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Solid state characterization of the structure of rod-like micelles and their mixtures with associating polymers

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The supermolecular structure or morphology of a series of solid state films of colloidal rod-like micelles, covering a range of hydrophobic activity, i.e. methylene chain length, was studied by small angle light scattering (SALS) complemented by polarized light microscopy. The SALS results on the colloidal rod-like micelles parallel those formed in rod-like polymers. A comparison with theoretical calculations shows that the individualized rod-like structures in solution aggregate into a supermolecular rod-like structure which is preserved in the concentrating process. The experimentally observed anisotropic patterns are discussed in terms of scattering models and are related to the way in which the rod-like entities are oriented in the supermolecular rod-like morphology. The analysis is extended to include intimate mixtures of colloidal rod-like micelles and hydrophobically (and nonhydrophobically) associating water soluble copolymers.

(Keywords: rod-like micelles; associating-type copolymers; polymer–colloid interactions; small angle light scattering; viscoelastic fluid)

INTRODUCTION

The need to modify the properties of both fluid and bulk polymeric systems in a predictable manner has led to the utilization of associating-type polymers[1–6]. In general, these polymers contain low levels ($\leqslant 10$ mol%) of associating-type monomer units. At least in qualitative terms, these moieties are characterized as possessing solubilities that are quite different (or even completely opposite, i.e., oil *versus* water soluble groups) from the parent polymer. In most instances of practical importance, the level of functionalization is relatively low ($\leqslant 5$ mol%), however, dramatic changes in physical properties are observed. A number of publications have focused on the aqueous and nonaqueous solution behaviour of these polymers as well as the utilization of this concept in the preparation of new miscible and partially miscible blends[1–8]. In our continuing pursuit of polymeric materials with technologically useful properties, a series of new hydrophobically associating copolymers and polymerizable viscoelastic fluids were developed[7–10]. These former materials are broadly characterized by markedly enhanced rheology at low polymer concentrations, brine and shear stability. The latter 'monomeric' systems are characterized as a rod-like structure in which the individual units are 'ordered' along the 'symmetry axis' of a long thread-like structure. The water soluble head group with its associated counterion lies on the surface of the micelle, while the long alkyl tails are hydrophobically associated in the interior of the rod (*Figure 1*). The oleophilic character of the interior of a micelle is well-known to impart interesting solubilization phenomenon to solutions containing these structures. Recently[11] it was shown that this phenomenon is useful in 'bridging' hydrophobically associating polymers with rod-like micelles. Enhanced dilute and semi-dilute solution properties result. It is, however, important to investigate the morphology of bulk films formed from this mixture and compare these results with those of the individual components. These results should help clarify the solution behaviour of these interesting fluids and possibly enhance their usefulness in a variety of thin film applications and as 'free-standing' films in both their unpolymerized and polymerized state.

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EXPERIMENTAL

The synthesis and characterization of several families of polymerizable viscoelastic fluids and hydrophobically associating polymers in aqueous environments has recently been detailed[9,10]. The cationic viscoelastic monomer fluid used as a model system in this work is formed from the reaction of allyl bromide and the appropriate *N*,*N*-dimethylalkyl amine (tetradecyl-, hexadecyl-, and octadecyl-amine). In these representative examples, the methylene sequence is 13, 15, and 17, respectively. Subsequently the bromide counterion is displaced (i.e. ion-exchange) with salicylic acid–sodium salt.

The cationic hydrophobically associating copolymers were synthesized via the aqueous solution copolymerization of acrylamide and a surfactant-type monomer formed by the reaction of dimethylaminopropylmethacrylamide and the appropriate alkyl bromide. In this study, two specific materials were used: ethyl bromide (methylene sequence is unity, i.e. $n=1$) and dodecyl bromide, i.e. $n=11$.

