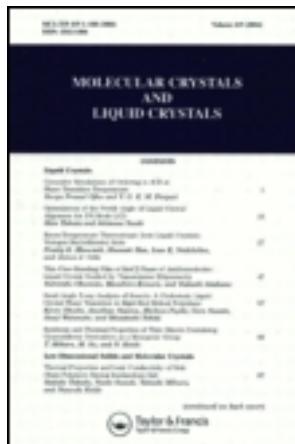


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Organizational and Aggregational Characteristics of Some Monomeric and Polymerized Quaternary Ammonium Salts

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ORGANIZATIONAL AND AGGREGATIONAL CHARACTERISTICS OF SOME MONOMERIC AND POLYMERIZED QUATERNARY AMMONIUM SALTS

C.M. PALEOS, G. MARGOMENOU-LEONIDOPPOULOU AND ANGELOS
MALLIARIS

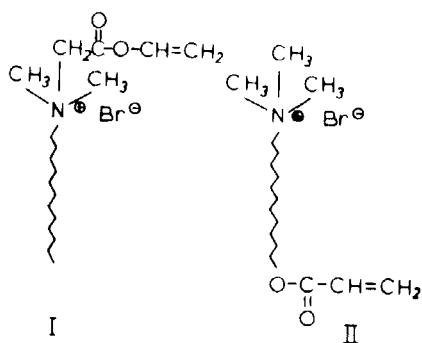
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Abstract In the present study two micelle forming polymerizable quaternary ammonium salts bearing the double bond either at the ionic head, or at the end of the aliphatic chain were prepared. Furthermore, the structure of the polymerizable group was different in the two cases, one being $\text{CH}_2=\text{CH}-\text{O}-(\text{C}=\text{O})-$ and the other $\text{CH}_2=\text{CH}-(\text{C}=\text{O})-\text{O}-$. By means of this functionalization it was possible to study the effect of minor molecular modification on micellization of these surfactants on one hand and their mesomorphic behavior on the other. It was found that the position of the double bond on the monomers affects the extent of constraints which are imposed on the polymers. These constraints subsequently influence, both the micellization of polymerized micelles as well as their behavior in the melt.

INTRODUCTION

A number of publications,¹⁻¹² primarily in recent years, have shown that amphiphilic compounds exhibit thermotropic mesomorphism in the melt in addition to the well-known aggregational and orientational properties which they show in solution.¹³ Specifically, they aggregate in aqueous solutions to form micelles, bilayers or vesicles and they also melt to smectic mesophases. In the present work we have prepared two micelle forming polymerizable quaternary ammonium salts bearing the double bond either at the ionic head (I) or at the

end of the aliphatic chain (II), Scheme. By means of this functionalization^{14,15} it was expected to study the effect of minor molecular modification on the micellization of these surfactants on the one hand, and their mesomorphic behavior on the other. Moreover, the corresponding properties of the polymerized materials were also investigated and compared to their non-polymerized counterparts.



Scheme

EXPERIMENTAL

Synthesis of monomers

I: To 0.01 mole of dodecyldimethylamine which was dissolved in ethylacetate, 0.0125 mole of distilled vinylbromoacetate (Polyscience) was added. The precipitated quaternary ammonium salt was filtered, recrystallized from ethylacetate and dried under vacuum over phosphorus pentoxide. Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{NBr}$: C, 57.17%; H, 9.52%; N, 3.70. Found: C, 57.54%; H, 9.82%; N, 3.60%.

II: Into ω -bromoundecylacrylate (which was prepared by the reaction of ω -bromoundecanol with acryloyl chloride) dissolved in ethylacetate, trimethylamine gas was bubbled. The

precipitated salt was filtered, recrystallized and dried over phosphorous pentoxide. Anal. Calcd for $C_{17}H_{34}NO_2Br$: C, 56.08%; H, 9.33%; N, 3.84%. Found: C, 56.15%; H, 9.73%; N, 3.78%.

Polymerization

The monomers were easily polymerized by UV irradiation in degassed micellar solutions. Their polymerization was monitored by the decrease of NMR intensity of the polymerizable groups.

