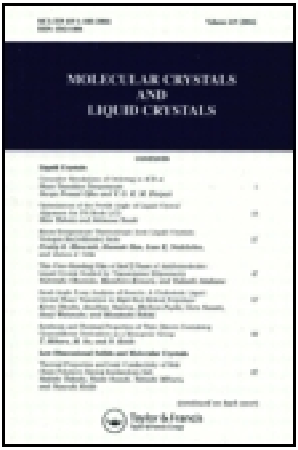

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Phase Behavior and Polymerization of Lyotropic Binary Liquid Crystals. A Positron Annihilation Study

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Phase Behavior and Polymerization of Lyotropic Binary Liquid Crystals. A Positron Annihilation Study

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Positron lifetimes and cross-polarized microscopic measurements have established the presence of hexagonal, nematic, and lamellar phases in 43%, 53–63%, and greater than 60% sodium decyl sulfate liquid crystals, respectively, at 65°C. These techniques also revealed hexagonal, nematic, and anisotropic phases in liquid crystals formed from 52% (w/v) sodium 10-undecanoate at 20°C, 30°C, and 44°C. Liquid crystalline sodium 10-undecanoate has been polymerized by ultraviolet irradiation, as well as by heating in the presence of ammonium persulfate as initiator. Irradiation resulted in a sequential change from hexagonal to mixed hexagonal-lamellar, and finally to lamellar phases. Polymerization by heating in the presence of ammonium persulfate resulted in a sequential change from hexagonal to mixed hexagonal-lamellar, and finally to isotropic phases. Cooling of the isotropic phase of polymerized liquid crystalline sodium 10-undecanoate to 20°C reformed the lamellar phase.

INTRODUCTION

Positron annihilation[3] has been found to be a highly sensitive method for investigating micelles, microemulsions, polyelectrolytes, and liquid crystals.[4–15] This technique has been profitably employed for characterizing subtle phase changes in sodium dodecyl sulfate (SDS)-water binary liquid crystals as a function of surfactant concentration and temperature.[14] Significantly, the presence of a previously unobserved nematic phase has been established in this system.[14]

Investigation of the phase behavior of other binary liquid crystals[16–27] and their subsequent polymerization[28,29] are the subject of ongoing research in our laboratories. Results on sodium decyl sulfate (sds) and sodium 10-undecanoate binary-liquid-crystal systems are reported here. Polymerization of the latter system by irradiation and by means of an initiator has also been investigated. Phase changes were detected by positron lifetime measurements and the phases were characterized by cross-polarized light microscopy.

EXPERIMENTAL SECTION

Purification and characterization of sodium decyl sulfate (sds) and 10-undecanoic acid have been described.[30] Liquid crystals were prepared by the established technique.[14] Sodium 10-undecanoate liquid crystals were obtained in their hexagonal phase at 52:48 = surfactant:water (w/v).

Hexagonal liquid-crystalline 52% (w/v) sodium 10-undecanoate has been polymerized by two different methods. In the first method, samples were aligned 8 cm from the central axis of a 4 W ultraviolet lamp and irradiated for different times at room temperature. In the second method, ammonium persulfate had been used to initiate the high temperature polymerization. Appropriate amounts of sodium 10-undecanoate have been dissolved in 0.05 M ammonium persulfate to give 52%