Thin films of the viscoelastic monomer fluid and the mixture of this fluid with the appropriate copolymers were formed by spreading a 10.0 g/dl concentrate onto a clean glass slide and slowly air drying at 25°C. Typically

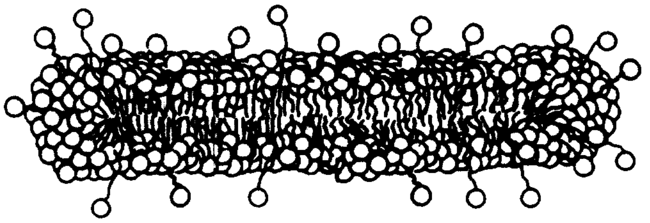

Figure 1 Schematic representation of the cross-section of an individual rod-like micelle. The head groups (denoted by circles) define the surface and the methylene chain units constitute the oleophilic, hydrophobic interior

the drying procedure lasted 60 min. In all instances, measurements were not performed on thoroughly dried films since a relatively small amount of moisture is needed to obtain clear SALS patterns. Measurements are continuing in order to explore whether this phenomenon is due to marked surface roughening of thoroughly dried films producing high levels of multiple scattering and/or a small amount of water is required to insure that the hydrophobic associations are sufficiently strong in order to retain the structural integrity of the rod-like micelles.

The light scattering measurements were photographically recorded on a Polaroid type 57 film because the whole scattering pattern is of interest. The technique and theory has been extensively described by Stein *et al.*[12–16]. A Spectra Physics Model 155 He–Ne laser was used as the monochromatic ($\lambda_0 = 632.8$ nm) light source. The film was placed between an analyser and polarizer with their respective optic axis at specific directions with respect to each other. The H_V denotes vertically polarized incident light and horizontally polarized scattered light and V_V denotes both vertically polarized incident and scattered light. The sample detector distance was typically between 20–35 cm.

RESULTS AND DISCUSSION

The solution behaviour of viscoelastic micellar fluids is dominated by presence of long rod-like structures which possess contour lengths that are, under certain conditions, larger than conventional flexible macromolecules. One intriguing feature of the previously described polymerizable viscoelastic fluids is that a distinct clearing temperature is observed. The specific temperature is inversely proportional to the methylene chain length. The octadecyl derivative, i.e. $n = 17$, has a 30°C clearing transition. An examination of the turbid fluid reveals that long macroscopic, needle-like aggregates are present (*Figure 2A*). Each aggregate is highly birefringent with the principal polarization direction located approximately normal to the long axis (small aggregates) and less than normal in larger aggregates. These needle-like aggregates appear to be composed of a large number of individual rod-like structures. The negative birefringence of rod-like micelles is experimentally observed because the individual molecules are typically directed perpendicular to the largest axial dimension[17].

Increasing the micelle concentration through slow solvent evaporation results in a marked increase in the number of aggregates (*Figure 2*). Eventually, these structures become so highly 'overlapping' that the field of view is too confused for a clear determination of the film morphology.

Small angle light scattering (SALS) offers some distinct advantages over the polarized light microscopy technique. The subjectiveness of interpretation of the morphological types is eliminated as well as any artifacts related to the use of thin films. Furthermore, a detailed morphological description, i.e. spherulitic, rod-like, discs, etc., can be clearly obtained utilizing SALS even if the scattering entities are overlapping each other. Typical light scattering patterns are shown in *Figure 3* with the corresponding micrograph of the dried film. A microdensitometer scan of these H_V patterns shows that there is no maximum in the scattered intensity, but only a monotonic decrease. This scattering pattern is typical of anisotropic rods[13,18–20]. The V_V pattern further confirms that the anisotropy contribution is more important than density correlations.

The scattered intensity for a random assembly of anisotropic rods should decrease monotonically with scattering angle. However, its azimuthal dependence is determined by the direction of the maximum polarizability (i.e. optical axis) for the rod as measured from the long axis of the rod[18,19]. If this angle, for example, is between 33°33′ and 70°07′ the pattern is of the (+) type with intensity maxima at 0, 90, 180, and 270° with respect to the polarizer direction. Alternatively, the V_V scattering pattern should be of the (X) type with intensity maxima at 45, 135, 225, and 315° with respect to the polarizer direction. The film formed from the rod-like colloidal micelles display such characteristics. Therefore, these materials are composed of superstructures which scatter light as thin rods with a mean optical anisotropy of approximately 45°. Experimentally, this corresponds to the angle between the alkyl chain axis and the longer lateral axis of the aggregate. The V_V scattering patterns is of the (X) type suggesting that the optical axis of the rods is about 45°. Since the principal polarizability of an individual monomer unit in the rod-like micelle is parallel to the methylene units, the SALS results indicate that the rods within an aggregate are aligned and stacked side by side at approximately 45° to the long axis of the aggregate. As for the orientation of the optic axes within the fibrils, Kawai *et al.*[19] have theoretically considered two types of polymeric fibrils. The first model (model A) assumes the optic axes orientation is fixed in a plane within the fibrils and the other (model B) assumes that the orientation is cylindrically symmetric around the fibril axis. As in collagen films, the +-type scattering must be interpreted as arising from fibrils of model A rather than those of model B. Consequently, the fibrils formed from these physically-associated colloidal rods have their optic axes essentially oriented in a plane of the fibrils (model A) in the angular range between 33°33′ and 70°07′. This appears to be a typical SALS pattern of rod-like entities, i.e. polymers and colloidal rods, in general.

