

Polycondensation in liquid crystalline phases of nonionic surfactants. Kinetics and morphology

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Abstract

We have investigated acid-catalyzed polycondensation of alkoxy silane monomers in liquid crystalline phases of nonionic CnEm surfactants. The liquid crystalline phase is retained when the monomers polymerize. The high molecular weight molecules formed phase separate from the mesophase and are subsequently organized by it to form micron-sized particles. A variety of particle morphologies are formed by organization of the polymer particles in the mesophase. For condensation of dimethyldimethoxysilane (DMS, with trimethoxysilane, TMS as crosslinker) in hexagonal and lamellar phases, specific reaction conditions, viz. slow condensation kinetics and low crosslink density, give rod-like particles in hexagonal phases and sheet-like structures in lamellar phases. However, when higher acid concentrations are used, the reaction kinetics accelerates and irregular particles form. Irregular particles also form when the fraction of trifunctional crosslinker is increased, and finally complex flower-like structures form for condensation of trimethoxysilane in the hexagonal phase. The particle morphology formed is crucially dependent on the details of the polycondensation rate, crosslinker density and surfactant-monomer/oligomer interactions.

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1. Introduction

The morphology of polymers synthesized in liquid crystalline media is dictated by the interaction between the growing polymer and the matrix liquid crystal phase [1, 2]. This interaction is dependent on the chemical nature of the polymer and the liquid crystalline matrix phase, and on the ordering in the liquid crystal. Lyotropic surfactant liquid crystals show hexagonal, lamellar, cubic and inverse phases [3,4], and therefore, represent interesting matrices for examining the influence of liquid crystalline order on the synthesis of polymers. Polymerization of monomers localized in surfactant liquid crystalline media typically lead to phase separation of the polymer from the matrix phase. Therefore, synthesis of polymers in surfactant liquid

crystalline phases might offer a route to control of polymer morphology.

There is considerable interest in synthesizing polymeric structures with well-defined nano- and meso-scale morphologies. High internal surface area materials with well-defined and controllable nanostructure are of relevance for separations and as supports for catalysts. Therefore, considerable effort has been devoted to attempts to template the surfactant liquid crystalline structure by polymerization of monomers localized in the mesophase [2,5,6]. There are a few reports where thermoset polymers have been synthesized that perfectly template the original ordered morphology of a surfactant hexagonal phase [7] (templated by phenol-formaldehyde resin) or an ordered block copolymer phase [8,9] (viz. a higher molecular weight analog of surfactants, templated by biphenol-A epichlorohydrin epoxy resin). However, such one-to-one direct templating is rare. Typically, the morphology of polymers synthesized in these surfactant phases rarely resembles the original ordered structure. As molecular weight builds up, the polymer phase separates from the surfactant liquid crystal, driven by a thermodynamic penalty for confinement in an ordered, chemically dissimilar matrix [10–17]. The

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phase separation observed here is similar to that when monomer is loaded in surfactant bilayer vesicles and polymerized. This phenomenon has been investigated in detail and it has been shown that, with a few exceptions [18, 19], the polymer phase separates rapidly to form compact polymer beads on the time scale of the polymerization [20] in most polymer-surfactant systems. These polymer beads sometimes remain associated with the bilayer vesicle (the so-called parachute morphology [21]). Recently, there have been reports of the synthesis of poly(3,4-ethylenedioxythiophene) [22] and polyaniline [23] in the form of nanowires by electropolymerization in surfactant hexagonal mesophases. In these reports, the polymer nanowires obtained were about an order of magnitude larger than the characteristic size scale of the hexagonal phase indicating that they were not formed by a direct templating.

Most reports of polymerization in surfactant liquid crystal phases have focused on free radical polymerization of monomers [5,10–12,16,18–21]. However, our group has previously shown that polycondensation presents a route to the formation of interesting, novel morphologies. We have previously reported [24] the synthesis of crosslinked polysiloxanes by acid-catalyzed condensation of alkoxy-silane monomers in hexagonal and lamellar phases of nonionic surfactants. The polymer particles formed in our experiments matched the geometry of the surfactant mesophase, viz. polymer rods were formed in hexagonal phases while sheets were formed in lamellar phases. However, these polymer particles were three orders of magnitude larger than the characteristic size of the mesophase—thus, the polysiloxane rods and sheets are not formed by direct templating, but rather by phase separation of polymer particles and their assembly in the liquid crystal phase. Interestingly, the morphologies observed in our polycondensation experiments differ from those observed previously in free radical polymerizations in surfactant mesophases [16] and from those predicted by theories of organization of colloidal inclusions in liquid crystalline mesophases [25]. The exact mechanism for the formation of the polysiloxane particle morphologies observed in our experiments is not understood, neither is it clear why these morphologies differ from those predicted by theories of ordering of colloids in liquid crystals, and observed in free-radical polymerizations in mesophases.