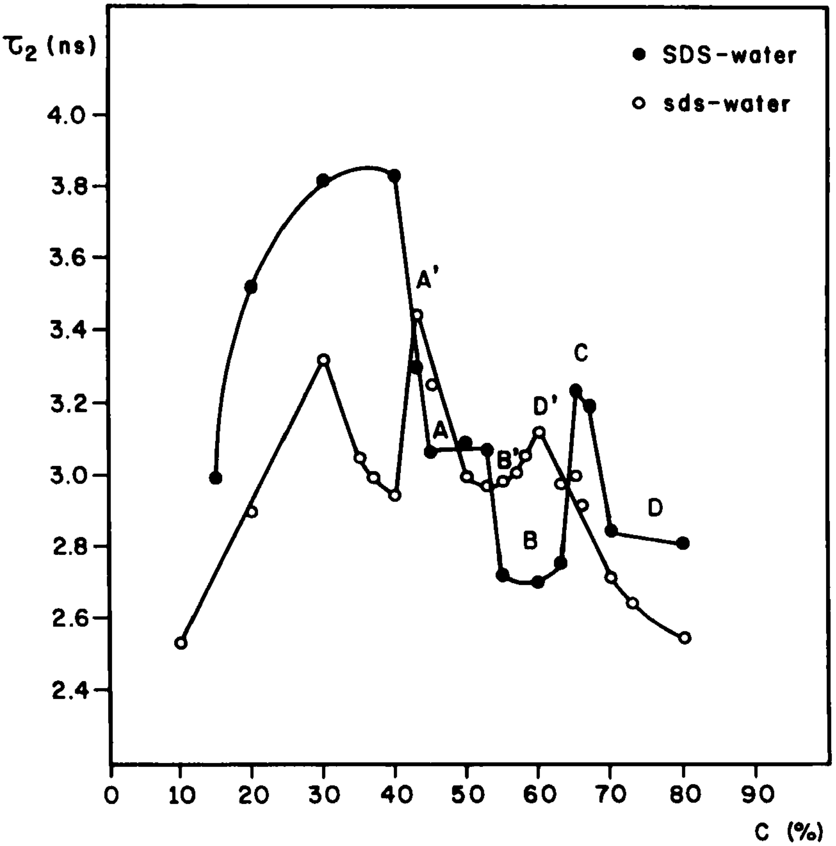


FIGURE 1 Plots of observed τ_2 values against concentrations (weight % in water) of sodium dodecyl sulfate (SDS) at 75°C (●) and against sodium decyl sulfate (sds) at 65°C (○). For SDS, the letters A (covering the 43–52% surfactuant range), B (covering the 54–62% surfactant range), C (covering the 65–68% surfactant range), and D (above 71% surfactant) indicate isotropic, nematic, complex-hexagonal, and lamellar phases, respectively. Similarly, for sds, the latters A' (43% surfactant), B' (covering the 53–63% surfactant range), and D' (above 60% surfactant) indicate hexagonal, nematic and lamellar phases, respectively. Data for SDS are taken from Reference 14.

surfactant (w/v) solutions, which were then heated at 65°C for different amounts of time.

Positron lifetime measurements were carried out by the usual fast coincidence technique, as described previously.[10-12] The resolution of the system, measured by the prompt time distribution of ^{60}Co source, was found to be 250 ps fwhm. Corrections for the positron absorption on the vial wall, which has an intensity of less than 3%, were made by the usual way by using conventional computational methods.[3] Positron lifetime and distributions were obtained by standard techniques.[3] The lifetime spectra was resolved, as previously described, into two components: a short-lived component (the result of p-Ps annihilation, free positron annihilation, and epithermal positronium interactions) and a long-lived component (with a lifetime τ_2 and its associated intensity I_2 which originates from reactions and subsequent annihilation of thermalized or nearly thermalized o-Ps).[3]

Optical microscopy was performed on a Zeiss K-7 Model microscope with a magnification of 2.5 × 10 × 1.25 coupled to a Canon A-7 camera charged with 35-millimeter Kodak color film (100 ASA). Samples for optical microscopic observation were prepared as previously reported.[14] Optical microscopy was performed under conditions identical to those used in the positron annihilation experiments.

RESULTS AND DISCUSSION

The phase behavior of the sds binary-liquid-crystal system was examined in the 15–80% surfactant concentration range by monitoring the positron lifetime parameter (τ_2). Figure 1 shows a plot of τ_2 versus sds concentration. Increasing the surfactant concentration is seen to result in an initial increase of the τ_2 value from 2.5 to 3.3 nsec at 30% sds, after which τ_2 decreases rapidly down to a minimum of 2.95 nsec at 40% sds concentration. This represents a turning point after which the τ_2 value increases again to a maximum of 3.45 nsec at 43% surfactant concentration. Subsequently, the τ_2 value decreases, once again, prior to reaching a final maximum at 52% surfactant concentration. Changes in the positron lifetime are related to phase changes. Cross-polarized microscopy, performed under identical conditions, allows the structural assessment of the appropriate phases present. Thus, at sds concentrations lower than 30%, isotropic micellar phases predominate. At this concentration, the phase change signals the appearance of other structures. Micrographs taken in the 43–53% sds range correspond to a hexagonal liquid crystalline phase, while those taken between 53–63% sds can be attributed to a nematic phase. The maximum in the τ_2 value (indicated by D′) corresponds to the onset of a lamellar phase which became predominant at higher surfactant concentrations. Entirely similar phase behavior has been obtained for sds at 65°C and 75°C.