An example of the typical scattering pattern of a rod-like polymer, i.e. hydroxypropylcellulose (HPC), is shown in *Figure 4*. Again a H_V pattern of the (+) type is found and has been interpreted in terms of the scattering of anisotropic rods which have their optic axis at 45° to the rod axis. In HPC[21] the maximum polarizability is along the molecular axis. These chains are organized into long microfibrils. Therefore the direction of maximum polarizability in the microfibril should be also parallel to the long axis of the microfibril. Subsequently, the microfibrils associate into larger mor-

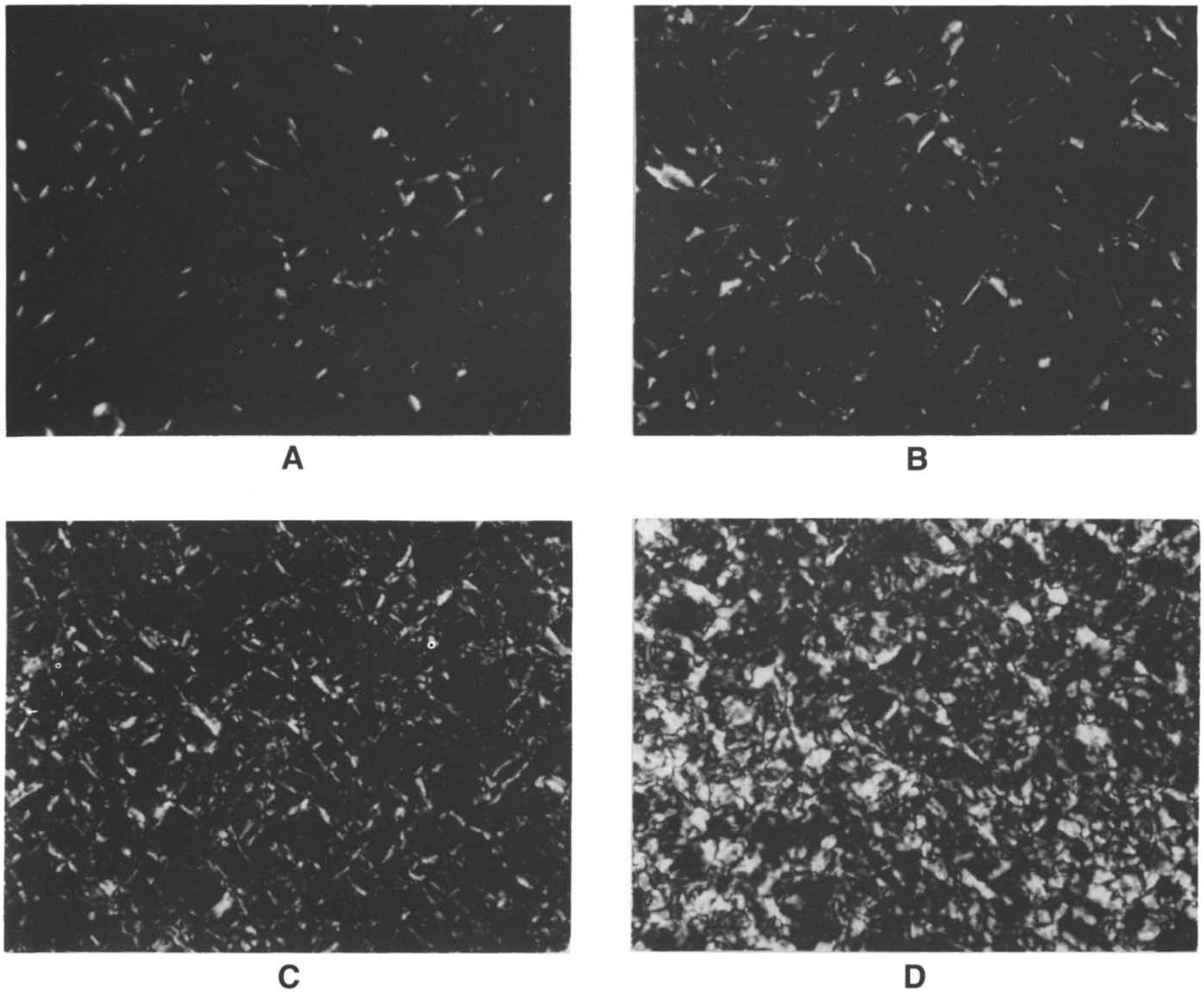

Figure 2 Polarized micrographs (160×) showing the morphology of a visoelastic monomer fluid (methylene sequence is 17) as the concentration is increased via slow air drying. (A) 0 minutes; (B) 10 minutes; (C) 20 minutes; and (D) 30 minutes. Measurement temperature is 25°C and initial concentration is 10.0 g/dl

phological rod-like entities in the microns size range. SALS suggests that these rods have their maximum polarization direction at about 45° to the rod axis, which implies the microfibrils are oriented with their long axis 45° from the axis of the rod. The specific mechanism for the behaviour in rod-like structures, including the rod-like micelle, is unclear but a mechanism invoking a longitudinal displacement of the microfibrils forming the rods can account for the direction of the maximum polarizability at 45° to the long geometrical axis of the rod. A longitudinal displacement and packing of the microfibril axis would force them to align at about 45° (i.e. between 33°33′ and 70°07′) to the long axis of the rod. The results shown here confirm the usefulness of this technique with regard to determining the morphology of nonpolymeric rod-like structures.

