Supramolecular structure of certain amphiphilic liquid crystalline polymers*

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Poly(maleic anhydride) was reacted with long-chain aliphatic amines in a 1:1 molar ratio (as per monomer unit) resulting in the formation of amphiphilic polymers bearing the carboxylic group on their polymer backbone. On the other hand, poly(acryloyl chloride) was interacted with ω-amino or ω-hydroxy carboxylic acids affording polyamphiphiles with the carboxylic polar group at the tail of the pendant group. In addition, the carboxylic group was replaced by the extremely polar quaternary group at the end of the lipophilic chain. Liquid crystalline textures were exhibited by these polymers as determined by optical microscopy and d.s.c. studies while the supramolecular structures, formed through hydrogen bonding of carboxylic groups, were responsible for the formation of mesomorphic phases.

(Keywords: amphiphilic liquid crystalline polymers; supramolecular structure; reactive polymers; poly(maleic anhydride); poly(acryloyl chloride))

INTRODUCTION

Several years ago we introduced a convenient method for the preparation of thermotropic liquid crystals by the interaction of reactive polymers with aromatic mesogenic moieties[1,2]. Specifically, poly(acryloyl chloride) was reacted with aromatic mesogenic moieties bearing phenolic or amino groups. The advantage of this method lies in the use of usually well-characterized reactive polymers which subsequently interact with a variety of substrates, affording diversified speciality polymers such as polymeric drugs, liquid crystalline polymers, etc. Following the rather extensive work performed on amphiphilic-type thermotropic liquid crystals[3–12], recently some work has been performed on the synthesis and characterization of thermotropic, amphiphilic-type liquid crystalline polymers where the preparation was primarily based on the use of poly(maleic anhydride)[13–16].

In the present study, poly(maleic anhydride) and poly(acryloyl chloride) have been employed to introduce the carboxylic group on the polymer backbone and at the end of the lipophilic pendant group, respectively. Poly(maleic anhydride) was reacted with long-chain amines in a 1:1 molar ratio (as per monomer unit) according to *Scheme 1*. Poly(acryloyl chloride) was reacted with long-chain ω-amino or ω-hydroxy carboxylic acids to introduce the carboxylic group at the end of the side chain (*Scheme 2*). In addition, poly(acryloyl chloride) reacted with 11-bromoundecanol and the polymer obtained was subsequently quaternized with trimethylamine leading to the preparation of the polyquaternary shown in *Scheme 2*. The supramolecular structure of the polymers was elucidated by *FT*i.r. spectral analysis and the mesomorphic character by optical microscopy and d.s.c. studies.

EXPERIMENTAL

Polymer synthesis

Poly(maleic anhydride). A polymer having a degree of polymerization (*DP*) of ~70 obtained[17] by γ-irradiation of sublimed maleic anhydride was used for subsequent experiments.

Poly(acryloyl chloride). This polymer, with *DP* of 140, was prepared by the catalytic polymerization of acryloyl chloride according to the method of Schultz *et al.*[18,19].

Preparation of I and II. These polymers were prepared by methods reported recently by the interaction of poly(maleic anhydride) with didodecylamine[14] and octadecylamine[15], respectively.

Preparation of III. To a solution of 0.012 mol of 11-aminoundecanoic acid and 0.022 mol of triethylamine in dry dioxane, 0.01 mol (corresponding to monomer) of poly(acryloyl chloride), also dissolved in dioxane, were added. The reaction mixture was allowed to react for several hours at room temperature. The precipitated material was treated with water to remove triethylammonium chloride, and the remaining polymeric material was allowed to dissolve by stirring for several hours and finally filtering. The water from the filtrate