It is instructive to compare the liquid crystalline phase behavior of sds with that of SDS (Figure 1). Most importantly, the nematic phase is observable in both surfactant systems. A difference of eight carbon atoms in the surfactant chain-length manifests, however, in marked dissimilarities. In the SDS liquid-crystalline system, there is only one (rather than two) phase transition in the isotropic micellar solution in the 15–38% surfactant concentration range. Furthermore, in contrast to SDS, the onset of a complex hexagonal phase in the sds liquid-crystalline system could not be observed. Micrographs taken at sds concentrations higher than 60% revealed only the presence of a lamellar structure (this is indicated by the absence of C′ in Figure 1).

Positron lifetimes determined in 52% (w/v) aqueous sodium 10-undecanoate are plotted as a function of temperature in the left-hand side of Figure 2. Cross-polarized micrographs taken at different temperatures are illustrated in the right-hand side of Figure 2. These data are explicable in terms of temperature-dependent phase transitions of sodium 10-undecanoate liquid crystals. Hexagonal structures predominate in the 20–28°C temperature range. An increase of temperature results in a transition to the nematic phase which prevails in the 32–33°C temperature range. The plateau of τ_2 values at 2.84 nsec in the 38–50°C range corresponds to a transition to an anisotropic phase which is followed by isotropic structures at temperatures above 51°C.

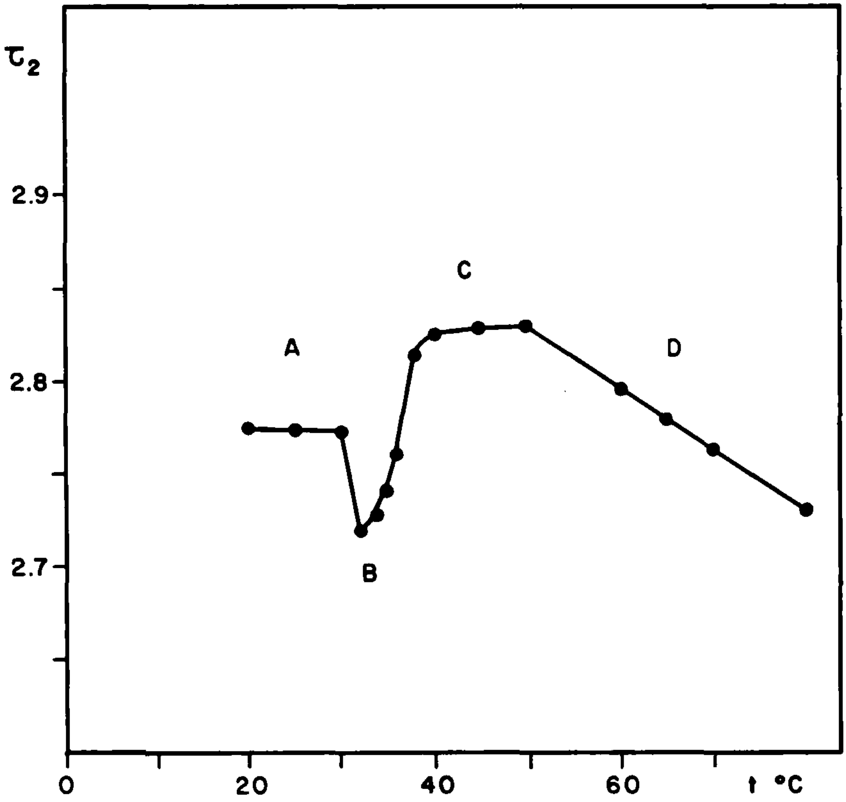
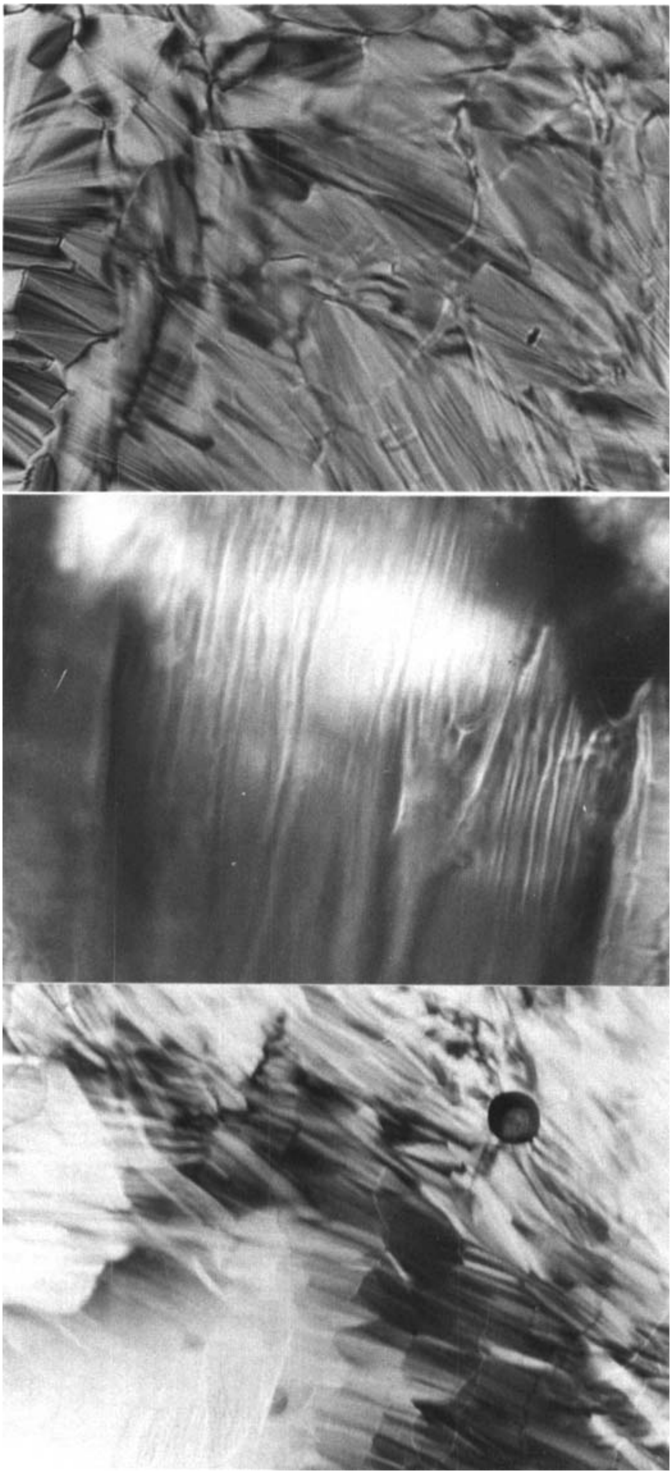