Although these rod-like micelles are held together by hydrophobic-type interactions and are, undoubtedly, quite dynamic in nature, polymeric-type solution behaviour is observed. In a previous manuscript, the specific rheological characteristics were described[9]. A salient feature of these fluids is the marked decrease in the viscoelastic behaviour with a decrease in hydrophobic character. In this monomer structure, the hydrophobic character is directly related to the length of the methylene sequence, *n*. At an alkyl length of 13, for example, the solution properties were badly deteriorated and, in fact, began to rapidly approach wholly Newtonian behaviour at low shear rates[9]. This leads to the conclusion that the rod-like structures were very dynamic resulting in relatively short rod lengths. Substantially improved properties are observed at higher methylene sequences. In *Figure 5* is shown SALS patterns as a function of hydrophobic character. These results parallel the solution behaviour in that a marked deterioration in the (+) pattern is observed at $n = 13$. In fact, a circularly symmetrical pattern is found at $n = 11$ indicating the formation of an ill-defined superstructure lacking any preferred correlations between the rod-like entities. It is noteworthy, however, that the scattering pattern spans approximately the identical angular range.

Another salient feature of these colloidal rod-like structures is their ability to 'solubilize' long chain methylene units, i.e. hydrophobic units, into its oleophilic interior. These hydrophobic units can be chemically bound onto a chain backbone[11]. The specific number of

