Poly(4-vinyl pyridine)/Zinc Dodecyl Benzene Sulfonate Mesomorphic State Due to Coordination Complexation

Janne Ruokolainen, Juha Tanner, Gerrit ten Brinke,[†] and Olli Ikkala*

Department of Technical Physics, Helsinki University of Technology,
FIN-02150 Espoo, Finland

Mika Torkkeli and Ritva Serimaa

Department of Physics, Helsinki University, P.O. Box 9, FIN-00140 Helsinki, Finland

Received June 15, 1995; Revised Manuscript Received August 8, 1995[®]

ABSTRACT: Recently, it has been shown that the properties of flexible and semi-rigid polyelectrolytes can be tailored by using specific surfactants. In these cases, mesomorphic structures in bulk and in solution and network morphologies in blends have been achieved. In polyelectrolytes, the available electrostatic interaction to bond the surfactants is large due to the charges bound to the polymer backbone. In this work, we show that mesomorphic behavior of even noncharged flexible polymers can be achieved if the interaction between the polymer and the surfactant is selected properly. The model system is atactic poly(4-vinyl pyridine) (P4VP) in combination with zinc dodecyl benzene sulfonate ($Zn(DBS)_2$). FTIR measurements indicate that transition metal coordination between the Zn cation and the pyridine amines takes place. SAXS and birefringence show that mesomorphic structures are obtained, the long period being 27.8 Å in the nominally fully complexed case and 26.1 Å when the degree of complexation is 25%. Also pure $Zn(DBS)_2$ is mesomorphic with the long period of 23.7 Å. The difference between the layer thicknesses of $Zn(DBS)_2$ and $P4VP(Zn(DBS)_2)_x$ can be explained by the atacticity of the polymer.

Introduction

Functionalization of semi-rigid and flexible polymers by suitable surfactants has recently opened new possibilities to tailor polymer properties in bulk, in solution, and in blends. In the case of polyaniline, which is a semi-rigid polymer, special amphiphilic dopants to yield relatively high electrical conductivities and liquid crystalline structures in solution and in bulk have been introduced.[1–3] Continuous network morphologies in blends can also be achieved.[4] Although these exciting materials properties have been amply demonstrated, the detailed mechanisms are still not sufficiently understood.[5,6] For example, doped polyaniline can be regarded as a polyelectrolyte, and the effect of the distributed charges along the backbone on its conformation in solution is not yet known in detail. Mesomorphic structures of semi-rigid polypyrrole due to surfactants have been reported.[7]

Also in more flexible polyelectrolytes, mesomorphic behavior has recently been achieved: Motivated by the intriguing properties of polyelectrolytes and surfactants separately in solutions, sodium-neutralized poly(styrene sulfonate) (Na-PSS) complexed with alkyltrimethylammonium salts have been studied.[8] The surfactant causes spatial organization in the form of mesomorphic structures. The highly ionic and nonpolar alkyl layers alternate, with the layer thickness depending on the surfactant chain length. The surfactants are able to cause a drastic conformational change of the random coil polymer. Although not discussed in the ref 8, one of the crucial requirements is a strong secondary interaction between the surfactant and the polymer, because relatively large work has to be exerted against the conformational entropy to organize the initially unordered polymers to layers. Both Na-PSS and alkyltrimethylammonium surfactant are ionic, containing positive and negative charges, easily leading to the required excellent bonding due to the large available electrostatic interaction.

In our previous paper, we have shown that both atactic poly(4-vinyl pyridine) (P4VP) and atactic poly(2-vinyl pyridine) (P2VP) can be protonated by *p*-dodecyl benzene sulfonic acid (DBSA) to yield P4VP(DBSA) and P2VP(DBSA) complexes, respectively.[9] DBSA is an example of amphiphilic strong protonic acid. At full protonation, poly(vinyl pyridine) is converted to poly(vinyl pyridinium), which contains a positive charge at each repeat unit, i.e., it is a polyelectrolyte. The overall electroneutrality is achieved by the negative dodecyl benzene sulfonate counterions. We observed mesomorphic behavior of this cationic polyelectrolyte/anionic surfactant system with the long period of 27–29 Å, depending on the protonation level. We also studied P4VP(DBSA) and P2VP(DBSA) complexes in xylene, which is a good solvent for the alkyl chains. Fredrickson has suggested that polymer/alkyl surfactant systems would stretch in a good solvent of the alkyl chains to yield liquid crystallinity.[10] Accordingly, the alkyl tails of the surfactants tend to avoid contacts with each other. If there is a high loading of surfactants along the polymer backbone, it should stretch leading to nematic behavior. However, we observed that, for example, P4VP(DBSA) complexes in xylene show layered structures even at 50 w/w % xylene. The analysis of the behavior of the long period as a function of the xylene concentration indicated that considerable stretching of the P4VP chains occurs in agreement with Fredrickson's arguments.[9]

