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Orientation of Supramolecular Self-Organized Polymeric Nanostructures by Oscillatory Shear Flow

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ABSTRACT: Macroscopic orientation of self-organized supramolecular polymeric materials has been demonstrated by oscillatory shear flow using in-situ small-angle X-ray scattering (SAXS). In the case when a homopolymer poly(4-vinylpyridine) and pentadecylphenol molecules are stoichiometrically complexed to form comb copolymer-like supermolecules, the self-organized lamellar local structures align parallel when sheared below the order–disorder transition temperature at 56 °C using 0.5 Hz frequency and 100% strain amplitude. Therefore, the hydrogen bonds between the phenolic and pyridine groups are strong enough to withstand the applied flow. In the case of a diblock copolymer of polystyrene and poly(4-vinylpyridine) stoichiometrically complexed with pentadecylphenol molecules to form the supermolecules, the self-organization yields lamellar-*within*-lamellar local structure near room temperature. The larger lamellar diblock copolymer structure showed a parallel orientation relative to the shearing plates upon shearing at 125 °C (i.e., above the order–disorder transition of the short length scale comb copolymer-like structure) with initially 0.5 Hz and finally 1 Hz, both at 50% strain amplitude. On cooling, the short length scale lamellar structure, consisting of poly(4-vinylpyridine) block and pentadecylphenol, is formed inside the layers of the comb copolymer-like material in perpendicular orientation.

Introduction

Self-organization has received much attention recently as a means to achieve nanoscale structures in bulk materials and on surfaces.¹ In particular, block copolymers are able to form lamellar, cylindrical, spherical, and gyroid structures due to repulsive forces between the different blocks.² Special properties can be incorporated for the domains by introducing functionalities in the separate blocks.^{3,4} However, the self-assembled nanostructures formed by microphase separation in block copolymer melts are local structures, and therefore the material is globally isotropic. To extend the local structure (e.g., lamellar, cylindrical) over macroscopic distances, one needs additional mechanisms, for example by imposing oscillatory shear flow. This is widely investigated both for diblock copolymer melts^{5–16} and for different kinds of liquid crystalline polymers.^{17–19}

Recently, another way to form self-organized nanoscale structures by using supramolecular materials has been introduced, where the repulsive moieties are physically complexed to the polymer chains,^{20–24} allowing a facile route to hierarchically ordered materials.^{3,25,26} The simplest example consists of the hydrogen-bonded complex of homopolymer poly(4-vinylpyridine)

(P4VP) and an alkylphenol.²⁷ The resulting comb copolymer-like supermolecules²⁸ exhibit a lamellar morphology below the order–disorder transition (ODT) occurring around 70 °C in the present experiments. We have further shown that if diblock copolymer structures (e.g., diblocks of polystyrene and poly(4-vinylpyridine) (PS-*block*-P4VP)) are combined with such hydrogen-bonded amphiphiles, structures with two different length scales can be achieved.^{25,26} For the block copolymer structure, long periods of 200–1000 Å are obtained depending on the molecular weights of the blocks. The architecture of one of the blocks corresponds again to that of a comb copolymer, due to the strong hydrogen bonding between the phenol and pyridine groups. It therefore microphase separates and forms lamellae with a long period of 36 Å (Figure 1). Transmission electron microscopy (TEM) shows that the smaller structure aligns perpendicular to the large structure.^{25,26}

Our structures resemble those in side chain liquid crystalline polymers²⁹ and liquid crystalline side group block copolymers^{1,30,31} where, however, the structure formation is due to the mesogenic groups, absent in our case.