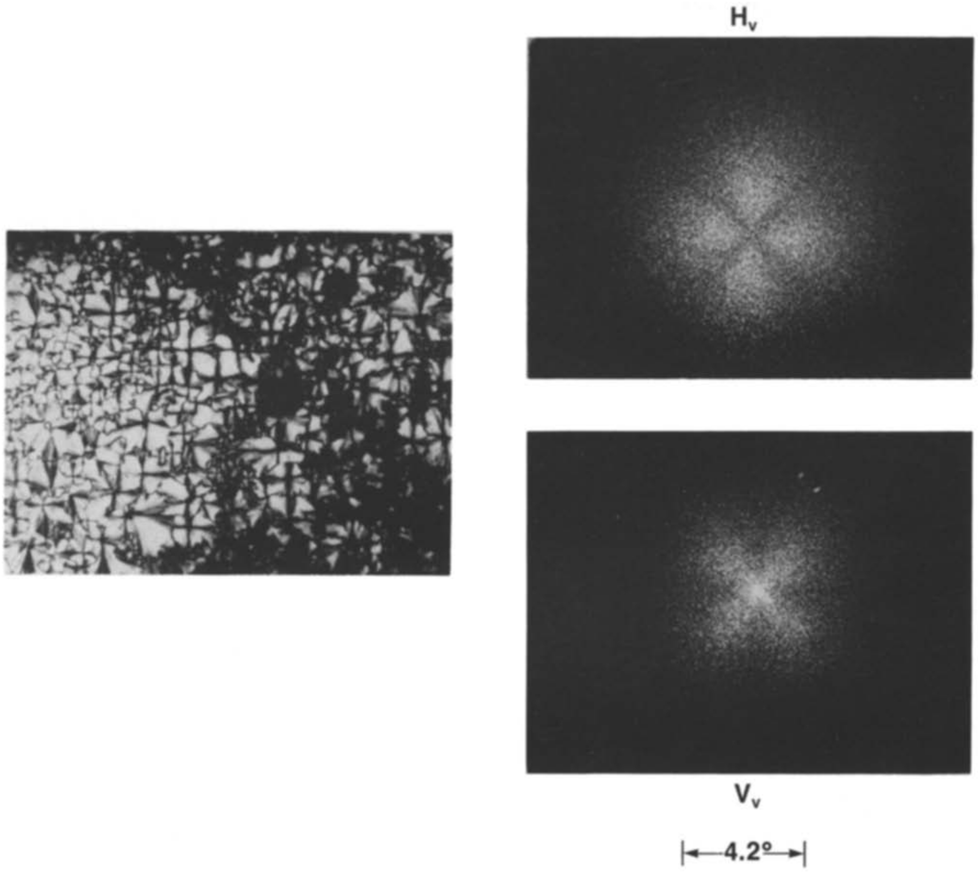

Figure 3 Small angle light scattering patterns and the corresponding polarizing micrograph (160×) from a solid state film of colloidal rod-like micelles. The methylene sequence is 15

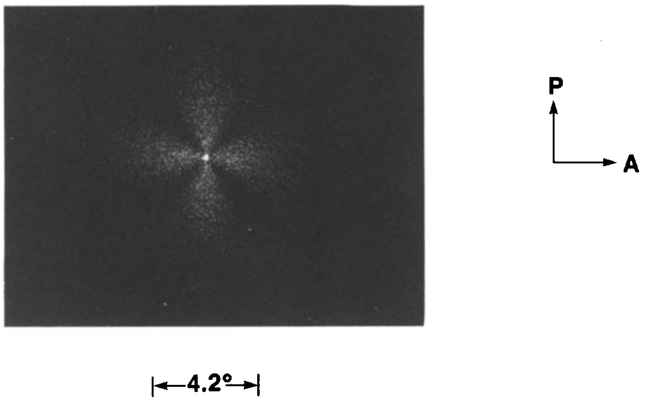

Figure 4 Small angle light scattering pattern (H_V) from a solid state film of hydroxypropylcellulose

these units can be easily varied, but on the average, there is about 1 unit per 100 acrylamide units. The acrylamide monomer units are not strongly associating with the rod-like structures. As anticipated, the rheological characteristics of the rod-polymer mixture is improved considerably with long methylene sequences attached to the polymer chain. The exact morphology of the fluid mixture is presently being explored but it is certainly clear that some sort of 'bridging' between the hydrophobically associating copolymer and rods is taking place (*Figure 6*).

