Nanometric Sieving of Polymer Coils by a Lamellar Liquid Crystal: Surfactant AOT and Polydimethylacrylamide

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ABSTRACT: The liquid crystal formed by surfactant AOT/water mixtures in its lamellar mesophase at a spacing between lamellae, d, equal to 8 nm, is mixed with poly(dimethylacrylamide) (PDMAA) polymers of low molecular weight in the range $\bar{M}_n = 2-20 \times 10^3$; the polymers are synthesized by living radical polymerization. The lowest molecular weights do not affect d significantly, indicating that the polymer coils penetrate inside the lamellar phase and dissolve in the water layers. With higher molecular weights, d decreases with added polymer, this decrease being stronger as the molecular weight of the polymer is higher, and the mixture becomes microheterogeneous. This indicates that the higher-molecular-weight polymers are segregated in a separate microphase that partially deswells the lamellae and that this segregation increases with the molecular weight of the polymer. The law, which governs the deswelling of lamella with added polymer, is deduced assuming that a fraction of each polymer can dissolve in the lamellar phase, while the rest of the polymer is segregated from it. This latter fraction is then obtained for each polymer simply by fitting to this law the experimental d as function of polymer concentration. It is proposed that the reason for this fractionation of polymer is that the lamellar structure acts as a grating which sieves the polymer coils according to their size relative to d, chains with molecular weight above a certain cutoff value, determined by d, being excluded from the interlamellar space. The fraction of chains excluded from the lamellae is calculated comparing the experimental molecular weight distributions (from SEC) of the polymers with the cutoff values determined by d. The results show that the polymer samples synthesized here cover the whole spectrum of behaviors, from almost total penetration to almost total exclusion. Both this method of cutting off the molecular weight distribution according to d and the other method of fitting d to the law for lamellar deswelling give similar results for the fraction of polymer that is segregated from the lamellae.

Introduction

The study of polymers in lyotropic liquid crystals has received considerable attention recently.[1,2] Some surfactant/water systems form ordered mesophases having hexagonal and lamellar structures. The order or spacing of these ordered structures is in the range of a few nanometers. A similar nanometric range is covered by the sizes of the macromolecular coils of common polymers when their average molecular weight is in the oligomer-to-polymer region.

In the case of noncharged polymers solubilized in a electrostatically stabilized lamellar phase, several behaviors have been proposed: (i) the formation of two coexisting lamellar phases,[3,4] (ii) the separation into a lamellar phase and a polymer rich aqueous solution,[5,6] and (iii) the solubilization of the polymer in the water layer of the lamellar phase.[5,6]

If the interaction between bilayers is strong, the sample remains monophasic, while if the interaction is weak, the sample separates in two phases: a surfactant-rich phase and a polymer-rich phase. Some authors propose that polymers can dope the lamellar phase when there is no interaction between the polymer and the surfactant[5] and that, in those conditions, it is possible the confinement of polymers in lyotropic lamellar systems having a pitch much smaller than the average size of the macromolecules,[7] although this is not a general rule, and in some cases a phase separation occurs.

Here we propose a simple model: for polymers not interacting attractively with the surfactant and having low molecular weights, the macromolecular coils penetrate the ordered structures of the mesophases driven mainly by the entropic force, which tends to disperse any component in all the space available, and this dispersion should be limited only by the steric restriction imposed on macromolecular coils with dimensions larger than the spacing of the ordered structure. Under this assumption, it is envisaged that the ordered structure could act as a sieve for the macromolecular coils: smaller coils, with diameters up to the value of the spacing in the ordered structure, could penetrate inside the mesophase, while coils with diameters larger than the spacing should stay out of the mesophase, forming a different phase.

We have already observed that very high molecular weights (coil diameter 80 nm) of the polymer poly(dimethylacrylamide) (PDMAA) suffer complete segregation from the lamellar structure of the surfactant Aerosol OT (AOT) in water and form a separate isotropic microphase.[8−12] However, in the case of low-molecular-weight (6×10^3 and 20×10^3) polyoxyethylene[13] (PEO), it has been observed that the polymer penetrates into

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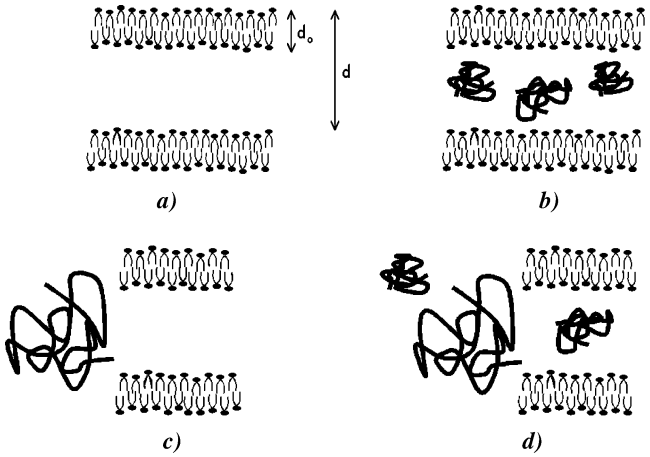
the aqueous domains of lamellar AOT, this solubilization being smaller for the higher-molecular-weight polymer.

Our point of departure here is: does PDMAA of molecular weight smaller than the one used previously actually penetrate inside the lamellar structure and, if this is the case, at which molecular weight can a crossover from coils that can penetrate to coils that cannot penetrate the lamellar structure be found? To answer these questions, it is necessary to have samples of different molecular weights covering an ample range of coil diameters. The adequate range of coil diameters should be that which embraces the value of the thickness of the water layers in the ordered structure of the mesophase. Our previous studies with high-molecular-weight PDMAA used AOT/water interlamellar spacings in the range 3−9 nm,[9,10] which correspond to water-layer thickness 1−7 nm. The purpose of the present communication is to study the steric exclusion of coils from the mesophase structure, using polymer samples with coil diameters embracing this 1−7 nm range. Because PDMAA is neutral and lacks the hydrogens of amides, it shows no specific or binding interaction with the surfactant so the size or steric effects should be the main driving force controlling the access of macromolecular coils to the spacing of the ordered mesophase.