In this paper, we explore in detail the influence of reaction parameters on the kinetics and morphology of the particles formed. The rod-like and sheet-like particles previously reported by us form only under conditions where hydrolysis and condensation of monomers is slow and where the polysiloxane is only lightly cross-linked. The rate of hydrolysis of the alkoxy-silane monomer and its subsequent condensation depend on the pH of the reaction medium. First, we report the influence of acid concentration on the kinetics and morphology of particle formation. Then, we examine the influence of cross-link density (viz. concentration of trifunctional monomers) on the

morphology of the polymer particles, and then explore how varying the organotrialkoxysilane changes the morphology of particles.

2. Experimental part

2.1. Materials

Nonaethylene glycol monododecyl ether ($C_{12}E_9$) was procured from Sigma. Polyoxyethylene(2) oleyl ether ($C_{18}E_2$) and polyoxyethylene(10) oleyl ether ($C_{18}E_{10}$) were purchased from Aldrich. The commercial nonionic surfactants used here are not chemically pure, and are available only as mixtures with the nominal composition specified by C_nE_m . HPLC characterization of the surfactants used in our experiments has been reported previously [24]. When C_nE_m surfactants having different n and m are mixed, the resultant materials show phase behaviour characteristic of the volume averaged n and m [4,24]. Therefore, $C_{18}E_6$ prepared by a mixture of equal parts of $C_{18}E_2$ and $C_{18}E_{10}$ shows the same phase behaviour as pure $C_{18}E_6$. Dimethoxydimethylsilane (DMS, purity 99.5%), methyltrimethoxysilane (TMS, purity 98%), trimethoxypropylsilane (purity 98%), trimethoxyoctylsilane (purity 96%) and trimethoxyphenylsilane (purity 97%) were obtained from Aldrich. All chemicals were used without further purification. Distilled deionized water (resistivity = 18.2 M Ω -cm) from a Milli-pore Milli-Q system was used for all experiments. We prepared a stock solution of 1 M sulphuric acid and diluted it as required for our experiments.

2.2. Sample preparation

1:1 parts by weight of $C_{12}E_9$ and aqueous acid solutions at the desired acid concentration were used to prepare the hexagonal phase. Lamellar phase was prepared from 0.7:0.3 parts by weight of $C_{18}E_6$ and acid solutions. The liquid crystalline phases were highly viscous gels with a few air bubbles trapped in them. Liquid crystalline phases were identified by the textures observed when the sample is viewed between crossed polarizers, and by the characteristics peaks observed in X-ray scattering (viz. for the hexagonal phase, the second order peak appears at a d -spacing corresponding to $1/\sqrt{3}$ the d -spacing of the primary peak). We have previously described the detailed characterization of the liquid crystalline mesophases [24].

Polymerization was carried out in the following manner. The appropriate quantity of monomer was thoroughly mixed with surfactant in a clean screw-cap glass vial. Then, acid solutions were added to this and the mixture was vortexed for about a minute. All our polymerisations were catalysed using sulphuric acid. The acid concentrations used were 0.01, 0.2 and 1 M. The monomer comprised of mixtures of DMS and trifunctional silanes, with the fraction of trifunctional monomer ranging from 1 to 100%. For

example, a typical polymerization reaction in hexagonal phase was carried out by mixing 40 μl (8% by volume) of silane with 230 μl (46% by volume) C_{12}E_9 and vortexing, followed by addition of 230 μl (46% by volume) of aqueous acid to the mixture. Note that the density of the surfactant is close to that of water. Vortexing was repeated to give homogeneous mixing. In case of polymerisation in lamellar phases, the fraction of silane was fixed at 5% by volume.

2.3. Characterization

Polysiloxane particles were separated from the liquid crystalline gel phase for analysis using FTIR (Perkin–Elmer 16-PC FT-IR). The gel containing particles was washed thoroughly with acetone to remove the surfactant and the polymer particles were allowed to settle down. This process of washing and separation was repeated thrice, after which the particles were vacuum dried at 50 $^{\circ}\text{C}$. The dry particles were taken in chloroform for FTIR. FTIR confirms that the particles comprise cross-linked siloxanes—this data is presented in the Supplementary information.

Characterization of the samples was done by polarized optical microscope (Olympus-BX50) and small angle X-ray scattering (Rigaku D-MAX-2500 using $\text{Cu K}\alpha$ radiation). For TEM, the gel was dispersed in ethanol and further crosslinking was terminated by addition of a large excess of trimethylmethoxy silane. TEM grids were prepared by spotting this dilute solution onto them. TEM was done on a JEOL1200-EX at an accelerating voltage of 80 kV.

