophilic and polar layers, is practically preserved [4]. This is due to the fact that ionic-type bonding of the solid phase, between the quaternaries and the counter-ions, remains intact while the long aliphatic chains melt and the material appears macroscopically as a melt. The material therefore does not behave as a typical liquid-crystalline phase, and it is characterized as being a mesomorphic-like substance, in which free molecular motion of the surfactants is prevented. In lyotropic liquid-crystalline phases, water molecules interpenetrate the lamellar structure and associate with the polar head layers.

Extending our previous work [3] on the polymerization and aggregational as well as the organizational characteristics of polymerizable head and tail quaternary ammonium salt surfactants, we deal here with a comparative polymerization study of a ‘head–tail’ pair in which the polymerizable group is methacrylate (see the scheme). In contrast with the previous work in which the polymerizable groups at the head and the end of the hydrocarbon chain were different, one being $-(O=)C-O-CH=CH_2$ and the other $-O-(O=)C-CH=CH_2$, in this case both monomers bear the same polymerizable methacrylate group. Thus any differentiations observed in the polymerization of head and tail monomers and their polymer products can be attributed to the position of the polymerizable group. For comparison, the same polymerizations were conducted under isotropic conditions. The characterization of the polymers involved

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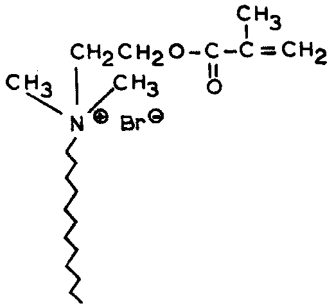
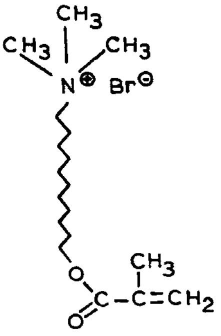


A



B

primarily their mesomorphic character as compared with that exhibited by the monomeric counterparts.

2. Experimental

2.1. *Synthesis of monomers*

ω-Bromoundecyl methacrylate was prepared by reacting ω-bromoundecanol with freshly distilled methacryloyl chloride, at room temperature, in the presence of triethylamine in dry ether solution. The molar ratio of reactants, i.e. of ω-bromoundecanol : methacryloyl chloride : triethylamine was (1 : 1·2 : 1·25) and the reaction mixture was allowed to stay for several hours at room temperature, with *p*-methoxyphenol as polymerization inhibitor, before it was worked up in the usual way, affording the monomer. The compound was used for the next quaternization step as received.

2.2. *Synthesis of A*

N,*N*-Dimethylaminoethyl methacrylate (0·01 mol) was quaternized by reacting with 0·011 mol of bromododecane, in acetone, at room temperature for several hours in the presence of inhibitor. The precipitated material was recrystallized from ethanol : ethyl acetate (1 : 10) solution and dried over phosphorus pentoxide. Its structure was established by proton N.M.R. Thus the assignment of the various resonances of the monomer relative to TMS based on peak intensities and homonuclear decoupling is as follows: CH_3, 0·95 (broad triplet due to virtual coupling); $(CH_2)_9$, 1·24; α-CH_2, 3·40(t); β-CH_2, 1·54(m); N–CH_3, 3·11(s); N–CH_2–CH_2–, 4·51(b); N–CH_2–CH_2–, 3·73(t). The methyl group of the vinyl moiety absorbs at δ 1·90, whereas the *geminal* protons appear at δ 6·08 (proton *trans* to methyl group) and 5·73 (proton *cis* to methyl group).

2.3. *Synthesis of B*

This monomer was prepared by conducting trimethylamine gas into a solution of ω-bromoundecy methacrylate in ethyl acetate at 0°C in the presence of polymerization inhibitor. The precipitated material was filtered and dried and its structure was also established by N.M.R. The resonances were assigned as follows: $(CH_2)_7$, 1·27; α-CH_2(–$N(CH_3)_3$), 3·30(t); β-CH_2(–$N(CH_3)_3$), 1·60(m); α-CH_2(–O–C–), 4·06(t); β-CH_2(–O–C–), 1·60(m); N–CH_3, 3·05(s). The methyl group of the vinyl residue absorbs at δ 1·87, whereas the *geminal* protons appear at δ 5·99 (proton *trans* to methyl group) and δ 5·65 (proton *cis* to methyl group).