The first task would be to synthesize a series of polymers, with different molecular weight averages, that presumably can cover the whole range of coil sizes, from the small ones that enter freely in the mesophase spacing to the large ones that are completely excluded from it. To this end, we resort to the methods of living or controlled radical polymerization, as described in the Experimental Section. Once we have synthesized and characterized the polymers, our study focuses on the degree of penetration of these polymers in the ordered mesophase. With this aim, we determine the spacing of the ordered structure (by SAXS), as a function of polymer concentration, for all the molecular weights. In our case, the ordered structure is lamellar, each lamella being formed by the regular packing of the surfactant molecules in a bilayer separated by water layers. We expect that the spacing between these bilayers would act as a grating which sieves the polymer coils according to their size (Scheme 1). For a two-component sample, containing only surfactant and water, the long period, d, depends on composition by a simple dilution law:[14] $d = d_0/\phi_S$, where d_0 is the bilayer thickness, and ϕ_S is the surfactant volume fraction. When a polymer with high molecular weight is added, the polymer is excluded from the mesophase, forming an isotropic phase. This polymer-rich phase exerts an osmotic compression[6,9] that reduces the water content in the lamellar phase, and the repeat distance is then shortened (although the bilayer thickness is not altered).

Scheme 1. (a) Molecules of AOT Forming a Lamellar Structure: d, Spacing between Lamellae; d_0, Thickness of Bilayers. The Spacing between Bilayers Can Act as a Grating Which Sieves the Polymer Coils According to Coil Size: (b) All Chains Smaller than Spacing; (c) All Chains Larger than Spacing; (d) Some Chains Larger, Some Chains Smaller than Spacing



Experimental Section

Materials. AOT (1,4-bis(2-ethylhexyl) sodium sulfosuccinate) was obtained from Sigma, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and DMAA (99%) from Aldrich, and the initiator AIBN (α,α′-azobis(isobutyronitrile)) from Fluka. AIBN was recrystallized from methanol, while all other products were used as received. Solvents were toluene (from Carlo Erba), diethyl ether (from Panreac), *N*,*N*-dimethylformamide and tetrahydrofuran (both from Aldrich, HPLC quality), and water (Milli-Q, reactivity quality).

Polymerization. Different methods of living or controlled radical polymerization are available for PDMAA: atom transfer radical polymerization (ATRP),[15−21] reversible addition−fragmentation chain transfer (RAFT),[15,22−24] and nitroxide-mediated radical polymerization (NMRP).[15,25−28] The method of NMRP using TEMPO, as described by Li and Brittain,[28] has proven useful for our purposes. We take this polymerization method from the literature, adjusting the conditions so as to obtain the molecular weight values in the desired range.

Table 1. Polymerization Conditions: Feed Mixture Composition in AIBN, DMAA, and AIBN/TEMPO Relation

polymer	AIBN mol/L	DMAA mol/L	AIBN/TEMPO mol/mol
6	0.0057	1.963	0
5	0.0232	2.243	0.598
4	0.0233	2.249	0.806
3	0.1454	2.272	0.517
2	0.1461	2.248	0.745
1	0.1455	2.254	0.946

The feed mixtures (see Table 1), with toluene as solvent, were closed inside 50 mL Erlenmeyer flasks, sonicated for 15 min, and put in an oven at 84 °C for 14 h. At the end of the synthesis, the polymer was precipitated in ether, filtered, and vacuum-dried for 3 days at 55 °C.

Polymer Characterization. Polymers were characterized by different techniques to obtain their molecular weight average, ($\bar{M}_n$), molecular weight distribution (MWD), and dimensions (hydrodynamic radius).

Viscometry. Intrinsic viscosity of polymers ([η]) in methanol and water were determined from efflux time measurements with an Ubbelhode modified viscometer fitted in a Lauda Viscoboy automatic viscometer. The temperature was kept at 25.00 ± 0.05 °C, and [η] was determined by Huggins and Kraemer extrapolations.

Size Exclusion Chromatography (SEC). SEC was performed in a modular system with HP 1100 pump, an injector rheodyne of 20 μL, and a Waters 410 differential refractometer as detector. The apparent molecular weights and MWDs were determined using a Styragel HR4 column from Waters, calibrated with six narrow polystyrene standards, from Showa Denko, with molecular weights ranging from 1.30×10^3 to 70.6×10^3. The flow rate was 1 mL/min, in THF, and the temperature was kept at 40 °C.

Vapor Pressure Osmometry (VPO). Number average molecular weights, $\bar{M}_n$, were determined with a Knauer vapor pressure osmometer in *N*,*N*-dimethylformamide. The osmometer was previously calibrated with a polystyrene standard ($\bar{M}_n = 2.87 \times 10^3$ and polydispersity index, $r = 1.04$) from Showa Denko.