In general, the locally microphase-separated material will be macroscopically isotropic due to the polydomain structure with random orientation. The next example, however, shows that new possibilities open if the

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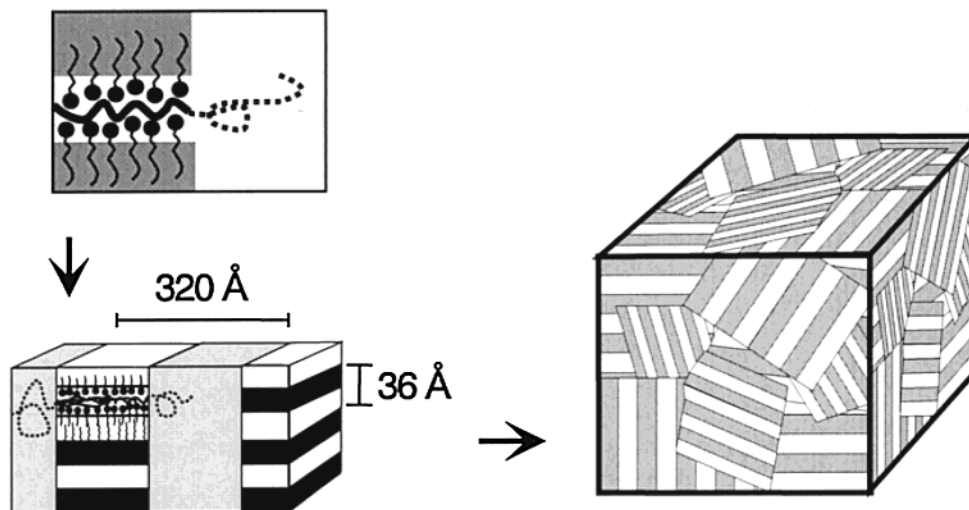


Figure 1. Illustration of the characteristic two length scale structure of PS-*block*-P4VP(PDP)_{1.0}. The larger, i.e., diblock structure, forms lamellae with a long period of 320 Å; the smaller supramolecular structure has a long period of 36 Å. The sample is macroscopically isotropic, due to the different orientations of the polydomain structure.

orientation of the local structures could be extended over macroscopic distances: The pyridine groups of PS-*block*-P4VP diblock copolymers are first protonated by methanesulfonic acid (MSA), and pentadecylphenol (PDP) molecules are hydrogen bonded to the sulfonate groups.³ The domains containing the polyelectrolytic P4VP(MSA) chains are ionically conducting. The material shows a sequence of order–disorder and order–order transitions as a function of temperature, where the dimensionality of the conducting domains changes which reflects in the overall conductivity. The switching is so strong that it is observable even without macroscopic orientation. However, it is expected to become even more pronounced if one could control the orientation of the conducting domains over macroscopic distances. This latter example illustrates that macroscopic orientation of such structure-*within*-structure materials might open routes to new applications.

In this paper we will restrict ourselves to the simplest systems involving hydrogen bonding only. The first one is the P4VP(PDP) homopolymer-based material with nominally one amphiphilic PDP molecule hydrogen bonded to each repeat unit of the polymer. This will demonstrate how the hydrogen bonds behave in the oscillatory shear flow. The second system consists of the diblock copolymer PS-*block*-P4VP with the amphiphilic PDP molecules stoichiometrically hydrogen bonded to P4VP. The samples are studied by ex-situ and in-situ SAXS with simultaneous rheology.

Experimental Section

Materials. Two kinds of samples were studied: the first one was based on the homopolymer poly(4-vinylpyridine), P4VP, and the second one based on the diblock copolymer poly(styrene)-*block*-poly(4-vinylpyridine), PS-*block*-P4VP. To both samples a stoichiometric (with respect to the number of pyridine groups) amount of 3-*n*-pentadecylphenol, PDP, was added. The schemes for the two complexes are presented in Figure 2.

P4VP was obtained from Polyscience Inc. with $M_v = 50\,000$ g/mol. The PS-*block*-P4VP used was obtained from Polymer Source Inc. with $M_w = 40\,000$ g/mol and 5600 g/mol for the PS and P4VP blocks and $M_w/M_n = 1.09$ for the complete polymer. PDP was purchased from Aldrich and originally 98% pure. It was twice recrystallized with petroleum ether and dried at 40 °C in a vacuum for 4 days.

