

The influence of grain size on the alignment of hexagonally ordered cylinders of self-assembled diblock copolymer-based supramolecules

Sasa Bondzic^a, Evgeny Polushkin^a, Arend Jan Schouten^a, Olli Ikkala^b, Gerrit ten Brinke^{a,*}

^a *Laboratory of Polymer Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands*

^b *Department of Engineering Physics and Mathematics, Center for New Materials, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo, Finland*

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Abstract

In situ SAXS is used to investigate the shear-induced alignment of a supramolecular system consisting of a polyisoprene-*b*-poly(2-vinylpyridine) diblock copolymer and octyl gallate (OG), where OG is hydrogen-bonded to the vinylpyridine block of the PI-*b*-P2VP copolymer. Due to microphase separation, the PI-*b*-P2VP(OG) system self-assembles forming a domain structure of hexagonally ordered P2VP(OG) cylinders embedded in the PI matrix. The results of the alignment showed that the orientation mobility of the cylinders, lying within the (10) planes parallel to the shear plane, is strongly dependent on the size of the cylindrical domains. Subjected to large amplitude oscillatory shear for 15 min a freshly loaded sample with a small grain size structure exhibited much better alignment compared to that of a pre-aligned/squeezed sample with a considerably larger grain size where the orientation had been first partly destroyed by squeezing.

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1. Introduction

Since 1970s of the last century it is well known that shearing can produce global alignment in microphase separated block copolymers, while under quiescent conditions they tend to form a randomly oriented multi-domain morphology [1]. In the latter case, block copolymer properties are macroscopically isotropic, although the local structure within each domain, or grain, is anisotropic. In this regard, shear flow used to be considered as a very attractive technique to align the initially isotropic morphology of block copolymers, in order to use them in a number of applications such as optoelectronics, membrane or nanotemplate technologies. During the past years great progress has been made in our understanding of the main features of the rheological properties and the mechanism of alignment of block copolymer systems, which both are found to be extraordinarily complex and dependent

on a large number of factors [2–4]. In particular, when oscillatory shear is used, rather than steady flow being apparently effective only until a certain strain [1,5], the final alignment is determined by at least four important parameters. These are the frequency, strain amplitude, duration of shear, and the alignment temperature [6–8]. Besides, such characteristics as the molar mass of the block copolymer and the number of blocks, the nature of the microphase separation (ranging from weak to strong segregation) and the rheological properties of the material, including the “mechanical contrast” between the blocks, are known to influence the mechanism and kinetics of alignment. Note that the rheological properties themselves depend in turn on the alignment state and, hence, on all the above-mentioned parameters. It is also known that the size and shape of the ordered domains strongly affect the rheology of a block copolymer sample [2,4]. Therefore, a dependence of the shear-induced alignment of block copolymer systems on the domain size might be expected.

So far, however, very little attention has been paid to this topic and we are not aware of any paper where the direct

* Corresponding author. Tel.: +31 050 363 4509; fax: +31 050 363 4400.

E-mail address: g.ten.brinke@rug.nl (G. ten Brinke).

influence of the initial domain size on the final alignment is reported. There are apparently several reasons for this. First of all, in many experimental studies the alignment has been investigated on samples initially heated to above the order–disorder transition temperature, T_{ODT} , to erase the thermal and deformation history. Prepared in this way the macroscopically isotropic fine-grain morphology of the samples allowed to obtain reproducible experimental data on further shearing [7,9–15].

On the other hand, it has been pointed out that thermal history, or more exactly the pre-annealing of block copolymers at temperatures far below T_{ODT} but above the glass transition temperature, T_g , is a “hidden” parameter that can significantly affect the orientation behavior under large amplitude oscillatory shear (LAOS) [8]. In particular, it has been observed that after low frequency shearing at a temperature roughly 15 K below T_{ODT} , a pre-annealed PS-*b*-PI sample showed a much better ‘parallel’ alignment of the lamellar microstructure than another sample quenched to the same experimental temperature from the disordered state. This influence of pre-annealing was interpreted in terms of the coherence length of the ordered regions, i.e. grains. The size of grains which, in turn, is determined by the annealing history [16], has been suggested to be a critical parameter for the reorientation process of the lamellae oriented more or less randomly in the initial samples [8,17]. In this particular case, the observation of such a nearly isotropic initial morphology was likely due to the fact that the pre-annealed samples were plane sheets first molded at a quite low temperature, well below the T_g of the PS-block. Other investigators have reported that a slight global ‘parallel’ alignment of lamellar domains is normally observed in samples prepared by molding [5,18]. Nevertheless, the degree of such initial alignment is quite low and the initial size of the ordered domains is rather small compared to those to be achieved on further shear. Because of this, the slight anisotropy of the initial state is often considered as a parameter that has little influence on further shear-induced alignment [5,19].

The second point why the influence of the initial domain size on the alignment of block copolymers has been practically disregarded so far is the fact that most of the experimental studies have been devoted to *lamellar* morphologies [2–4,8]. Depending on the alignment parameters three possible, mutually orthogonal, lamellar orientations have been observed: the above-mentioned ‘parallel’ alignment with lamellae oriented parallel to the shear plane and the ‘perpendicular’ and ‘transverse’ alignments. It has been reported that ‘flipping’ from one alignment to another can occur on varying the frequency and strain of the oscillatory shear imposed. The mechanism of this realignment involves at least partly the destruction of the initial orientation and the reformation of domains of the new alignment, rather than the rotation of domains as a whole [3,8]. Therefore, the flipping phenomenon is apparently rather insensitive to the initial domain size.

Another important feature of the lamellar morphology is its “primitivity” in comparison, for instance, with the cylindrical one. Essentially the type of lamellar alignment is only determined by the preferred orientation of the lamellar layers, and within each of the three possible alignments the perfection

of the anisotropy with time proceeds via the coarsening of the domains of the favored alignment on the expense of all other alignments. In other words, the initial domain size is supposed to simply determine the time to achieve the final alignment.