The above mesomorphic P4VP(DBSA) and P2VP(DBSA) systems in bulk or in solution are polyelectrolytes[11] in the sense that, due to protonation, high amounts of bound positive charges have been introduced into the polymer backbone. In other words, poly(vinyl pyridines) are ionized in the DBSA-solvent, as would be characteristic for cationic polyelectrolytes. Polyelectrolytes form a rather specific group among polymers:

[†] Also at the Laboratory of Polymer Chemistry and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

[®] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-7779$09.00/0

first, large electrostatic charges are available to bond the surfactants; second, the bound charges, although screened by the oppositely charged counterions, may have influence on the available conformations. Our general aim is to identify new potential concepts where polymers in general (i.e., other than polyelectrolytes) can be rendered mesomorphic by suitable surfactants. Therefore, it is essential to identify strong feasible interactions between polymers and surfactants. The first step is to remove the requirement of *bound* ionic charges along the polymer backbone, characteristic of polyelectrolytes. Keeping poly(vinyl pyridine) as the model system, we therefore search other schemes where the pyridine rings are not converted to pyridinium rings.

In this paper, we study whether coordination complexation between the basic amines in pyridine rings and suitable surfactants could be used to yield mesomorphic behavior. The concept of using coordinate complexation to modify polymer properties is not new. Aminic cosolvents have been used for sulfonate ionomers with transition metal cations.[12] Coordination complex formation between Zn(II), Co(II), Ni(II), and Cu(II) and polyvinyl pyridines have been studied to achieve cross-linking.[13,14] Transition metal complex formation has also been used to improve the properties in polymer blends, such as compatibilization of EPDM to amine-containing polymers, by incorporating a small amount of Zn-neutralized sulfonate moieties to EPDM.[12,15,16] The coordination complexation of zinc to P4VP and P2VP has been studied by using low molecular weight model compounds (such as zinc acetate, zinc laurate, and zinc stearate), and has been compared to magnesium acetate.[17] Accordingly, zinc is coordinated to the pyridine ring via the nitrogen lone electron pair. Also, other metal complexes have been studied.[18]

In this paper, we show a novel concept where coordination complexation can be used to achieve mesomorphic structures of flexible polymers. Atactic poly(vinyl pyridine) (which is *not* in the charged polyelectrolyte state) is complexed by using zinc salt of dodecyl benzene sulfonic acid, and the resulting mesomorphic structures are characterized by using FTIR, X-ray scattering, and optical microscopy. The present concepts can potentially be used to develop new methods to obtain interconnected network morphologies in polymer blends.

Experimental Section

Materials. The atactic P4VP was acquired from Polyscience Europe GmbH. The viscosity-averaged molar mass M_v was measured in ethanol[19] to be 49 000. The DBSA is of laboratory purity and was obtained from Tokio Kasei. ZnO (purity 99.0%) was acquired from J. T. Baker B.V. The solvents were of analysis grade.

Optical Microscopy. The optical observations were carried out with a Nikon Optiphot 66 microscope in transmission mode with a Linkam TMS 91 hot stage. Birefringence was studied by adjusting the analyzer at the angle of 90° with respect to the polarizer. The samples were prepared as thin films between two glass plates. To observe liquid crystallinity, shearing was used to achieve orientation in the samples by sliding the microscope cover glass slip. The temperature was scanned between 25 and 200 °C at a heating rate of ca. 5 °C/min.

Small Angle X-ray Scattering. SAXS was used to analyze the mesomorphic behavior. The CuK_α radiation was monochromatized by means of totally reflecting mirror (Huber small angle chamber 701) and Ni filter. The sealed Cu anode fine focus X-ray tube was powered by Siemens Kristalloflex 710 H. The scattered radiation was detected by a linear one-dimensional position sensitive proportional counter (MBraun OED-50M). A narrow slit was used before the sample to minimize background scattering. The primary beam is narrow (the full width at half maximum, fwhm < 0.002 Å^{-1}) compared to its length (fwhm = 0.027 Å^{-1}) at the sample. Together with the detector height profile, the fwhm of the instrumental function was determined to be 0.048 Å^{-1}. The smallest achievable k is only ca. 0.02 Å^{-1} by using this setup. The instrumental broadening was corrected by an iterative desmearing procedure.[20] In some of the experiments, the range of k was extended down to 0.004 Å^{-1} by increasing the distance between the sample and the detector from 15 to 116 cm. For this purpose, a new vacuum chamber was inserted with 13-μm polyimide windows and a tantalum beam stopper, as was used in our original setup.