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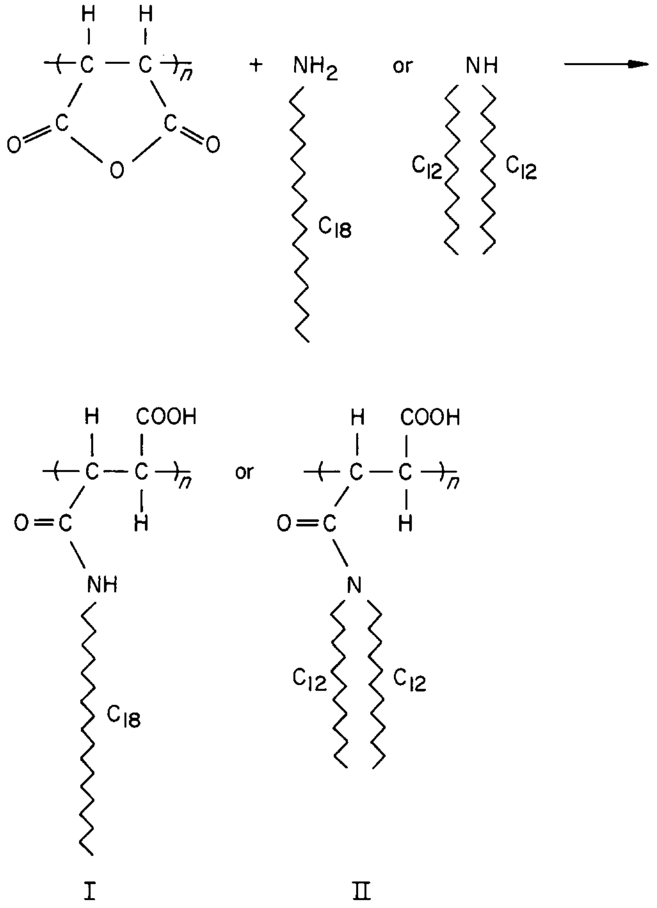


Scheme 1

was removed under vacuum and the remaining solid was treated with dioxane and ethyl acetate to remove solubles.

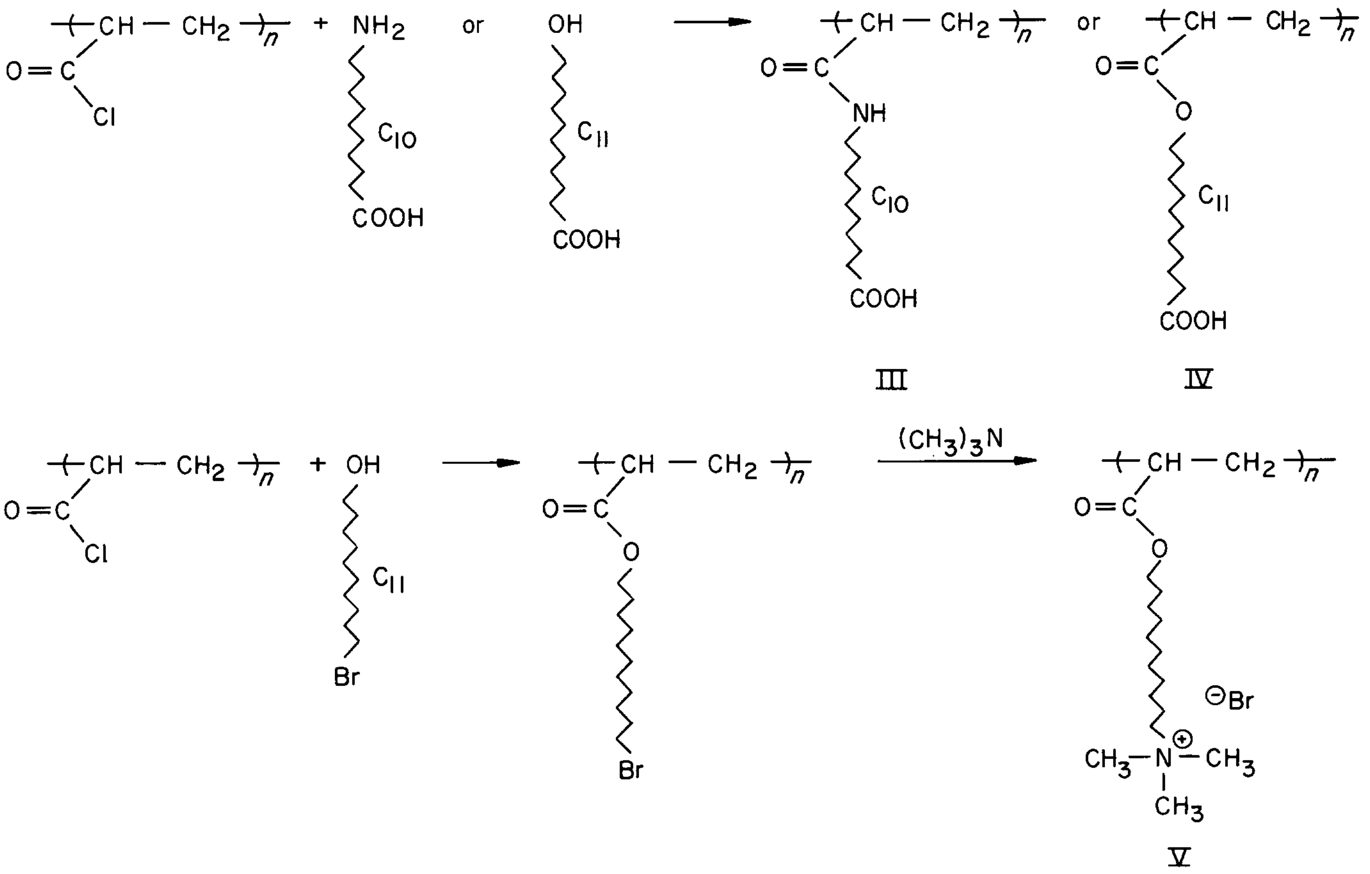
Analysis. Calculated for $C_{14}H_{25}O_3N{\cdot}0.5H_2O$: C 63.60, H 9.91, N 5.30%. Found: C 63.35, H 10.35, N 5.90%.