In our view, the situation is much more complex in the case of a cylindrical morphology. First, two features, the *ordering* of cylinders within a domain and the *orientation* of domains with respect to the shear direction, should be taken into account to characterize the alignment. The most favorable ordering for cylinders is known to be a hexagonal symmetry packing. Therefore, the observation of a 6-spot scattering pattern from a cylindrical self-assembled block copolymer system is a sign of good macroscopic alignment of the sample. As to the orientation of the cylinders, it is well established that they tend to orient along the shear direction. Two types of orientation have been found, the ‘parallel’ alignment with the (10) plane of the hexagonal unit cell parallel to the shear plane, and the ‘perpendicular’ alignment in which the (11) plane is parallel to this plane [19]. Since cylinders are most densely packed in the (10) plane, the parallel alignment is commonly observed in the experiments [2]. The second thing we would like to note with respect to the alignment of cylindrical morphology is that the relationship between the three following features: (a) the perfection of the hexagonal order on a local scale, (b) the orientation of the cylinders along the shear direction and (c) the choice between the parallel and perpendicular alignment, is still not clear. Our experimental data presented below suggest that once the cylindrical domains are formed the flow along the (10) planes is the first stage of alignment, which is in accordance with most of the literature data [1,2,4,11]. The orientation of the cylinders, the perfection of the hexagonal order and the coarsening of the domains seem to occur afterwards, during the so-called ‘slow’ alignment [3]. The most important observation of this work, discovered probably for the first time, is that the orientation mobility of cylinders within the (10) planes is strongly dependent on the size of the cylindrical domains.

In this paper we report on the orientation behavior of a very specific class of block copolymer systems consisting of so-called comb-shaped supramolecules. Here non-mesogenic amphiphiles are hydrogen-bonded to one of the blocks of a suitable diblock copolymer [20,21]. In our case octyl gallate (OG) is in this way attached to the vinylpyridine block of a polyisoprene-*b*-poly(2-vinylpyridine) diblock copolymer. The choice of this particular supramolecular system, hereafter referred to as PI-*b*-P2VP(OG)_{*x*}, where *x* denotes the ratio between the number of OG molecules and the pyridine groups, is based on the results of our previous work [22,23], showing that at *x* = 0.5 the microphase separation between the PI ‘coil block’ and the P2VP(OG) ‘comb-like block’ results in the formation of hexagonally packed cylinders of P2VP(OG)_{0.50} within the PI matrix. It is important to note that in general the rheological and orientation behaviors of such hydrogen-bonded supramolecular systems are similar in many aspects to that of ‘common’ block copolymers [24–27].

The results on the alignment of the PI-*b*-P2VP(OG)_{0.50} system presented in this study have been obtained at a synchrotron

SAXS beamline, using a homemade tooth rheometer [28,29]. The advantage of this rheometer is the possibility to perform in situ SAXS measurements in two different directions using only a small amount of sample.

2. Experimental section

The system under investigation is a complex between a PI-*b*-P2VP diblock copolymer, i.e., poly(1,4-isoprene)-*block*-poly(2-vinylpyridine), and octyl gallate (OG), i.e., 4-octyl-3,4,5-trihydroxybenzoate, where the OG molecules are attached to the vinylpyridine block via hydrogen bonding [22,23]. The PI-*b*-P2VP copolymer with a weight average molar mass of 30 and 2.8 kg/mol for the PI and P2VP blocks, respectively, and with $M_w/M_n = 1.15$, was purchased from Polymer Source, Inc., and used as received. OG was obtained from Sigma–Aldrich, Inc., and prior to use it was recrystallized from 9:1 volume ratio mixture of ethanol and chloroform. The PI-*b*-P2VP(OG)_{0.50} supramolecular system studied was prepared according to the following procedure [22]. First, the PI-*b*-P2VP copolymer is dissolved in chloroform to a concentration less than 2% (w/w). Then the required amount of OG, i.e., one OG molecule per two vinylpyridine groups, is added into the solution, and the system is allowed to form the complex for 24 h. Although chloroform is not a good solvent for OG, its dissolving in the chloroform solution of PI-*b*-P2VP was readily performed due to the hydrogen bonding between OG and the P2VP block. After slow evaporation of the solvent in air, the as-cast sample is additionally dried in a vacuum at 40 °C for 48 h. Note that the glass transition temperature (T_g) of pure P2VP is about 100 °C, while that of a P2VP(OG)_{0.50} complex made from a homopolymer of P2VP with high molar mass is ca. 60 °C. Due to the low molar mass of the P2VP block ($M_w = 2800$ g/mol) contained in the PI-*b*-P2VP diblock copolymer used here, the T_g in the self-assembled PI-*b*-P2VP(OG)_{0.50} complex is even lower than this, approximately 50 °C.

SAXS measurements were performed at the DUBBLE beamline of ESRF in Grenoble, France [30]. The sample-detector distance was ca. 7.7 m, and the X-ray wavelength was 1.24 Å ($E = 10$ keV). Values of the scattering vector have been calculated as $q = (4\pi/\lambda) \sin \theta$, where θ is one-half of the scattering angle. The q -range covered by the 2D-detector was as broad as 0.07–0.80 nm⁻¹.

Using a Linkam hot stage, a macroscopically isotropic sample was initially examined by SAXS during a heating–cooling run performed with a rate of 10 °C/min. The measuring time in these experiments was 30 s per frame.

Shear-induced alignment of the samples was conducted using a homemade tooth rheometer described in detail elsewhere [28,29]. The instrument, operated in an oscillatory strain controlled mode, is a kind of plate–plate rheometer, specially designed to perform in situ SAXS studies on the alignment of complex fluids induced by large amplitude oscillatory shear (LAOS). Instead of relatively large plates normally used in rheology, in this rheometer small tooth-like plates of 5×3 mm² in size are employed (see Fig. 1). Despite of this

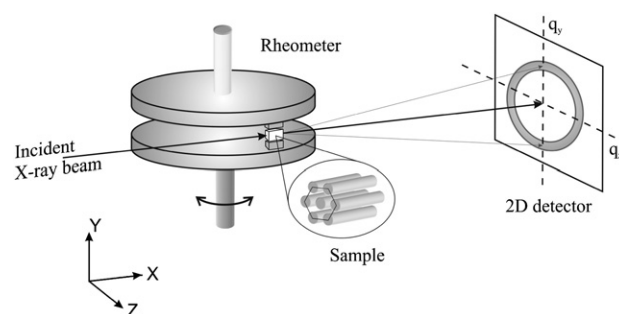


Fig. 1. Set-up with the tooth rheometer used in the in situ SAXS experiments during shear-induced alignment.

small-size geometry, the rheometer allows to perform adequate rheological measurements [29].