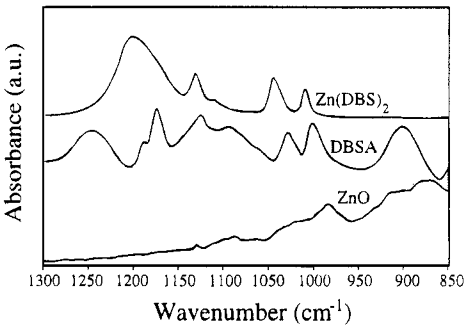

Figure 1. Infrared spectra of ZnO, DBSA, and Zn(DBS)$_2$.

Wide Angle X-ray Scattering. Scattering intensities were measured with using a symmetrical reflection geometry with monochromatized CuK_α radiation (from quartz crystal face 10 $\bar{1}$ 1) with a scintillation counter and a pulse height analyzer. The samples were pressed pellets with a thickness of 1 mm and a diameter of 20 mm. The measurements were done at 25 °C. Pure Zn(DBS)$_2$ and ZnO samples were measured with symmetrical reflection geometry from 10° to 105°, using an angle step of 0.25° in 2θ. P4VP(Zn(DBS)$_2$)$_{0.75}$ was measured with symmetrical transmission geometry from 2 to 120° using an angle step of 0.1°. The width of the receiving slit was 1 mm, and the height of the primary beam in the sample position was 6 mm. The intensity curves were corrected for absorption.

Infrared Spectroscopy. Infrared spectra were obtained using a Nicolet 730 FTIR spectrometer with Nic-Plan IR microscope. Samples were prepared by DMF casting directly onto zinc selenide crystals followed by evaporation at 80 °C and drying in vacuum at 60 °C for several hours. In pure P4VP, overnight drying was required to remove the remainders of DMF. ZnO was measured from pressed pellets.

Sample Preparation. Our first aim was to prepare zinc dodecyl benzene sulfonate according to

$$\mathrm{ZnO} + 2\mathrm{DBSA} \rightarrow \mathrm{Zn(DBS)_2} + \mathrm{H_2O} \qquad (1)$$

ZnO powder was first added to anhydrous ethanol (99.5%) both by ultrasonic treatment and vigorous mixing at 70 °C to form a "milky" suspension of concentration of ca. 1 w/w %. A total of 2 mol of DBSA vs 1 mol of ZnO was added, which caused the sample to become clear during continued mixing. The ethanol was first evaporated at 78 °C on a hot plate. The sample was dried overnight at 70 °C in vacuum and finally at the relatively high temperature of 100 °C for 16 h in vacuum to evaporate the rest of the removable water. The above drying procedure was selected according to a previous study: In zinc *p*-toluene sulfonate, 6 molecules of water can be absorbed, four of which can be removed at 78 °C and the remaining two at 100 °C at 1 atm.[21] Note, however, that small unknown amounts of water may still be bound to the sulfonates due to their large polarity even after the drying.

Two methods were used to confirm that reaction 1 takes place. Figure 1 shows the FTIR spectra of ZnO, DBSA, and their reaction product. DBSA shows the characteristic SO$_3$H band at ca. 900 cm^{-1}. In the reaction product, no such band is observed, indicating that there remains essentially no amount of unreacted sulfonic acid. In contrast, a large new

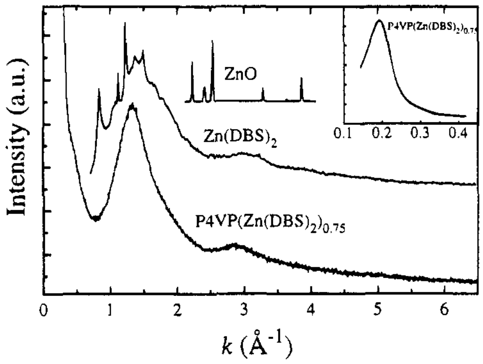

Figure 2. WAXS data of ZnO, $Zn(DBS)_2$, and $P4VP(Zn(DBS)_2)_{0.75}$.