The critical micelle concentration of A was found [19] to be equal to $5{\cdot}93 \times 10^{-3}$ mol l^{-1}. That of B was determined by the conductivity method employing a Metrohm Herisau E512 conductometer and found to be $5{\cdot}53 \times 10^{-3}$ mol l^{-1} at 25°C.

2.4. *Polymerization*

Polymerization was accomplished by employing a U.V. immersion lamp (2537 Å, 2·5 W) in a reactor that was cooled by circulating water. 0·05 M micellar or aqueous-alcoholic solutions were used, and polymerization was monitored by determining the decrease in N.M.R. intensities of protons of the methacrylate group.

Proton N.M.R. spectra were recorded on a Varian FT 80A spectrometer operating at 80 MHz. Solutions 0·1 M in DMSO-d_6 were used. Chemical shifts were measured relative to the deuteriated solvent at δ 2·49 from TMS.

2.5. *Mesomorphic phase characterization*

Optical-microscopic investigation was performed with a Reichert Thermopan polarizing microscope. D.S.C. studies were performed using a Du Pont 910 Calorimeter with a R90 Programmer at a scanning rate of 5°C/min.

2.6. *Characterization of polymers*

Molecular weights were determined with a Varian GPC chromatography system (2010 Liquid Chromatograph Isocratic Pump with a RI-3 Refractive Index Detector) employing Micropack TSK 4000 PW column.

3. Results and discussion

Polymerization in micellar media, which was performed photochemically, was completed in about 40 min for both head and tail monomers. In order to investigate the effect of micellar medium on polymerization, the same monomers were polymerized under isotropic conditions. In the latter case the destruction of the micellar structure was accomplished by the addition of 50 per cent ethanol. In this way it became possible to employ the same concentration as in micellar experiments, because if water had been used as solvent then concentrations below the critical micelle concentration would have had to be employed. Thus isotropic experiments in water could not be compared with micellar ones, at least as far as the concentration of the monomer is concerned. Nevertheless, the dielectric constant of water : alcohol 1 : 1 solution is about 50 at 20°C, compared with about 80 for water [20], and hence polymerization may be affected. However, since the addition of a sufficient quantity of ethanol eliminates the effect of topochemical factors, the observed differentiations in polymerization and polymer products should be attributed to the medium only. A major differentiation observed during polymerization is that, while polymers remain practically soluble up to the completion of polymerization in micellar media, partial precipitation does occur in isotropic experiments with the head methacrylate. For the same head monomer a slight turbidity is observed during polymerization. The precipitation in isotropic media may be attributed to a branched polymer, whose formation may be favoured in this case. Addition of ethanol results in complete dissolution of the polymers resulting from the isotropic polymerization.

Molecular weights that were determined in aqueous media by G.P.C. were found to be greater than 300 000 for both the micellar and isotropically obtained polymers (except for the head polymer, which precipitates under isotropic conditions). Since in these preliminary experiments the aggregation situation of the polymers is not known, one cannot decide whether high-molecular-weight polymer formation, as determined by G.P.C., is attributed to intermicellar polymerization or simply to the assembly of the macromolecules. Further work is in progress for determining molecular weights by modifying the eluent solvents in G.P.C. and by measuring the aggregation numbers for both monomeric and micellar solutions.