FIGURE 2 Left-hand side: A plot of observed τ_2 against temperature for 52% (w/v) sodium 10-undecanoate as a function of temperature. Right-hand side: Cross-polarized micrographs taken at 20°C, 30°C, and 44°C corresponding to hexagonal, nematic, and anisotropic phases, respectively.



See Color Plate V FIGURE 2 (*continued*)

Liquid crystals prepared from unsaturated carboxylic acid have been shown to polymerize. The progress of polymerization of liquid crystals of 52% (w/v) sodium 10-undecanoate was monitored by following changes in τ_2 values. The variation of τ_2 values as a function of exposure time to ultraviolet radiation is shown in the left-hand side of Figure 3. The initial decrease of τ_2 corresponds to the inhibition of positronium formation by the free radical generated by the ultraviolet irradiation. Free radicals are known to interact with e^+ and e^-, the positronium precursors.[31-33] Subsequently, the free radicals are removed by cross-linking (i.e., forming the polymer) and, thus, they no longer interfere with the positron formation. This manifests in the exponential build-up of τ_2. Typical micrographs taken at different irradiation times are illustrated in the right-hand side of Figure 3. Polymerization is seen to cause a change in sodium 10-undecanoic liquid crystals from a hexagonal (0–10 minutes of irradiation) to a lamellar (40 minutes and longer irradiation) phase. At intermediate times, hexagonal and lamellar structures coexist.

