

SYNTHESIS AND AGGREGATION PROPERTIES OF IONIC AMPHIPHILIC SIDE CHAIN SILOXANE POLYMERS

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INTRODUCTION

Amphiphilic polymers have attracted considerable attention of late for their application as associative thickeners.^{10,22} Comb or regular side chain polymers offer a variety of uses in thermotropic liquid crystalline form as media for optical data storage, electrooptic display devices, nonlinear optical devices, photoconductors, solid polymer electrolytes and stationary phases in chromatography applications.¹⁵

Recently, efforts to synthesize side chain lyotropic liquid crystal-forming polymers with either amphiphilic or rigid thermotropic mesogenic side chains have revealed that lyotropic liquid crystallinity can be greatly enhanced by attaching the lyotropic LC-forming group to a flexible polymeric backbone. This enhanced stability manifests itself in terms of both enlarged compositional and thermal extent of individual LC phases.^{8,9,13,14} Using polymethylhydrosiloxane (PMHS) as a derivatizable hydrophobic backbone, Finkelmann and coworkers have attached a variety of both rigid and flexible amphiphilic side chain groups to this polymer by hydrosilylation.

Finkelmann and Rehage⁷ reported the synthesis of several liquid-crystal-forming polysiloxanes with rigid mesogenic side-chains. The mesogenic group was either a substituted biphenyl or a substituted phenyl ester of benzoic acid. These were attached by propyloxy or butyloxy groups to the siloxane backbone, and the end of the side chains consisted of either a methoxy, a hexyloxy or a nitrile group. These side chain polymers all exhibited thermotropic liquid crystallinity, with lower glass transition temperatures than their hydrocarbon analogues because of the flexibility in the backbone.

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Finkelmann *et al.*⁸ first reported on solvent-induced or lyotropic liquid crystallinity of polysiloxane with amphiphilic side chains. The amphiphilic side-chain was the ester of 10-undecenoic acid and either tetra-, hexa-, or octaethylene glycol monomethyl ether. This nonionic amphiphile was added to the PMHS backbone by hydrosilylation. The monomer undecenyl-octaethylene glycol monomethyl ether (UOG) exhibits a hexagonal lyotropic LC phase at concentrations from 49-70 wt % surfactant in water and at temperatures from -10 to 20°C. The amphiphilic side-chain polymer in which UOG is coupled to the PMHS backbone of degree of polymerization (DP) 95 exhibits a large region of lyotropic hexagonal phase from 40-75 wt % polymer and from -10 to 50°C. In addition, at higher concentrations (70-90%) and over a wider temperature range (-10 to 65°C), there exists a stable lamellar LC phase. Thus, the polymeric amphiphile was observed to have lyotropic LC phases of enlarged compositional and thermal extent than the analogous monomeric amphiphile. Finkelmann *et al.*⁸ speculated that this enhanced stability may be due to restricted translational and rotational mobility of the amphiphilic groups when they are anchored to a polymeric backbone.

Luhmann and Finkelmann¹⁴ documented a similar enhancement of lyotropic liquid crystallinity upon attachment of nonionic amphiphiles to PMHS in which the hydrophobic portion of the amphiphile consisted of a propyloxy or hexyloxy group linked to a biphenyl moiety. The hydrophilic portion of the amphiphilic side-chain was a monomethyl ether of nonaethylene glycol or undecaethylene glycol. As with the flexible hydrophobic side chain, greatly enhanced thermal and compositional extents of the hexagonal and lamellar LC phases were observed. Moreover, this effect was apparent even at very small DPs of 3-6.

Based on the successful attempts of Finkelmann and coworkers to synthesize nonionic polymeric surfactants that exhibit lyotropic mesomorphism with enhanced stability over the corresponding monomer, it seemed reasonable that ionic amphiphilic side chain polymers based on PMHS could also be synthesized that might exhibit comparable enhanced lyotropic mesomorphism. In this chapter, we describe the synthesis of polymeric surfactants comprised of PMHS functionalized with undecenoic acid side chains, which are subsequently neutralized to yield the corresponding cesium salts of the polymeric carboxylic acid. These materials have been characterized by ¹H-NMR spectroscopy to determine the number average molecular weight and the degree of side chain functionalization. The aggregation properties of these materials in water have been studied indirectly by surface tensiometry and directly by quasi-elastic light scattering (QLS). The lyotropic liquid crystallinity has been probed by making aqueous solutions with deuterated water (D₂O) and observing the resulting deuterium NMR spectra and their dependence on composition. The phase behavior at high concentration and the aggregation behavior at low concentration of the polymeric surfactants are compared to those of the monomeric surfactant, cesium undecenoate.

EXPERIMENTAL PROCEDURES

Materials

The hydrophobic polymer backbone, polymethylhydrosiloxane (PMHS) was obtained from Aldrich Chemicals (catalog no. 17,620-6, DP = 30) and Petrarch Systems (catalog no. PS119, $M_w = 1500$). 10-Undecenoic acid, sodium hexachloroplatinate, and dicyclopentadiene were the purest grades available from Aldrich Chemicals. The reaction and separation solvents tetrahydrofuran, toluene, methanol and 1-propanol were HPLC grade materials from Fisher Scientific. Cesium hydroxide was from Carus Chemicals, D_2O was 99.8% isotopic purity from Wilmad Glass and $CDCl_3$ and CD_3OD were from MSD Isotopes. Undeuterated water was drawn through a four-stage Nanopure filtration system and stored in glass bottles.