After loading a sample in the rheometer at 90 °C a required gap width Δy (see Fig. 4a) between the rheometer teeth was set and any excess of the sample around the tooth edges was always removed prior to shear. All in situ SAXS experiments with the rheometer were performed at a frequency of 0.5 Hz and a constant temperature of 120 °C. The maximal angular deflection of the moving bottom plate was limited to $\Omega = 20$ mrad, and in most of the experiments it was set to this maximal value. The primary X-ray beam of ca. 0.2×0.2 mm² in size was directed into the rheometer gap along the shear vector (X axis). Thus, the beam passed through a 5 mm long sample and all SAXS images were obtained as ‘tangential’ patterns recorded in the q_y – q_z scattering plane by a 2D-detector (Fig. 1). The gap width Δy , i.e., the thickness of the sample in the shear gradient direction (Y axis, see Fig. 4a), could be varied between 1.2 and 0.4 mm, while in the vorticity direction (Z axis) the size of the sample was 3 mm. Changing the gap Δy allowed us to readily control the shear strain amplitude γ_0 in the range of 40–120%, since $\gamma_0 = \Omega R / \Delta y$, where $R = 25$ mm is the distance of the teeth to the center of the rheometer plates (see Fig. 1). Typical time limit for the alignment was 15–30 min, while the measuring time per SAXS frame was 30 s. The broadness of the direct beam peak was estimated to be below 0.01 nm⁻¹ and due to such a small value it was neglected in the analysis of the SAXS data obtained.

Rheological characteristics, such as the storage and loss moduli G' and G'' , respectively, as well as the phase angle φ , were also recorded during the in situ experiments. Note, since samples were subjected to LAOS, the rheological parameters measured were most probably obtained in a non-linear deformation mode. Therefore, they were not truly G' and G'' and should be considered only as convenient quantities to follow the alignment of the samples.

3. Results

3.1. SAXS measurements under quiescence conditions

At room temperature the as-cast sample of PI-*b*-P2VP(OG)_{0.50} shows two broad scattering peaks at $q^* = 0.247$ and ca. $q = 0.48$ nm⁻¹ (Fig. 2). The position of the

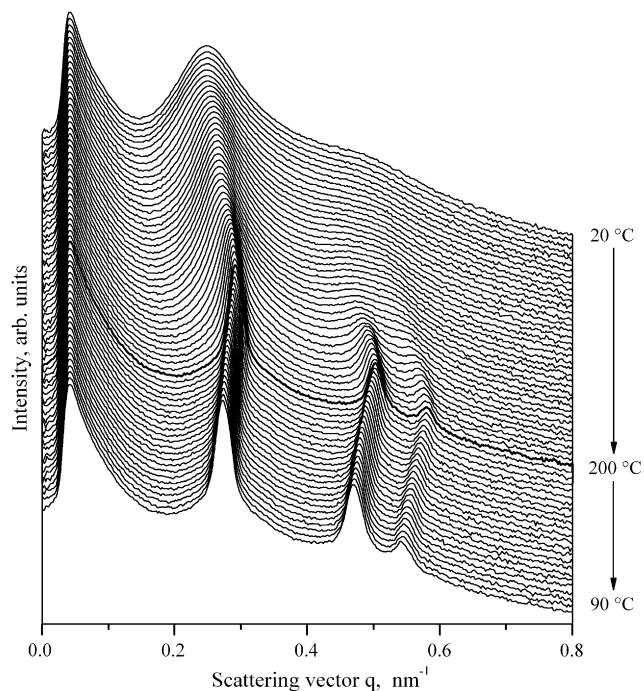


Fig. 2. SAXS integration patterns obtained from PI-*b*-P2VP(OG)_{0.50} on heating from 20 to 200 °C and cooling from 200 to 90 °C with a rate of 10 °C/min under quiescent conditions. The bold line is the SAXS profiles obtained at 200 °C.

peaks and their transformation on further heating suggest that a very poorly ordered cylindrical structure is present in the initial sample. To specify, at this amount of OG added the system microphase separates to form a hexagonally ordered array of P2VP(OG)_{0.50} cylinders embedded in the PI matrix [22]. The *d*-spacing corresponding to the *q**-peak decreases from ca. 25 to 23 nm when the temperature increases from 20 to 220 °C.

The temperature dependence of the full width at half maximum (FWHM) of the principal scattering peak, also referred to as *q**-peak above and below, is presented in Fig. 3. For the initial sample the width is about 0.06 nm⁻¹ and it remains

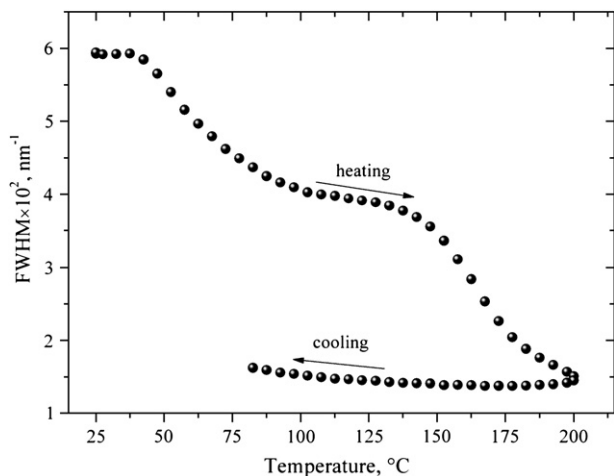


Fig. 3. Temperature dependence of the FWHM of the main scattering peak observed on heating the PI-*b*-P2VP(OG)_{0.50} sample under quiescent conditions.

about that value up to ca. 50 °C, which is in close proximity of the *T*_g of the P2VP(OG)_{0.50} block. Above this temperature the FWHM starts to decrease, reaching a plateau value of 0.04 nm⁻¹ at ca. 100 °C. On further heating the width of the peak remains relatively constant up to 150 °C, where once again it starts to decrease abruptly until a temperature of 180 °C is reached. At the maximal temperature of 200 °C the peak width reveals its minimal value of 0.015 nm⁻¹, which remains relatively unaltered on subsequent cooling.

The width of the *q**-peak is known to be a suitable parameter to estimate the perfection of the sample structure, while the decrease of the FWHM observed on heating is a clear evidence for healing of the structural imperfections with temperature. To interpret the SAXS data in more detail, it is convenient to use a simplified model [31,32], describing the peak width ΔS , which is in fact related to the FWHM measured in our experiments by $\text{FWHM} = 2\pi\Delta S$, in terms of the inherent domain order and the average grain size *Nd*:

$$\Delta S \approx \sqrt{\left(\frac{\pi^2\delta^2}{d^3}\right)^2 + \left(\frac{1}{Nd}\right)^2}$$

Here *N* is essentially the number of scattering centers of a one-dimensional lattice spaced on average at a distance *d* and δ is the half-width of the assumed Gaussian distribution in the real distance between two neighbor scattering centers. Thus, the parameter δ is a quantity to characterize the structural imperfections inside the grains.

