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In Situ *Radial* Small Angle Synchrotron X-ray Scattering Study of Shear-Induced Macroscopic Orientation of Hierarchically Structured Comb-Shaped Supramolecules

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During recent years we have introduced a new concept to prepare functional polymeric materials based on self-assembly of comb-shaped supramolecules.[1] They are obtained by attaching "short" chain molecules via physical interactions (hydrogen bonding, ionic bonding or a combination thereof) to either a homopolymer or to one of the blocks of a diblock copolymer. In the latter case, one of the most interesting aspects of our approach is the possibility to construct hierarchically structured materials, i.e., structures at different length scales.[2−4] Most of our studies are based on diblock copolymers of polystyrene (PS) and poly(4-vinylpyridine) (P4VP) with pentadecyl phenol (PDP) hydrogen bonded to the P4VP-block, i.e., PS-*b*-P4VP(PDP)$_{1.0}$. Here, the subscript indicates the ratio between pyridine and phenol groups. In the simplest case of a so-called lamellar-*within*-lamellar structure, the material consists of alternating lamellae (the *large* length scale) of which every other one, containing the comb-shaped P4VP(PDP)-blocks, is in turn again internally self-organized in the form of alternating lamellae (the *short* length scale). Besides this structure, many others (lamellar-*within*-cylinders, lamellar-*within*-spheres, etc.) have been constructed and imaged by transmission electron microscopy as well.[2−5] In all cases the microphase separation in the P4VP(PDP) domains is in the form of a lamellar structure with a periodicity of ca. 3.5 nm.[5−6]

Almost all applications, such as functional membranes,[7] anisotropic proton conductivity,[8] dielectric stacks,[9] etc., require the comb-shaped supramolecules based materials to be macroscopically aligned.[1] This alignment may in principle be induced using external fields like shear fields,[10−15] electric fields[16−18] or special surfaces.[19−22] However, little is known about the consequences of the supramolecular nature of the constituents with respect to the effect of external fields. Moreover, many of the hierarchically structured materials constructed so far (e.g., lamellar-*within*-lamellar) are characterized by two structures that are oriented perpendicularly with respect to each other. The macroscale ordering by external forces of both levels of organization present will therefore frequently involve frustration, since the external field may promote for instance parallel orientation of both structures with respect to the field, whereas thermodynamics dictates a mutually perpendicular orientation. Previously, we have succeeded in creating some macroscopic alignment by applying large amplitude oscillatory shear on a macroscopically isotropic multidomain PS-*b*-P4VP(TSA)$_{1.0}$(PDP)$_{1.0}$ system.[8] Here toluenesulfonic acid (TSA) forms a salt with the P4VP-blocks and PDP is subsequently hydrogen bonded to the TSA groups. The P4VP(TSA) salt acts as a proton conductor and the improved macroscopic orientation manifests itself in tridirectional proton conductivity.[8]

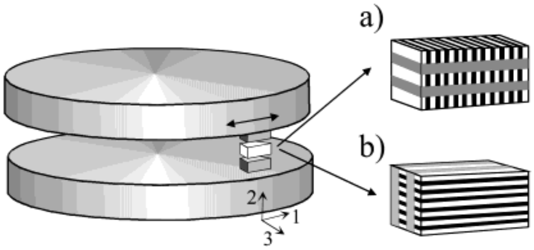

Figure 1. Illustration of shearing plates used and bimodal distribution of lamellar-*within*-lamellar structure. Two "teeth" of the same size are positioned on top of each other and the sample of characteristic thickness of 0.5 mm is put in between. Here 1 is the tangential direction (shear direction), 2 the normal direction and 3 the radial direction. In part a, the large length scale ordering is parallel and the short length scale ordering is transverse; in part b, the large length scale ordering is perpendicular and the short length scale ordering is parallel.

To study the influence of large amplitude oscillatory shear on the macroscopic orientation of these systems in more detail and in particular to study the pathways toward macroscopic orientation we recently completed the development of a novel rheometer (a modification based on a Bohlin rheometer). This instrument enables us to investigate the orientation process in situ in the X-ray beam in two directions, i.e., not only in one direction as it is customary in the case of block copolymer systems.[23,24] The rheometer was equipped with two large metal disks. These were thinned down in such a fashion that, on their outer rim, several teeth of varying dimensions were left. The disks were mounted on the rheometer in such a way that the teethed sides were facing each other. Samples can now be placed between opposing teeth of the same size. This configuration allows for free radial and tangential access of the X-ray beam to the sample (see Figure 1). The shearing device is further surrounded by an oven to allow temperature scans. Details of the apparatus will be published elsewhere. We have used this device on the Dutch−Belgian (DUBBLE) beamline BM26B at ESRF in Grenoble, France.[25] This work reports the first *radial* SAXS patterns of a hierarchically structured material recorded during large amplitude oscillatory shear.