Methods

Polymer Synthesis

Hydrosilylation of the PMHS backbone by 10-undecenoic acid was performed according to the procedure described by Apfel *et al.*¹ PMHS and 10-undecenoic acid (4.7-11.6 % excess) were dissolved in one of the three solvents, THF, toluene or 1-propanol. The solution was warmed to the reaction temperature (50-100°C), and the catalyst added (150-6600 ppm). For four of the reactions, the catalyst components (NaPtCl \cdot 6HO and dicyclopentadiene) were added directly in solution form to the reaction mixture. For the other two reactions, the catalyst product (dicyclopentadienylplatinum chloride) was synthesized prior to being introduced to the reaction mixture¹. Active catalyst was prepared by dissolving 0.33 g of NaPtCl \cdot 6HO in 7 mL of glacial acetic acid, diluting with 14 mL of water, adding 0.38 g of dicyclopentadiene, heating to 70°C and stirring vigorously for 24 hours. The product catalyst was centrifuged, decanted and washed three times with THF. The hydrosilylation reaction, which ran for 2-24 hours with a nitrogen sparger to agitate the mixture and prevent oxidation, should form predominantly the anti-Markovnikov product. Hydrosilylation was carried out in a 500-mL three-necked round bottom flask. Inserted into the vertical neck of the flask was a 50 cm Allihn drip tip condenser with glass wool in its outlet to reduce the escape of solvent. The reaction mixture was sparged continuously with nitrogen and the reaction temperature was continuously monitored. A Glas-Col heating mantle, controlled by a Staco 120 volt variable transformer, was used to heat the reaction mixture.

Polymer Isolation

Following reaction, solvents were replaced with methanol by diafiltration of the reaction mixture through a YM-5 cellulose acetate membrane (5000 MW cutoff) in an Amicon 8400 stirred cell ultrafiltration system. The acidic form of the polymer - poly(methyl undecanoic acid siloxane), or PMUS - was converted to the cesium salt form by stoichiometric addition of cesium hydroxide in methanol. The neutralized cesium salt form of the polymer (PMCsUS) was converted to an aqueous solution by diafiltration with either deuterated or undeuterated water.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to monitor the course of the reaction and reaction solvent replacement during diafiltration. The setup included a Perkin-Elmer Series 10 liquid chromatography pump, supported by a Perkin-Elmer LC-25 differential refractive index (RI) detector, and a Fisher Recordall Series 5000 chart recorder. One GPC column used was a Waters Associates μ Syrage!TM linear gel permeation column with a reported molecular weight range of 500-1,000,000. The second GPC column used was a DuPont ZORBAX porous silica microsphere (PSM) 60S high performance size exclusion column (HPSEC) with a molecular weight range of 100-10,000.

Nuclear Magnetic Resonance Spectroscopy

Two nuclear magnetic resonance (NMR) spectrometers were used to characterize the polymer and to probe for evidence of liquid crystallinity: a General Electric GN-300 Omega spectrometer and an IBM-CX 100 spectrometer. The GE GN-300 Omega spectrometer was equipped with a 5 mm dual probe with a proton resonance frequency of 300.522 MHz. Chemical shifts of protons are reported relative to TMS. The IBM-CX 100 spectrometer was equipped with an IBM VTU temperature controller, an Aspect 3000 software package and a drum plotter. A 10 mm deuterium probe with a resonance frequency of 15.371 MHz was used with this spectrometer. Typical spectral conditions in obtaining deuterium spectra were a 5000 Hz spectral width, 12 μ s pulse width (corresponding to about 45°), 0.5-1.0 seconds acquisition time and 500-1000 transients.

Surface Tensiometer

Surface tensions were measured by the DuNuoy Ring detachment method with a Fisher 215 Autotensiomat Surface Tension Analyzer and a 6.005 cm circumference platinum-iridium DuNuoy ring. A Fisher Recordall Series 5000 chart recorder was used to display the results of the analyses. A Lauda RC 20 refrigerating circulator was used to maintain constant temperature.

Quasielastic Light Scattering

The quasielastic light scattering (QLS) Instrument used was comprised of an Innova 70-3 argon ion laser (Coherent) equipped with a Brookhaven Instruments (BI)- 200 SM Automatic Goniometer, a BI-2030 digital correlator, a BI computer, a BI high voltage power supply and a Newport 815 power meter. The system temperature was controlled by a BI RTE-5DD refrigerated circulating bath.

RESULTS

Surface Tension Measurements of Cesium Undecenoate-Water Solutions

In order to determine the efficacy of lowering surface tension and the critical micelle concentration (CMC) of the monomer cesium undecenoate, surface tension measurements were made on aqueous solutions of cesium

undecenoate in the concentration range from 80 μM to about 0.1 M. The surface tension decreases monotonically (Figure 1) with increasing concentration below about 0.06 M. Above this concentration, the surface tension is virtually independent of concentration. We attribute this leveling of the surface tension to micellization of the surfactant. Application of the Gibbs adsorption isotherm to the surface tension data² yields a surface excess concentration for cesium undecenoate just below the CMC of 0.239 nmol/cm². This corresponds to an area/molecule of approximately 69 \AA^2 .