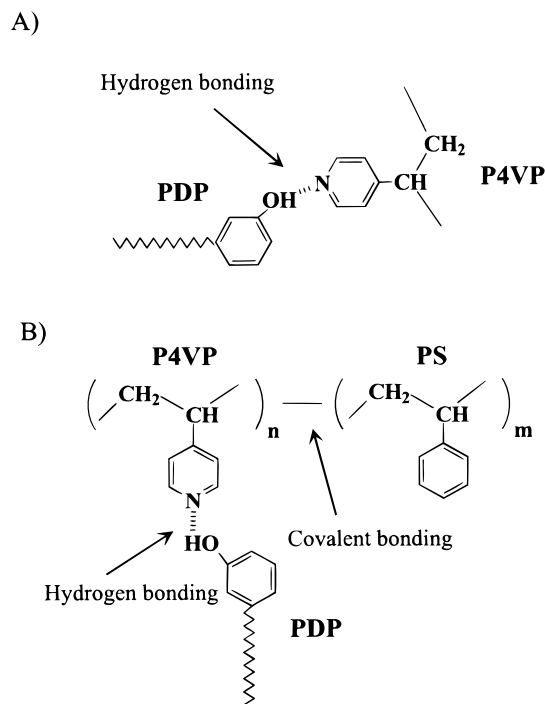


Figure 2. Chemical scheme for the homopolymer supermolecule P4VP(PDP)_{1.0} (a) and the diblock copolymer supermolecule PS-*block*-P4VP(PDP)_{1.0} (b). In both supermolecules the oligomers are hydrogen bonded to the pyridine groups in P4VP.

Sample Preparation. The complexes were prepared by dissolving both components, P4VP and PDP, for the homopolymer complex and PS-*block*-P4VP and PDP for the diblock copolymer complex, in analysis grade chloroform. The solvent was evaporated at 60 °C on a hot plate; thereafter, the samples were vacuum-dried at 60 °C for at least 12 h.

The homopolymer-based and diblock copolymer-based samples were heated to 90 °C (homopolymer) and 120 °C (diblock) in a mold of 10 mm in diameter and 1 mm in thickness. During half an hour no pressure was applied, and the samples were allowed to flow to fill the mold. Subsequently, the samples were pressed into tablets at 10 bar and immediately cooled to 50 °C with compressed air, before removing from the press.

Small-Angle X-ray Scattering. SAXS was performed at the Max Planck Institute for Polymer Research in Mainz,

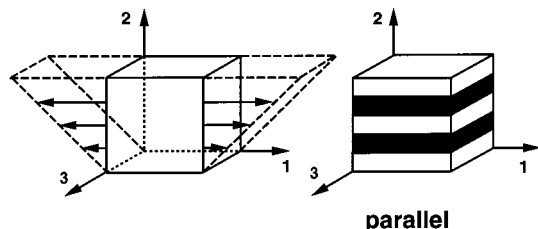


Figure 3. Shearing coordinates, where 1 is the shear direction, 2 is the shear gradient direction, and 3 is the vorticity direction. The *tangential* SAXS intensity patterns were taken with the incident beam along the 1-direction; in the *normal* SAXS patterns the X-ray beam was along the 2-direction. Illustration of the parallel alignment.

Germany. The SAXS instrument consists of a Rigaku Rotaflex 18 kW rotating anode X-ray source with a graphite double monochromator at a wavelength of $\lambda = 1.54 \text{ \AA}$ (Cu K α). Three pinholes collimate the beam over 1.5 m to a diameter of about 1 mm at the sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 1.2 m (homopolymer) and 0.93 m (diblock), yielding an angular resolution of $\Delta 2\theta \approx 0.07^\circ$ or $\Delta q \approx 0.005 \text{ \AA}^{-1}$. The scattering vector q is defined as $q = 4\pi/\lambda \sin \theta$ with 2θ being the scattering angle. The measurements were corrected for nonuniformities in spatial distortion.