The broadness of the *q**-peak (Fig. 3) and the presence of only faint higher order peaks at room temperature (Fig. 2) are a clear signature of a very short range order of the cylindrical structure. This implies that the size of grains is small, not more than 100 nm, and the majority of the sample is not well ordered (i.e., *Nd* is small, while δ is large).

The decrease of the width observed above 50 °C, where after passing the *T*_g the molecular mobility of the system significantly increases, is mostly due to the healing of structural imperfections inside the grains. No significant change in the higher order peak region is observed in the SAXS patterns, implying the very short range ordered cylindrical morphology to persist. The peak width reaches a plateau value at ca. 100 °C, where apparently most of the imperfections inside the grains have disappeared. Therefore, a decrease in δ takes place in this temperature region while the increase in *Nd* is still not substantial: the grain size is estimated to be 150 nm.

At above 150 °C the energy barrier for the coarsening of different grains can be overcome. As a result the coherence length of the ordered structure increases up to 450 nm (i.e., a strong increase in *Nd* and further decrease of δ). All this gives rise to the appearance of the higher order peaks of the cylindrical structure (Fig. 2) and the significant decrease of the FWHM (Fig. 3). The hydrogen-bonded nature of the complex seems to be the main reason for the specific behavior of the sample observed at these high temperatures. As shown in our previous work [22] the hydrogen bonding between OG and P2VP block considerably weakens on heating above

140 °C. This increases the molecular mobility of the P2VP(OG)_{0.5} block, leading to a significant decrease in the viscosity of the PI-*b*-P2VP(OG)_{0.5} complex.

It is important to notice that no order–disorder transition (ODT) has been observed on heating to 200 °C and above, implying that the sample is most likely in the strong segregation limit (SSL) for which the disordered state is highly unfavorable.

As a summary of this part: the initial as-cast sample is far from the equilibrium state and its structure consists of a large number of small grains of hexagonally packed cylinders. On heating under quiescent conditions most of the structural imperfections located inside the grains are healed by 120 °C, while the grain coarsening takes place only at temperatures above 150 °C. The perfection of the hexagonal order achieved on heating is retained on subsequent cooling.

The results of our shear experiments, on which we will concentrate next, were obtained at 120 °C, where on the one hand the grains are still small in size, while on the other hand the structural imperfections inside the grains have been minimized.

3.2. In situ SAXS during the LAOS alignment

First, we recall that the loading of the PI-*b*-P2VP(OG)_{0.50} samples into the rheometer was performed at 90 °C and then any excess of the sample partially flowing out of the gap between the rheometer teeth was removed (see Fig. 4a). All in situ SAXS experiments on shear were performed at a frequency of 0.5 Hz and temperature of 120 °C. A typical SAXS image of a freshly loaded sample obtained at this temperature prior to shear is shown in Fig. 5a. Two prominent arc reflections corresponding to the principal q^* -peak in Fig. 2 are observed on the meridian against an isotropic scattering ring as background. Besides, close inspection reveals another low intensive ring corresponding to the $\sqrt{3}q^*$ -peak. The anisotropy of the first scattering ring is a clear evidence that the deformation of the sample on closing the gap is enough to slightly align the P2VP(OG)_{0.50} cylinders in the horizontal x – y plane (see Fig. 1). On the other hand, the relatively large width of the ring in the radial direction (the FWHM of the q^* -reflection is 0.03–0.05 nm⁻¹, depending on the azimuthal

position on the scattering ring) and the rather faint and isotropic higher order reflections strongly suggest that the initial sample consists of relatively small grains (of ca. 120 nm) of poorly ordered cylinders that are slightly aligned in the horizontal plane, as schematically depicted in Fig. 4b.

SAXS images of two samples after 15-min LAOS alignment performed with two different shear strain amplitudes of 41 and 81% are shown in Fig. 5b and c, respectively. In contrast to the freshly loaded sample, both sheared samples reveal a 6-fold pattern characteristic of a macroscopically aligned cylindrical structure. The appearance of the first order spot-like reflections and, in addition, well-separated higher order reflections, which as shown below are much more intensive as well as narrower than those in Fig. 5a, is a clear indication for a shear-induced increase in the grain size of the two aligned samples, as schematically illustrated in Fig. 4c.

Before discussing the SAXS images further, we present in Fig. 6 the changes in the ‘apparent’ storage G' and loss moduli G'' and the phase angle φ , measured for the sample aligned with the shear strain of 81%. Similar dependences were observed for the sample sheared at 41% strain. As the shear starts, a dramatic decrease in G' and G'' and a significant increase in φ (from 55° to 65°) were observed during the first 4–5 min of the alignment. Accompanied with a significant modification of the SAXS patterns, these strong changes in rheology are in accordance with the ‘fast process’ usually observed for LAOS alignment of block copolymers [3,7]. The further alignment is a typical ‘slow process’ characterized by rather gradual changes in the rheological parameters. For instance, the phase angle φ increases only from 65 to 67 for the next 10 min. After 15 min all three dependences presented in Fig. 6 reveal a strong tendency to reach asymptotic values. The SAXS pattern of the sample recorded at this point is shown in Fig. 5c. No significant changes in SAXS were observed on further shear.

Compared to each other, the SAXS patterns presented in Fig. 5b and c are good examples to demonstrate the influence of the shear strain amplitude on the final degree of alignment achieved. In both cases, the q^* -reflections observed on the meridian are more intensive than that of the off-meridian ones. This means that not all of the hexagonally packed P2VP(OG)_{0.50} cylinders are aligned parallel to the X-ray beam, conforming to the statement that “alignment is never perfect” [2]. On the other hand, the sample sheared with the 81% strain revealed a much lower difference in the intensity of the meridional and off-meridian reflections than that observed for the sample aligned at the strain of 41%. This is clearly visible from Fig. 7, where linear-scaled 3D-analogues of the 2D SAXS patterns of Fig. 5 (plotted in fact in a logarithmic scale) are shown. We note in passing that the meridional reflections are assumed to originate from all the hexagonally packed cylinders lying within the (10) planes parallel to the shear plane, but only some of the cylinders, that are parallel to the primary X-ray beam, are supposed to produce the off-meridian reflections.