Micellar characterization

Critical micelle concentrations (cmc) at $25^\circ C$ were determined by electrical conductivity. For both monomers cmc was found approximately equal to 5×10^{-3} mole/lit. Polymerized surfactants did not show cmc, as expected, evidently due to the fact that they form intramolecular micelles even at the lowest concentration. Fluorescence measurements of micelle associated pyrene were recorded for both monomers, before and after polymerization, on a previously reported instrument¹⁶.

Liquid Crystalline Characterization

Optical microscopy was performed with a Reichert "Thermopan" polarizing microscope. For thermal studies a Du Pont 910 Differential Scanning Calorimeter system with R90 Programmer was employed.

RESULTS AND DISCUSSION

The organizational and/or aggregational characteristics of both monomeric and polymerized micelles were investigated by fluorescence studies. Thus the parameters obtained from fluorescence measurements are shown in Table I. The ratio I_3/I_1 , which is an excellent index¹⁷ for the polarity of the micellar interface, does not change upon micellar polymerization

of (I) and therefore the micropolarity in the vicinity of solubilized pyrene remains unaffected by the polymerization. It is concluded therefore that, with or without the polymer backbone, carbonyl-hydration water is kept inside the interface creating in both cases the same polarity in the immediate environment of the probe.

TABLE I Micellar parameters obtained from fluorescence measurements

Surfactant	I_3/I_1 ^a	N_s ^b
Monomeric I	0.83	62
Monomeric II	-	-
Polymerized I	0.85	24
Polymerized II	0.72	42

^aIntensity ratio, peak I_3 to peak I_1

^bAggregation Number

Comparing the I_3/I_1 ratio between the polymerized surfactants (I) and (II) we note that it is smaller in (II) than in (I). Therefore solubilized pyrene senses higher polarity in polymerized micelles (II) than in micelles (I). In micelles of (II) it is easy for water to penetrate into the interior, thus giving rise to higher polarity in the former than in the latter case.

It should be noted that pyrene solubilized in monomeric micelles of (II) does not give any fluorescence. Since it had been found that the group $\text{CH}_2=\text{CH}(\text{C=O})-$ quenches the fluorescence of pyrene (unpublished data), in this case it may safely be assumed that the long aliphatic chain of the monomer bends in such a way that the effective group $\text{CH}_2=\text{CH}(\text{C=O})-$ is located in the interfacial region. There it can encounter solubilized pyrene molecules and quench their emission. After micellar polymerization of (II), micelle-

bound pyrene fluoresces normally.

By steady-state quenching of the fluorescence of pyrene with cetylpyridinium chloride, in micellar solutions of (I) and polymerized (I) and (II) it was possible to determine the mean micellar aggregation number of N_s of these micelles (Table I).¹⁸ Determination of N_s of monomeric (II) by fluorescence was not possible as discussed above. It is seen that N_s for monomeric (I) is 62 which is in agreement with the value expected for a micelle built from surfactant which has a twelve carbon atom chain.¹⁹ However, N_s for the polymeric micelle of (I) is only 24 which probably reflects the structural constraints arising when the polymeric bonds form at the interface. N_s for polymerized (II) is 42 i.e. almost twice as large as N_s for polymerized micelles of (I). In this case the structural constraints are not so serious since the polymer backbone is formed at the micellar core.

Peculiar anisotropic phases Fig. 1 and Fig. 2 were observed during the melting of I and II. In analogy with other long-chain functionalized quaternary ammonium salts^{8,11} these

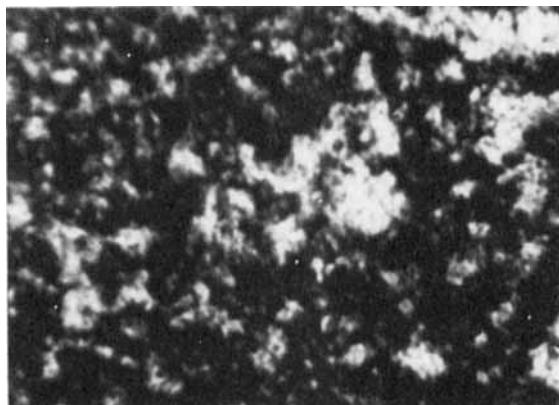


FIGURE 1. Smectic-like texture of monomer I. See Color Plate X.

compounds exhibit the so-called smectic-like textures. In these phases the ionic bonding of polar heads with counter-ions is preserved up to the mesomorphic-isotropic transition. It



FIGURE 2. Smectic-like texture of monomer II. See Color Plate XI.

is also interesting to note that the solid lamellar structure of the surfactants is retained above the first transition temperature, which corresponds to the melting of the long alkyl chains, and it is necessary to press the cover slip on the specimen in order to observe the smectic phases. The DSC diagrams of I and II are shown in Fig. 3 and Fig. 4. For surfactant I the small endothermic peak at 32°C is attributed to the melting of the alkyl chains whereas the respective transition for II is buried within the peak of the mesophase-isotropic transition. The latter transition is due to the breakage of the ionic bonding between polar heads and counterions.