2.4. Model experiments to establish localization of alkoxy silane monomers

When the alkoxy silane monomers are added to the surfactant mesophase, it is difficult to establish where they localize. Therefore, model experiments were conducted wherein the monomers were added to a test tube containing

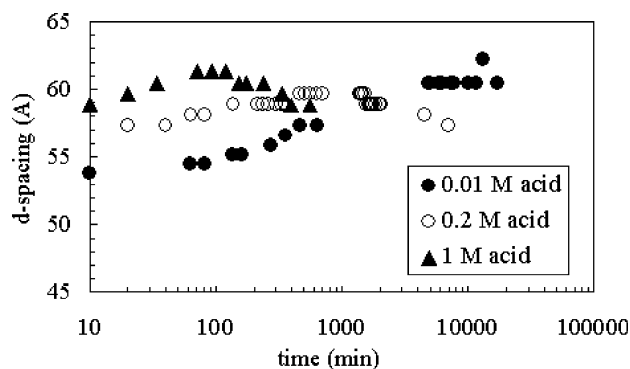


Fig. 1. Variation in d -spacing of the C_{12}E_9 -water hexagonal phase as monomer is condensed in it, at acid concentrations of 0.01, 0.2 and 1 M. The d -spacings are obtained from the primary peak of the X-ray diffraction pattern from the hexagonal phase.

a dodecane (oil) and acidified water (0.2 M sulphuric acid). The oil phase is less dense and is on top of the aqueous phase. Samples are withdrawn from the oil phase as a function of time and are analysed using FTIR (Perkin–Elmer 16-PC FT-IR) to determine the presence of the monomer, and to check whether oligomers have formed. We also visually monitor the mixture for the onset of turbidity that signifies phase separation.

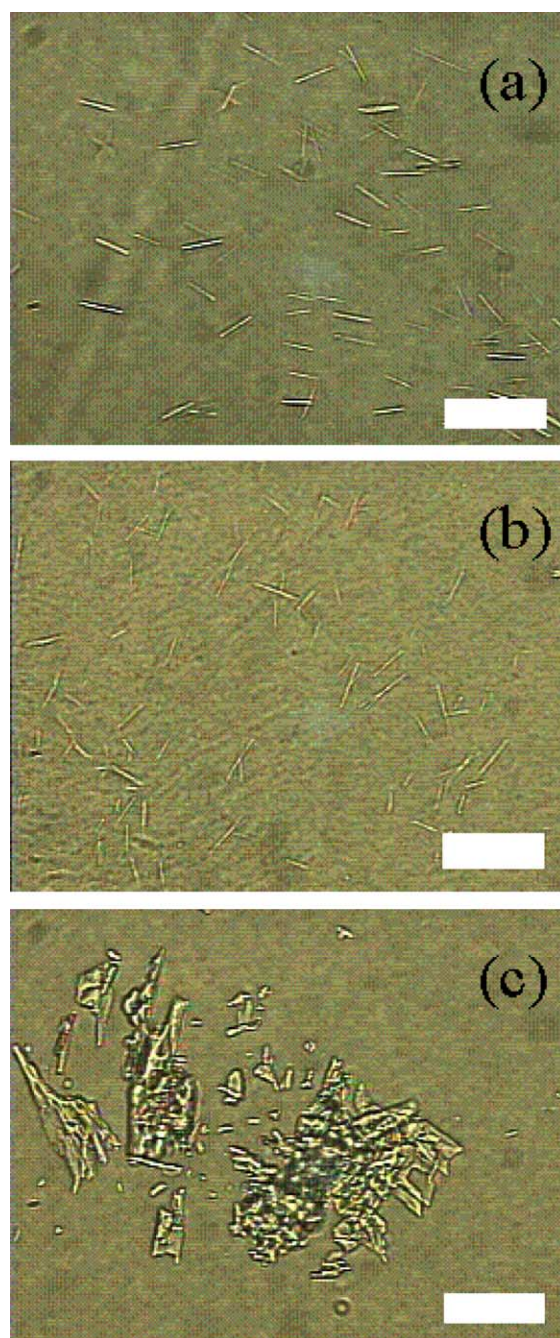


Fig. 2. Optical micrographs of polysiloxane structures formed after condensation of 4:1 DMS:TMS mixtures in a C_{12}E_9 -water hexagonal phase at acid concentrations of (a) 0.01 M, (b) 0.2 M and (c) 1 M. Scale bars represent 50 μm .