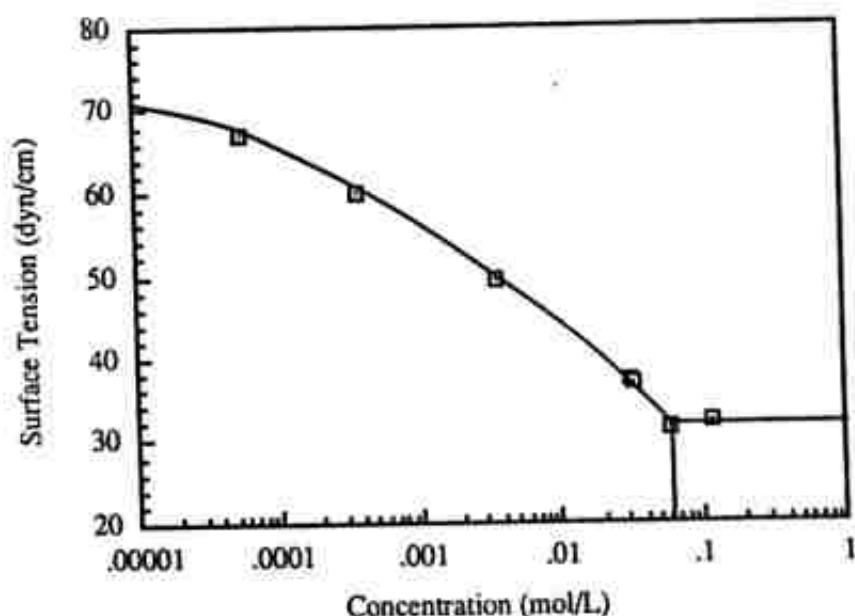


Figure 1. Dependence of surface tension on surfactant concentration of cesium 10-undecenoate-water solutions.

²H NMR Spectroscopy of Cesium Undecenoate-D₂O Mixtures

Evidence for lyotropic liquid crystallinity of concentrated (50-90 wt %) samples of cesium undecenoate in deuterated water was obtained by deuterium quadrupole NMR spectroscopy.^{4,11,17,19} By measurement of the net anisotropy of D₂O molecules bound to the surface of the anisotropic liquid crystalline aggregates as gauged by the quadrupole splitting, it is possible to construct a plot of quadrupole splitting with increasing concentration which delineates liquid crystalline phase boundaries. This is shown in Figures 2 for cesium undecenoate-water mixtures at 298 and 333 K. Below approximately 50 wt % surfactant, the deuterium nmr spectrum consists of a narrow (< 15 Hz line width) isotropic peak and the mixture is fluid and freely flowing. We

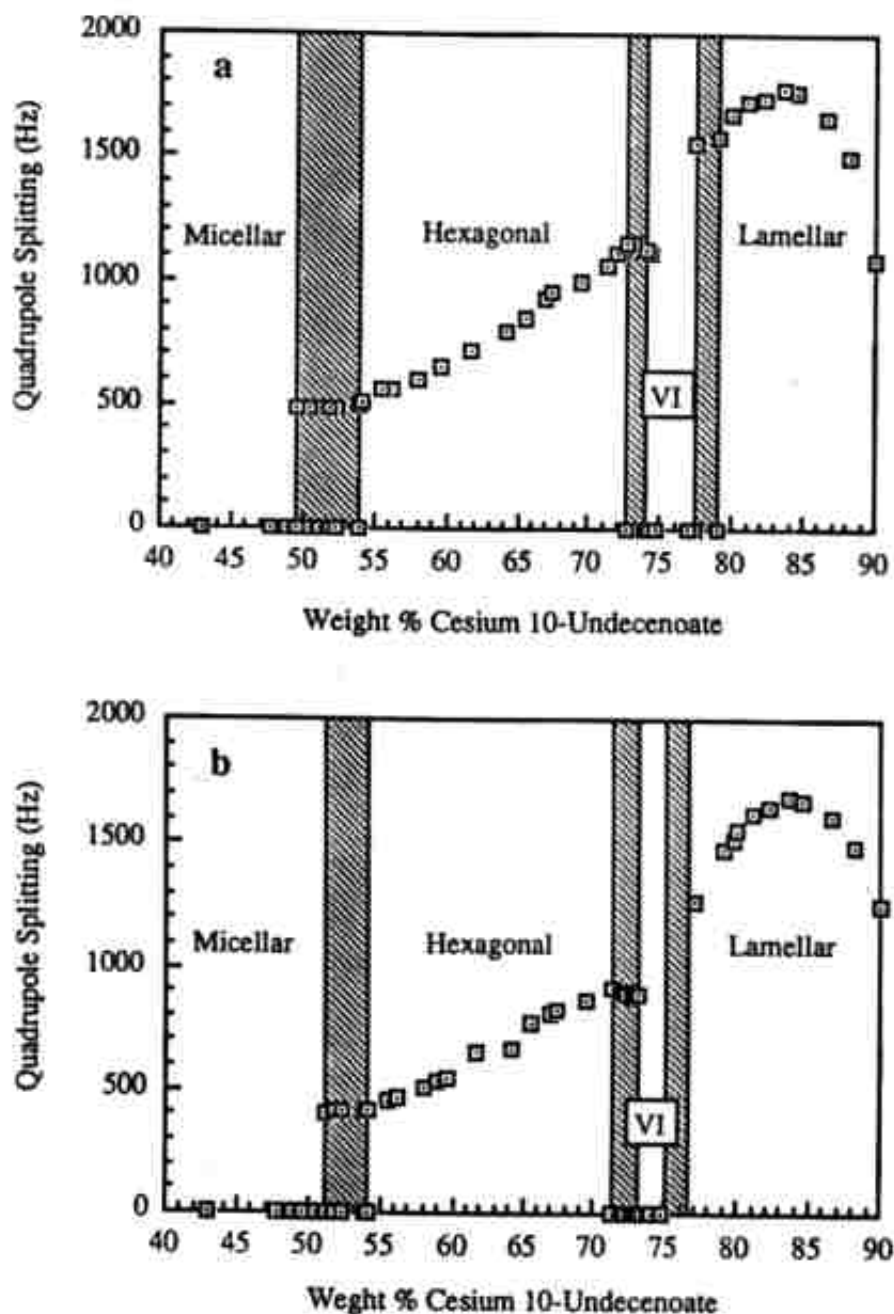


Figure 2. Dependence of ^3H NMR quadrupole splitting in Hz on concentration of cesium-10-undecenoate-D₂O solutions at (a) 298 K and (b) 333 K. VI denotes the region of stable viscous isotropic liquid crystal. Crossed-hatched regions denote two-phase regions.