Rheology. Shear flow was exerted by a Bohlin CSM-50 stress-controlled rheometer in oscillating mode using parallel plate geometry. In the case of P4VP(PDP)_{1.0}, the sample was heated to 80 °C before the shear experiments to obtain a homogeneous sample with a good contact with the rotor and stator of the rheometer. SAXS data were recorded at 56 °C in-situ in the tangential direction, during the shearing at 0.5 Hz and a strain amplitude of 100% for 6.5 h.

In the case of PS-*block*-P4VP(PDP)_{1.0}, the sample was heated to 150 °C and then kept at 125 °C for 2 h also to obtain a

homogeneous sample and a good contact to the plates. The shear was performed with 0.5 Hz and 50% strain amplitude for 8.3 h and then at 1 Hz and 50% strain amplitude for 2.4 h at 125 °C, to further increase the amount of orientation. The temperature was above the ODT for the small length scale complex structure but below the structural transition temperature of the larger structure.

Before and after shearing the SAXS intensity patterns for both materials were measured ex-situ in both the tangential (2-3 plane) and normal (1-3 plane) directions near room temperature, i.e., below the ODT of the smaller complex structure (see Figure 3). For this, the samples were cut so that the path length through the sample was approximately 1 mm in each direction.

Results and Discussion

Homopolymer Complex P4VP(PDP)_{1.0}. First the homopolymer complex P4VP(PDP)_{1.0} was investigated to study the orientational behavior of the hydrogen-bonded structure under oscillatory shear flow. At quiescent conditions, the P4VP(PDP)_{1.0} complex exhibited an ODT at about 70 °C from a high-temperature homogeneous phase to a microphase-separated lamellar phase. This T_{ODT} is slightly higher than the previously reported value,²³ which might be due to the additional purifying (recrystallization) steps applied to the PDP. Furthermore, at room temperature, which is well above the T_g of the complex, side chain crystallization of the PDP takes place.³² Note that FTIR measurements show that most of the hydrogen bonds are still present at temperatures near the T_{ODT} , and therefore the ODT is not related to broken hydrogen bonds.²⁶

Before the shearing started, a SAXS measurement was performed, demonstrating that the sample has a macroscopically isotropic microphase-separated mor-