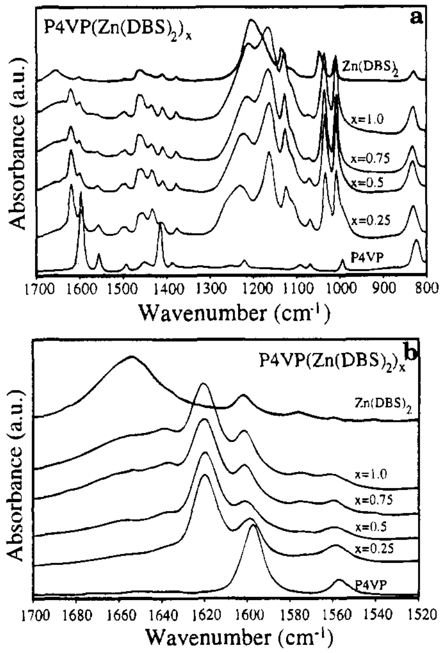

Figure 3. Infrared spectra of $P4VP(Zn(DBS)_2)_x$, $x = 0.25$, 0.50, 0.75, 1.00, P4VP, and $Zn(DBS)_2$ (a) in the 800–1700 cm^{-1} region and (b) in the 1520–1700 cm^{-1} region.

band is observed at ca. 1200 cm^{-1}, indicating sulfonate groups. WAXS analysis shows that no characteristic diffraction peaks of ZnO remain in the reaction product, as is shown in Figure 2. Therefore, FTIR and WAXS data indicated that reaction 1 was accomplished. The resulting $Zn(DBS)_2$ is transparent and "waxy".

P4VP was dried at 60 °C in vacuum for at least 1 day. $Zn(DBS)_2$ and P4VP were dissolved into dry DMF at proportions of x mol of $Zn(DBS)_2$ vs 1 mol of P4VP repeat units to form $P4VP(Zn(DBS)_2)_x$ complex. DMF had first been carefully dried by 3-Å molecular sieves. The nominal degree of complexation x was selected to be 0.25, 0.50, 0.75, and 1.00 where $x = 1.00$ corresponds to the case where nominally 100% of the pyridine rings have been complexed with Zn^{2+}. DMF was first evaporated on a hot plate at 80 °C. The complexes were further dried at 60 °C in vacuum for 2 days and thereafter stored in desiccator.

Results and Discussion

The complex formation between P4VP and $Zn(DBS)_2$ is studied by using FTIR. Figure 3a shows spectra of $P4VP(Zn(DBS)_2)_x$ with $x = 0.25$, 0.50, 0.75, and 1.00 as well as the pure P4VP and $Zn(DBS)_2$. The 1600 cm^{-1} region is illustrated in more detail in Figure 3b. A characteristic carbon–nitrogen stretching absorption band due to the *pyridine* ring in P4VP is observed at 1597 cm^{-1}, in agreement with the previous studies.[22,23,15,17] Note, that in $Zn(DBS)_2$ there is a nearby absorption at 1600 cm^{-1} due to its two *phenyl* rings, not to be confused in the spectra. Therefore, for $x > 0$, the absorption bands of the phenyl rings of $Zn(DBS)_2$ and the uncomplexed pyridine rings of P4VP yield a broad combination peak at ca. 1597–1600 cm^{-1}. When the degree of complexation x is increased, the pristine pyridine band gradually disappears. Noteworthily, a shifted band in $P4VP(Zn(DBS)_2)_x$ samples is observed at 1617 cm^{-1}, which is not observable in P4VP or in $Zn(DBS)_2$. Previous investigations can be used to interpret this shift: First, by FTIR it has been shown that the 1596–1597 cm^{-1} aromatic carbon–nitrogen stretching band of P4VP is shifted to 1615–1617 cm^{-1} when the pyridine group participates in metal ligand π-bonding.[17,15] Second, NMR shows that the zinc cation is able to coordinate to the pyridine ring.[17] Therefore, it seems justified to assume that the observed FTIR shifts also in the present system are due to the coordination complexation between Zn^{2+} and nitrogen lone electron pair in the pyridine ring.

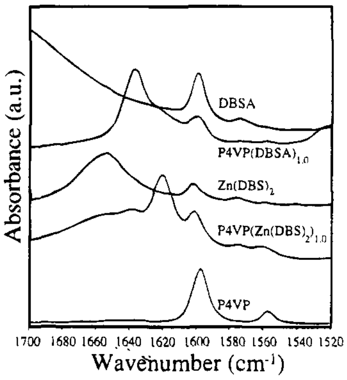

Figure 4. Infrared spectra of the fully $Zn(DBS)_2$ complexed and the fully DBSA protonated P4VP in the 1520–1700 cm^{-1} region.