A preliminary examination of films comprising a mixture of nonassociating and an associating copolymer with the colloidal rods shows a striking modification in the SALS patterns (*Figure 7*). With the former copolymer the initial (+) scattering pattern is 'rotated' by 45° to the (X) type. This occurs even at relatively low levels of copolymer ($\leqslant 1$ g/dl). At high copolymer concentrations the nonassociating structure destroys the (+) pattern completely. The pattern persists with the hydrophobically associating copolymer even up to high concentrations. These SALS results confirm the 'compatibility' of the associating-type copolymer with the rod-like micelle. However, the detailed explanation for the change in the SALS pattern is still a matter of speculation. It is important to note that phase separation of the two associating components in solution does not occur. If one assumes that phase separation does not take place during film formation, then the copolymer could simply behave as a nonvolatile, high molecular weight diluent. The rod-like structures would be unable to aggregate into the larger rod-like superstructure, but remain, to a first approximation, as individualized fibrils. Because these latter moieties would be unable to be longitudinally displaced with respect to the long axis of the aggregate, then a (+) pattern would result. Certainly, this mechanism needs to be further detailed in these systems.

CONCLUSION

SALS has been used to examine the solid state morphology of colloidal rod-like entities as a function of methylene chain length (hydrophobic units) and with the addition of hydrophobically associating and nonassociating co-

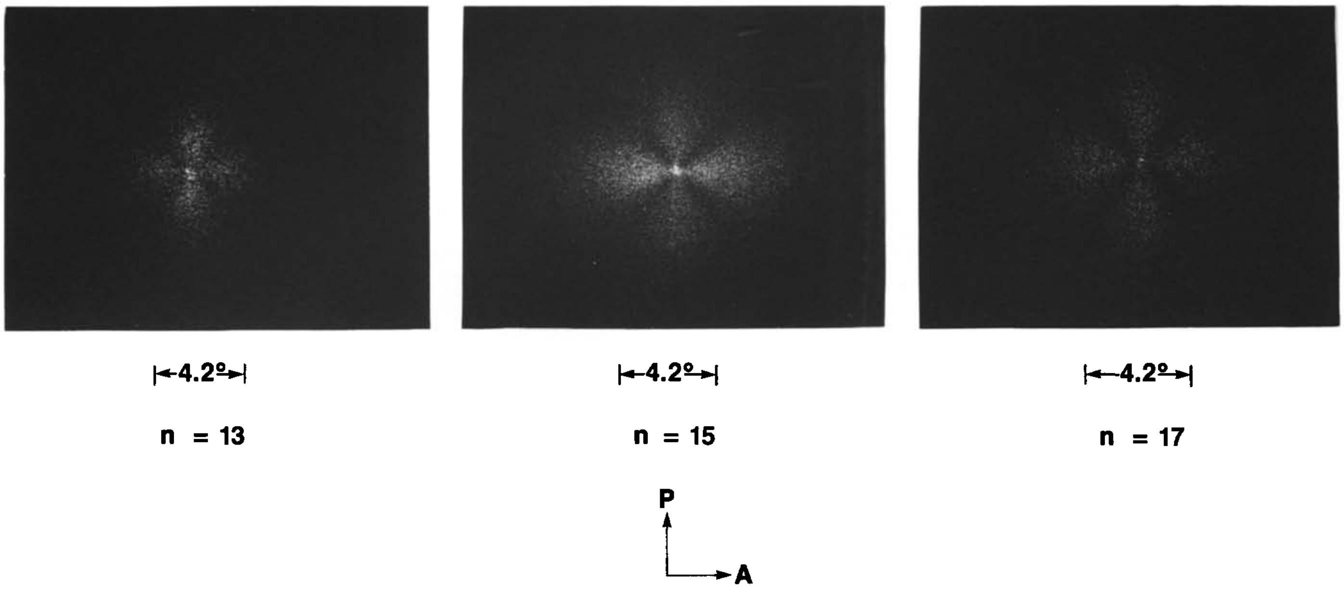

Figure 5 Small angle light scattering patterns (H_V) from a series of solid state films comprising rod-like micelles spanning a range of methyl sequence (n) lengths