The exhibition of mesomorphic-like character by the monomers was expected in general since several long-chain functionalized quaternary ammonium salts have been reported to show liquid-crystalline properties [1–6]. Similar mesomorphic behaviour was also exhibited by other classes of compounds exhibiting distinct lipophilic and hydrophilic moeities. It is precisely this feature that induces the formation of lamellar structures in both the solid phase and in the melt. Thus smectic behavior has been exhibited by metal carboxylates [7, 12], *n*-alkylammonium halides [8, 21] and bis(*n*-alkylammonium) salts [22]. For quaternary ammonium salts, it has previously been established [5] that the replacement of a methyl group in *n*-alkyltrimethylammonium salts with functional groups of greater lipophilicity and specifically (in this case with the polymerizable groups $-CH_2C-O-CH=CH_2$, $-CH_2CH_2-O-(O=)C-CH=CH_2$ or $-CH_2CH_2-O-(O=)C-C(CH_3)=CH_2$) lowers their clearing point, and therefore decomposition does not occur before the clearing point. In line with this observation is the fact that the clearing point of the tail monomer is higher than that of the head monomer. Figure 1 depicts the mesomorphic textures, with spherulitic domains, of monomers A and B observed during their cooling from the isotropic melt. The microphotograph of monomer A was taken at 82°C and that of B at 110°C during their cooling cycle from the isotropic melt. These textures are not typical smectic, as also discussed in §1 for other quaternaries [2–6], since ionic bonding is preserved in the mesomorphic range. Thus materials do not melt immediately following the first transition temperature, as determined by D.S.C., and therefore mesomorphic-like textures are not observed. Without being a prerequisite, the appearance of mesomorphic phase is induced by exerting pressure on the glass covers, during microscopic observation, at temperatures exceeding the conformational melting of the chains as determined by D.S.C. However melting does occur at higher temperatures, without pressure, within the mesomorphic phase as determined by D.S.C.

The thermotropic behaviour of the monomers is also established by DSC diagrams, as shown in figure 2, with phase transitions corresponding to microscopic observations, at least as far as their clearing point is concerned. In this transition the complication of the preservation of ionic bonding during solid–mesomorphic transition apparently does not exist.

The position of the polymerizable group with respect to the polar head significantly affected the mesomorphic character of polymerized surfactants, which in general were broader than their monomeric counterparts. Thus, as shown in figure 3, the polymer resulting from monomer B, with the backbone at the end of the lipophilic chain, exhibited a broader and more thermally stable mesomorphic phase than that resulting from the monomer with the methacrylate group at the head. However, even in the case with the backbone at the lipophilic end, there is significant modification