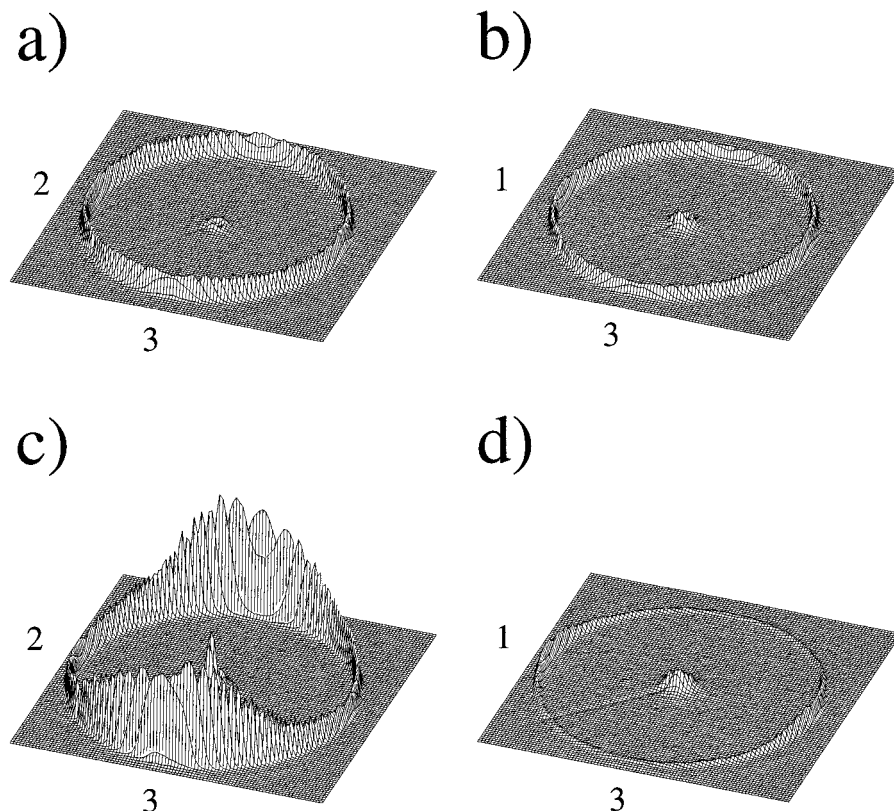


Figure 4. SAXS intensity patterns of P4VP(PDP)_{1.0} in linear scale taken before and after shearing for 6.5 h, measured in the tangential (a and c) and normal directions (b and d), respectively. The frequency used was $f = 0.5 \text{ Hz}$, the strain amplitude $\gamma = 100\%$, and temperature = 56 °C. The first-order scattering peak is located at $q = 0.17 \text{ \AA}^{-1}$, corresponding to a lamellar spacing of 36 Å.