interpret these observations as evidence of isotropic micellar solutions. At concentrations from 50 to 54 wt %, the deuterium nmr spectrum consists of a superposition of an isotropic peak and a Pake pattern of quadrupole splitting of 500 Hz. Beyond 54 wt %, the deuterium NMR spectrum is a Pake pattern with quadrupole splitting, which increases monotonically with increasing concentration. The visual appearance of the sample is that of an extremely viscous birefringent phase. This phase exhibits striation textures typical of hexagonal LC phases when viewed between crossed polarizers in an optical microscope. This hexagonal phase is stable up to concentrations of 72 wt %. Between 72 to 74 wt %, deuterium NMR spectra consist of a superposition of an isotropic peak and a Pake pattern with a quadrupole splitting equal to that of the hexagonal phase at 72%. The phase which is stable beyond 74% is isotropic, extremely viscous, and exhibits strain birefringence. We interpret these observations as evidence of a viscous isotropic liquid crystalline phase. It is stable to concentrations of 77%, whereupon an additional anisotropic phase with quadrupole splittings of 1500 Hz is observed. This highest concentration phase is less viscous than hexagonal or viscous isotropic, and exhibits textures typical of a lamellar LC phase when viewed under crossed polarizers in the optical microscope. Using these NMR data and visual observations, a partial phase diagram of cesium undecenoate-D₂O was constructed and is shown in Figure 3.

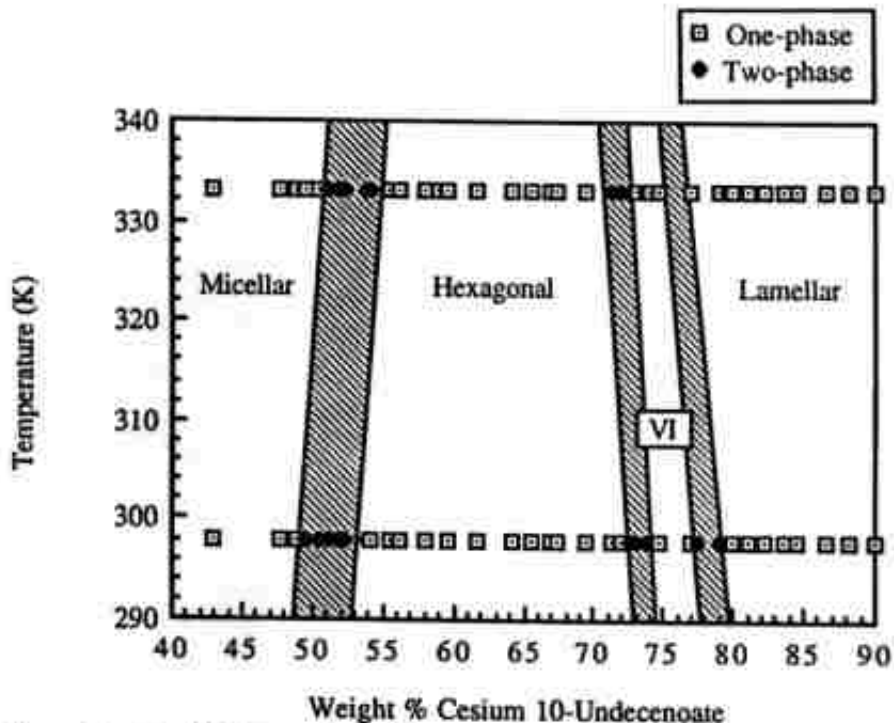


Figure 3. Partial binary phase diagram of cesium 10-undecenoate-water mixtures as determined by ²H NMR spectroscopy.

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¹H NMR Analysis of PMHS Backbone

¹H-NMR spectra of the parent backbone PMHS polymers from Aldrich and Petrarch were acquired to determine their number average molecular weights (M_n) and to aid in identification of ¹H-NMR spectral peaks of the functionalized polymer. Two readily resolved resonances were observed: a peak at 4.76 ppm corresponding to protons that are directly attached to the silicon atoms in PMHS and a peak at 0.13 ppm corresponding to methyl protons directly attached to the backbone and capping the ends of the polymer. A linear PMHS backbone of infinite molecular weight would possess a ratio of methyl to silyl protons of 3. The degree of polymerization (DP) can thus be determined by forming the ratio of methyl proton peak area to backbone proton peak area, subtracting the contribution due to backbone methyls and dividing into the relative peak area of the end cap methyls:

$$DP = \frac{18}{\left(\frac{MP}{BP} - 3\right)} \quad (1)$$

where MP and BP denote the integrated peak areas of methyl and backbone silyl protons, respectively. Applying equation (1) to the peak areas obtained for the two PMHS samples gives degrees of polymerization of 25 and 28 for the Aldrich and Petrarch materials, respectively. The number average molecular weights, determined from the structures corresponding to these degrees of polymerization, are 1666 and 1846, respectively.