Fig. 8 shows the decrease of the FWHM of the meridional q^* -reflection in time obtained for the two samples aligned at

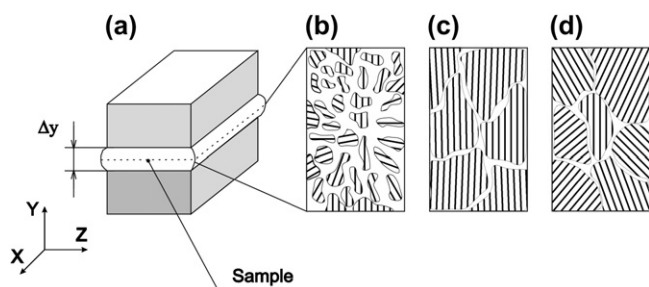


Fig. 4. (a) Loading a sample into the Δy gap between the rheometer teeth of 3×5 mm in size. Drawings for the grain size and the orientation of cylinders: (b) prior to shear, (c) after an initial shear alignment and (d) after the partial destroying of the initial alignment on reducing the gap by 50% (see the text).

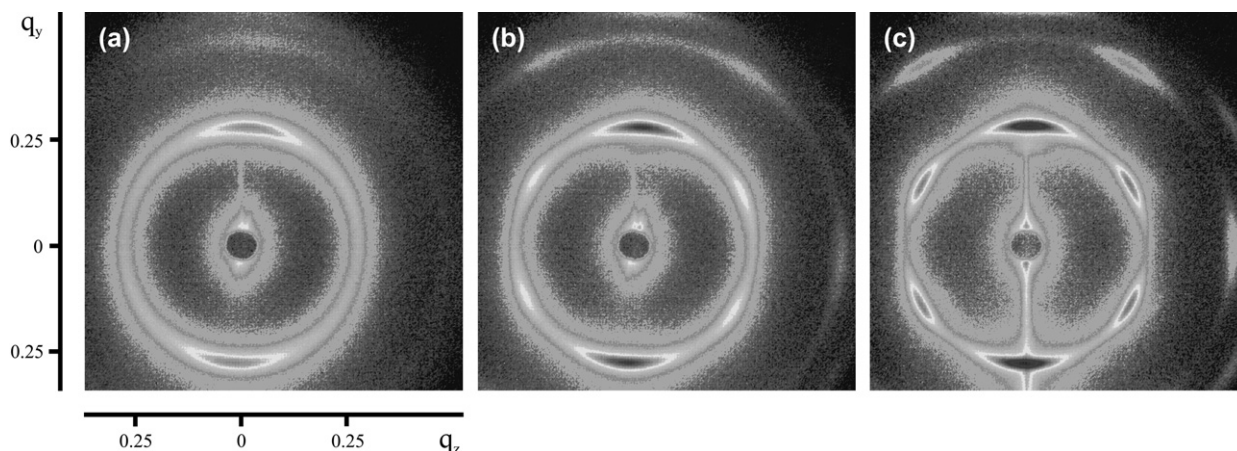


Fig. 5. SAXS images obtained at 120 °C: (a) prior to shear, just after loading the PI-*b*-P2VP(OG)_{0.50} sample between the rheometer teeth, and after 15-min oscillatory shear with a frequency of 0.5 Hz at a shear strain of (b) 41% and (c) 81%.

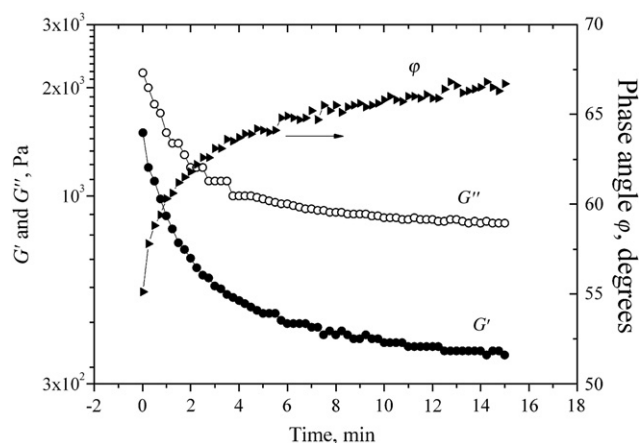


Fig. 6. Changes of the dynamic G' and G'' moduli and the phase angle ϕ in time at 120 °C during the LAOS alignment of a freshly loaded PI-*b*-P2VP(OG)_{0.50} sample, performed at $f = 0.5$ Hz and $\gamma = 81\%$.

41 and 81% strain (full and open circles, respectively). The final peak width of 0.015 nm^{-1} achieved during the 81% alignment corresponds to the grain size of 420 nm, while the width of 0.020 nm^{-1} found for the sample sheared at the lower strain suggests the formation of 310 nm grains. When shear

starts, both samples exhibit an instantaneous increase in the peak width compared to the initial value. This increase is most probably due to the destruction of grains not favorably oriented along the flow. On further shear, a rapid decline of the peak width is observed that coincides in time with the ‘fast alignment process’ changes in the rheological parameters (Fig. 6) and the most prominent changes in the SAXS pattern. The initial broadening and the decrease of the peak width in time are strongly dependent on the applied shear strain. At 81% strain, the initial 12% increase of the peak width is followed by a 50% decrease in the course of the 15-min alignment. These percentage values are nearly twice as large as those observed at the lower strain of 41%.

Thus, prior to the alignment both samples reveal a slightly anisotropic hexagonally ordered cylindrical structure consisting of rather randomly oriented grains, which are small in size (Fig. 4b). Under the LAOS imposed for 15 min, considerable macroscopic alignment of the samples is achieved by means of the destruction and rotation of the small, disoriented grains accompanied by the coarsening of the favorably oriented grains. At the higher shear strain of 81% the degree of the final alignment is higher and the size of the grains is larger than those obtained under the 41% strain. This is in agreement