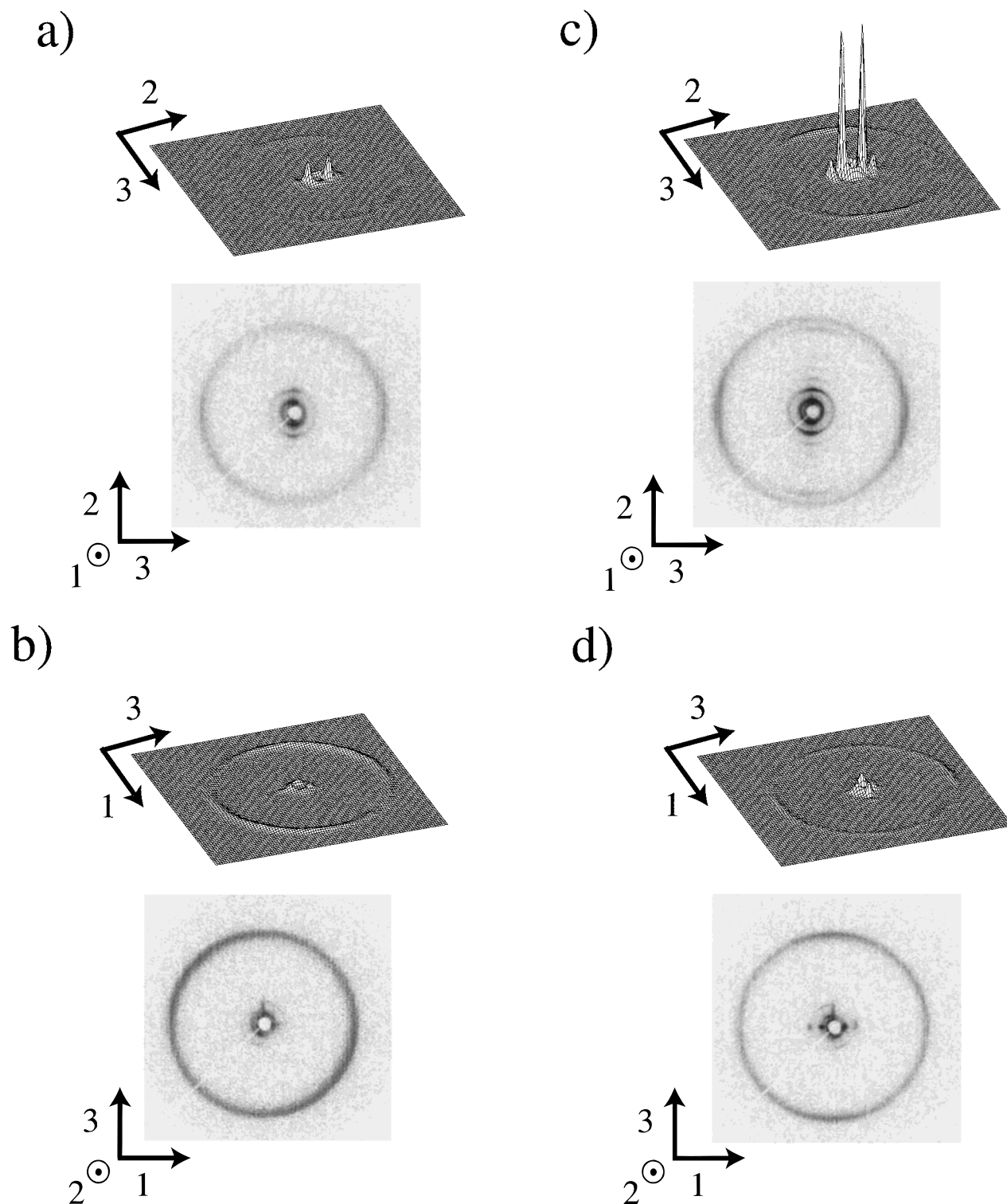


Figure 5. SAXS intensity patterns of PS-*block*-P4VP(PDP)_{1.0} taken in the tangential direction and the normal direction before (a and b) and after (c and d) shearing. The scattering intensities are in the linear scale in the uppermost figures and in the logarithmic scale in the bottom figures. The diblock structure has a long period of 320 Å; the corresponding first-order peak is located close to the beam stop at $q = 0.02 \text{ \AA}^{-1}$. The initial sample already exhibited a preference for the parallel orientation as is clear from the presence of the two peaks along the 2-direction in (a). After shear (c), sharp first-order and higher-order peaks are visible along the 2-direction for the diblock structure, indicating that the parallel alignment was further enhanced. The smaller complex structure shows a preferential perpendicular orientation. The presence of the small peaks at $q = 0.02 \text{ \AA}^{-1}$ in (d) shows that the sample contained some additional defect structures.

phology (Figure 4a,b). The intensity maximum occurs at $q = 0.17 \text{ \AA}^{-1}$, which corresponds to a structure with a long period of 36 Å. The corresponding second-order SAXS peak indicating lamellar structure becomes resolvable using synchrotron radiation.²⁷ The sample was

subsequently exposed to oscillatory shear of 0.5 Hz and 100% strain amplitude at 56 °C, which is well within the microphase separated regime. P4VP(PDP)_{1.0} was easily oriented as shown by the SAXS pattern taken after 6.5 h of shearing which demonstrates that the

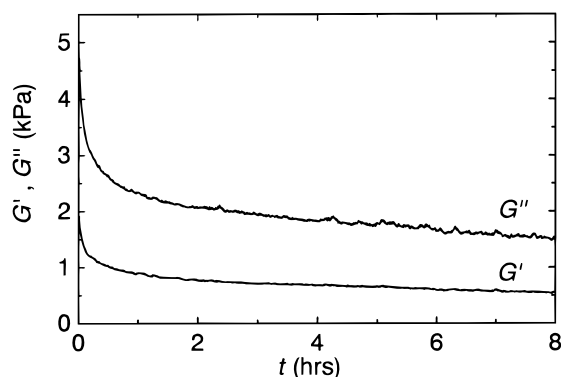


Figure 6. Change in the dynamic storage modulus G' and the dynamic loss modulus G'' of PS-*block*-P4VP(PDP)_{1.0} during the shearing process at 125 °C. Frequency $f = 0.5$ Hz, strain amplitude $\gamma = 50\%$.

sample is highly oriented parallel to the shear flow (Figure 4c,d). Such orientation is similar to the conventional diblock copolymers where parallel alignment is also commonly observed well below the T_{ODT} .^{5,8,13,14,33} Note that in our case we are dealing with supramolecular comb copolymer-like structures where the most important new aspect concerns the nature of the bond between the chemically different species, i.e., hydrogen bonding rather than covalent bonding. The fact that also in the present case good orientation is obtained indicates that the hydrogen bonds are strong enough to withstand the applied oscillatory shear flow. If a large number of hydrogen bonds were broken due to the shear flow, the repulsive interaction between the alkyl tails and the P4VP would most likely have resulted in macrophase separation as the shearing was performed only about 10 °C below the T_{ODT} .