Synthesis and Isolation of Side Chain Polymers

Four different sets of reaction conditions were employed to determine the effects of reaction temperature, catalyst concentration and reaction time on the degree of functionalization of the side chain polymer. These reaction conditions are summarized in Table 1. The determination of the degree of functionalization of each of these polymers by ¹H NMR is described in the following section. After completing the reaction, the reaction mixtures were cooled to ambient temperature and converted to methanolic solutions by dilution and rotary evaporation. Residual undecenoic acid was removed by diafiltration in methanol. The disappearance of the acid monomer was monitored by GPC. The acid side chain polymer (PMUS) was converted to the saponified form by stoichiometric neutralization with CsOH in methanol. The solvent was then replaced by diafiltration with either water or D₂O through a YM5 ultrafiltration membrane (5000 MW cutoff). Complete retention of the polymer was taken as indirect evidence of resistance of the polymer backbone to chain scission upon contact with the basic CsOH solution.

Table 1.

Reaction Conditions for Acid Side-Chain Functionalized Polysiloxanes (PMCsUS)

	PMCsUS 1	PMCsUS 2	PMCsUS 3	PMCsUS 4
PMHS (gms)	2.61	13.7	9.98	8.00
Excess 10-undecenoic acid (%)	6.6	4.7	9.0	11.6
Catalyst (ppm)	150	6600	340	150
Reaction time (hrs)	5	24	12	24
Reaction temp. (°C)	50	50	100	90
Solvent	THF	THF	Toluene	i-Propanol
Percent functionalization	----	41.1	55.3	28.2
Molecular weight	----	4885	6154	4354

PMCsUS 2 and PMCsUS 3 were synthesized using the Aldrich Chemicals PMHS (DP 25). PMCsUS 4 was synthesized using the Petrach Chemicals PMHS (DP 28). PMCsUS 3 and PMCsUS 4 were synthesized by preparing the catalyst according to the method of Apfel *et al.*¹

¹H NMR Analysis of Functionalized Polymer PMCsUS

In order to identify the peaks in the ¹H NMR spectra for the side chain functionalized polymers, it was first necessary to make spectral assignments for the 10-undecenoic acid side chain. This compound is indexed in the Sadtler library of proton NMR spectra and these assignments were taken directly from this source. The acidic proton was not observed experimentally due to exchange with the deuterated methanol solvent. ¹H-NMR spectra of the acidic (PMUS 2) and saponified polymers (PCsUS 2) were also obtained. The residual unfunctionalized backbone protons were not observed in these spectra as they are unresolved from the methanol solvent peak. Evidence of the reaction is provided by the appearance of a peak at 0.59 ppm which represents protons on the eleventh carbon of the acid side chain and which is directly attached to the siloxane backbone. This assignment was made by comparing the chemical shift to that of methylene protons directly attached to siloxane silicon in tetraethylsilane indexed in the Sadtler library. The other peaks in the PMCsUS spectra are common to the 10-undecenoic acid or PMHS spectra.

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The percent functionalization (PF) (i.e., the percent of the siloxane backbone protons functionalized by 10-undecenoic acid) can be determined from the peak areas of protons in the PMCsUS spectrum. By taking the ratio of the area of the peak at 0.13 ppm (the methyl protons, MP) to the area of the peak at 0.59 ppm (the protons on the eleventh carbon of the attached acid, C¹¹H₂), the percent functionalization is obtained from:

$$\% \text{ Functionalization} = \frac{3(\text{C}^{11}\text{H}_2)(\text{DP} + 6)}{2(\text{MP})(\text{DP})} \quad (2)$$

In equation (2), DP is the degree of polymerization obtained from analysis of the ¹H-NMR spectra of the parent PMHS backbone polymers. Applying equation (2) to the spectra of the functionalized polymers, PMCsUS 2, 3 and 4 were found to have percent side-chain functionalizations of 41.1, 55.3 and 28.2% , respectively. These results are reported along with the reaction conditions in Table 1.

The primary difference in the spectra of the acidic and ionic forms of the functionalized polymers appears to be broadening of the peaks of the saponified polymer, which is most likely due to aggregation of the polymer in aqueous solution. It should be noted that the acidic side-chain polymers are not water-soluble to any appreciable extent. This line broadening was quantified by noting that the peaks corresponding to the eleventh carbon on the undecanoate chain directly attached to the siloxane backbone and the unresolved methylenes corresponding to carbons 4 through 10 have half-line widths of 21.6 and 8.7 Hz for the acidic polymer PMUS 2 and 39.3 and 19.8 Hz, respectively, for the saponified polymer.

Surface Tension Measurements of PMCsUS-Water Solutions

In an effort to monitor aggregation of saponified polymer in aqueous solution, surface tensions were measured for isotropic solutions of PMCsUS 2, 3 and 4 at varying concentrations (10⁻⁵-10⁻¹ M) (Figure 4). As Figure 2 indicates, the polymers are about equally effective in lowering solution surface tension. Solutions of the two functionalized polymers with the lower % sidechains, PMCsUS 2 and 4, were observed to be translucent at concentrations of 0.01 M and greater. Solutions of PMCsUS 3, which had a % sidechain of 55%, were transparent at all concentrations. Solutions of PMCsUS 2 and 3 exhibited concentration-independent surface tensions at sufficiently high concentrations. Surface excess concentrations (Γ) and area per molecule (σ) were calculated for the three saponified polymers by applying the Gibbs adsorption isotherm² to the surface tension data in the concentration regime over which the surface tension was linear with the logarithm of the polymer concentration. These results are reported in Table 2.