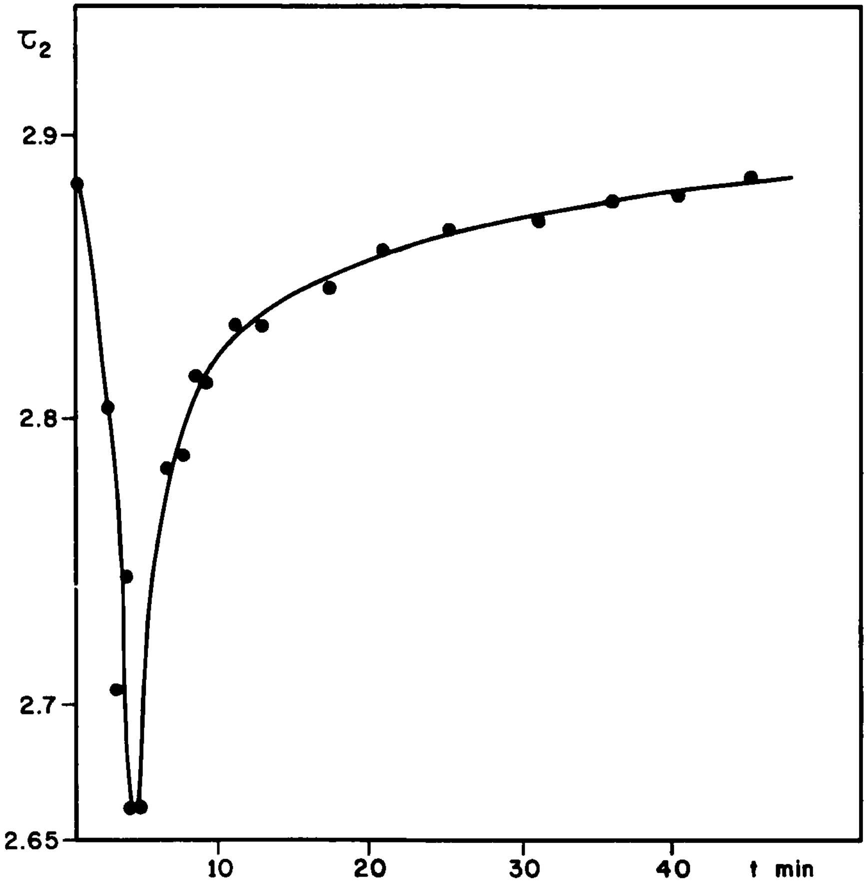
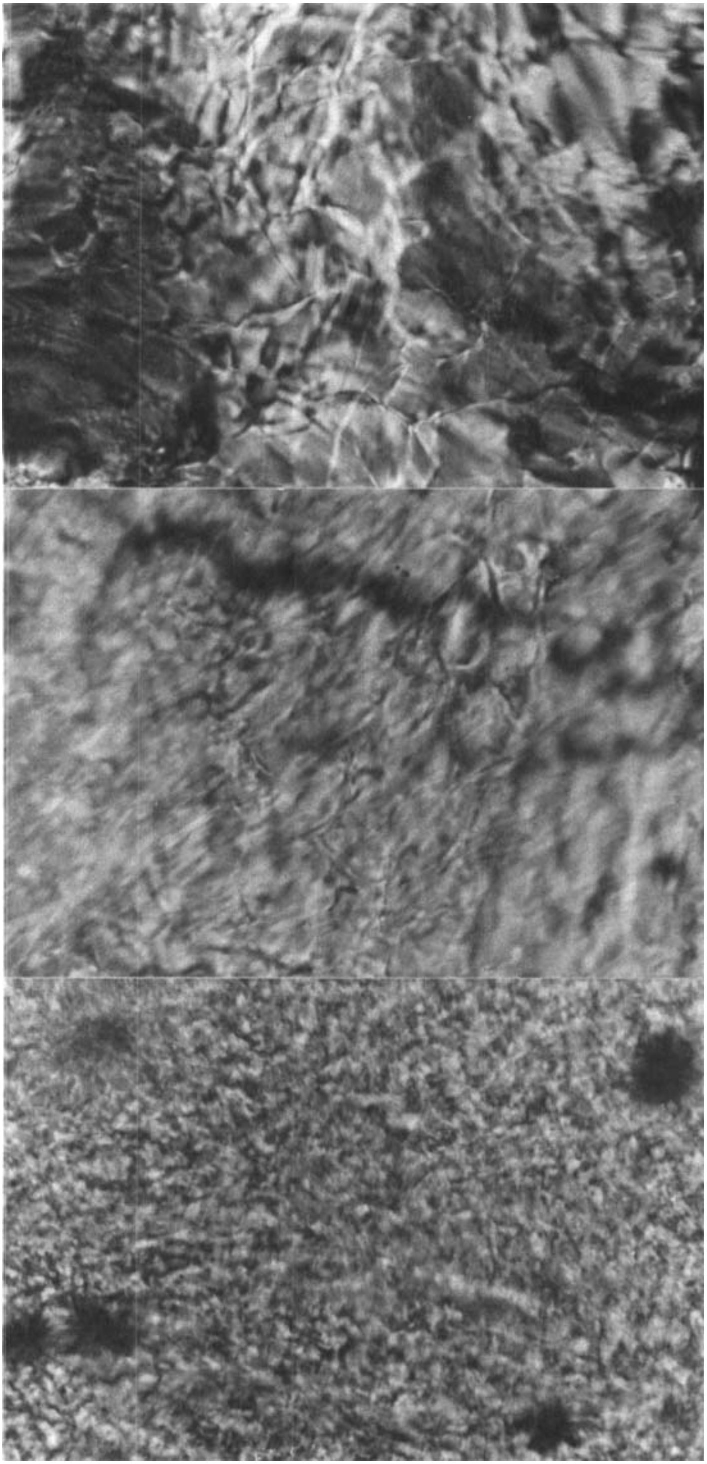