Table 2. Number-Average Molecular Weight ($\bar{M}_n$) and Polydispersity Index (r), Determined by Size Exclusion Chromatography (SEC), $\bar{M}_n$ from Vapor Pressure Osmometry (VPO), Intrinsic Viscosities ([η]) in Water and Methanol at 25 °C, and Hydrodynamic Radius (R_h), Measured by PGSE-NMR

	$\bar{M}_n \times 10^{-3}$		r	[η] (dL/g)		
polymer	VPO	SEC	SEC	methanol	water	R_h (nm)
6	20	18	2.25	0.31	0.34	5.5
5	6.3	7.3	1.65	0.15	0.16	2.9
4	5.0	7.6	1.65	0.13	0.17	2.9
3	2.2	3.0	1.70	0.066	0.079	1.5
2	2.3	2.8	1.48	0.058	0.076	1.5
1	2.2	2.6	1.34	0.053	0.071	1.4

Pulsed Gradient Spin−Echo NMR (PGSE-NMR). The self-diffusion coefficients of polymers (D), in deuterated water, were measured on an Avance DMX200 spectrometer from Bruker, operating at 200 MHz, at 25 °C. A stimulated echo pulse sequence was evaluated by using a Stejskal−Tanner analysis. D was then transferred to a hydrodynamic radius, R_h, by using the Stokes−Einstein equation, $R_h = kT/6\pi\eta D$.

Sample Preparation. The AOT/PDMAA/water mixtures were prepared by weighing proper amounts of the three components directly into vessels with lids. The samples were homogenized by repeated centrifugation of the mixtures, back and forth, for more than 5 h and then were left for 20 days at 25 °C before any measurements were conducted. The concentration of AOT was set at an approximately fixed value of 25% (v/v), and the concentration of PDMAA was varied in the approximate range 0.2−3.5% (v/v).

Optical Microscopy. A microscope (Zeiss Axiopan) provided with a Hamamatsu camera (Model: L2400-08) and crossed polarizers was employed to determine the anisotropy of the samples. During these measurements, the samples were placed between a glass slide and a cover-slip.

Small-Angle X-Ray Scattering (SAXS). SAXS measurements were performed on a Kratky compact small-angle system equipped with a position-sensitive detector (OED 50M, Mbraun, Graz, Austria) containing 1024 channels, each with a width of 53.6 μm. Cu Kα radiation of wavelength 1.54 Å was provided by a Seifert ID-300 X-ray generator operating at 50 kV and 40 mA. A 10-μm-thick nickel filter was used to remove the Kβ radiation, and a 1.5 mm tungsten filter was used to protect the detector from the primary beam. The sample-to-detector distance was 277 mm. To minimize scattering from air and to increase the signal-to-noise ratio, the volume between the sample and the detector was under vacuum. During the measurement, the samples were placed in a capillary and the temperature (25 °C) was controlled to within 0.1 °C by using a Peltier element. The smearing was taken into account to determine the peak position.

Molecular Weights of Polymers

The molecular weight averages, polydispersities, and hydrodynamic coil radii for the polymers are given in Table 2. The number average molecular weights and polydispersities determined from SEC were calibrated with polystyrene (PS) standards. Usually, the values obtained with this simple calibration are only approximate, but for the present system (PDMAA in THF), it has been proven that it is an excellent approximation.[29] Furthermore, the number average molecular weights thus determined by SEC agree very well with the same averages determined independently by vapor pressure osmometry (see Table 2).

All the measurements ($\bar{M}_n$ from SEC and VPO, R_h from NMR, and intrinsic viscosities) show that we have three groups of polymers, according to their macromolecular size: (i) polymers 1, 2, and 3 that are very similar and have the lowest sizes; (ii) polymers 4 and 5 that are similar too, and have intermediate sizes; and finally, (iii) polymer 6 that is the largest one. With this set of samples, we will cover the range of sizes in which we are interested to determine what is the limiting value to penetrate or to be excluded from the lamellae. Additionally, the similarity of molecular weights in each group will give us an idea of the reproducibility of the measurements.

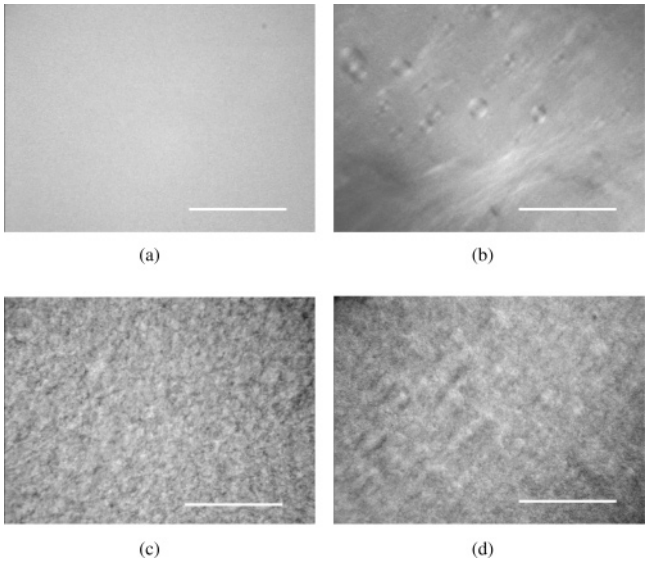


Figure 1. Optical micrographs for polymers 1 (upper) and 6 (lower), at concentrations of 3.5 and 3% w/w, respectively. On the left, without crossed polarizers; on the right, with crossed polarizers. Bar = 100 μm.

The intrinsic viscosities in water correspond to overlap concentrations ($c^* = 1/[\eta]$) ranging from 141 g/L for polymer 1 to 29.5 g/L for polymer 6, indicating that, in all the cases, the samples we are studying are below this critical concentration. It means that, in this process of exclusion or penetration, each coil can act separately, without overlapping interferences from neighboring coils.