Diblock Copolymer Complex PS-*block*-P4VP-(PDP)_{1.0}. Below the T_{ODT} of the supramolecular comb copolymer-like P4VP(PDP)_{1.0} species, the block copolymer complex PS-*block*-P4VP(PDP)_{1.0} has a lamellar-*within*-lamellar morphology characterized by two different length scales. The alternating lamellae of PS and P4VP(PDP)_{1.0} are stacked with a long period of 320 Å, whereas in the P4VP(PDP)_{1.0} containing layers, alternating layers of polar and nonpolar material with a long period of 36 Å are present²⁶ (Figure 1). The most appropriate temperature range for shearing is dictated by two opposite requirements. First, since the PS blocks have a glass transition temperature of approximately 100 °C, the shearing should take place above this temperature. Under this conditions the P4VP(PDP) layers are disordered, since the T_{ODT} of the short length scale structure is around 70 °C. Second, an upper limit to the shearing temperature is set by the fact that the PDP side chains of the supramolecular comb copolymer-like blocks are attached to the P4VP by hydrogen bonding. This hydrogen bonding diminishes strongly at elevated temperatures, while at the same time PDP becomes miscible in PS above 130 °C.^{3,26} On the basis of these considerations, a shearing temperature of approximately 125 °C was selected. At this temperature more than 50% of the hydrogen bonds are still present on the basis of FTIR.²⁶

Since the initial orientation might have an effect on the final alignment, the initial sample should preferably be completely isotropic. However, the PS-*block*-P4VP-(PDP)_{1.0} cannot be heated above the T_{ODT} of the diblock structure for the reasons mentioned above. (At elevated

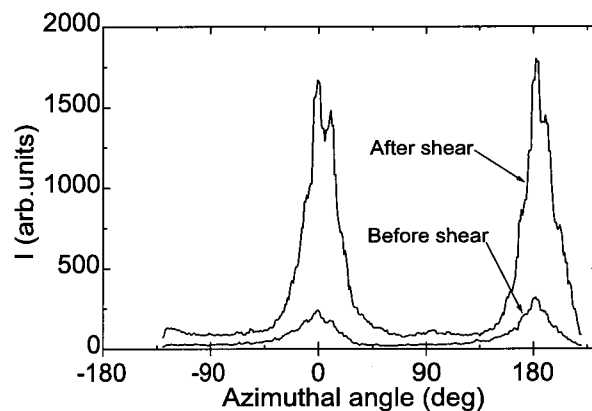


Figure 7. Azimuthal scan of the first-order peak of the diblock structure before and after shearing in the 1-direction. Maxima at 0° and -180° correspond to the parallel alignments, whereas 90° and -90° correspond to the perpendicular alignments. The intensity ratio before and after shearing is 1:6. The division of the peak at 0° into two intensity maxima is not real and is probably due to some problems with the detector response.

temperatures the PDP will either partly evaporate or partly diffuse into the PS phase, in both cases inducing a transition from the lamellar structure to the potentially cylindrical morphology.²⁶) The initial orientation for each sample was checked by SAXS at room temperature. Figure 5a,b demonstrates that the sample preparation induces already a slight parallel orientation. This is most likely due to the solvent evaporation stage; subsequent pressing into tablets at 10 bar did not influence the degree of orientation.

The shearing of the diblock copolymer complex PS-*block*-P4VP(PDP)_{1.0} was performed at 125 °C at 0.5 Hz and 50% strain and then at 1 Hz and 50% strain to further increase the amount of orientation. The applied amplitude was lower than in the case of P4VP(PDP)_{1.0}, because of the higher tendency for instabilities during flow. Because of the higher viscosity of the material, the orientation process was slower than that for the homopolymer case. Figure 6 shows the change in the shear moduli G' and G'' during the oscillatory shearing. Both of them show an initial drop followed by a gradual decrease, as commonly found for diblock copolymer samples.¹⁰ The initial drop is believed to be associated with the formation of well-defined lamellae out of poorly organized regions.^{8,10} The subsequent slow process may be due to growth of the domain sizes.⁸ After 8 h of shearing G' and G'' still continued to decrease.