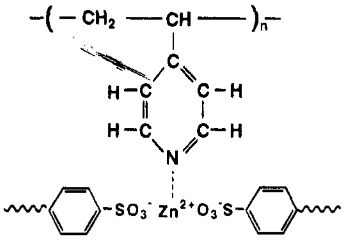

Figure 5. Schematics of complexation of $Zn(DBS)_2$ with P4VP. Possible residual water is not shown.

Further understanding on the nature of the bonding is acquired when our previous results are incorporated.[9] Figure 4 depicts the shift of the carbon–nitrogen stretch band to 1617 cm^{-1} in P4VP due to the nominally fully complexation with $Zn(DBS)_2$. In this case, the backbone of P4VP is not positively charged, i.e., it is not a polyelectrolyte. If, instead, the strongly acidic DBSA is used for complexation, the absorption band is changed to 1637 cm^{-1}.[9] In this case, the pyridine rings are converted to positively charged pyridinium rings, due to the protonation by the acidic DBSA, leading to larger shift with more strengthened carbon–nitrogen bond.

The suggested coordination complex is shown schematically in Figure 5. Note that the scheme is oversimplified. In reality, $Zn(DBS)_2$ probably has the form of a "crankshaft" instead of being linear (see also ref 24), and its direction is approximately in straight angle relative to the P4VP backbone, as are also the pyridine rings. In the literature, the possible coordination

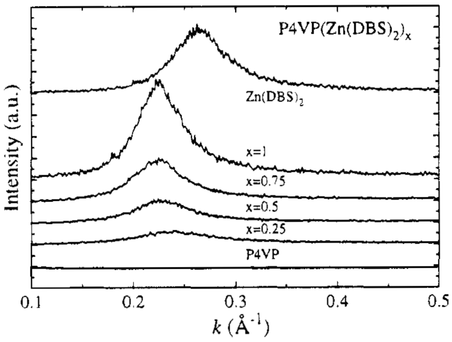

Figure 6. SAXS spectra of P4VP(Zn(DBS)$_2$)$_x$, x = 0.25, 0.50, 0.75, 1.00, P4VP, and Zn(DBS)$_2$.

Table 1. SAXS Data of P4VP(Zn(DBS)$_2$)$_x$ Complexes

x	Bragg law k_0 (Å^{-1})	$2\pi/k_0$ (Å)	fwhm (Å^{-1})	Scherrer eq. 5.9/ fwhm (Å)	correlation function no. of layers
0.25	0.241	26.1	0.098	60	3
0.50	0.229	27.4	0.072	82	3
0.75	0.225	27.9	0.064	93	3
1.00	0.226	27.8	0.052	113	4
Zn(DBS)$_2$	0.265	23.7	0.057	103	4

number of Zn cations in related systems has been discussed. For example, Zn^{2+} is able to coordinate to four monomeric vinyl pyridine rings.[13] However, incorporation of pyridine rings in the polymer backbone causes steric hindrances, and in this case, the coordination number can be less.[12] In the present case, Zn^{2+} is coordinated to at least one pyridine ring and two sulfonates. Whether or not additional coordinations take place to bond possible residual water remains an open question.

Figure 6 depicts the SAXS results. The intensity curve of Zn(DBS)$_2$ shows a diffraction maximum arising from a layered, i.e., mesomorphic structure at 23.7 Å, as determined by means of Bragg's law. In the WAXS regime, mostly amorphous halo is recorded, as is shown in Figure 2. In addition, small diffraction maxima corresponding to d-spacings of 7.5, 5.1, and 4.2 Å can be observed. Zn(DBS)$_2$ also shows birefringence in optical microscopy, as is indicated in Figure 9.

It is not unexpected that Zn(DBS)$_2$ is mesomorphic.[25,26] Mesomorphic behavior of soaps and esters of organic acids have been widely studied previously. As an example, DBSA has smectic A ordering with characteristic 26.5- and 13.3-Å WAXS peaks, interpreted as the first- and second-order diffraction peaks. The layer thickness has therefore been suggested to be 26.5 Å in agreement with the approximate length of 25 Å of the DBSA molecule. The results indicate that within each layer, there is only a poor order. The amount of the residual water is not discussed, but based on their relatively inefficient drying procedures, one may expect it to be large. The authors also show that 20–40 w/w % NaDBS in water forms a lyotropic solution with a typical spacing of 26.5 Å.