Lamellar Structure of Samples

All the samples studied here show at least one lamellar phase, as expected from the surfactant concentration.[30] For polymers with the lowest molecular weights (1, 2, and 3), there is no phase separation, irrespective of the polymer concentration. The samples are clear; in fact, micrographs without crossed polarizers do not show any texture (Figure 1a), while with polarizers, the anisotropy of samples is evident, showing the typical L_α marbled texture (Figure 1b) and the presence of spherical domains, so-called Focal Conic Domains II (FCDII). The FCDII were first observed for isotropic matrixes dispersed in a lamellar phase, but later they were also detected, as in this case, in single-phase lamellar systems.[31]

For the polymers with highest molecular weight (4, 5, and 6), the samples are turbid and the micrographs obtained without crossed polarizes show a phase-separated pattern (Figure 1c), which becomes more evident as the polymer concentration increases. Despite this, macroscopic phase separation could not be obtained; the reason is the high viscosity that makes the kinetics at phase separation too slow.[8] In fact, the separate phase domains are large enough to scatter light (above 10−100 nm) but are smaller than 10 μm. The micrographs with crossed polarizers with these higher-molecular-weight polymers (see Figure 1d) show ani-

sotropy, but the lamellar texture is not so clear due to the disturbance produced by the phase separation.

SAXS measurements provide information about the ordered structure of the samples. Diffractograms have a common pattern in all the samples. Usually, two peaks can be seen, with the position of the second (k_2)- to first (k_1)-order Bragg peaks in agreement with that expected for the lamellar structure, namely: $k_2/k_1 = 2$. Nevertheless, for some compositions only the second-order peak appears, which is a characteristic of the AOT/water lamellar system,[32] and there is also another feature typical of the AOT system: the existence of a broad hump for a wave vector between 0.1 and 0.5 $Å^{-1}$. From the position of the first and/or second Bragg peaks, the repeat distance or long period (d) of the lamellar stacking can be obtained from a simple relationship ($d = 2\pi/k_1$ or $d = 4\pi/k_2$).

Polymer Penetration in the Lamellar Spacing

For a polymer that does not associate strongly with the surfactant, the exclusion or not of the polymer from the lamellar structure depends on the interactions between bilayers, and four different regimes of confinement[33,34] have been proposed, depending on the size and the concentration of the polymer. However, in the system studied here, the exclusion/penetration of the polymer from the surfactant lamellar structure can be analyzed in terms of just steric or geometric factors, as shown below.

The polymer coils can be dispersed inside the lamellae if the macromolecular coils are small enough compared to the lamellar spacing; in contrast, the polymer coils will keep outside of the lamellae if their diameters are larger than the distance of empty space (solvent) between two consecutive bilayers. Thus, for the surfactant−polymer pair lacking strong attraction, the lamellar phase and the polymer will mix or demix depending on the relative size of macromolecular coil-to-lamellar spacing. The lamellar spacing is determined by the concentration of surfactant. The dimensions of macromolecular coils are determined mainly by the length of the polymer chain, namely, by the molecular weight. Since a polymer is not a unique species but contains a distribution of molecular weights, it is possible that a fraction of the polymer, the one corresponding to the shorter chains, can disperse inside the lamellae, while the rest of the polymer, the one corresponding to the longer chains, keeps segregated out of the lamellae. Let f be the fraction of the polymer which corresponds to the longer chains that cannot penetrate inside the lamellar structure. Then, $1 - f$ is the fraction of polymer which corresponds to the shorter chains that are able to penetrate inside the lamellar structure.

It should be noted that the fraction f is governed both by the molecular weight distribution of the polymer and by the lamellar spacing because the spacing selects the part of the distribution that is not allowed to penetrate the lamellar structure. For a given polymer, its molecular weight distribution is fixed and does not depend on the total amount of polymer present. However, the lamellar spacing depends on polymer concentration whenever some segregation of the polymer takes place. In fact, if segregation occurs as the polymer concentration increases, the lamellar spacing decreases. Therefore, as more polymer of a given molecular weight distribution is present in the system, a smaller fraction of that distribution is being allowed in the lamellar structure due to the diminished spacing, and the fraction f should be an increasing function of polymer concentration.

In this study, we have determined: (*a*) the molecular weight distribution of the polymers and (*b*) the lamellar spacing as a function of total polymer concentration. So, in principle, we can determine the fraction of polymer corresponding to longer chains that remains excluded outside the lamellar structure. This applies provided we have a means of converting molecular weights into coil diameters that allows us to compare such coil diameters with the thickness of the water domains in between bilayers. This full comparison is accomplished in the section Size of the Coils that Penetrate. However, first we shall develop a short-cut way for the determination of such fractions of polymer that does not require information about the coil diameters or molecular weight distributions but uses only the lamellar spacing data. For this short-cut method, we have to deduce the law which governs the variation of lamellar spacing with polymer concentration when two phases are present, lamellar and isotropic, and both contain a fraction of the polymer. This is done in the following section.

Law for the Lamellar Spacing

When the average molecular weight of the polymer is so low that all chains of the distribution are smaller than the lamellar spacing ($f = 0$), the dilution law is simply:

$$1/d = (1/d_0)\phi_S \tag{1}$$

where d is the lamellar spacing in the ternary system surfactant + water + polymer, d_0 is the surfactant bilayer thickness, and ϕ_S is the volume fraction of surfactant in the ternary system.

In the opposite extreme, when the average molecular weight of the polymer is so high that none of the chains occur between the lamellae and all the polymer stays apart in a different isotropic phase ($f = 1$), the lamellar phase is binary (the surfactant plus water), and the dilution law is

$$1/d = (1/d_0)\varphi_S' \tag{2}$$

where φ_S' is the volume fraction of surfactant in the surfactant lamellar phase. In this lamellar phase, there is only a fraction of the total water, the rest being in the isotropic phase. In the isotropic phase, the volume fraction of polymer is φ_P''.