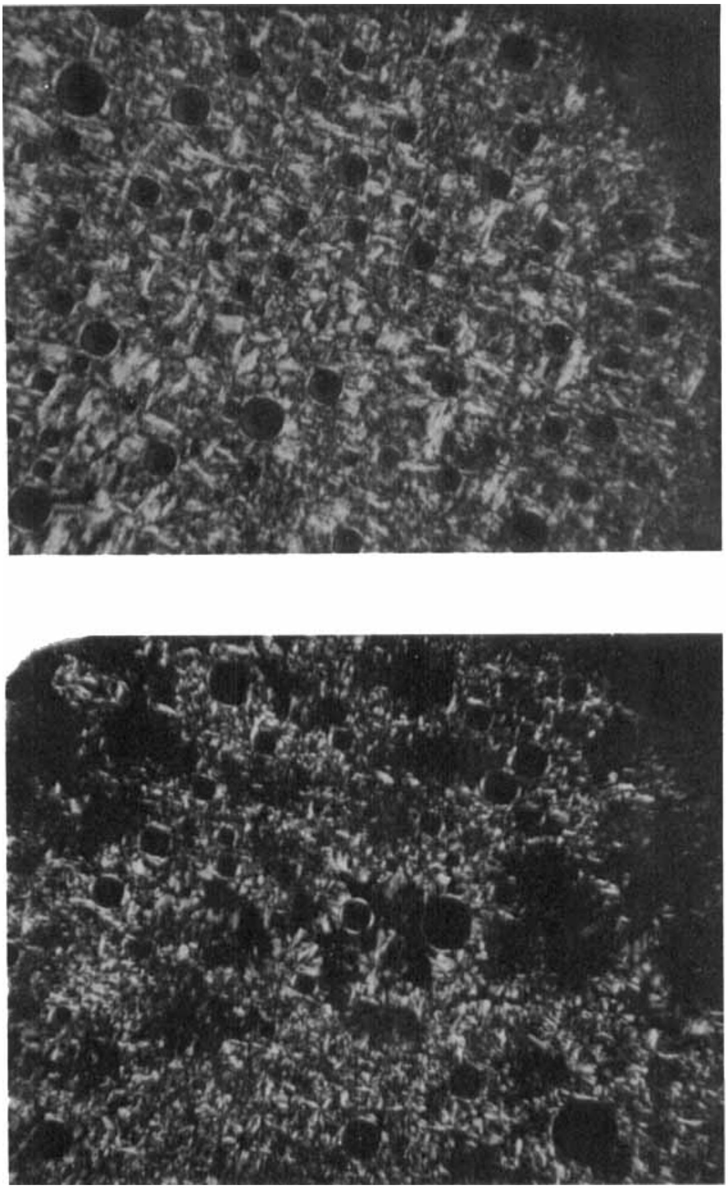


Figure 1. Mesomorphic-like textures of monomers A and B under crossed polarizers.

of the texture, with spherulitic domains disappearing, as compared with that of its corresponding monomer. The binding of the aliphatic chains at the backbone and the limitation of free movement possibly result in a distortion of the lamellar structure, leading to changes in the texture. For the polymer resulting from the head monomer, the texture is destroyed even before the clearing point is reached. This shows the same behaviour as the polymer derived from the monomer [3] bearing the polymerizable group $-CH_2C(=O)-O-CH=CH_2$ at the polar head. In the latter case, in which the spacer is shorter than that of monomer A, a glassy polymer

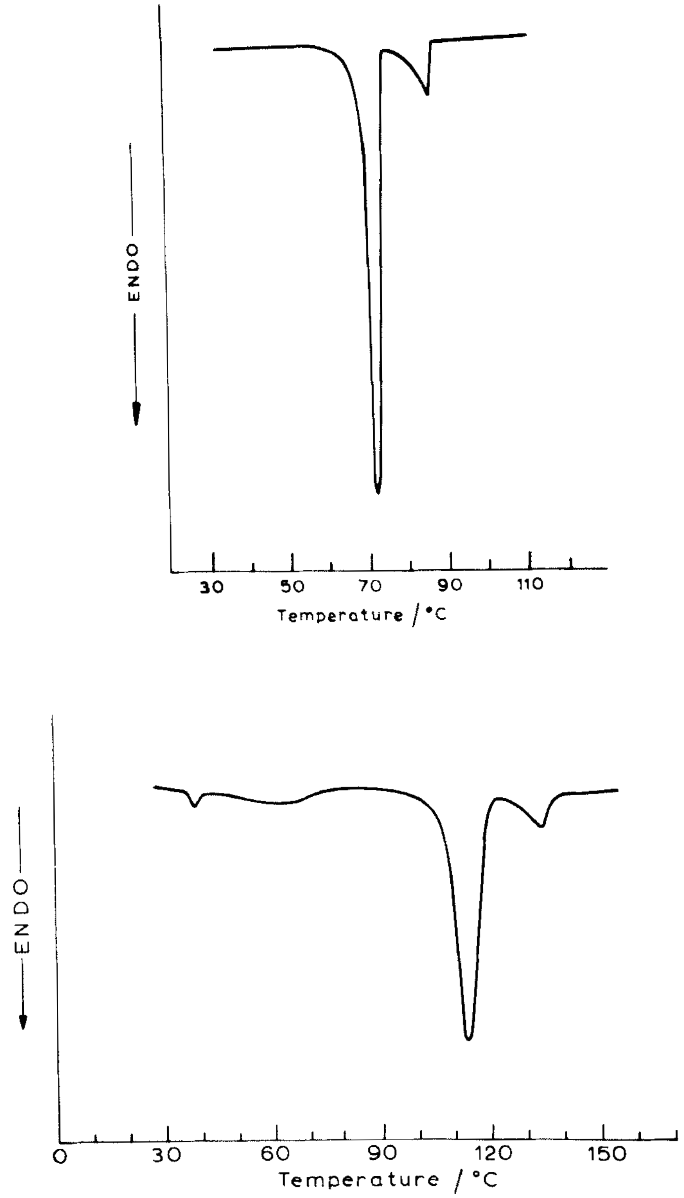


Figure 2. D.S.C. diagrams of monomers A and B.

is obtained, which completely decomposes before melting. It has also been found that the acrylate counterpart [3] of the tail methacrylate afforded a polymer that exhibited a thermally stable mesomorphic phase. Thus, for these polymer surfactants, bearing the backbone near the polar quaternary head, decomposition is a common property. In this case the unfavourable interaction, caused by the proximity of the positively charged quaternary nitrogens owing to their attachment to the backbone, is relieved by the destruction of the polymer.