The PS-*b*-P4VP(PDP) system discussed above has certain drawbacks due to the relatively high glass transition temperature of the PS-block ($T_g \cong 100$ °C for the PS layers). The order−disorder transition temperature T_{ODT} of the short length scale structure, which corresponds to microphase separation between the alkyl tails and the more polar part of the comb-shaped P4VP(PDP) blocks, is around 65 °C. Therefore, it is actually

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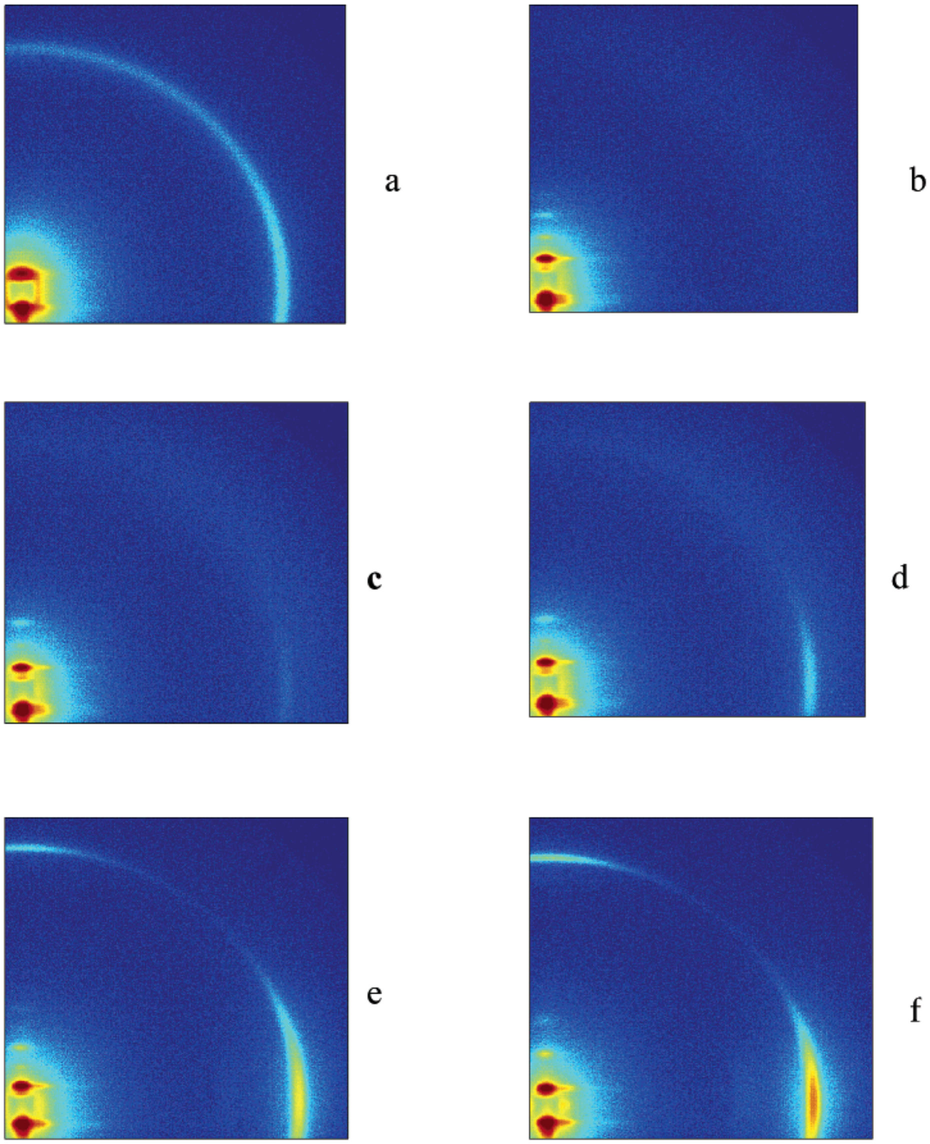

Figure 2. In situ *radial* scattering patterns of PI-*b*-P4VP(PDP)$_{1.0}$: (a) at room temperature before shear; (b) at 85 °C during shear; (c) at 70 °C during shear and cooling; (d) at 62 °C during shear and cooling; (e) at 54 °C during shear and cooling; (f) at the end at room temperature. The cooling rate is ca. 0.4 °C/min, the sample of thickness 0.5 mm is confined between two "teeth" of 8 mm length and 3 mm width, the shear strain amplitude is 75%, and the frequency is 1 Hz.

difficult to continue the shearing process through the transition region. Indeed, the P4VP(PDP) layers remain fluid down to room temperature where the alkyl tails start to crystallize.[6,25] However, it cannot be excluded that the macroscopic ordering of the thin layers formed inside the P4VP(PDP) layers at the T_{ODT} will be hampered by the glassy PS layers. Note that this problem did not arise for the above-mentioned PS-*b*-P4VP(TSA)$_{1.0}$(PDP)$_{1.0}$ system, since here the ODT of the short length scale structure occurs at ca. 120 °C, and the shear procedure involved cooling through 120 to ca. 115 °C. However, that is a rather complex system due to the combination of ionic bonding and hydrogen bonding and therefore hardly the first choice to start a systematic study. Hence, we selected a diblock copolymer of polyisoprene and poly(4-vinylpyridine) to prepare a PI-*b*-P4VP(PDP)$_{1.0}$ supramolecules sample, which remains in the melt state down to room temperature.