These volume fractions, φ_S' and φ_P'', refer to single phases. They can be converted into volume fractions referring to the whole system, ϕ_S (surfactant) and ϕ_P (polymer), through the relationship:

$$\phi_S/\varphi_S' + \phi_P/\varphi_P'' = 1 \tag{3}$$

Hence, the dilution law, equation [2], is converted to

$$1/d = (1/d_0)[\phi_S + \phi_P(\varphi_S'/\varphi_P'')] \tag{4}$$

or

$$1/d = (1/d_0)\{\phi_S + \phi_P[(1 - \varphi_W')/(1 - \varphi_W'')]\} \tag{5}$$

with φ_W' and φ_W'' being the volume fractions of water in the lamellar and isotropic phases, respectively ($\varphi_W' = 1 - \varphi_S'$; $\varphi_W'' = 1 - \varphi_P''$). Previously, we have shown[10]

that the partitioning of water between the two phases gives a ratio $(1 - \varphi_W')/(1 - \varphi_W'')$ which stays practically constant for a wide range of surfactant and polymer concentrations. Hence, the ratio was written as a constant, K. The constancy was checked with a polymer of very high molecular weight average ($\bar{M}_v = 3 \times 10^6$), corresponding to a coil diameter of about 80 nm, which was much larger than the lamellar spacing values, in the range 3−9 nm. Hence, in this limit where no polymer enters into the lamellar structure, the dilution law is

$$1/d = (1/d_0)(\phi_S + K_\infty \phi_P) \tag{6}$$

where we have added the subindex ∞ to show that K is the constant corresponding to the limit of polymers having very high average molecular weight.

In the general case where the distribution of polymer chain sizes is such that the shorter chains can enter in the lamellar structure, while the longer chains stay out of it ($0 < f < 1$), the polymer can be treated as a mixture of two species: the shorter chains which mix with the surfactant and the longer chains which do not mix with the surfactant. Now, each of the two microphases in equilibrium contains three components: the lamellar phase has surfactant plus water and short chain polymer, and the isotropic phase has long chain polymer plus water and short chain polymer.

We have now the equilibrium between two ternary phases in a system of four components. The surfactant and the long-chain polymer are in separate phases, while water and the short-chain polymer are present in both.

The dilution law for the lamellar phase should follow the same equation (2) because the spacing is determined by the volume fraction of the surfactant in the lamellar phase, φ_S'. The difference is that now this volume fraction refers to a lamellar phase with short chain polymer in it. It is easy to show that:

$$\phi_S/\varphi_S' + \phi_H/\varphi_H'' = 1 \tag{7}$$

where subindex H denotes the long-chain polymer. Thus, φ_H'' is the volume fraction of long-chain polymer in the isotropic phase, and ϕ_H is the volume fraction of long chain polymer in the whole system.

We substitute φ_S' in eq 2 for its value, given in eq 7, and obtain

$$1/d = (1/d_0)[\phi_S + \phi_H(\varphi_S'/\varphi_H'')] \tag{8}$$

Using the definition of f as the fraction of polymer having long chains:

$$\phi_H = f\phi_P \tag{9}$$

We finally get the lamellar spacing, d, expressed in terms of experimental volume fractions for the surfactant, ϕ_S, and the polymer, ϕ_P:

$$1/d = (1/d_0)[\phi_S + \phi_P f(\varphi_S'/\varphi_H'')] \tag{10}$$

This result can be written in the same form as eq 6:

$$1/d = (1/d_0)(\phi_S + K\phi_P) \tag{11}$$

but with the coefficient K now redefined as

$$K = f(\varphi_S'/\varphi_H'') \tag{12}$$

In the case of total segregation of polymer, we had $K_\infty = (\varphi_S'/\varphi_P'') = (1 - \varphi_W')/(1 - \varphi_W'')$. Now that segregation is only partial, it is $K/f = (\varphi_S'/\varphi_H'') = (1-\varphi_W' - \varphi_L')/(1 - \varphi_W'' - \varphi_L'')$, (with φ_L' and φ_L'' volume fractions of short-chain polymer in the lamellar and isotropic phases, respectively). The difference is that the volume fraction of water is now replaced by the volume fraction of water plus short chain polymer in each phase. If the system is dilute in polymer, the volume fraction of short-chain polymer is much smaller than the volume fraction of water and we can approximate K/f by K_∞. Then, under this approximation, eq 10 can be written as

$$1/d = (1/d_0)(\phi_S + fK_\infty \phi_P) \tag{13}$$

Thus, if with a sufficiently large polymer we can determine the limiting partition coefficient for total segregation, K_∞, then, for any other smaller polymer, we can get which fraction of the polymer segregates from the lamellar structure, f, by measuring the spacing, d, as a function of surfactant and polymer concentrations, ϕ_S and ϕ_P (in a range similar to that in which K_∞ was determined). The advantage of this method is that we do not need to know the molecular weight distribution of the polymer, not even its average molecular weight, all we need is the lamellar spacing as a function of polymer concentration.

The experimental results for the lamellar spacing, d, as a function of polymer concentration, ϕ_P, are given in Figure 2. The volume fraction of surfactant is very similar in all the cases (around $\phi_S = 0.25$); so, the main reason for the variation of d is the influence of the polymer. Nevertheless, ϕ_S is not exactly the same in all the cases, and this explains the scatter of some points (notably, the one for the lowest polymer concentration of polymer 2).