Preparation of IV. This polymer was prepared by reacting poly(acryloyl chloride), dissolved in dry dioxane, with 12-hydroxydodecanoic acid as reported recently[16].

Preparation of V. Polymer V has recently been prepared[16] according to the reactions shown in *Scheme 2*.

Polymer characterization

Optical microscopy studies were performed with a Reichert Thermopan polarizing microscope equipped with a hot-stage. D.s.c. studies were performed with a Perkin-Elmer DSC-4 in conjunction with a System-4 programmer. Attenuated total reflection (ATR) *FT*i.r. spectra were recorded on a Bomem Michelson 100 *FT*i.r. spectrometer at a resolution of 4 cm^{-1}. ATR *FT*i.r. studies were performed using a Hamilton ATR unit with a horizontally mounted KRS-5 crystal. A minimum of 30 scans were signal averaged. For the ATR *FT*i.r. studies the sample was applied on the crystal from a 1% (w/v) polymer solution in chloroform and the film formed after the evaporation of the solvent was used to obtain the spectra. (The complete absence of solvent was confirmed by the absence of its most intense bands.) ATR *FT*i.r. spectra at elevated temperatures were obtained using a specially constructed thermostatically controlled cell with an accuracy of ±3°C.



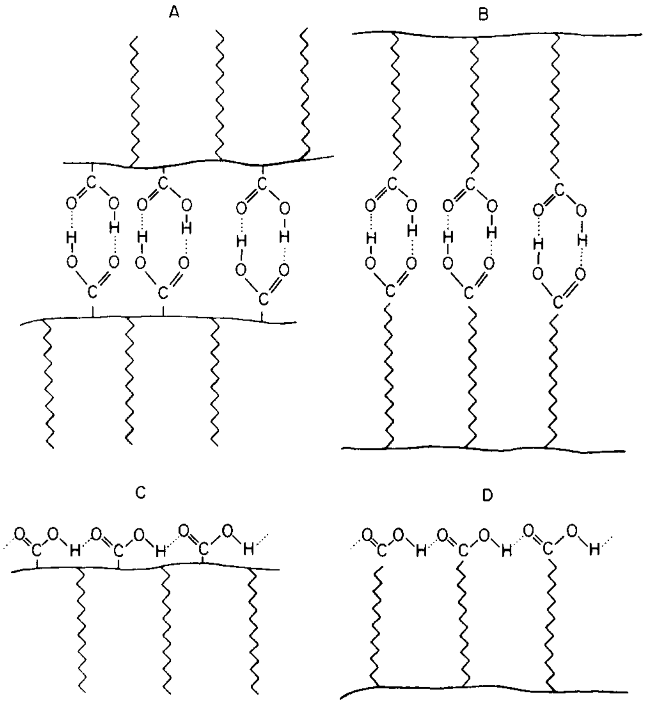
Scheme 2

RESULTS AND DISCUSSION

In our previous studies, a series of amphiphilic polymers[14,15] were prepared by reacting poly(maleic anhydride) with dodecylamine, didodecylamine, octadecylamine, biphenylamine, dodecanol and octadecanol. Copolymers were also prepared[15] by reacting the same polymer with mixtures of the above compounds. In analogy with the dimers formed by aromatic acids[20,21], such as cinnamic acid derivatives, the exhibition of liquid crystalline character by certain of the above derivatives was proposed[14,15] to be due to the formation of supramolecular structures originating from association through hydrogen bonding of polymeric chains. The observed smectic-like behaviour was attributed to the lamellar structure formed by lipophilic and hydrophilic layers which were formed, respectively, from the aliphatic chains and the facing hydrogen-bonded carboxylic groups.