Figure 6 further shows that all samples except the pure P4VP are mesomorphic. At the fully complexed case (x = 1), the distance between the layers is 27.8 Å and is reduced to 26.1 Å in the case when only 25% of the pyridine rings are complexed with Zn(DBS)$_2$, see also Table 1 and Figure 7. Two aspects are worth pointing out: First, only one SAXS peak is observed as the coverage of the surfactant is reduced. Second, the long period of P4VP(Zn(DBS)$_2$)$_x$ is ca 3–4 Å larger than that of the pure Zn(DBS)$_2$. A tentative explanation is

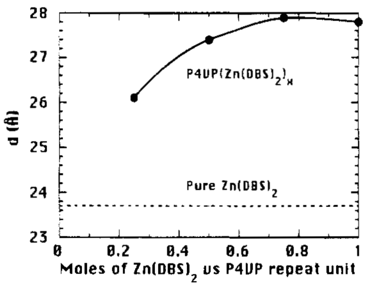

Figure 7. Long period d for P4VP(Zn(DBS)$_2$)$_x$ as a function of x.

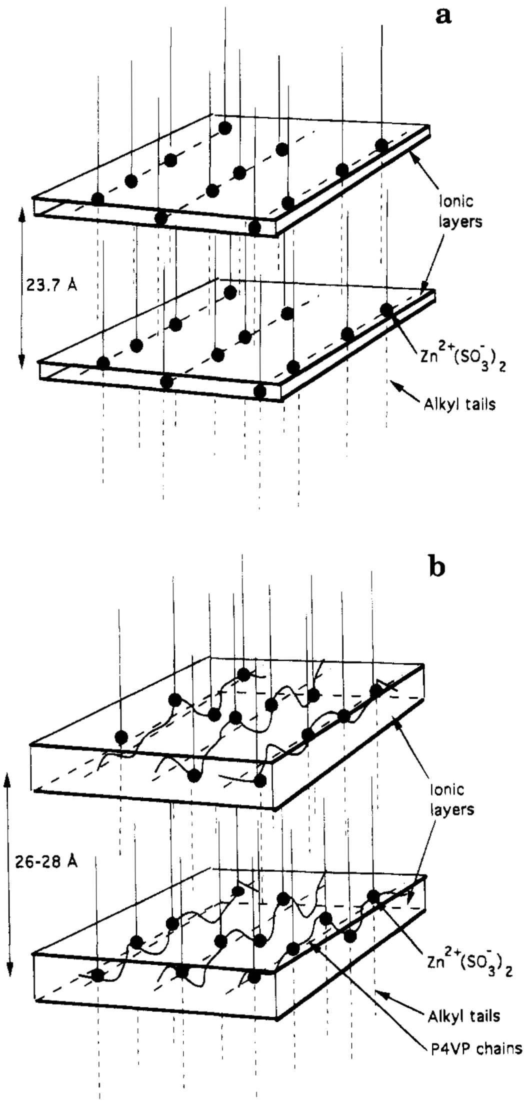

Figure 8. (a) Suggested mesomorphic structure of Zn(DBS)$_2$ with a relatively thin ionic layer. (b) Suggested mesomorphic structure of P4VP(Zn(DBS)$_2$)$_x$ with a relatively thick ionic layer. The black dots show the locations of the ionic moieties of Zn(DBS)$_2$, i.e., Zn^{2+}(SO$_3^-$)$_2$.

shown in Figure 8a,b. The nonpolar alkane groups of Zn(DBS)$_2$ molecules are schematically illustrated by lines whereas their polar ionic groups are depicted as dots. In P4VP(Zn(DBS)$_2$)$_x$, the dots also visualize the locations where the surfactants complex along the atactic P4VP chains. Figure 8a shows schematically the mesomorphic structure of Zn(DBS)$_2$. We suggest that the large electrostatic interactions between the individual Zn^{2+}(SO$_3^-$)$_2$ moieties of Zn(DBS)$_2$ are able to yield relatively thin ionic layers. Within the ionic layers, there may be only a poor order, due to the suggested