As we can see, the spacing starts at values around 8.0 ± 0.1 nm for vanishing polymer concentrations and either stays constant or decreases as polymer is being added, this decrease being steeper as the molecular weight of the polymer increases. Finally, the spacing decreases down to 6.3 nm at 3.3% of polymer 6 (the one of highest molecular weight). To interpret these results, we can use the relationships deduced above. To this end, we calculate $d\phi_S$, as a function of ϕ_P. If complete penetration of the polymer in the lamellar structure takes place ($f = 0$), then $d\phi_S$ should be independent of ϕ_P (eq 1), while if the polymer is partially or totally segregated from the lamellar structure ($f > 0$), then $d\phi_S$ should be a decreasing function of ϕ_P. This is so because the polymer that stays out of the lamellae carries with it some of the water (to form the other isotropic microphase) and, consequently, deswells the lamellar structure. This deswelling is increasingly important as the concentration of polymer grows. In Table 3 are shown the results of $d\phi_S$ as a function of ϕ_P.

We can see that $d\phi_S$ is virtually constant, independent of ϕ_P for polymers 1 and 2, showing that these two polymers are unrestricted to penetrate in the lamellar structure, and $d\phi_S$ is very nearly constant, but with a very small change downward as ϕ_P grows for polymer 3, indicating that for this polymer there is a very small segregation. The other three polymers show a clear decrease of $d\phi_S$ with ϕ_P that gets more pronounced as

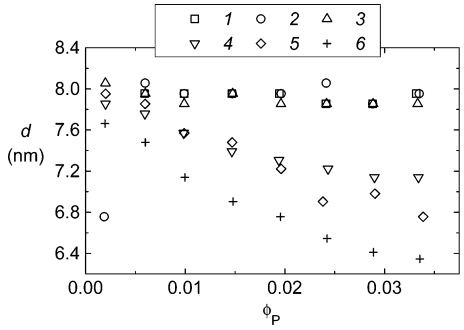


Figure 2. The lamellar spacing, d, as a function of the polymer concentration, ϕ_P, for the six polymers studied.

Table 3. Product of Lamellar Spacing, d, Times the Surfactant Volume Fraction, ϕ_S, as Function of the Polymer Volume Fraction, ϕ_P

	$d\phi_S$ (nm)					
	polymer					
ϕ_P	1	2	3	4	5	6
0.002	–	2.00	2.02	1.96	1.99	1.91
0.006	1.99	2.02	1.99	1.94	1.95	1.87
0.010	1.99	1.99	1.97	1.89	1.89	1.78
0.015	1.99	1.99	1.99	1.85	1.88	1.72
0.020	1.99	1.99	1.96	1.83	1.81	1.69
0.024	1.96	2.01	1.96	1.80	1.81	1.64
0.029	1.96	1.97	1.96	1.77	1.74	1.60
0.033	1.99	1.99	1.96	1.79	1.69	1.59

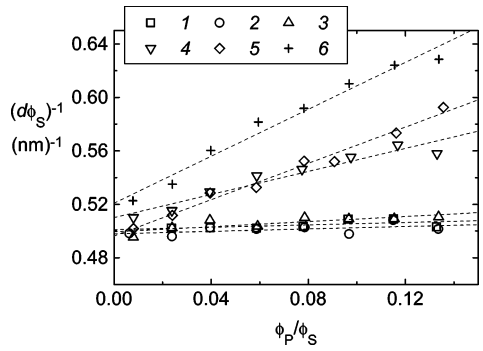


Figure 3. The deswelling of the lamellar structure by the polymer, plotted as $(d\phi_S)^{-1}$ versus ϕ_P/ϕ_S, for all six polymers. Experimental results and linear fits according to eq 13.

the molecular weight average of the polymer grows. This indicates that more polymer is restricted to enter in the lamellar structure as the average molecular weight gets larger.

To estimate the fraction of polymer that is hindered to enter the lamellar phase, we could in principle apply eq 11 to follow the decrease of $d\phi_S$ with ϕ_P. As a practical approximation, we would consider, for the moment, the fraction, f, as constant for each polymer (the variation of f with ϕ_P will be studied in the next section). Under such an assumption, the plot of $(d\phi_S)^{-1}$ versus ϕ_P/ϕ_S should be linear. From the fit of such a linear plot, the values of d_0 and K can be obtained, and from K and K_∞, the value of f can be calculated, according to eq 13. In Figure 3 are shown the results of $(d\phi_S)^{-1}$ versus ϕ_P/ϕ_S for all the polymers studied. Table 4 summarizes the values of d_0 and K that are obtained from the intercept $(1/d_0)$ and slope (K/d_0) of the linear fits shown in Figure 3.

Two points are to be noted in these results. First, with all the polymers, we get the same consistent value of d_0 for the pure AOT. Second, K is an increasing function

Table 4. Bilayer Spacing for the Pure Surfactant, d_0, and Partition Coefficient, K, for the Equilibrium between the Lamellar and Isotropic Microphases, Both Deduced from the Intercepts and Slopes of the Linear Plots in Figure 3, and Fraction of Polymer that Is Segregated from the Lamellar Microphase, f, Deduced with Eq 13 Considering $K_\infty = 1.7$ and 1.9

polymer	d_0 (nm)	K	f ($K_\infty = 1.7$)	f ($K_\infty = 1.9$)
1	2.00	0.09	0.05	0.05
2	2.00	0.09	0.05	0.05
3	2.00	0.19	0.11	0.10
4	1.96	0.85	0.50	0.45
5	2.01	1.37	0.81	0.72
6	1.92	1.69	0.99	0.89

of the average molecular weight of the polymer. It starts at $K = 0$ for the small polymers that penetrate completely and grows as the size of the polymer increases, reaching $K = 1.69$ for the largest polymer. This value is a third important point to consider. When studying a polymer with average molecular weight much larger than any of those considered here, we obtained values[10] of K in a narrow range, $K = 1.7-1.9$, depending on the calculation method. Now, the value obtained for polymer 6 is in the lower limit of that range. This coincidence with a much larger molecular weight allows us to assume that polymer 6 is already very close to the limit of total segregation from the lamellar structure. Taking the bound values $K = 1.7$ and 1.9 as the limiting K_∞ ($f = 1$), we can get f for all the polymers studied as $f = K/K_\infty$. The corresponding values of f are shown in the fourth and fifth columns of Table 4. According to these values, in the molecular weight range corresponding to polymers 3, 4, 5, and 6, part of the polymer penetrates in the lamellar structure and part of the polymer is segregated from such structure. The fraction of polymer being segregated, f, increases as the average molecular weight of the polymer grows.