However, in addition to the facing polymers A and B for poly(maleic anhydride) and poly(acryloyl chloride) derivatives, respectively, one may envisage that these polymers may form structures C and D characterized as sideways polymers (*Scheme 3*). In both cases, hydrogen bonding among carboxylic groups is responsible for the formation of the supramolecular structures.

Following a discussion on the mesomorphic behaviour of these polymers, *FT*i.r. spectral analysis will be used to rationalize the formation of their lamellar structure. The relatively stable liquid crystalline character of poly(maleic anhydride) derivatives seems to result from the interplay of two factors[15]: (1) the presence of strongly lipophilic moieties, by the incorporation, for instance, of an octadecyl moiety or two dodecyl groups. The latter derivative results from the reaction of poly(maleic anhydride) with didodecylamine; and (2) the presence of the amide group which induces the formation of liquid crystalline phases. The same group however, decreases the water solubility as compared to the corresponding polyamphiphiles bearing an ester linkage and therefore it is not possible to study their aggregational properties in water[16]. The strongly lipophilic moieties, on the one hand, lower the melting point of the polymers so that their liquid crystalline phases appear before their decomposition and, on the other hand, form quite distinct areas segregated from the polar segments. The amide group, in contrast to the ester linkage, apparently forms intramolecular hydrogen bonding resulting in the stabilization of the layer structure of the polymers.



Scheme 3

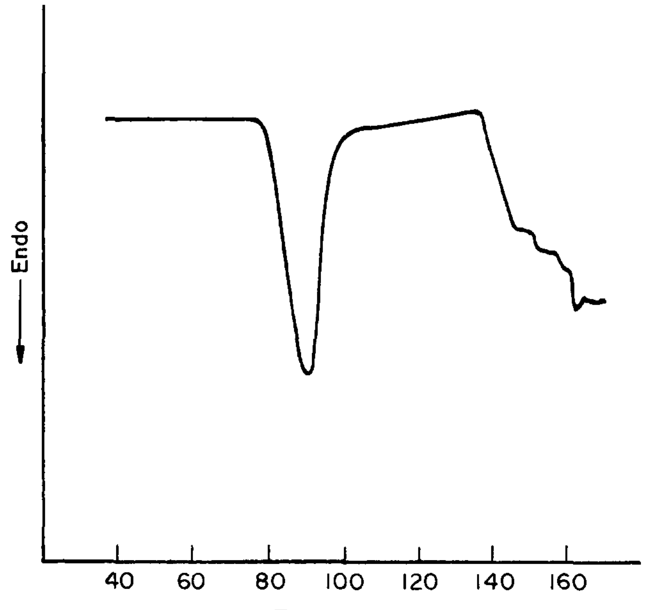


Figure 1 D.s.c. trace of polymer III

The mesomorphic behaviour of I[15] and II[14] poly(maleic anhydride) derivatives was investigated by optical microscopy and d.s.c. studies as reported recently. In this case, as mentioned above, the presence of the amide moiety and also the strong lipophilic character due to the presence of the octadecyl or the two didodecyl alkyl chains were of crucial significance and these polymers exhibited thermotropic liquid crystalline behaviour.