3. Results and discussion

The hexagonal phase of the liquid crystalline $C_{12}E_9$ -acidified water system is preserved as polysiloxane forms by co-condensation of a 4:1 mixture of dimethyldimethoxysilane (DMS) and trimethoxysilane cross-linker (TMS) within the mesophase [24]. The X-ray diffraction (XRD) pattern characteristic of the hexagonal phase (showing primary and secondary peaks with a d -spacing ratio of $\sqrt{3}:1$) is observed throughout the experiment as the

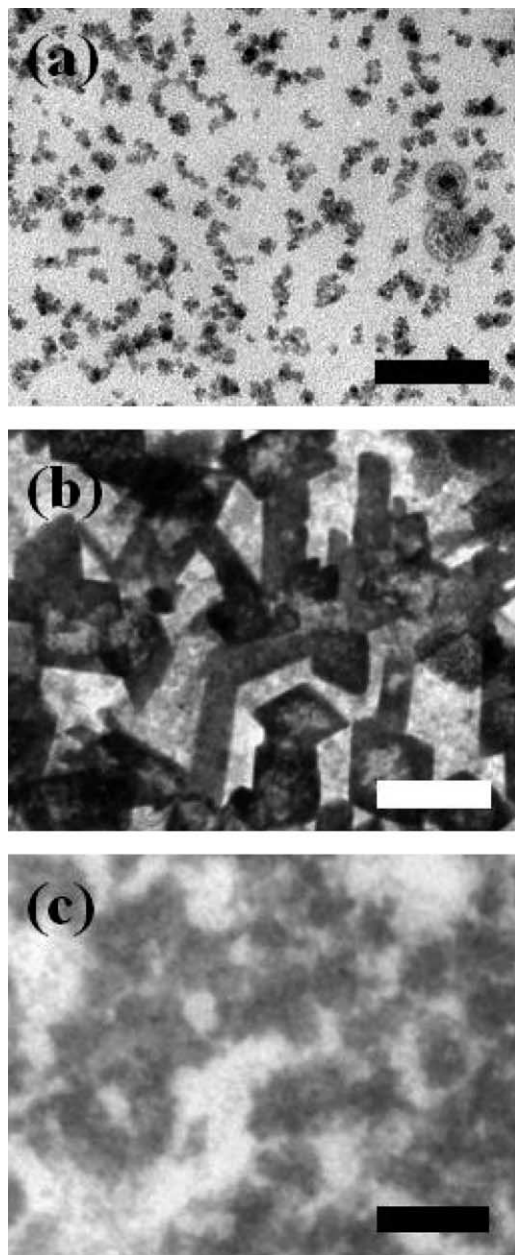


Fig. 3. Transmission electron micrographs of particles observed during condensation of 4:1 DMS:TMS mixtures in a $C_{12}E_9$ -water hexagonal phase at (a) early (1 h) and (b) late stages (6 days) at an acid concentration of 0.2 M, and (c) at a late stage (10 days after monomer addition) at an acid concentration of 1 M. All scale bars represent 200 nm.

monomer is converted to polymer. After addition of the monomers, the d -spacing of the hexagonal mesophase initially increases and then decreases (Fig. 1). We have explained this trend in d -spacing on the basis of a mechanism that emerged from model experiments described previously [24]. We showed that monomers are confined to the organophilic (C_{12}) region upon addition to the mesophase. However, they quickly hydrolyse and move into the aqueous region. As they condense and form hydrophobic siloxane oligomers, they move back into the organophilic cylinders and swell the d -spacing. The oligomers continue to increase in molecular mass with time, and eventually phase separate from the mesophase to form colloidal particles that are a few tens of nanometers in size. Thus, the d -spacing of the hexagonal phase decreases at later times. The qualitative trend in d -spacing is similar as the concentration of acid in the aqueous phase is increased from 0.01 to 0.2 to 1 M—however, the time scale decreases dramatically. The time at which the d -spacing shows a maximum (which we use as a characteristic time for this process) decreases by two orders of magnitude, from 10,000 min (for 0.01 M) to 1000 min (for 0.2 M) to 100 min for the highest acid concentration (1 M) (Fig. 1). Thus, it appears that polysiloxane is formed more rapidly at higher acid concentrations, and that the rate of hydrolysis and condensation is increased.

Large polysiloxane particles, with dimensions on the order of microns are formed several days after addition of monomer to the hexagonal phase, and subsequent to the swelling/deswelling of the mesophase. The particle morphology observed is a function of the concentration of acid used for condensation. For acid concentrations of 0.01 and 0.2 M, where the rates of hydrolysis and condensation are slow, the colloidal particles that separate from the surfactant mesophase assemble to form larger (micron-sized) rod-like morphologies (Fig. 2(a) and (b)). For 1 M acid, where the swelling/deswelling of the hexagonal phase is about ten times faster than at 0.2 M, the final morphology is irregular (Fig. 2(c)). Thus, regular, rod-like morphologies are formed only at acid concentrations where the rates of hydrolysis and condensation are relatively slow.