Polymerized surfactants exhibited completely different behavior in the melt. Thus the polymer resulting from the polymerization of II exhibits mesomorphic texture (Fig. 5) the clearing point of which, as also seen in its DSC diagram,

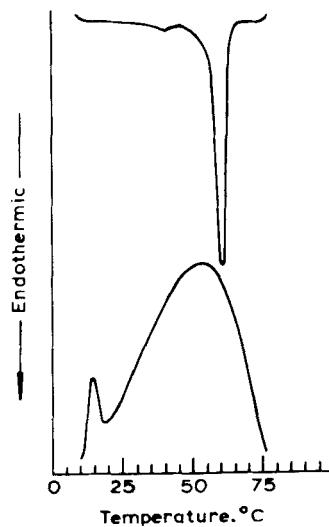


FIGURE 3. DSC diagram of monomer I.

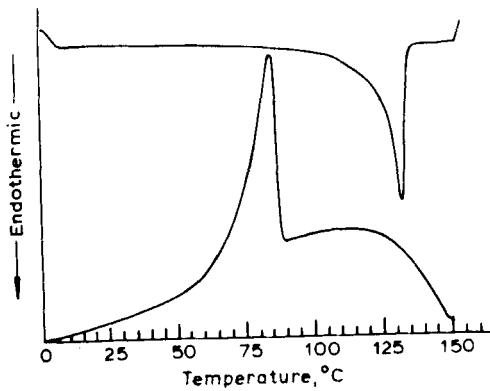


FIGURE 4. DSC diagram of monomer II.

occurs at significantly higher temperature compared to its monomeric counterpart. Apparently the binding of the aliphatic

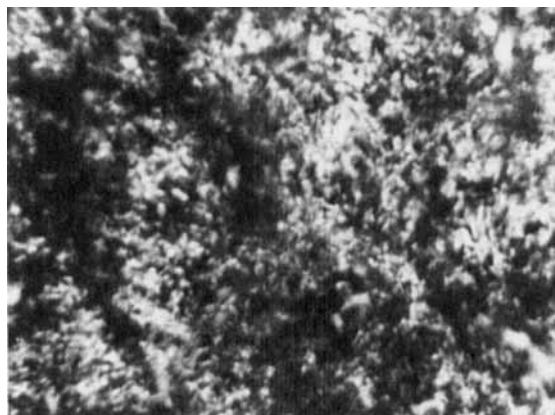


FIGURE 5. Smectic-like texture of the polymer derived from monomer II. See Color Plate XII.

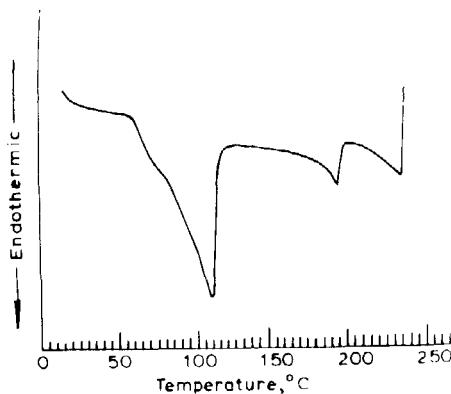


FIGURE 6. DSC diagram of the polymer derived from monomer II.

tic chains on the backbone results in the demonstration of mesomorphic behavior at higher temperature. On the contrary a completely different material is obtained by the polymeri-

zation of I. A glassy material results which decomposes before melting. It is therefore seen that the position of the polymerizable group, in the monomers I and II, affects significantly the thermal behavior of the resulting polymerized counterparts.

CONCLUSION

The main conclusion of this investigation is that the position of the double bond on the monomers affects the extent of constraints which are imposed on the macromolecules. These constraints in turn influence both the micellization of polymerized products as well as their behavior in the melt.

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