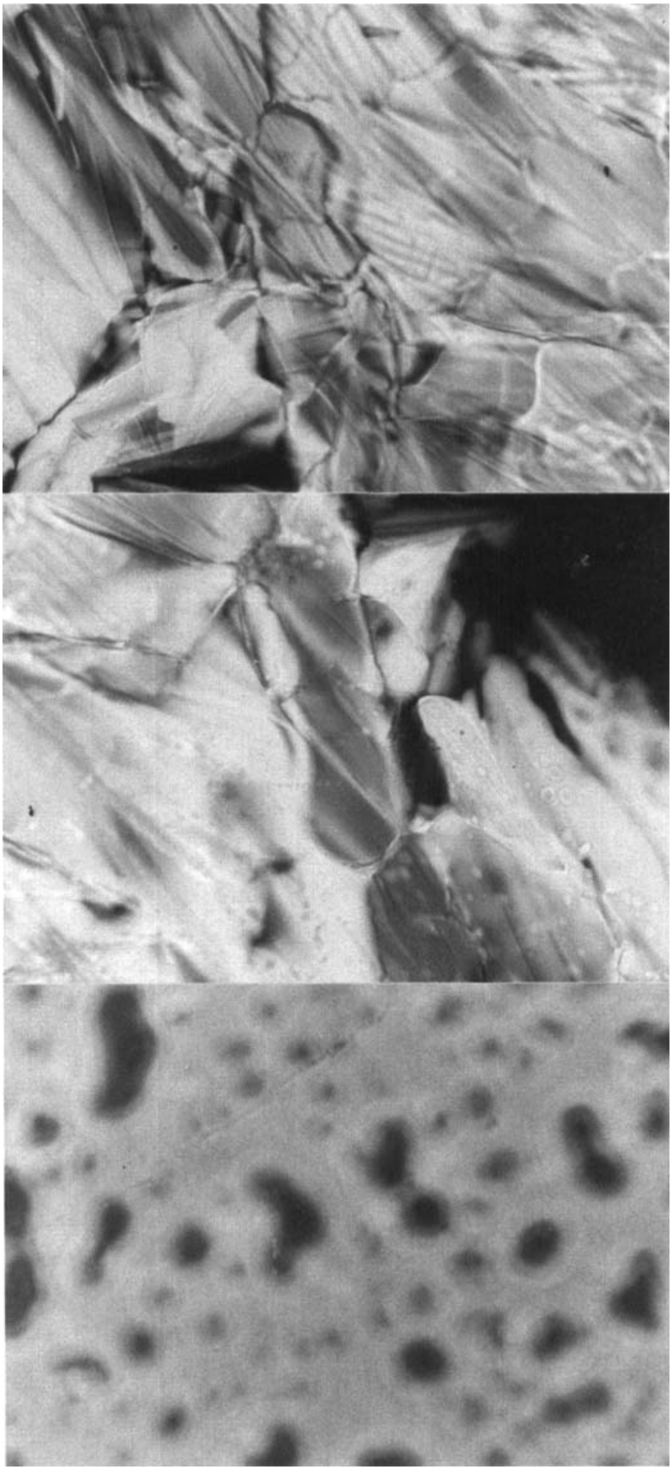