TEM reveals further details of the formation of these structures. At an acid concentration of 0.2 M, small siloxane particles around 20–40 nm in size form about 1 h after addition of monomer (Fig. 3(a)). These particles assemble in the liquid crystal matrix and form larger (≈ 100 nm), geometrically regular particles over a period of several days (Fig. 3(b) shows TEM at 6 days from the addition of monomer). Under these conditions, the hexagonal phase starts deswelling after about 1000 min (approximately 1 day, Fig. 1). There is a large polydispersity in sizes of the particles observed in the TEM and 50–100 nm particles co-exist with large micron-sized rods. For an acid concentration of 1 M, irregular aggregates that are 50–100 nm in size are observed after 10 days (Fig. 3(c)). Thus, at low acid concentrations when polycondensation is slow,

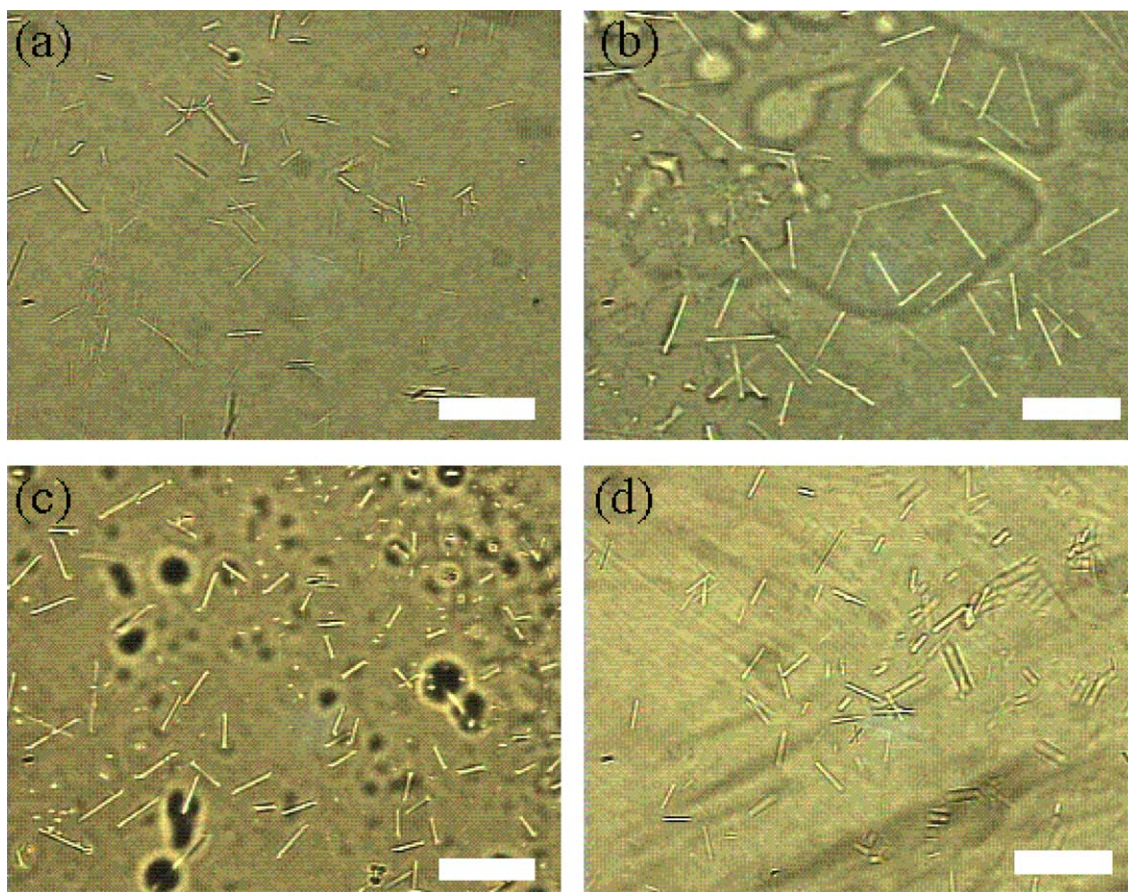


Fig. 4. Optical micrographs to track the change with time of rod-like polysiloxane particles observed for condensation of a 4:1 DMS:TMS mixture in a $C_{12}E_9$ -water hexagonal phase at an acid concentration of 0.01 M. Micrographs are taken (a) 10 days, (b) 20 days, (c) 30 days and (d) 50 days after addition of monomer. Scale bars represent 50 μm .

the siloxane particles are able to organize in the liquid crystalline medium to form geometrically regular particles. At higher acid concentrations (1 M), when polycondensation is more rapid than at 0.2 M (by about an order of magnitude based on the data in Fig. 1), the colloidal particles aggregate to form disordered structures.