These results refer to the particular values of the lamellar spacing that we are using here, about 8.0 nm in the absence of deswelling by segregated polymer. The spacing can be varied by changing the AOT/water ratio, hence, the grating that selects which polymer coils get in the lamellar structure and which are kept out.

The model seems simple but in fact gives comparable results as the one proposed by Ligoure et al.[33,34] Using the expressions given by them, we can calculate the contribution of the polymer in the bilayer−bilayer interactions to the layer compression modulus for the different regimes of confinement that would have the polymer. The total layer compressions modulus ($\bar{B}_\mu$) is the addition of the two contributions: the polymer one ($\bar{B}_{pol}$), which is negative, and the electrostatic ($\bar{B}_{el}$), which is positive. In a simple lamellar system, the sum of these contributions should be positive, although if the lamellar phase of the mixed system is unstable against phase separation, the total compression modulus should be negative.

The results obtained by calculating these two contributions for the two polymers of opposite behavior (polymers 1 and 6), at concentration $\phi_P = 0.020$, are as follows. For polymer 1, it is in the three-dimensional dilute regime (3D D): $\bar{B}_{el} = 2.31 \times 10^5$ Pa and $\bar{B}_{pol} = -2.515 \times 10^3$ Pa. Therefore, $\bar{B}_\mu > 0$, meaning that polymer 1 mixed with the lamellar system is stable. Oppositely, for polymer 6, it should be in the two-dimensional dilute regime (2D D): $\bar{B}_{el} = 3.64 \times 10^5$ Pa and $\bar{B}_{pol} = -3.82 \times 10^5$ Pa. Thus, the sum of these two contributions is negative, which means that polymer 6

mixed with the lamellar system is unstable and separates in two phases, according to our results. The total layer compressions modulus is also negative at higher concentrations of polymer 6, but it turns positive at lower polymer volume faction. This discrepancy with the experimental results can be due to the simplifications introduced in the theoretical model of $\bar{B}_\mu$. In the case of polymer 1, the same result $\bar{B}_\mu > 0$, with values approximately constant, is obtained at all concentrations.

Size of the Coils that Penetrate

In the approach developed above, no information about the molecular weight or coil diameter of the polymer has been used. Let us now consider a more direct determination of the fraction of polymer that stays out of the lamellar structure (at each polymer concentration) by comparing the lamellar spacing (at that concentration) with the sizes of the chains which compose the polymer sample. The information about the sizes of the chains in a polymer sample is obtained from its chromatogram determined by SEC. In fact, what we have from SEC is a distribution of molecular weights, $W(M)$. So, we have to determine which molecular weight, M_C, corresponds to the cutoff between the chains that can penetrate from those that stay outside the lamellae. The fraction of polymer that is segregated from the lamellae, f, is then calculated from the distribution of molecular weights as

$$f = \int_{M_C}^{\infty} W(M)\, \mathrm{d}M \tag{14}$$

To relate this M_C with the lamellar spacing, we assume that the polymer fits exactly in the lamellar structure when its root-mean-squared radius of gyration, $\langle s^2\rangle^{1/2}$, is equal to one-half the distance of empty space (solvent) between two consecutive lamellae:

$$\langle s^2\rangle^{1/2} = (d - d_0)/2 \tag{15}$$

Then, M_C is the value of M which corresponds to this value of $\langle s^2\rangle$. The task now is to convert radius of gyration into molecular weight.

For high-molecular-weight polymers in Θ solvents, the easiest way of converting coil size into molecular weight is through the characteristic ratio, C_∞, which gives the mean-squared end-to-end distance, $\langle r^2\rangle$ ($C_\infty = \langle r^2\rangle/Nl^2$, where l is backbone bond distance and N the number of backbone bonds in the chain: $N = 2M/M_0$, with M_0 being the molecular weight of a monomer unit), and from this, the mean squared radius of gyration, $\langle s^2\rangle$-($\langle s^2\rangle = \langle r^2\rangle/6$). The value of C_∞ is known for PDMAA in water, but this method is not applicable here because we are dealing with low-molecular-weight polymers, while C_∞ is an asymptotic limit for very long chains. Our short-chain polymers may deviate substantially from this limiting behavior. A much better method should be to use data for short-chain PDMAA, but unfortunately, these data are not available. An alternative method is to use short-chain data for another polymer which is expected to have a similar dependence of dimensions with molecular weight as PDMAA.

It is well-known that SEC separates polymer molecules according to their size in dilute solution. The fact that the calibration with PS standards gives such excellent approximation allows us to conclude that the size of PDMAA in THF is nearly the same as the size of PS in the same solvent. Therefore, the mean-squared radius of gyration, $\langle s^2\rangle$, for PDMAA may be calculated from the following empirical relation, which has been obtained using experimental data for PS oligomers[35] in THF at Θ conditions:

$$\langle s^2\rangle^{1/2}(\mathrm{nm}) = 0.01455M^{0.57} \tag{16}$$

This relationship should also be valid in water, which is the solvent used here because, for short chains, values in good solvents and Θ solvents are nearly the same.[36] The deviations from the Gaussian $M^{1/2}$ behavior are due to persistence length effects and not to excluded volume, when the chains are short.