FIGURE 3 Left-hand side: A plot of observed τ_2 against irradiation time used to polymerize 52% (w/v) sodium 10-undecanoate at 25°C. Right-hand side: Cross-polarized micrographs taken subsequent to 5, 15, and 40 minutes of irradiation which correspond to hexagonal, mixed hexagonal-lamellar, and lamellar phases, respectively.



See Color Plate VI

FIGURE 3 (*continued*)



See Color Plate VII

Similar transitions can be affected if the polymerization is carried out by heat using an initiator. Typical micrographs taken at different times of heating (at 65°C) a 52% solution of sodium 10-undecanoate in 0.05 M ammonium persulfate are shown in Figure 4. Cooling the polymerized samples gradually (after 24 hours of heating) to 20°C results in the reformation of the lamellar phase (micrographs are similar to that shown on the bottom right-hand side of Figure 3).

Increasing the temperature of polymerized liquid crystals caused reversible changes in the polymeric chain which manifested in changes in τ_2 (left-hand side of Figure 5). There is a gradual increase of τ_2 up to 40°C; at this temperature τ_2 decreases somewhat and then rises to a maximum at 55°C. Micrographs taken at 43°C, 45°C, and 48°C (right-hand side of Figure 5) correspond to mixed hexagonal-lamellar, predominantly lamellar, and anisotropic phases, respectively.

CONCLUSION

Positron annihilation techniques have, once again, shown subtle differences in the concentration-dependent phase behavior of sodium dodecyl sulfate and sodium decyl sulfate. The same method has been used to monitor the polymerization of sodium 10-undecanoate. Temperature-dependent phase changes of polymerized liquid crystals indicated relative mobilities of the polymeric chains. Structures of different phases have been established by cross-polarized microscopy.

Acknowledgment

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FIGURE 4 Cross-polarized micrographs of 52% (w/v) sodium 10-undecanoate in 0.05 M ammonium persulfate subsequent to 30 minutes, one hour, and five hours of heat at 65°C which correspond to hexagonal, mixed hexagonal-lamellar, and isotropic phases, respectively.