With respect to poly(acryloyl chloride) derivatives, polymer III (amide derivative) forms some anisotropic areas above 90°C which become completely isotropic at ~150°C with simultaneous decomposition as evidenced by yellowing of the sample during microscopic observation and the d.s.c. trace shown in *Figure 1*. Polymer IV, i.e. the ester derivative, is a glassy material with a glass transition at ~20°C which becomes isotropic at ~44°C as determined by the thermogram shown in *Figure 2*. An unidentifiable texture is observed on heating, at ~30°C, and is shown in *Figure 3*. For the polyquaternary derivative V we may assume, in analogy with simple quaternaries[6,11], the formation of lamellar structures in which the polar layers consist of quaternary groups sandwiched between lipophilic chains. This polymer is rubbery and hygroscopic and also shows an unidentifiable anisotopic texture (*Figure 4*) from room temperature when pressure was exerted on the cover glass during microscopic observation. It becomes isotropic at ~135°C with simultaneous partial decomposition. The d.s.c. trace, due to the high hydrophilicity of the material, showed a broad endothermic peak centred at ~90°C.

Concerning the supramolecular structures of the polymers as determined by *FT*i.r. spectroscopy polymer I showed a broad band centred at 1712 cm^{-1}, having also a small shoulder at ~1723 cm^{-1}. Upon heating to the liquid crystalline region two peaks start appearing at 1723 and 1710 cm^{-1} attributed to the formation of sideways and facing polymeric supramolecular structures[22–24]. In *Figure 5*, the *FT*i.r. spectra of polymer I at various temperatures are shown. The two bands are clearly resolved at 110°C and their intensities begin to rise with temperature up to 180°C indicating that the amorphous material disentangles, finally organizing in the form of facing and sideways polymeric structures. As the polymer undergoes its second transition at 130°C a shift of the peak at 1710 to 1705 cm^{-1} is observed. This is accompanied by a further increase in its intensity. After cooling at room temperature the two peaks remain resolved having strong intensities. This is explained by the fact that the material supercools. On the other hand the peak at 1637 cm^{-1}, assigned to amide I band, behaves in an analogous manner. The band shifts to the left with temperature while at temperatures above 110°C a second peak starts to appear at 1675 cm^{-1} at the expense of the former band. This band, which is assigned[25] to the non-hydrogen-bonded NH group, predominates above 130°C. After cooling, the peak at 1675 cm^{-1} remains strong. We may assume therefore that above 130°C hydrogen bonds between NH and C=O are substantially broken resulting in 'mobile' COOH groups which are able to form facing polymer dimers (1710→1705 cm^{-1}). At temperatures above ~180°C new bands begin to appear indicating decomposition of the polymer.

In analogy, polymer II also shows peaks at 1728 and 1700 cm^{-1} attributed to sideways and facing polymeric structures, while the band at 1621 cm^{-1} is assigned to the C=O amide group. On heating the sample at temperatures above the first transition, i.e. at ~50°C, the peak at 1728 cm^{-1} attributed to sideways polymeric supramolecular structure decreases while the peak at 1775 cm^{-1}, which was weak at room temperature, drastically increases. This may be rationalized by the formation of anhydride groups originating from the dehydration of adjacent carboxylic groups. The intensity of the peaks at 1357 and 2922 cm^{-1} attributed to CH_2 and CH_3 stretching absorptions, respectively, decreases above 50°C, i.e. at the melting transition of the long aliphatic chains.