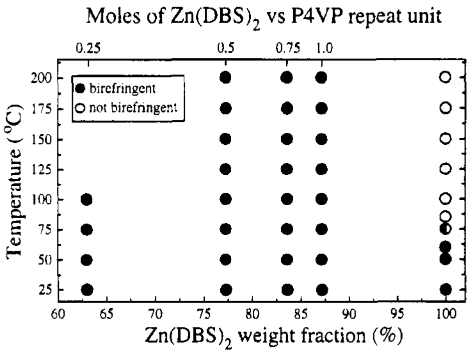

Figure 9. Phase diagram of P4VP(Zn(DBS)$_2$)$_x$.

crankshaft form of the molecules. The situation is totally different when the Zn^{2+}(SO$_3^-$)$_2$ moieties do not associate with each others but with the pyridine rings belonging to P4VP. Due to its atacticity, the directions of the 4VP rings are statistically varying, leading to thick polar layers, as illustrated in Figure 8b.

The domain thickness D consisting of the layers was estimated from the full width of the SAXS intensity maximum using the Scherrer equation $D = 5.9/\text{fwhm}$ in k-scale. Table 1 shows that it is 113 Å in the nominally fully complexed case and reduces to 60 Å at the 25% complexed case. Therefore, the number of layers varies from ca. 4 to ca. 2, correspondingly. Approximately the same number of layers was found also by using correlation functions. The SAXS results resemble those obtained previously with different systems, i.e., liquid crystalline polymers with phenyl benzoate side chains[27,28] and DBSA protonated poly(vinyl pyridines).[9]

Polarization microscopy was used to preliminarily determine the liquid crystalline/isotropic phase diagram. Samples were examined as a function of temperature from the room temperature to 200 °C. Figure 9 shows that pure Zn(DBS)$_2$ is birefringent at the room temperature, the phase transition to the isotropic state taking place between 60 and 90 °C. The fully Zn(DBS)$_2$ complexed P4VP is birefringent from the room temperature to at least 200 °C, indicating liquid crystalline order even at the high temperatures. Same phenomena were observed when the Zn(DBS)$_2$ mole fraction vs P4VP repeat unit was reduced from 1.0 to 0.75 and 0.5. When the mole fraction was only 0.25, birefringence was observed at room temperature, but due to its faintness, the behavior could not be reliably determined at the highest temperatures. The X-ray diffraction measurements agree with the optical microscopy observations.

DSC analysis was attempted to reveal the main thermal transitions. The glass transition in pure P4VP was observed to be at 150 °C. However, in Zn(DBS)$_2$ complexed with P4VP, no clear transitions were observed between −100 and 200 °C. Similar behavior has been described in mesomorphic polyelectrolyte complexes.[8]

SAXS data may be further commented. The intensity curves of pure P4VP and P4VP(Zn(DBS)$_2$)$_x$ increase strongly when approaching the primary beam. This behavior can be attributed to pores in the bulk polymer, whose sizes exceed 600 Å and are too large to be determined with the SAXS setup. In the case of P4VP, the intensity obeys a power law $I \propto k^{-\alpha}$ with the exponent $\alpha = 4.0$, when k values range from 0.004 Å^{-1} to 0.10 Å^{-1}. In P4VP(Zn(DBS)$_2$)$_x$ similar analysis is disturbed by the intensity being smaller by a factor of 10 and because of the overlapping Bragg reflection. The curves obey the power law in the range $0.008 < k < 0.05$ Å^{-1}. The exponent α tends to decrease with increasing complexation to the value 3.5 in the case fully complexed case. The value of the exponent is assumed to reflect the dimensionality D_S of the pore surfaces by the formula $\alpha = 6 - D_S$.[29]

Concluding Remarks

From polymer blends, it is known that interesting properties may be achieved if one of the polymer components is able to percolate within the matrix phase at low concentrations. In oversimplified terms, the percolating polymer can be visualized as a "film" between the domains of the majority polymer. Our general aim is to study whether specific surfactants could offer a general route toward that direction. In addition to the sufficient surface activity and concentration, one of the crucial aspects is to identify strong enough secondary interactions to bond the surfactant to the polymer backbone. This is by no means a trivial question because if the secondary interactions are not strong enough, phase-separated systems are rendered. It has recently been observed that polyelectrolytes may become mesomorphic in bulk[8,9] and in solution[9] when used in combination with suitable surfactants. In this case, the strong bonding is achieved by the available large electrostatic interactions because the polymers contain bound charges. As the first step to find a potentially more general concept, we have studied transition metal coordination complexation to bond the surfactant to the polymer. In this case, one could relax from the requirement that the polymer should contain bound charges, i.e., being polyelectrolyte.