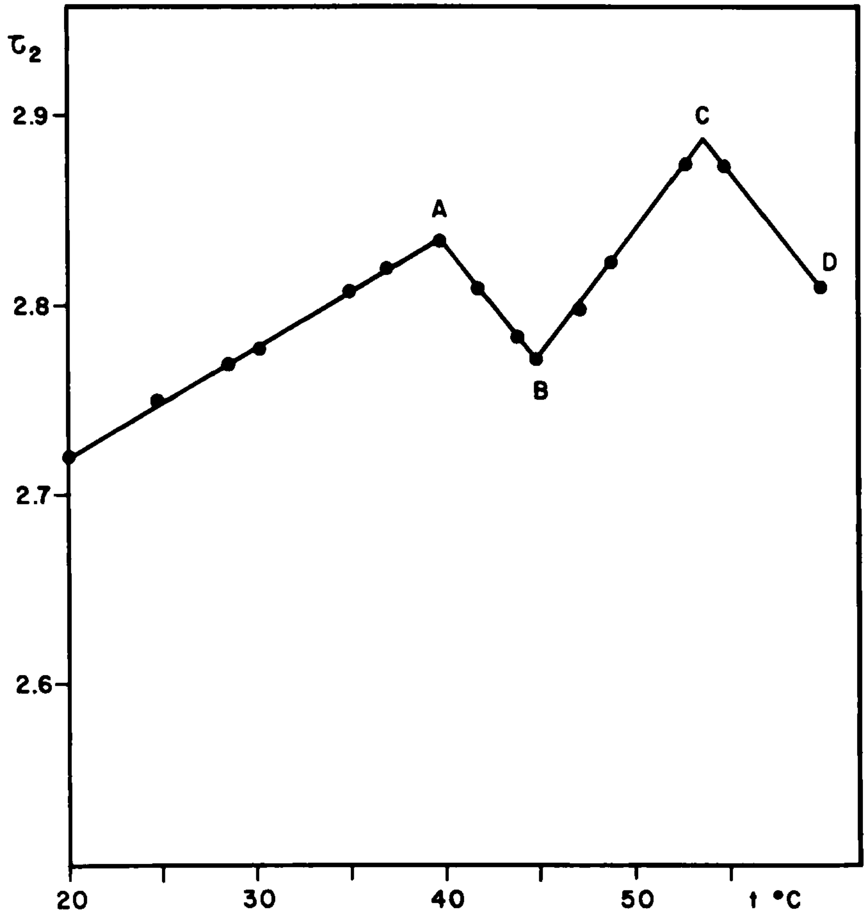
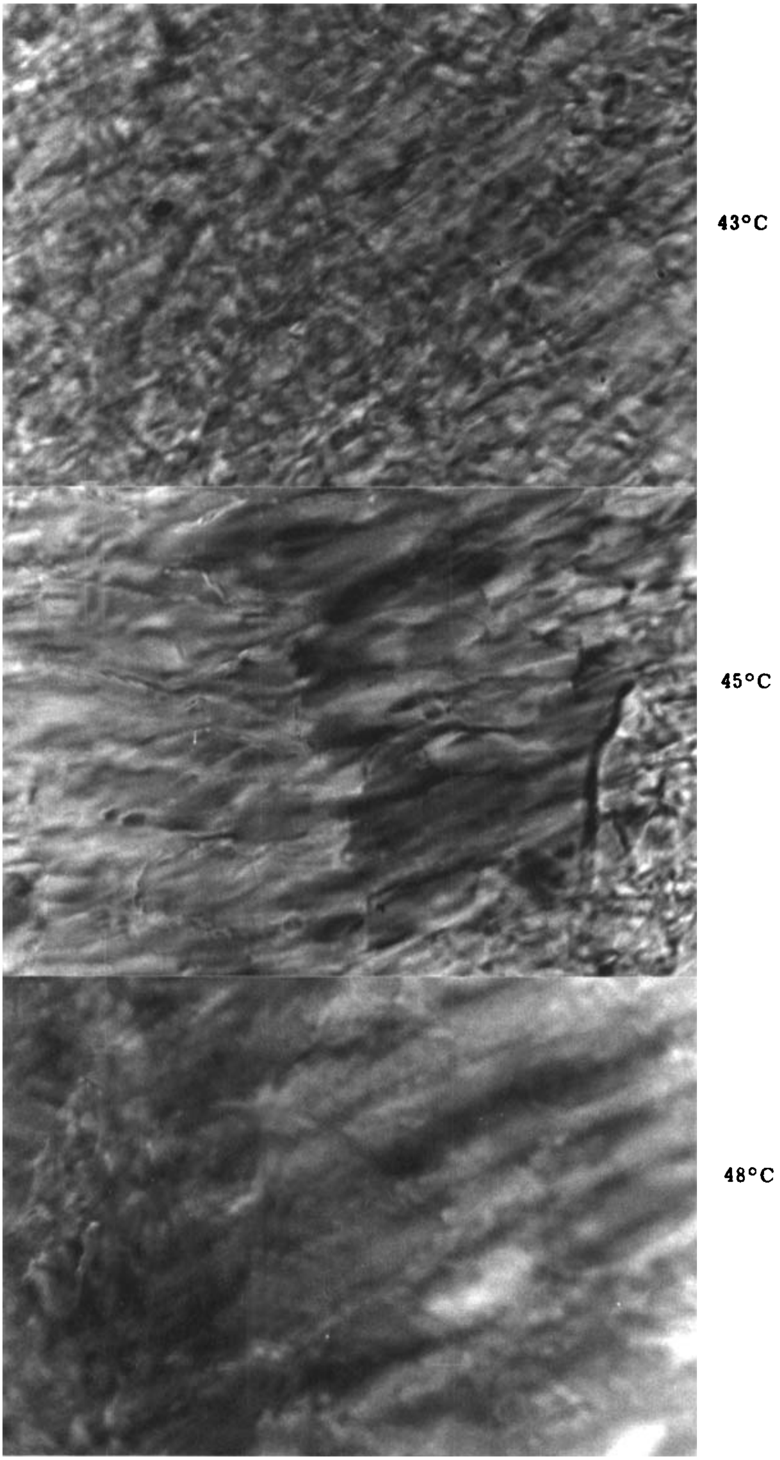


FIGURE 5 Left-hand side: A plot of observed τ_2 against temperature for light polymerized (40 minutes) 52% (w/v) sodium 10-undecanoate. Right-hand side: Cross-polarized microscopy taken at 43°C, 45°C, and 48°C which correspond to mixed hexagonal-lamellar, predominantly lamellar, and anisotropic phases, respectively.



See Color Plate VIII FIGURE 5 (*continued*)

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