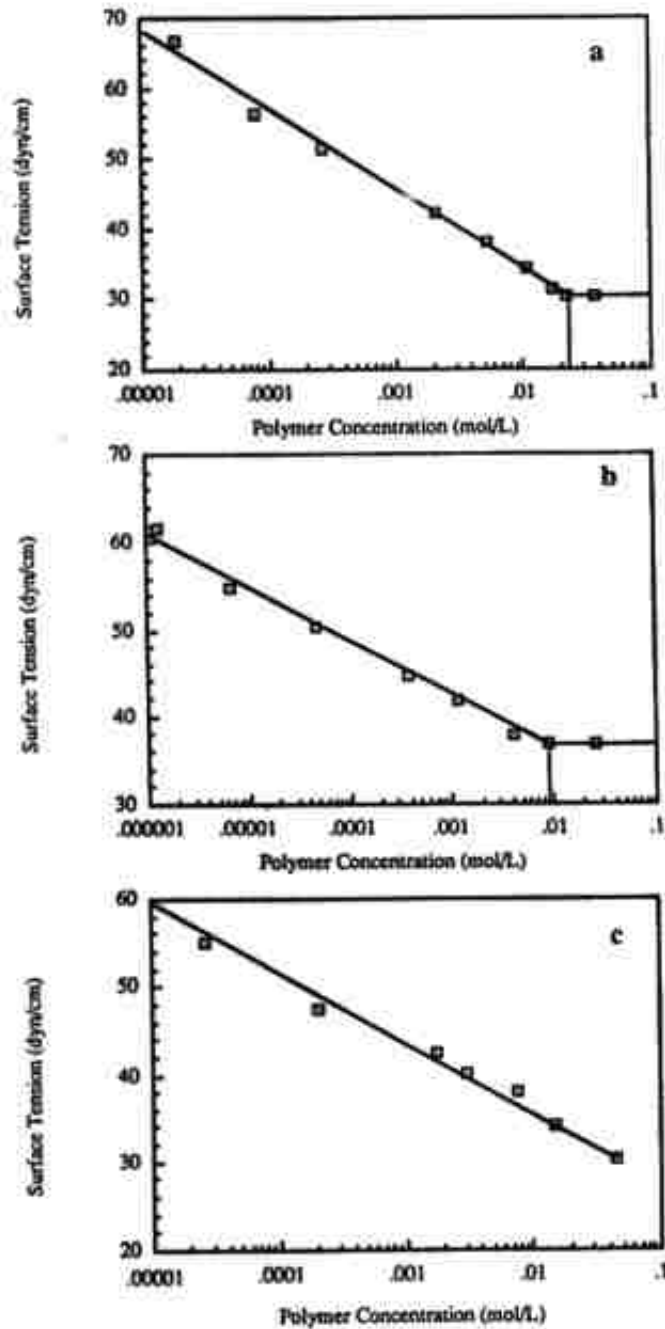


Figure 4. Dependence of surface tension on polymer concentrations at 25°C of PMCsUS-D2O solutions on polymer concentration for (a) PMCsUS 2, (b) PMCsUS 3 and (c) PMCsUS 4.

Table 2.

Size Transition Concentration, Surface Excess Concentration, and Area per Molecule at Air-Water Interface for the PMCsUS Polymers

	PMCsUS 2	PMCsUS 3	PMCsUS 4
Size transition concentration (mol/L polymer)	0.022	0.009	0.045
(weight % polymer)	1.07	.534	1.95
Γ (pmol/cm ²)	197	113	129
σ (Å ² /molecule)	84.3	147.3	128.5
Molecular weight	4885	6154	4354

QLS Measurements of PMCsUS-Water Solutions

QLS measurements were performed on samples of varying concentrations of aqueous solutions of the saponified PMCsUS polymers. The mean diffusion coefficient D was obtained directly from a cumulant fit to the scattered light intensity autocorrelation function.^{12,21} This diffusion coefficient was converted to an effective hydrodynamic diameter using the Stokes-Einstein equation.

Shown in Figure 5 are polymer aggregate diameters as a function of concentration for solutions of the three saponified polymers PMCsUS 2, 3 and 4. QLS measurements could not be performed on the most concentrated samples of the PMCsUS 2 and 4 polymers because these solutions were turbid. Upon centrifugation, these translucent solutions yielded an observable precipitate. Solutions of the polymer with the highest degree of side chain functionalization, PMCsUS 3, were transparent at high concentrations (> 0.01 M). The apparent polymer aggregate size varied continuously (from ≈ 200 Å at PMCsUS concentrations of 0.3-0.4 mM to ≈ 800 -900 Å at concentrations of 10 mM). With the most soluble polymer, PMCsUS 3, aggregate sizes of ≈ 4000 Å were measured at 20 mM. The approximate size of monomeric functionalized PMCsUS polymer should be no larger than 50 Å in diameter based on an end-to-end length of the PMHS backbone of 60-65 Å.³ It thus seems clear that the sizes observed by QLS correspond to aggregates of polymer rather than to monomeric polymer at all concentrations studied.