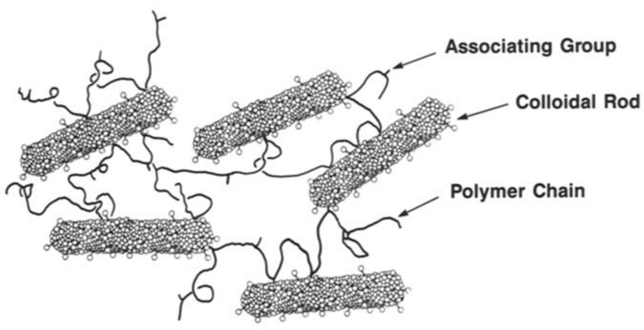

Figure 6 Schematic representation of a solution constituting a mixture of hydrophobically associating copolymers and colloidal rod-like micelles

polymers. The results clearly confirm that the rod-like structure present in an aqueous environment persists in the solid state. The SALS patterns confirm also that the individual rod-like entities aggregate into a superstructure that parallels observations on rod-like polymers, such as hydroxypropylcellulose. That is, the rod-like micelle aggregates orient within the superstructure in such a fashion as to position its optical axis approximately 45° to the long axis. It appears that the addition of water soluble copolymers prevents the longitudinal displacement of the rod-like aggregates in the formation of larger rod-like superstructures. Although more detailed information is required with regard to those complex solid state morphologies, SALS has been shown to be of

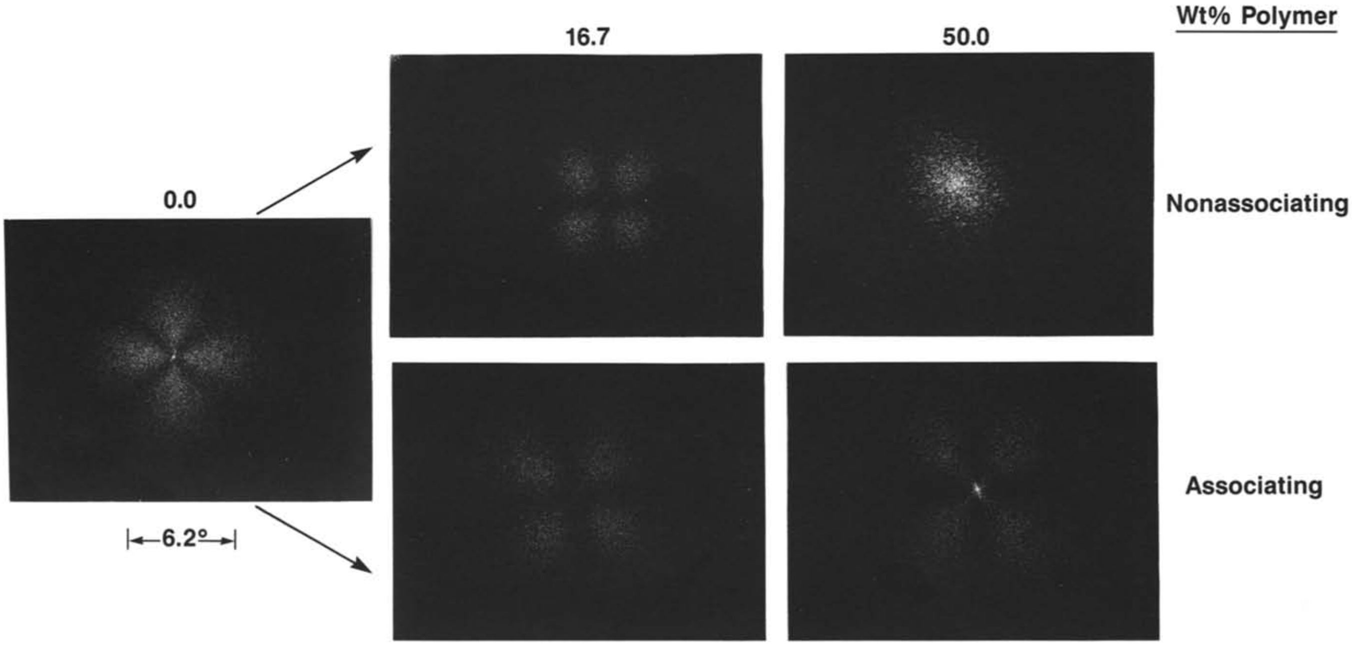

Figure 7 Small angle light scattering patterns (H_V) in the solid state of colloidal rod-like micelles (methylene sequence is 15) mixed with various amounts of a nonassociating copolymer ($n'=1$) and a hydrophobically associating copolymer ($n'=11$). Counterion associated with the rod-like micelle is salicylic acid–sodium salt

considerable utility in probing the morphology of these colloidal rod-like structures.

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