We now examine the development of the particles under conditions that give rise to rod-like morphologies. At the lowest acid concentrations examined (0.01 M), rod-like structures form on a time scale of days and are visible using the optical microscope between 5 and 15 days after monomer addition (Figs. 4 and 5). There is large sample-to-sample variation in the time at which particles can be observed under the optical microscope. This time does not appear to correlate with the rate of hydrolysis and condensation of monomers. Further, there is considerable spatial heterogeneity in the number density and size of particles at various locations in the liquid crystalline gel: Particles are found in some locations in the gel and are absent at others. Therefore, we present data on the size of the particles from three independent repeat experiments: Each data point in each experiment is obtained by averaging the size of particles from several different locations in the sample vial. We examined the evolution of

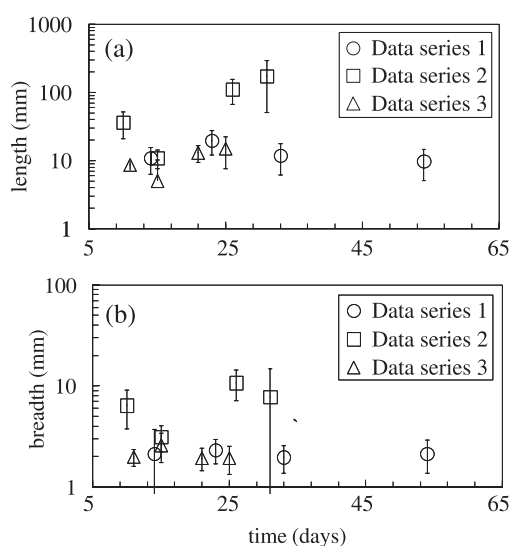


Fig. 5. The change in the (a) length and (b) breadth of the rod-like polysiloxane particles with time when a 4:1 DMS:TMS mixture is condensed in a $C_{12}E_9$ -water hexagonal phase at an acid concentration of 0.01 M.

these polysiloxane rods as a function of time by periodically sampling the hexagonal phase after addition of monomers. We observed the colloidal particles using optical microscopy and obtained the length and breadth of the particles (averaged over around one hundred particles). In two experiments (Fig. 5(a) and (b); data series 1, 3), there was essentially no change in the size of the rods with time after they were first observed. However, in one other case (Fig. 5(a) and (b); data series 2), there was a significant increase in the size of the rods with time, and an increase in the size-polydispersity (as is evident from the increase in the size of the standard deviation with time). Thus, while we obtain the same morphologies in each experiment, we cannot quantitatively reproduce the sizes obtained, neither can we reproduce trends in growth of these particles as a function of time.

The mechanism that emerges is that, at all acid concentrations, monomers condense and cross-link to form polysiloxane particles that phase separate from the liquid crystalline mesophase once their size is a few tens of nanometers. Further, aggregation and cross-linking of these particles to form the micron-scale structures is dictated by the mesophase. For low acid concentrations, condensation is slow and the colloidal particles phase separate from the mesophase over days. Under these conditions, they aggregate to form rod-like structures. For high acid concentrations, the condensation rate is rapid and the particles assemble into irregular structures. The time scale for the formation of the micron-sized particles shows large sample-to-sample variations and spatial variations within a sample, and might be strongly influenced by local spatial variations in the number density of the colloidal particles.

Varying the ratio of DMS to the trifunctional cross-linker, TMS changes the crosslink density in the

polysiloxane particles as well as the hydrophobicity of the oligomers, and hence the thermodynamics of oligomer–mesophase interactions. When the DMS:TMS ratio is low (at least up to a TMS concentration of 20%), the oligomers that form at initial stages of polycondensation are localized in the organic phase until their molecular weight increases and they phase separate. However, for pure TMS, oligomers are preferentially localized in the aqueous phase until phase separation [24]. We systematically varied the TMS concentration from 1% of the total monomer added to 100% and found that for condensation at an acid concentration of 0.2 M, the rod-like morphologies formed at low TMS concentrations gradually change to a mixture of rod-like and irregular particles above DMS:TMS ratio of 4:1, and finally form flower-like particles for 100% TMS (Fig. 6). It is worth noting that when pure TMS is condensed, structures large enough to be observed in the optical microscope form rapidly, in about 10 h, relative to the DMS:TMS mixtures that typically take a few days. Therefore, it appears that the higher functionality of the monomer leads to the formation of oligomers that are rapidly phase separated from the mesophase and that these arrange and cross-link to form the observed flower-like structures. Thus, the cross-link density and hydrophobicity of the particles formed strongly influence the particle morphologies obtained—however, the detailed mechanisms for this complex organization need further investigation.