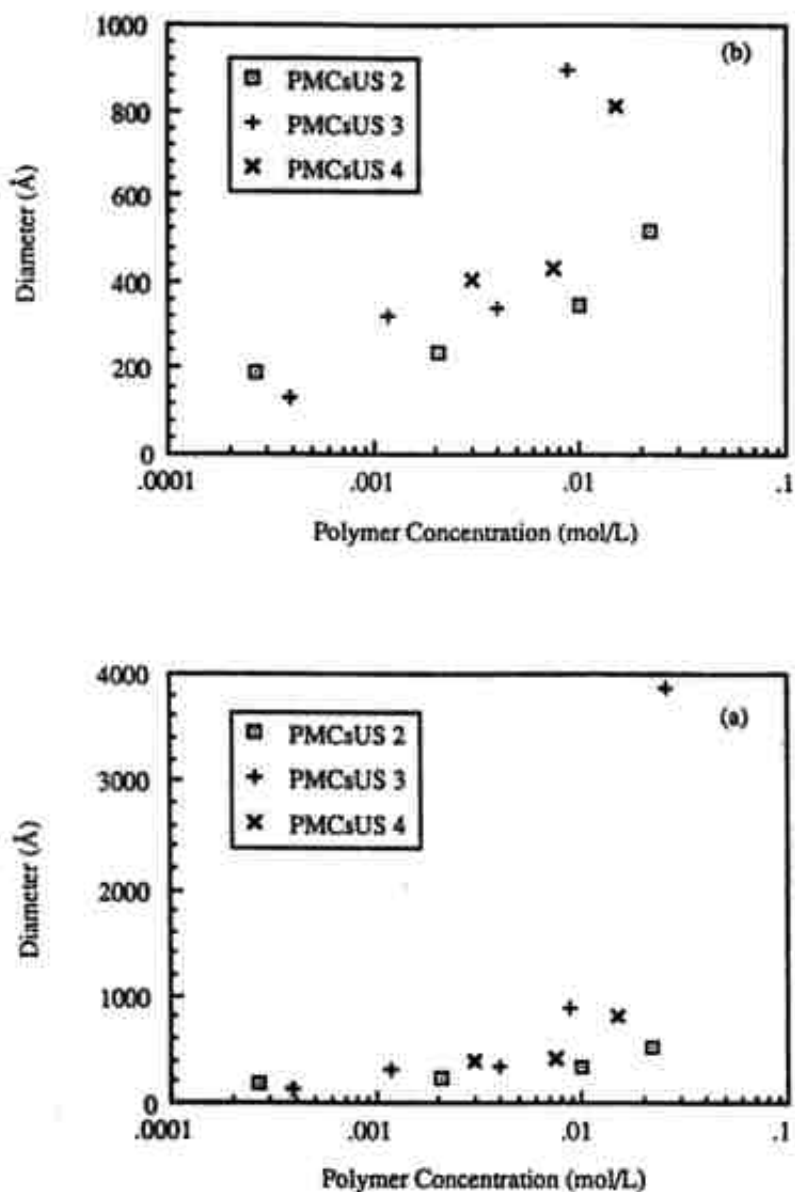


Figure 5. Variation in Stokes diameter as measured by quasi-elastic light scattering of PMCsUS polymeric aggregates. Plot (b) is an expanded version of plot (a).

^2H NMR Spectroscopy of PMCsUS- D_2O Samples

Binary PMCsUS- D_2O samples were prepared from each of the three polymers as described previously. Samples made from PMCsUS 2 and 4 remained macroscopically phase separated from the water after vigorous mixing. This is consistent with the visible precipitation observed in the light scattering samples commented on above. Samples made with PMCsUS 3 equilibrated rapidly (a few days) to yield optically clear homogeneous phases which were then analyzed by ^2H NMR spectroscopy. These experiments were performed at 298 and 333 K and from 10 to 80 wt % PMCsUS 3. From 10-32 wt % polymer, the samples were observed to be fluid and isotropic. Above 32% polymer, the samples became visibly viscous and ceased to flow under their own weight at concentrations greater than 36 wt %. All the deuterium NMR spectra on samples varying in composition from 10-70% polymer were isotropic peaks; there was no evidence of anisotropic LC formation from either the NMR experiments or from visual observations between crossed polarizers. However, the line shape was observed to change between 32 and 36% from a single Lorentzian to a superposition of two Lorentzian lineshapes: a broader Lorentzian ($\Delta\nu_{1/2} = 20$ Hz) and a narrower Lorentzian ($\Delta\nu_{1/2} = 10$ Hz). This is illustrated in Figure 6, a sample consisting of 34.25 % PMCsUS 3 and D_2O . The lineshape is clearly super-Lorentzian, and one interpretation of this is that of a phase transition from a less viscous fluid phase to a more viscous isotropic phase.

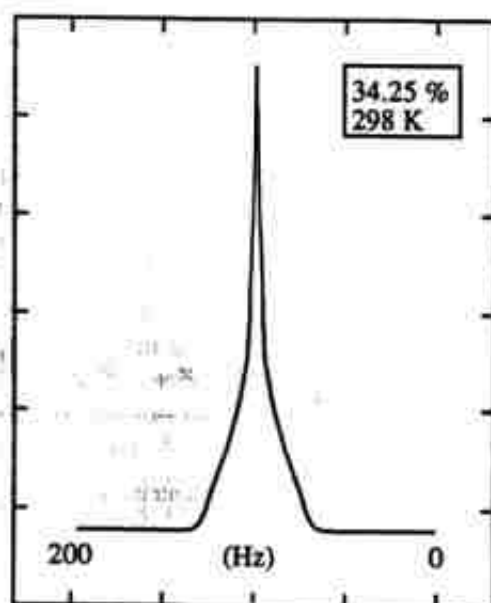


Figure 6. ^2H quadrupole NMR spectrum of mixture of 34.25 wt % PMCsUS 3 and 65.75 wt % D_2O .

DISCUSSION

The monomer cesium undecenoate lowers surface tension in a manner similar to other alkali metal carboxylates. Its CMC of 60 mM is lower by a factor of 2 than the comparable CMC of 117 mM determined for sodium undecenoate by Durairaj and Blum.⁵ This is consistent with the observed depression of the CMC of alkali metal carboxylates as the size of the bare counterion is increased from sodium to cesium.¹⁶ The monomer cesium undecenoate also exhibits lyotropic mesomorphism at higher concentrations which is typical of alkali metal carboxylates of short alkyl chain lengths. Sodium *n*-octanoate is observed to exhibit hexagonal, viscous isotropic and lamellar LC phases with increasing surfactant concentration⁶. We contrast this behavior with that of the functionalized polymers PMCsUS.