The diblock copolymer (Polymer Source Ltd) has a molecular weight of 30K for the PI-block and 11.7K for the P4VP-block. For a stoichiometric amount of PDP, with respect to the number of pyridine groups, the PI-blocks account for ca. 40 w/w% of the system. As a consequence, the large length scale ordering due to the microphase separation between the PI-block and the P4VP(PDP)-block corresponds to a lamellar structure. Its periodicity is ca. 35 nm. Because of the strong incompatibility, on heating this structure persists up to elevated temperatures. As always, the short length scale structure appears on cooling around 65 °C in the P4VP(PDP) layers and also corresponds to a layered structure, but of an order of magnitude smaller periodicity of ca. 3.5 nm. An illustration of the local structure containing both length scales can be found in Figure 1.

The system was first heated to 85 °C and subsequently subjected to large amplitude oscillatory shear. A frequency of 1 Hz and a shear strain amplitude of 75% was employed for a sample with a thickness of ca. 0.5 mm. During the shear, the sample was slowly cooled with a cooling rate of 0.4 °C/min and *radial* X-ray scattering patterns were recorded (1 min/frame). Figure 2 presents a series of X-ray patterns thus obtained. Before being heated to 85 °C, the system shows already some orientation of the alternating PI and P4VP(PDP) layers, whereas the layers inside the P4VP(PDP) domains have a more random orientation (Figure 2a). At 85 °C (Figure 2b), where the shearing starts, the short length scale structure is obviously not present anymore as $T > T_{\mathrm{ODT}}$ and the alternating PI and P4VP(PDP) layers have a strongly improved parallel orientation due to shearing (first, second, and third diffraction orders are clearly visible). The comb-shaped architecture of P4VP(PDP) gives rise to a broad correlation hole peak faintly present at "large" angles in Figure 2c taken at 70 °C (see also ref 6). On further cooling the layered structure inside the P4VP(PDP) layers starts to appear at ca. 64 °C (see Figure 2d for the situation at 62 °C). Compared to Figure 2a, we observe that the short length scale layers are no longer randomly oriented. The equatorial diffraction peak shows that at least a considerable fraction of these "thin" layers is oriented transverse to the shear flow. Obviously, the radial scattering pattern alone does not exclude all other orientations normal to the "thick" layers (180° rotational freedom). Strikingly, on further cooling an additional reflection peak corresponding to the short length scale ordering appears on the meridional at ca. 59 °C. This is illustrated in Figure 2e, which for clarity was taken at 54 °C. On further cooling the scattering pattern remains essentially the same (Figure 2f). This additional reflection peak cannot possibly be due to the formation of a layered structure inside the large length scale layers parallel to the shear direction. However, as far as the large length scale structure is concerned, the data presented show the presence of layers that are oriented parallel to the shear flow, but they do not exclude the presence of additional layers that are oriented perpendicular. This kind of orientation would not show up in a radial scattering pattern. The presence of layers that are oriented transverse, as observed in ref 23, is excluded, since these would show up as additional equatorial reflections (the apparent small angle equatorial scattering is simply forward scattering increasing on cooling). A tentative explanation for the presence of the meridional peak belonging to the short length scale ordering is therefore that also alternating PI and P4VP(PDP) layers are present that are oriented perpendicular with respect to the shear direction. The presence of the meridional reflections at "large" angles then corresponds to "thin" layers oriented parallel to the shear direction inside these "thick" P4VP(PDP) lamellar domains. Why the ODT temperatures of the differently oriented "thin" layers should differ by as much as 5° (64 and 59 °C, respectively) is not clear. An alternative explanation is that the perpendicular orientation of the alternating PI and P4VP(PDP) layers is actually induced at 59 °C by the shear flow. To confirm this, tangential scattering experiments, that have not yet been performed, are required. The two different orientations that could give rise to the scattering patterns observed are illustrated in Figure 1.

Therefore, these data seem to imply the presence of a bimodal orientation distribution of the "thick" alternating PI and P4VP(PDP) layers. Related bimodal orientation distributions are well-known as intermediate states toward macroscopic orientation in conventional PI-*b*-PS diblock copolymers.[13,23] Still, in our case, this is merely a tentative explanation. To obtain a more complete picture, a thorough study of this system is planned, where the pertinent parameters will be varied systematically and where in situ radial scattering experiments will be combined with in situ tangential scattering experiments following the same protocol. From such a systematic study, we expect to obtain unique insight in the pathways toward macroscopic orientation of this class of hierarchically structured materials. In particular, we hope to be able to answer the fundamental question whether it is possible to create true macroscale order in hierarchically ordered materials using large amplitude oscillatory shear, i.e., to align both type of layers.

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