The D.S.C. diagrams of head and tail polymers, obtained under micellar conditions, are shown in figures 4 and 5. In line with microscopic observations, the

Figure 3. Mesomorphic texture of the polymer derived from monomer B under micellar conditions.

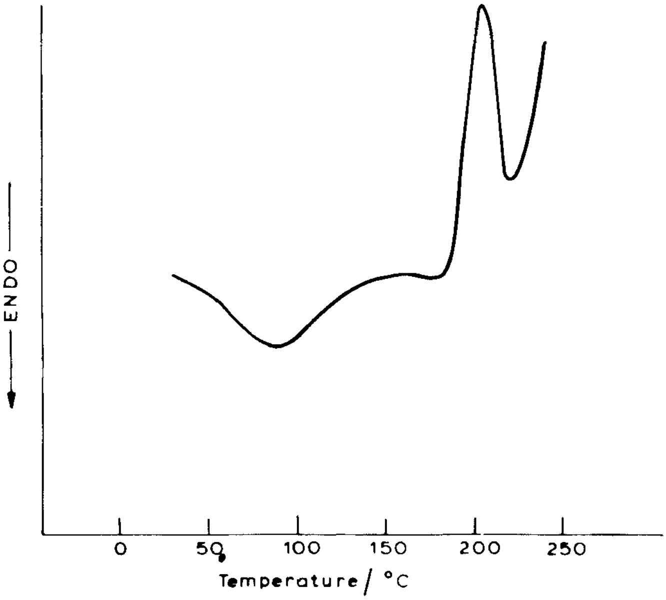


Figure 4. D.S.C. diagram of head polymer obtained in micellar media.

D.S.C. trace of the head polymer almost does not show the mesomorphic–isotropic endothermic transition (figure 4), since decomposition occurs simultaneously, as evidenced by the strong exothermic peak. In contrast, the tail polymer does show an endothermic peak corresponding to mesomorphic–isotropic transition at about 200°C. Decomposition occurs from the isotropic melt, as can be seen from the exothermic peak in figure 5.

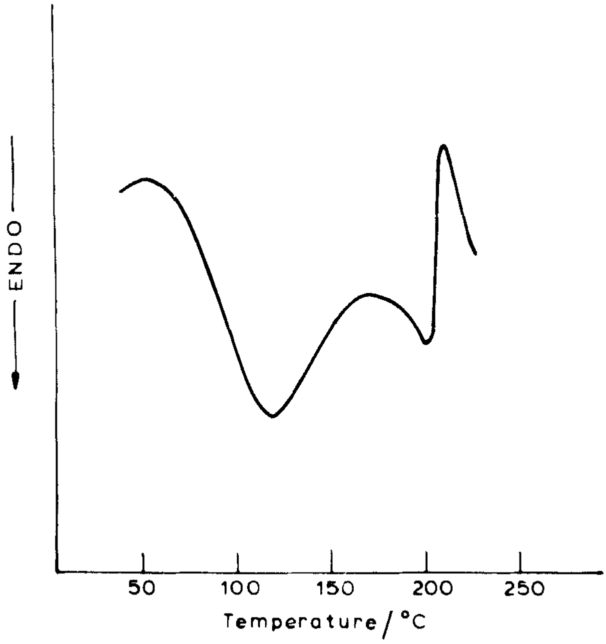


Figure 5. D.S.C. diagram of tail polymer obtained in micellar media.

4. Conclusion

The position of the methacrylate group at the polar head or at the end of the lipophilic chain affects the mesomorphic behaviour of the monomer surfactants discussed above, as well as that of their polymers. Micellar properties of the same monomeric and polymerized quaternaries are currently under investigation.

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