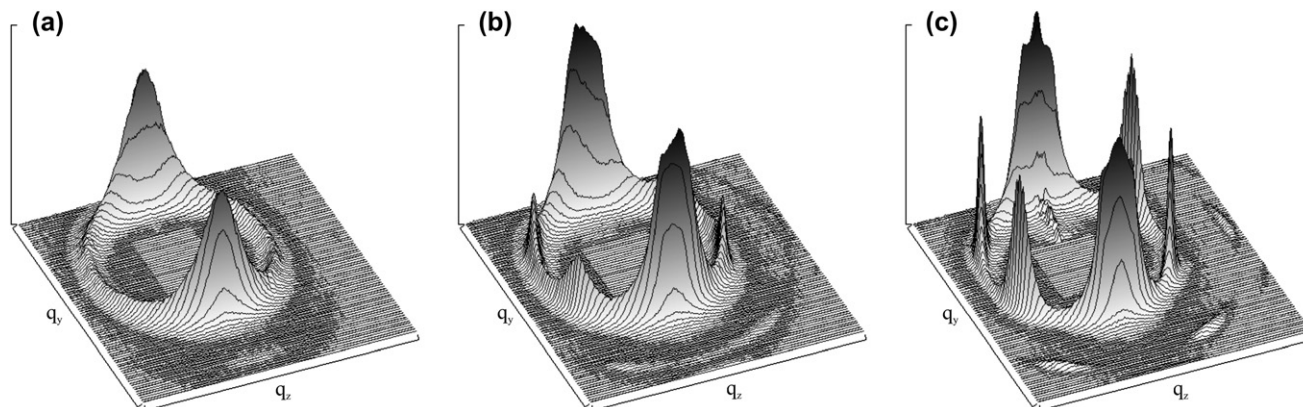


Fig. 7. Linearly-scaled 3D-SAXS images obtained at 120 °C: (a) prior to shear and on the alignment of PI-*b*-P2VP(OG)_{0.50} at the shear strain of (b) 41% and (c) 81% (more details in Fig. 5).

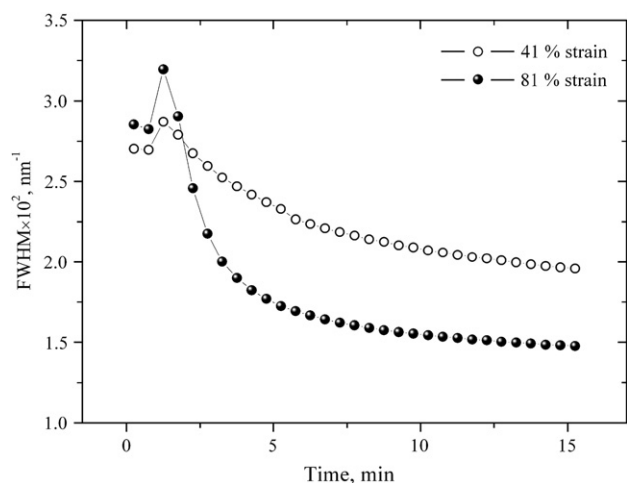


Fig. 8. FWHM of the main q^* -peak observed for the two PI-*b*-P2VP(OG)_{0.50} samples aligned at 120 °C with the shear strain of 41% (open circles) and 81% (solid circles).

with the observation made on the alignment of polystyrene-*b*-polyisoprene copolymers [15].

It is important to note that the SAXS images shown in Fig. 5b and c were obtained at two different rheometer gaps of ca. 1.2 and 0.6 mm, respectively. In these experiments, the angular deflection of the moving rheometer plate was kept constantly equal to 20 mrad, and the gap changes were used to set the desired shear strain amplitudes of 41 and 81%, respectively. Although not shown here, additional results were obtained in similar experiments with two other gaps of 0.8 and 0.4 mm, corresponding to shear strains of 61 and 122%. The general tendency found for the freshly loaded samples is that the higher the shear strain the better the alignment and the larger the grain size. Besides, the same tendency was found for samples aligned at a fixed gap width, when the shear strain was varied by changing the angular deflection of the rheometer plate. A last remark is to comment the vertical spikes observed in the SAXS image of Fig. 5c. They sometimes appear on closing the gap if the adjustment of the rheometer with respect to the primary X-ray beam is not completely optimized and the parasitic

instrumental scattering around the beam hits the working planes of the rheometer teeth.

In the rest of this section, we report on the most interesting in situ SAXS data obtained using the following alignment procedure. First, a freshly loaded PI-*b*-P2VP(OG)_{0.50} sample placed into a relatively large gap between the rheometer teeth was pre-aligned at a certain shear strain for 15 min. Then, the gap was gently reduced to a smaller value and the pre-aligned sample was subjected to an additional LAOS alignment procedure for another 15 min, using either the same or a higher shear strain amplitude.

Fig. 9a is a 3D-SAXS pattern obtained after the 0.8-mm gap alignment of a freshly loaded sample performed at 61% strain for 15 min. The pattern is very similar to that shown in Fig. 7c and, therefore, it also suggests the formation of a large grain hexagonally packed cylindrical morphology in the macroscopically aligned sample. Although the 6-fold pattern in Fig. 9a is not ideally symmetrical the degree of alignment achieved in this case is supposed to be quite high if compared with the slightly anisotropic state of the sample prior to shear (e.g., see a typical SAXS image in Fig. 7a).

The SAXS pattern of the sample obtained just after the gap was decreased from 0.8 to 0.4 mm is presented in Fig. 9b. Such a reduction in the sample thickness destroys the initial alignment significantly. In contrast to the highly anisotropic pattern in Fig. 9a, the anisotropy of the image shown in Fig. 9b is rather faint: quite broad arc reflections of the first order are observed on the meridian only, while off-meridian reflections are completely absent. This pattern resembles in some extent the one of a freshly loaded sample prior to shear (Fig. 7a), but there is also a significant difference clearly seen in the corresponding 2D patterns shown in Fig. 10. First of all, in addition to the q^* -reflection, two other very prominent reflections are observed at higher q -values just after the squeezing of the pre-aligned sample (Fig. 10b). Secondly, all the scattering reflections of the sample are quite narrow in the radial direction when compared to those of the initial freshly loaded sample (Fig. 10a). All this suggests that the grain size achieved during the pre-alignment is not very much