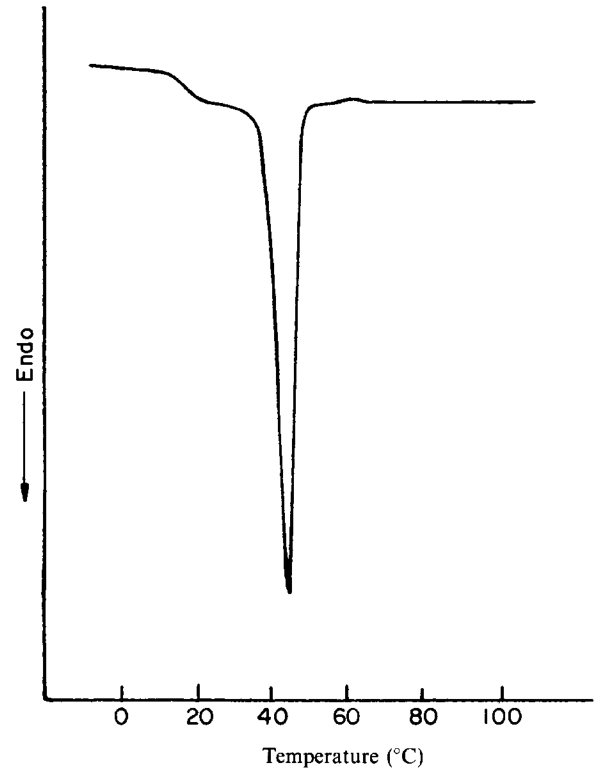


Figure 2 D.s.c. trace of polymer IV

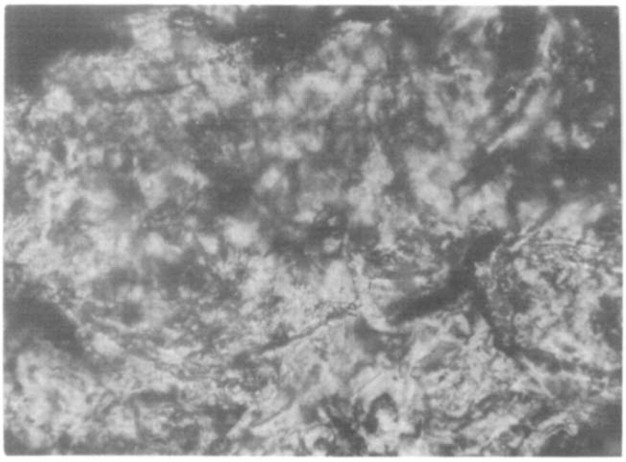


Figure 3 Liquid crystalline texture obtained for polymer IV

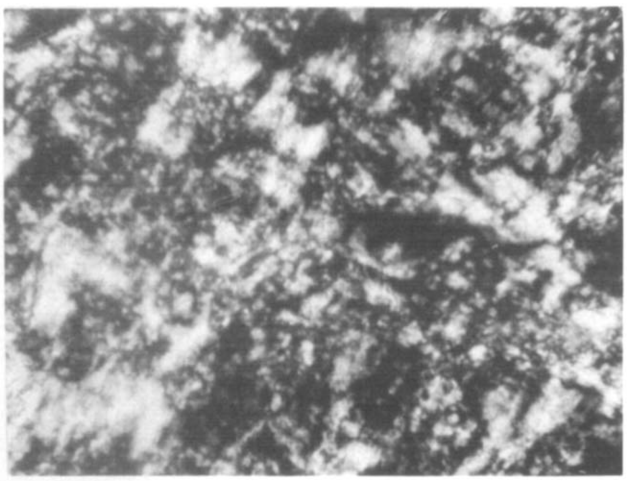


Figure 4 Liquid crystalline texture obtained for polymer V

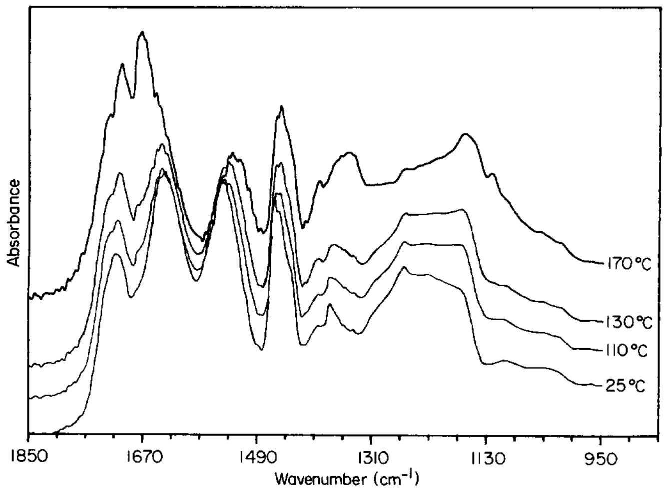


Figure 5 *FT*i.r. spectra of polymer I at various temperatures

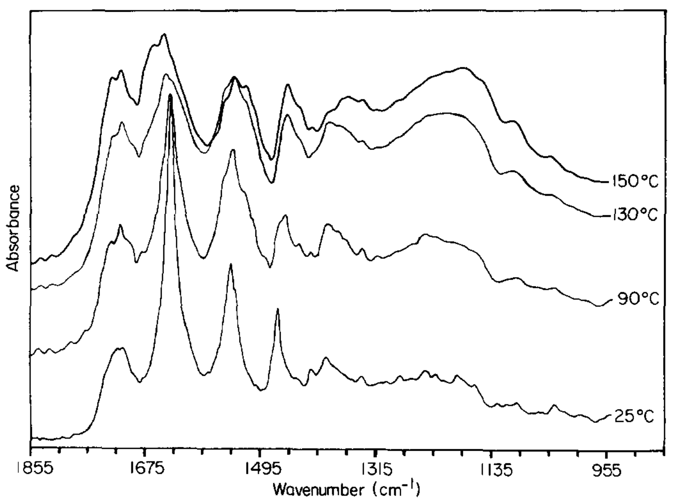


Figure 6 *FT*i.r. spectra of polymer III at various temperatures

It should be noted that in poly(maleic anhydride) derivatives, the attachment of the carboxylic group on the polymer backbone, in which amide or ester groups are also attached, is not typical of a common surfactant structure. Thus, the segregation of the hydrophilic and hydrophobic moieties is not straightforward in this case. For poly(acryloyl chloride) derivatives, however, the long aliphatic chain acts as a spacer for the polar groups and therefore there is the flexibility for the polar groups to be decoupled from the motion of the main chain and favourably segregate for the formation of the lamellar structure.

For poly(acryloyl chloride) derivatives, polymer III shows, in general, the same peaks as polymer I. Specifically the broad peak at 1716 cm^{-1} observed at room temperature splits at higher temperatures in to two bands, i.e. at 1728 and 1710 cm^{-1}. In addition, the peak at 1637 cm^{-1} decreases while the band at 1670 cm^{-1} increases. In *Figure 6* the *FT*i.r. spectra for the material at various temperatures are shown. Thus, sideways and facing polymeric structures are also formed by this polymer.

Polymer IV shows a shoulder at 1735 cm^{-1} attributed to C=O of the ester and two peaks at 1728 and 1708 cm^{-1} assigned, respectively, to sideways and facing polymeric structures. In an analogous manner, on heating, the peak at 1728 cm^{-1} diminishes in favour of the peak at 1708 cm^{-1}.

The *FT*i.r. spectrum of polymer V is in general analogous to monomeric long-chain quaternaries[26]. Further X-ray diffraction studies are planned for the elucidation of the solid and liquid crystalline structure of the polymers.

CONCLUSIONS

Amphiphilic polymers obtained using the 'method of reactive polymers' exhibited thermotropic liquid crystalline phases attributed to the formation of lamellar structures on the molecular level. For the polymers bearing the carboxylic group, as evidenced by *FT*i.r. spectral analysis, a layer structure is induced by the formation of facing or sideways supramolecular polymeric structures through hydrogen bonding. It is also clear that these two supramolecular architectures coexist in the solid and liquid crystalline phase and the temperature of the samples determines which structure prevails. In this context the unidentifiable textures observed in microscopic observation may be attributed to the simultaneous presence of both structures. The polymer with the quaternary group forms a lamellar structure due to the segregation of its lipophilic and hydrophilic moieties.

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