We further explored the mesophase-directed structures that formed for condensation of a variety of trifunctional monomers whose oligomers have different hydrophobicity as compared to TMS (based on their localization in oil–water mixtures). We condensed *n*-propyltrimethoxysilane, octyltrimethoxysilane and phenyltrimethoxysilane (8% by

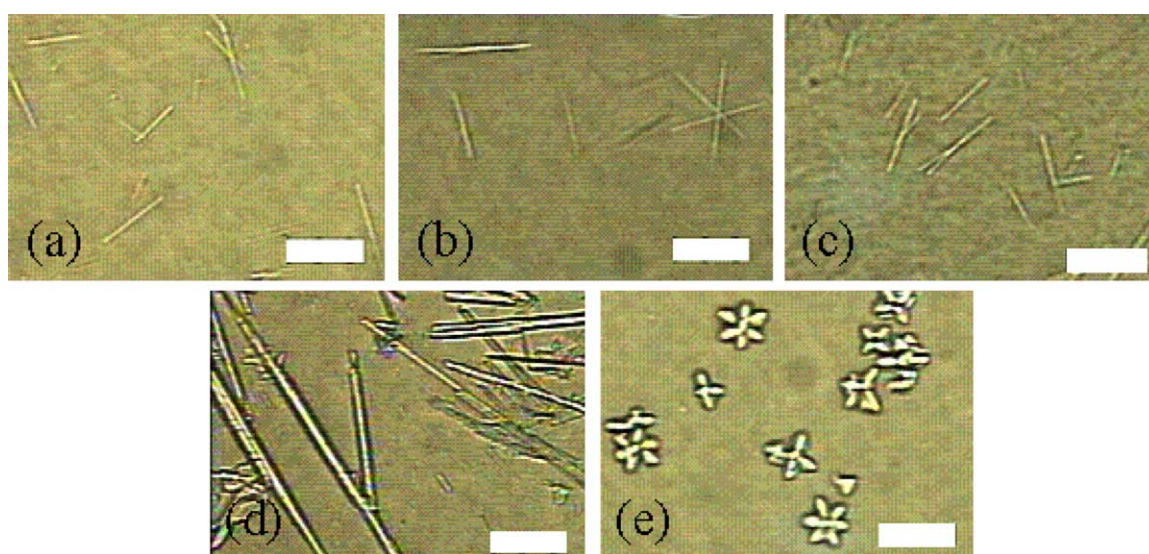


Fig. 6. Optical micrographs showing the change in particle morphology obtained when the DMS:TMS ratio is varied during condensation of monomer in a $C_{18}E_9$ -water hexagonal phase at an acid concentration of 0.2 M. When the percentage of TMS as a fraction of total silane added is increased from (a) 1% to (b) 5% to (c) 20% to (d) 50% and finally 100%, the particle morphology changes from rods to a mixture of rods and irregularly shaped particles to flower-like particles. Scale bars represent 25 μm .

volume) in the hexagonal phase at an acid concentration of 0.2 M and observed the formation of flat particles in all three cases (Fig. 7, compare with the flower-like particles observed for TMS in Fig. 6(e)). In model experiments (Section 2) where the location of the silanes were tracked using FTIR during condensation in a test tube containing dodecane (oil) and 0.2 M sulphuric acid (water) phases, we see that oligomers of TMS and *n*-propyltrimethoxysilane are localized in the aqueous phase during hydrolysis and condensation while oligomers of octyltrimethoxysilane are localized in the oily dodecane phase and oligomers of phenyltrimethoxysilane partition between oil and water phases (data not shown). In all cases, after ‘complete’ condensation (*viz.* for several hours), crosslinked particles visibly phase separated from both oil and water phases.

Our model experiments demonstrate that the localization behaviour of oligomers of various trialkoxysilanes is different, and is a function of the organic group attached