Since the shearing temperature is above the T_{ODT} of the P4VP(PDP)_{1.0} complex, only the larger diblock structure is directly affected by the flow. The ordering of the smaller complex structure takes place once the sample is cooled below the ODT of the small structure in the quiescent situation. Figure 5c,d demonstrates that the larger diblock copolymer structure orients parallel to the shear flow. The increased ordering can be appreciated from Figure 7 presenting the intensities of the first-order scattering peak before and after shearing as a function of the azimuthal angle. Because of the shearing, the intensity of the first-order peak has increased by a factor of 6.

The small length scale lamellar structure, as formed after cooling, has the tendency to align perpendicular to the interface between PS and P4VP(PDP)_{1.0}^{3,25,26} as is also clear from Figure 8 presenting the intensity of the corresponding scattering peak as a function of the azimuthal angle. The degree of orientation of the

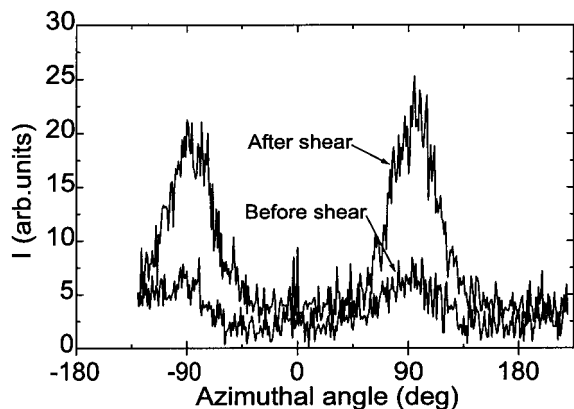


Figure 8. Scattering intensity due to the small structure as a function of the azimuthal angle before and after shearing.

smaller structure depends strongly on the degree of orientation of the large structure. If the large structure is macroscopically isotropic, no overall orientation for the small structure is found either. In this case, as demonstrated in Figure 5a, the SAXS pattern shows two isotropic rings, located at $q = 0.02 \text{ \AA}^{-1}$ for the large length scale lamellar structure and at $q = 0.17 \text{ \AA}^{-1}$ for the small length scale lamellar structure. When the diblock layers are macroscopically aligned, the orientational freedom of the small length scale lamellae is limited. However, the scattering peak corresponding to the small structure of the sheared sample is very broad, and only a modest increase in intensity is observed. Attempts to obtain a better alignment for the small structure by annealing the sample at $60 \text{ }^\circ\text{C}$, which is close to the ODT for the small structure, resulted only in a slight increase in the orientation for the large structure.

Conclusions

We have taken the first steps to macroscopically orient supramolecular self-organized polymer materials by imposing an oscillatory shear flow. By shearing at 0.5 Hz frequency and 100% strain amplitude the lamellar hydrogen-bonded complex of P4VP and PDP, P4VP-(PDP)_{1,0}, aligned parallel to the shear flow, showing that the hydrogen bonds between the amphiphiles and the P4VP are strong enough to withstand the flow. The diblock copolymer complex PS-*block*-P4VP(PDP)_{1,0}, having a hierarchical lamellar-*within*-lamellar morphology below ca. $70 \text{ }^\circ\text{C}$, was sheared above the ODT of the complex structure at $125 \text{ }^\circ\text{C}$ at 0.5 Hz and 50% strain amplitude and at 1 Hz and 50% strain amplitude. For the larger diblock structure, a parallel alignment was found. Upon cooling the sample, the smaller complex structure is formed inside the layers of the comb copolymer-like material oriented perpendicular with respect to the diblock structure. Finally, while probing other shear parameters, we found evidence for the existence of other alignments (e.g., perpendicular and transverse), which will be further investigated in the future.

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