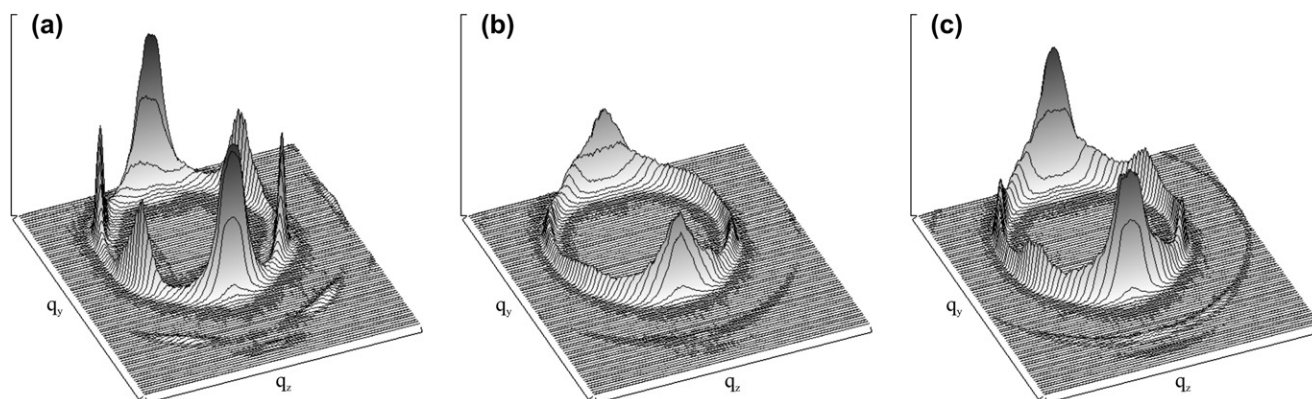


Fig. 9. 3D-SAXS images obtained at 120 °C: (a) after the 15-min LAOS alignment of a freshly loaded PI-*b*-P2VP(OG)_{0.50} sample performed with a strain of 61%; (b) just after the squeezing of the pre-aligned sample by decreasing the rheometer gap from 0.8 to 0.4 mm; (c) after the subsequent LAOS alignment of the pre-aligned/squeezed sample with a doubled strain of 122% for another 15 min.

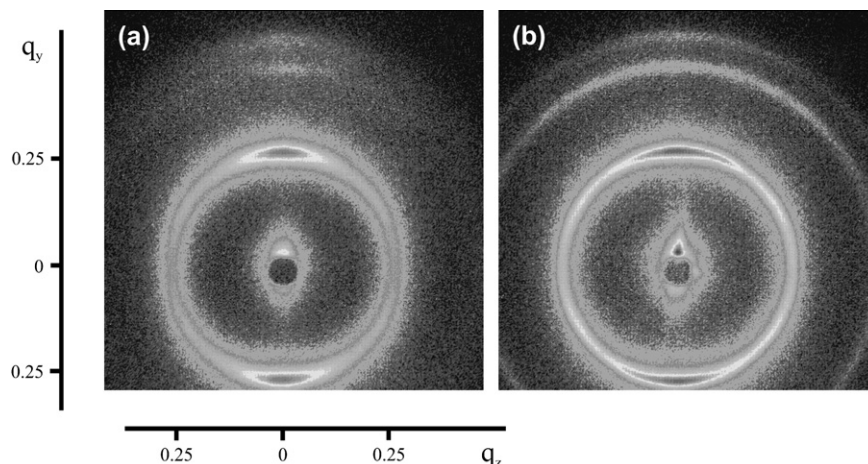


Fig. 10. 2D SAXS images obtained at 120 °C from (a) a freshly loaded PI-*b*-P2VP(OG)_{0.50} sample prior to shear and (b) just after the squeezing of the pre-aligned sample by decreasing the rheometer gap from 0.8 to 0.4 mm (more details in the text).

affected by the squeezing. On the other hand, the squeezing is enough to destroy the initial global orientation of the P2VP(OG)_{0.50} cylinders that were mostly parallel to the shear direction (*X* axis in Fig. 1) in the pre-aligned sample. In the squeezed state most of the hexagonally packed domains remain oriented with the (10) plane parallel to the shear plane (*X*–*Z* plane in Fig. 1), but the cylinders within the (10) planes are believed to be somewhat distributed along the shear direction (*X* axis). A model of the partially misaligned, coarse-grain morphology is depicted in Fig. 4d.

When the squeezed sample was additionally subjected to LAOS with a strain of 122%, i.e., twice as much as that used during the pre-alignment, for another 15 min, it was a big surprise to see its SAXS pattern, which is presented in Fig. 9c. The degree of macroscopic alignment in the sample was unexpectedly poor if compared to that of the freshly loaded sample sheared at the lower strain of 61% (Fig. 9a). Similar results were obtained for other pre-aligned samples squeezed from 0.8 to 0.6 mm and from 0.6 to 0.4 mm.

The above results on squeezing became even more intriguing after the observation of considerable alignment achieved in a special experiment when a freshly loaded sample was placed into a 0.6 mm gap at 120 °C, kept at this temperature under quiescent conditions for 10 min, then squeezed to a 0.4 mm gap and subjected to a 122% shear strain for 15 min. The specificity of this experiment consists in the presence of an excess of the material around the rheometer teeth (see Fig. 4a) produced by squeezing the sample from 0.6 to 0.4 mm prior to its alignment, like it was after squeezing the pre-aligned samples. Because of this, the path of the primary X-ray beam through the sample slightly increases. Such an increase is estimated to be not more than 1 mm just after squeezing the initially 5 mm long sample and then it gradually reduces in time as the excess sample flows down on the bottom plate. The azimuthal distribution in the intensity of the first order reflections of the freshly loaded sample sheared after squeezing is shown in Fig. 11 (a line). For comparison, the corresponding distribution of the pre-aligned sample obtained from the

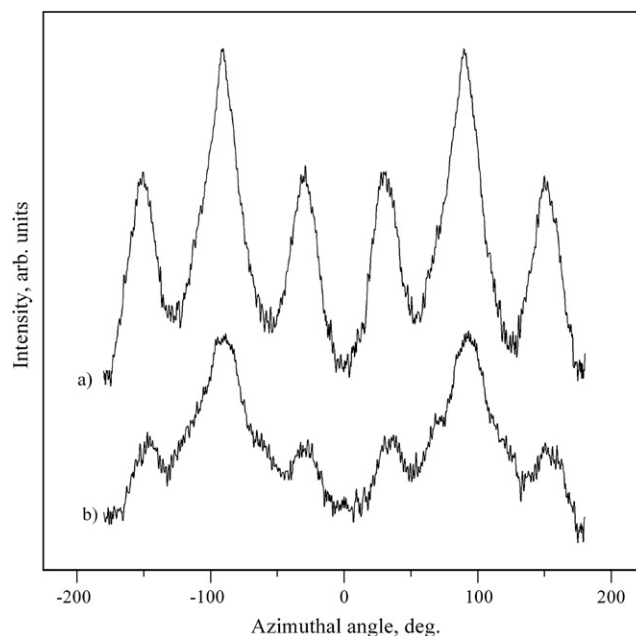


Fig. 11. Azimuthal distribution in the intensity of the main q^* -reflections observed in the SAXS patterns of two different PI-*b*-P2VP(OG)_{0.50} samples aligned at 120 °C for 15 min, using the same LAOS parameters ($f=0.5$ Hz, $\gamma=122\%$) and the same gap equal to 0.4 mm: (a) a freshly loaded sample squeezed from 0.6 mm; (b) a sample initially pre-aligned at a 0.8-mm gap and then squeezing to the gap of 0.4 mm (more details in the text).