Equations 15 and 16 enable us to estimate which molecular weight corresponds to chains having dimensions equal to the thickness of water layers between lamellae. The corresponding cutoff molecular weight is given by

$$M_C = \left(\frac{d - d_0}{0.0291}\right)^{1/0.57} \tag{17}$$

Putting the value $d \approx 8.0$ nm, which corresponds to the initial lamellar spacing without polymer, results in $M_C \approx 11.5 \times 10^3$. This means that the set of polymer samples used here cover the whole spectrum of relative sizes, from polymers much smaller than this cutoff imposed by the initial lamellar structure to polymers much larger than it. Thus, the relative positions of the molecular weight averages, $\bar{M}_n$ and $\bar{M}_w$ (Table 2), with respect to this M_C value, are as follows: for polymers 1, 2, and 3, both averages are smaller than this cutoff value, for polymers 4 and 5, the cutoff value is intermediate to the two averages, and for polymer 6, both averages are larger than this cutoff value.

The value of M_C may vary with polymer concentration. At each concentration, M_C is given by eq 17, using the actual value of d determined in the sample at that concentration. Then, the values of f for each polymer at a given polymer concentration are calculated with eq 14, using (a) the molecular weight distribution of the polymer, $W(M)$, derived from its corresponding SEC chromatogram and (b) the cutoff M_C value given by the experimental d at each polymer concentration. This procedure is exemplified in Figure 4 for one of the polymers.

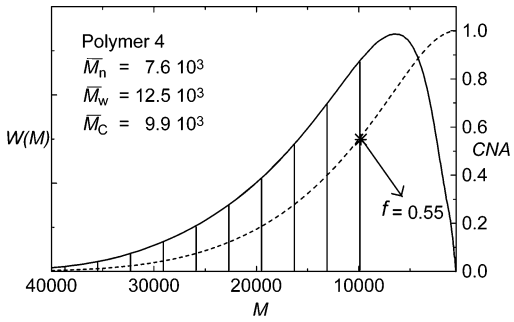


Figure 4. Molecular weight distribution obtained from SEC chromatogram of polymer 4 in THF (solid line) and cumulative normalized area, *CNA* (dash line), as a function of molecular weight, M. Lined area under molecular weight distribution corresponds to the polymer fraction that is expected to be excluded from the lamellar phase when the cutoff molecular weight is $M_C = 9.9 \times 10^3$ (this cutoff corresponds to a lamellar spacing $d = 7.4$ nm, according to eq 17). The value of *CNA* at this M_C yields f, the value of such fraction of total polymer having long chains that are excluded.

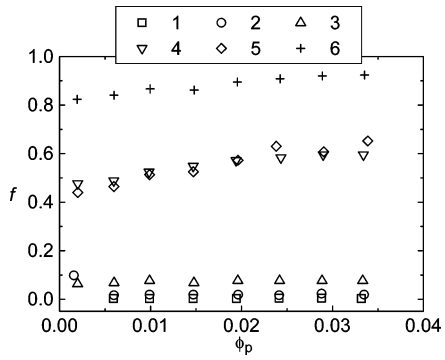


Figure 5. Fraction of long-chain polymer (of total polymer) that is excluded from the lamellar phase, f (calculated from the SEC chromatograms), as function of total polymer volume fraction in the mixture, ϕ_P.

The resulting f's are depicted in Figure 5 as a function of polymer volume fraction. These f values, obtained now by applying the cutoff imposed by the lamellar spacing on the molecular weight distribution of the polymers, can be compared with the previous ones (Table 3), obtained by fitting d to the dilution law without any information about molecular weights or coil sizes. We can see that the two methods yield very similar results. The only significant discrepancy is with polymer 5, which now gives lower values than before, but the present ones are more satisfactory since they come closer to those of polymer 4, and the two polymers have similar molecular weights and hydrodynamic radii.

With the present method, we calculate f independently at each polymer concentration and obviate the previous approximation of considering f to be constant. As we can see in Figure 5, the variation of f with polymer concentration is small (in this range of concentrations) and so the approximation is acceptable. In fact, for polymers 1, 2, and 3, which suffer very little exclusion from the lamellae, f remains unchanged. For the other polymers (4, 5, and 6), which have a significant fraction of polymer excluded from the lamellae, there is a slight positive slope in the variation of f with ϕ_P, This is due to the cooperative effect of the polymer in the exclusion since the segregated polymer deswells the lamellar structure and forces more (smaller) chains to be excluded (as was anticipated in previous section).

Conclusions

The macromolecules of the polymer PDMAA penetrate inside the lamellar structure of the surfactant AOT/water liquid crystal and dissolve in the water layers of such structure, without perturbing the AOT bilayers, when the dimensions of the macromolecular coils are small compared to the spacing between bilayers. If the macromolecular dimensions are larger than this spacing, the polymer chains cannot penetrate inside the lamellar structure and keep segregated, forming a separate isotropic polymer/water phase which partially deswells the lamellar structure. Polymers studied here have molecular weight distributions covering a range of macromolecular dimensions, which go from chains smaller than the spacing to chains larger than it. Then, a fraction of the molecular weight distribution that corresponds to chains larger than the spacing is excluded from the lamellar structure, while the rest of the polymer is able to penetrate inside. The lamellar structure acts thus as a sieve that fractionates the polymer according to the size of chains relative to spacing. Therefore, the nonadsorbing macromolecules cannot be deformed and aligned through dissolution in the water layers of the lamellar mesophase, and this result sets limitations on the idea that mesophases can be used as anisotropic templates in polymerization processes.

These conclusions have been obtained in a certain range of AOT and PDMAA concentrations, using low-molecular-weight polymers synthesized by nitroxide-mediated radical polymerization.

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