As is evident from the reaction data presented in Table 1, the conditions of the hydrosilylation reaction have a strong effect on the percentage of the PMHS backbone that is functionalized. The saponified polymer with the largest degree of undecanoate side chain functionalization, PMCsUS 3 (55% side chain), also exhibited the greatest water solubility (32 wt %), the largest aggregate size by QLS ($\approx 4000 \text{ \AA}$) and a viscous isotropic liquid crystalline phase at high concentrations in water (36-80 wt %). Apparently, the degree of functionalization plays a large role in solubility of the polymer, and this is likely attributable to the hydrophobicity of polymer.

All three functionalized polymers that were studied (PMCsUS 2,3 and 4) were effective in lowering surface tension of aqueous solutions. Polymers 2 and 4 were slightly more effective than polymer 3 as gauged by the surface excess concentrations (see Table 2). Again, this is likely attributable to the greater hydrophobicity of polymers 2 and 4, relative to polymer 3, which may lead to increased surface activity at comparable concentrations. With typical aqueous solutions of ionic surfactants, surface tension is observed to decrease in a nearly linear fashion with the logarithm of the surfactant concentration until the CMC, or critical micelle concentration, is reached. Beyond the CMC, additional surfactant participates in the formation of micellar aggregates and the surface tension is observed to change little with increasing concentration. The surface tension behavior of aqueous solutions of polymers 2 and 3 is typical of micelle-forming ionic surfactants and it is tempting to construe the break points in surface tension as ≈ 0.02 and ≈ 0.01 M, respectively, as CMCs. However, the QLS data indicate that at concentrations well below this breakpoint, there are aggregates of diameter 200 \AA and greater. Moreover, the size of these aggregates grows continuously with increasing concentration for all three polymers. These observations suggest that there are a distribution of polymer molecular weights and degree of ionic surfactant side-chain functionalization. At low concentrations, the polymer molecules with lowest CMC values (presumably those with greatest hydrophobicity) aggregate, while that fraction of the distribution with highest CMC values adsorb to the air-water interface and lower surface tension. Interestingly, the distribution of surface excess concentrations of the individual polymer species averages to yield a linear

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surface tension plot with logarithm of concentration. At sufficiently high concentrations, even the most functionalized of polymer species participate in aggregate formation.

At elevated concentrations of polymer 3 in water (10-30 wt %), solutions of the polymer remain fluid and isotropic. Beyond 32 wt % polymer, mixtures of polymer and water become viscous and at 36 % polymer, they gel into a viscous isotropic phase. The ^2H nmr lineshape of polymer 3- D_2O mixtures changes in this transition regime (32 to 36%) from a simple Lorentzian line shape of 15 Hz linewidth to a superposition of two Lorentzian line shapes in which the broader component is ca. 30-40 Hz in width. This suggests that a first-order phase transition separates low and high concentration polymer- D_2O mixtures. While we provide no evidence here of three-dimensional order, the high viscosity and optical isotropy of the high concentration polymer phase suggest that this is a viscous isotropic lyotropic liquid crystalline phase.

Unlike the nonionic amphiphilic side chain polysiloxanes synthesized and studied by Finkelmann *et al.*⁸ and by Luhmann *et al.*^{13,14} the ionic amphiphilic side chain polymers prepared here show no anisotropic liquid crystallinity at high concentrations (>30 wt%) of polymer. This may be due to incomplete functionalization of the PMHS backbone; the largest degree of side chain functionalization obtained was only 55%. With only partial functionalization, one might expect some intramolecular hydrophobic interactions, which may lead to globular aggregates. With more complete functionalization, the electrostatic repulsion between adjacent carboxylate moieties may favor a more distended polymer chain. This in turn might favor the formation of anisotropic aggregates. Clearly, future studies on ionic amphiphilic side chain polysiloxanes should address the issues of backbone chain size distribution and the distribution of side chain functionalization as determinants of aggregation in aqueous solution and possible lyotropic liquid crystal formation.

CONCLUSIONS

Cesium undecenoate (CsU) exhibits a CMC of 60 mM at 25°C and lyotropic LC formation typical of other short-chain alkali metal carboxylates. Two anisotropic phases are stable in the monomer-water system: a hexagonal and a lamellar phase. These phases have broad compositional and thermal extent. In addition, a narrow concentration range is observed in CsU- D_2O mixtures (72-76%) in which a viscous isotropic LC phase is stable. Polymethylhydrosiloxane (PMHS) polymers of DP 25-30 have been functionalized by hydrosilylation with the amphiphilic side chain: 10-undecenoic acid. The degree of side chain functionalization obtained varied from 30 to 55%. The acidic form of the side chain was neutralized with CsOH to yield the ionic carboxylate form. This polymer was water soluble while the acid form and the PMHS backbone were not. The carboxylated PMCsUS polymers were effective in lowering surface tension and associated in solution to yield aggregates of 200-800 Å in diameter. The surface excess

concentrations of the three PMCsUS polymers increased monotonically with decreasing ionic side chain percentage. Only PMCsUS 3 with the highest side-chain percentage (55%) was soluble in water above a concentration of 0.01 M (1-2 wt%). This polymer formed isotropic solutions in water up to concentrations of 32 wt %, beyond which a viscous isotropic phase was observed. The tendency of these ionic side-chain polysiloxane polymers to form isotropic rather than anisotropic phases may be due to a distribution in molecular weights and side-chain percentages.

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