2D-image in Fig. 9c is also presented in Fig. 11 by b line. Therefore, the presence of excess sample is not a limiting factor to obtain a highly anisotropic SAXS pattern.

Thus, the results shown in Figs. 9 and 11 indicate that the efficiency of the LAOS imposed to align the cylinder morphology samples is strongly influenced by the initial grain size of the structure. The freshly loaded samples, where the average size of the randomly oriented cylindrical domains is rather small, turned out to be more suitable to achieve considerable alignment than the pre-aligned samples characterized by significantly increased grain sizes.

4. Discussion

The flow alignment of block copolymer samples forming hexagonally ordered cylindrical structure has been the subject of a number of publications [1,9,11,33–36]. The two primary features of the alignment are the orientation of the cylinders along the shear direction and usually the formation of ‘parallel’ alignment where the (10) plane of the hexagonal lattice is parallel to the shear plane. Like the shear behavior of lamellar self-assembled systems, the alignment of cylindrically ordered samples can be divided into ‘fast’ and ‘slow’ processes clearly identified by means of rheology. From a structural point of view, the fast process is characterized by a significant transformation of the initial morphology of the sample, involving considerable orientation of the cylindrical domains along the flow direction, accompanied by coarsening of the favorably oriented domains and the relatively fast disappearance of domains with all other orientations. During the slow process the partly oriented sample is on its long-time way to reach the final state of alignment, showing gradual improvement in the positional and orientation order of the cylindrical domains and their further growth that proceeds mostly due to defect annihilation [2].

The results presented in this study are in general consistent with the above-mentioned findings. However, the discovered influence of the grain size on the kinetics and “the final degree” of alignment of the PI-*b*-P2VP(OG)_{0.50} system appear to be a new interesting experimental observation. In some respect, our results are in line with recent data obtained on thin films of lamellar self-assembled polystyrene-*b*-polyisoprene block copolymer solutions that were subjected to electric field alignment [37]. Also there, the initial degree of order in the system has been found to strongly affect the mechanism and kinetics of the orientational process. For a highly oriented sample, the perpendicular realignment of the lamellae occurs via “the nucleation and growth of newly oriented domains” and this process is rather slow. In less ordered samples, the re-orientation process is considerably faster, since it proceeds through a grain rotation mechanism. We realize that the *cylindrical* PI-*b*-P2VP(OG)_{0.50} system investigated in this work is rather different from the above-mentioned *lamellar* thin film samples in both its chemical and physical nature. Besides, the alignment techniques used, LAOS and electric field, are also different. Nevertheless, we believe that the comparison of these experimental data is relevant. In both cases, the initially less ordered samples are more responsive to the orientation pressure of an external field than the pre-aligned samples. We consider the former as samples of small grain size, i.e., ‘samples with high defect density’ [37] where *grain rotation* as the mechanism of alignment is well possible. As to the re-orientation of pre-aligned samples, we believe that in general the destruction/reformation mechanism [1,5,11] might be more appropriate here than *nucleation and growth of new domains* [37]. In our particular case, however, *destruction/reformation* is hardly the primary route to macroscopic orientation. As depicted in Fig. 4d, after squeezing the relatively large domains of the PI-*b*-P2VP(OG)_{0.50} samples are mostly oriented parallel to the shear plane and the cylinders within

these domains are assumed to be broadly distributed around the flow direction. Compared to the lamellar [37] and cylindrical [1] samples pre-aligned *orthogonally* to the desired orientation, such a morphology of our squeezed samples is a “half way” state towards the final alignment. From an energetic point of view [1,11] this state is already much more favorable for a sample to flow than any orthogonal alignment morphology. Therefore, the pre-aligned PI-*b*-P2VP(OG)_{0.5} samples may simply flow without significant destruction of the initial domains and, hence, without any noticeable improvement in their macroscopic alignment. On the other hand, aligning by means of the grain rotation mechanism is also hindered in the samples due to their increased grain size and decreased defect density compared to those in the freshly loaded samples.

5. Conclusions

The SAXS data obtained from the PI-*b*-P2VP(OG)_{0.50} supramolecular system investigated in quiescent state and under shear revealed that the system self-assembles into a domain structure of hexagonally ordered P2VP(OG) cylinders immersed in the PI matrix. The morphology of the as-cast sample is far from equilibrium, being a small grain structure of poorly ordered cylinders. On heating under quiescent conditions most of the structural imperfections inside the small cylindrical domains are healed by 120 °C. The coarsening of domains, leading to a considerable increase in the grain size, takes place only at temperatures above 150 °C.

The LAOS experiments carried out at 120 °C revealed that freshly loaded samples of PI-*b*-P2VP(OG)_{0.50} can be well aligned under shear imposed for 15 min. Due to the small grain morphology in the initial state, these samples readily respond to the orientation pressure and align by means of the destruction and rotation of the small, disoriented grains simultaneously with the coarsening of favorably oriented grains. Both the degree of alignment and the final grain size of freshly loaded samples increased with the shear strain amplitude, which was varied in the range of 41–122%.

Under similar shear conditions, the pre-aligned/squeezed samples showed an unexpectedly low degree of macroscopic orientation. This result has been explained in terms of the specific grain morphology. Those samples were first aligned using a relatively large gap width between the rheometer teeth. Then the achieved alignment was partially destroyed by setting a lower gap width. After this squeezing the pre-aligned/squeezed samples still reveal a large grain morphology and the (10) plane of the cylindrical domains is mainly parallel to the shear plane. However, the orientation of P2VP(OG)_{0.5} cylinders within the (10) planes was considerably diverged from the flow direction. On further shear the alignment of such morphology was hindered due to the increased size of the partially oriented cylindrical domains.

Thus, the experimental data obtained under shear are clear evidence that the degree of alignment of the PI-*b*-P2VP(OG)_{0.5} supramolecular system is strongly dependent on the initial size of the cylindrical domains. Depending on the deformation history, samples sheared under identical

conditions show quite different alignment kinetics and the final degree of alignment.

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