We studied the model system of zinc dodecyl sulfonate and atactic poly(4-vinyl pyridine) and showed that the transition metal coordination complex formation between the Zn cation and the amine of the pyridine ring is sufficient to yield mesomorphic behavior. The long period was studied by SAXS and is shown to be 27.8 Å in the fully complexed case. It becomes smaller at lower degrees of complexation. Pure Zn(DBS)$_2$ is also mesomorphic with the long period of 23.7 Å. The larger layer thicknesses in P4VP(Zn(DBS)$_2$)$_x$ are explained by the atacticity of P4VP. We did not study the corresponding systems with P2VP because we expected the coordination complexation being at least partly sterically hindered.

As a conclusion, we have shown that the transition metal complexation may open a new route to obtain mesomorphic structures. In a forthcoming paper, we will discuss its use in blending.

Acknowledgment. Several scientists of Neste Oy (Finland) are acknowledged: Alpo Toivo and Maarit Taka of Neste Oy (Finland) for FTIR analysis and Jukka Laakso for discussions. This work was supported by grants from Finnish Academy, Technology Development Centre (Finland), and Neste Oy Foundation.

References and Notes

(1) Cao, Y.; Smith. P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91.
(2) Cao, Y.; Smith, P. *Polymer* **1993**, *34*, 3139.
(3) Kärnä, T.; Laakso, J.; Savolainen, E.; Levon, K. European Patent Application EP 0 545 729 A1, 1993.
(4) Yang, C. Y.; Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *53*, 293.
(5) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103.
(6) Ikkala, O. T.; Pietilä, L-O.; Ahjopalo, L.; Österholm, H.; Passiniemi, P. J., submitted to *J. Chem. Phys.*
(7) Wegner, G. *Makromol. Chem., Macromol. Symp.* **1986**, *1*, 151.

(8) Antonietti, M.; Conrad, J.; Thünemann, A. *Macromolecules* **1994**, *27*, 6007.
(9) Ikkala, O. T.; Ruokolainen, J.; ten Brinke, G.; Torkkeli, M.; Serimaa, R. *Macromolecules*, in press.
(10) Fredrickson, G. H. *Macromolecules* **1993**, *26*, 2825.
(11) Eisenberg, A.; King, M. *Ion-Containing Polymers, Physical Properties and Structure*; Academic Press: New York, 1977.
(12) Agarwal, P. K.; Duvdevani, I.; Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 839 and references therein.
(13) Agnew, N. H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2819.
(14) Nishide, H.; Tsuchida, E. *Makromol. Chem.* **1976**, *177*, 2295.
(15) Peiffer, D. G.; Duvdevani, I.; Agarwal, P. K. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24,* 581.
(16) Lundberg, R. D.; Peiffer, D. G.; Phillips, R. R. U. S Patent 4,480,063, 1984.
(17) Belfiore, L. A.; Pires, A. T. N.; Wang, Y.; Graham, H., Ueda, E. *Macromolecules* **1992**, *25,* 1411.
(18) Belfiore, L. A.; McCurdie, M. P.; Ueda, E. *Macromolecules* **1993**, *26,* 6908.
(19) Berkowitz, J. B.; Yamin, M.; Fuoss, R. M. *J. Polym. Sci.* **1958**, *28*, 69.
(20) Lake, J. *Acta Crystallogr.* **1967**, *23*, 191.
(21) Bombin, M.; Guerrero, A.; Martinez-Zaporta, M.; Ramirez, A.; Jerez, A. *Thermochim. Acta* **1989**, *146*, 341.
(22) Takahashi, H.; Mamola, K.; Plyler, E. K. *J. Mol. Spectrosc.* **1966**, *21*, 217.
(23) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(24) Broomhead, J.; Nicol, A. D. I. *Acta Crystallogr.* **1948**, *1*, 88.
(25) Krishnamurti, D.; Somashekar, R. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 3.
(26) Tezak, D.; Strajnar, F.; Sarcevic, D.; Milat, O.; Stubicar, M. *Croat. Chem. Acta* **1984**, *57*, 93.
(27) Shilov, V. V.; Tsukruk, V. V.; Bliznyuk, V. N.; Lipatov, Yu. S. *Polymer* **1982**, *23*, 484.
(28) Shilov, V. V.; Tsukruk, V. V.; Lipatov, Yu. S. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 41.
(29) Schmidt, P. *J. Appl. Crystallogr.* **1991**, *24*, 414.

MA9508414