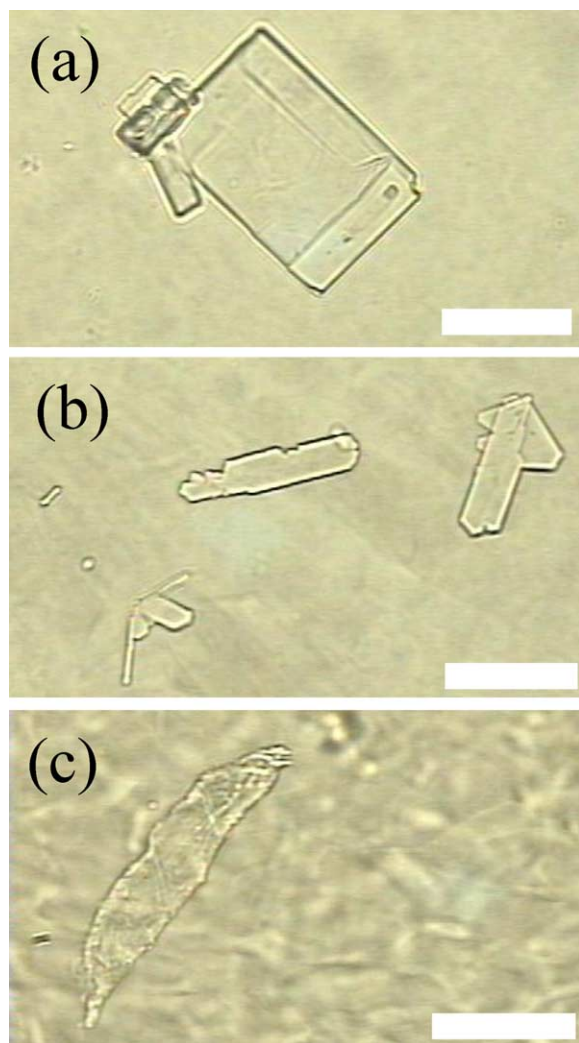


Fig. 7. Optical micrographs of particle morphologies formed by condensation of organotrimethoxysilane in a $C_{12}E_9$ -water hexagonal phase at an acid concentration of 0.2 M where the organo group is (a) *n*-propyl, (b) octyl and (c) phenyl. Scale bars represent 50 μm .

to the silicon. However, flat particle morphologies are observed for condensation of all trifunctional silanes investigated in the hexagonal mesophase, except TMS. Therefore, it is unlikely that the morphology is determined only by how the monomers and/or oligomers are localized in the surfactant mesophase.

The organic group on the monomers determines their interaction with the surfactant mesophase, and appears to govern the particle morphology. Sheet-like morphologies have also been observed for free-radical polymerization in hexagonal mesophases [16]. These morphologies can be rationalized by theories of organization of colloidal entities in liquid crystalline phases [16,24]. However, it is unlikely that the flat particles observed for condensation of TMS follow the same mechanism.

The unique flower-like morphologies observed for condensation of TMS in the hexagonal mesophase appears to result from a subtle balance of hydrophilicity and hydrophobicity of the TMS oligomers.

We observe similar behaviour to that described in the above hexagonal phases when we carry out polycondensation of alkoxy silanes in lamellar phases of a $C_{18}E_7$: Water lyotropic phase. There too, the lamellar liquid crystalline structure of the mesophase is preserved and higher acid concentrations lead to more rapid changes in the *d*-spacing. For polycondensation in the lamellar phase, varying the fraction of trifunctional cross-linker leads to a change in particle morphology from sheets to cubes (Supplementary information).

4. Conclusions

We report a route to a variety of morphologies when polymer particles are formed by acid-catalyzed polycondensation of alkoxy silane monomers in organized hexagonal and lamellar mesophases of nonionic C_nE_m surfactants. When dimethyldimethoxy silane (DMS) is crosslinked using 20% trimethoxymethylsilane (TMS) in a hexagonal phase, the *d*-spacing of the hexagonal phase first swells and then deswells. We interpret the swelling as resulting from the localization of oligomers in the hydrophobic domains of the hexagonal mesophase, and the subsequent deswelling as arising from phase separation of the polymers from the mesophase, as the molecular weight of the polymer increases. The rate of swelling/deswelling is dependent on the concentration of the sulphuric acid catalyst, and increases hundred-fold as we go from 0.01 to 1 M acid. The polymers that phase separate are organized by the mesophase-for acid concentrations up to 0.2 M, rod-like morphologies are formed. For acid concentrations of 1 M, irregular particles are observed. When the fraction of TMS relative to the total monomer added is increased at an acid concentration of 0.2 M, the rod-like morphology transforms to irregular structures, and finally flower-like particles are formed for condensation of pure TMS in the hexagonal

phase. Condensation of other trimethoxysilanes (with propyl, octyl and phenyl groups bonded to the silicon) give flat structures. Model experiments demonstrate that while oligomers of TMS and propyltrimethoxysilane localize in the aqueous phase, octyltrimethoxysilane oligomers localize in the hydrophobic phase while phenyltrimethoxysilane oligomers partition between both domains. Therefore, the particle morphologies observed are not governed by the localization of the monomers and oligomers in the surfactant mesophase. Flower-like morphologies are observed for condensation of TMS, probably resulting from a unique balance of hydrophobicity and hydrophilicity of the TMS oligomers.

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Supplementary data

Supplementary data associated with this article can be found at [doi:10.1016/j.polymer.2005.07.001](https://doi.org/10.1016/j.polymer.2005.07.001)

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