Chapter Three

Oscillatory shear flow-induced alignment of lamellar diblock copolymers

Abstract
The oscillatory shear flow-induced alignment of lamellar diblock copolymers, in particular PEP-block-PEE and PS-block-PI, has been investigated by many authors, leading to an overall mapping of the orientation with frequency, strain amplitude and temperature. Four regimes were found, three of parallel alignment and one of perpendicular alignment. Transverse alignment never proved stable and was only found en route to parallel alignment in the highest frequency regime. The trajectories towards final alignment consist of an initial fast process, followed by a slow process. The first is characterized by a strong decay in the shear elastic and loss moduli with time. In this process, two of the three alignments and everything in between are enhanced. Regions of poorly organized material transform into well-defined lamellae. In the following slow process, where the moduli are leveling off, all orientations but one are eliminated.
3.1 Introduction

Keller et al.\textsuperscript{1,2} and Hadziioannou et al.\textsuperscript{3,4} were the first to show that block copolymers can be macroscopically oriented when subjected to deformation or flow. Since then, a large number of authors have picked up the subject in a search for new applications, investigating the oscillatory shear flow-induced alignment of di- and triblock copolymers.\textsuperscript{5-41} Especially lamellar diblock copolymers have gained a lot of attention, leading to an overall mapping of the alignment with the oscillation parameters, like temperature, frequency and strain amplitude.\textsuperscript{11,18} This is the focus of this chapter.

3.2 Experimental set-up

3.2.1 Dynamic rheology

Oscillatory shear flow-induced orientation experiments are generally performed in the non-linear regime, i.e. at large amplitudes, to force the system out of its macroscopically isotropic state into the desired macroscopically oriented state. Typically, strain amplitudes of 100\% or higher are used.\textsuperscript{5-29} Still, Winey and Wiesner and coworkers showed that even small strain amplitudes as small as 3 to 5 \% could induce alignment,\textsuperscript{16,17,19,26} indicating that diblock copolymers are very susceptible to the applied flow. The plate-plate set-up is commonly used in literature, as it allows \textit{in-situ} characterization of the orientation of the sample. A typical sample thickness is 1 mm. For the cone-plate set-up the shear rate is constant throughout the sample; in a plate-plate set-up it increases linearly with the distance from the center. Before oscillation, the samples are heated above the order-disorder transition temperature, $T_{ODT}$, of the material, to erase all history including any orientation initially present. In this way, each new experiment has the same starting conditions.

3.2.2 Methods of characterizing the oriented structure

The orientation process can be followed in time by combining dynamic rheology with \textit{in-situ} scattering methods, such as small angle X-ray scattering (SAXS), light
scattering (SALS) and neutron scattering (SANS), or with optical methods such as birefringence. For practical reasons, these methods are commonly applied in one direction only, leaving a large uncertainty as to which alignment is actually developing in time (see Fig. 3.1). The time resolution of the scattering methods is in the order of tens to hundred seconds; more detailed information is lost. Birefringence has a time resolution in the order of microseconds, but it has much lower information content,\textsuperscript{11} and requires additional characterization methods to confirm the interpretation of the optical data.

\textit{Ex-situ} scattering methods can provide three-dimensional information, but after cessation of the oscillations, the material can relax and distortions of the structure during cooling, transportation and sample preparation may occur. Transmission electron microscopy (TEM) records the local structure in the material as well as the type and density of defects that define the domains in a block copolymer.\textsuperscript{9,15,19,21,26,42} The length scale of the uniformly oriented domains can vary from tens of nanometers for unaligned samples up to micrometer scale for aligned samples.\textsuperscript{9,26,42}

![Figure 3.1. Possible macroscopic alignments obtained upon the oscillatory shear flow orientation of an initially macroscopically isotropic lamellar diblock copolymer. a) and b) Experimental set-up and coordinate system. c) Layers with their normal along the shear gradient direction (2-direction): parallel alignment. d) Layers with their normal along the radial direction (3-direction): perpendicular alignment, and e) layers with their normal along the shear direction (1-direction): transverse alignment.](image-url)
3.3 The orientational behavior of lamellar diblock copolymers

3.3.1 Alignments

There are three possible macroscopic orientations for lamellar diblock copolymers (see Fig. 3.1), namely parallel, perpendicular and transverse, which can be distinguished by the way the normal on the lamellae is directed. In the case of parallel orientation, the lamellar normal is along $\nabla \nu$, the velocity gradient direction. For transverse orientation it is directed along $\nu$, the shear velocity direction. Perpendicular oriented lamellae have their normal directed along $\nabla \times \nu$, the radial or neutral direction. Throughout this thesis, these three directions are referred to as $I$, $2$- and $3$-direction respectively (See Fig. 3.1).

3.3.2 Dynamic moduli of ordered and disordered phases in the linear regime

Fig. 3.2 shows the storage modulus $G'$ of an unoriented PEP-block-PEE obtained over a temperature range of 35 to 170 °C as a function of the frequency at low strain amplitudes, i.e., in the linear regime. The data are time-temperature shifted to $T_o = 35$ °C. At a certain frequency, called $\omega_c$, the ordered and the disordered branch coincide, corresponding to the longest relaxation of the polymer chain. Below $\omega_c$, larger structures such as lamellae and domains of lamellae are probed. Above $\omega_c$, the chain distortion dominates the rheological behavior.

Guilock and Porter were the first to show that the ODT can be identified using dynamic rheology. Below $T_{ODT}$ both $G'$ and $G''$ scale as $\omega^{0.5±0.1}$, while above $T_{ODT}$ $G'$ scales as $\omega^2$ and $G''$ as $\omega$. Accordingly, it is clear from Fig. 3.2 that the $T_{ODT}$ of this material is at 96 °C. Nowadays, this method of obtaining $\omega_c$ and $T_{ODT}$ is commonly used for diblock copolymers as well as ABA triblock copolymers. It requires an experimentally accessible ODT and is valid only for a limited range of molecular sizes. After oscillation, the shear and loss moduli of the aligned samples show distinctly lower moduli as a function of frequency than the initial samples.
A second characteristic frequency, \( \omega_c \), exists, below which the relaxation of the lamellar domains becomes important. Koppi et al. were able to determine this frequency from the storage modulus in the shear plane (\( G'_{xy} \)).\(^{12}\) A small bump in \( G'_{xy} \) of a perpendicular oriented sample was attributed to defect motions. Zhang and coworkers offered an alternative approach of determining \( \omega_c \) and \( \omega_d \) out of the loss tangent (\( \tan \delta = G''/G' \)) and the dynamic viscosity (\( \eta'' = G''/\omega \)).\(^{18,27,29,48}\) They estimated \( \omega_c \) and \( \omega_d \) to be the upper and lower points in the \( \tan \delta \) versus \( \log \omega \) curve, between which \( \tan \delta \) has a loss peak. A change in the slope of \( \eta'' \) at high and
low frequencies gave rise to the same critical frequencies. These methods do not seem to work for unentangled diblock copolymers, as they gave inconsistent results when applied to unaligned, parallel aligned and perpendicular aligned PS-block-PI copolymers. The problem in determining \( \omega_d \) is the fact that its value is controlled by grain boundaries and defects, and thus depends on the texture and domain size. Increasing the domain size could reduce this frequency. For PEP-block-PEE copolymers \( \omega_d \) was estimated to be 0.03 \( \omega_c \), whereas for PS-block-PI copolymers \( \omega_d \approx 0.0001 \omega_c \).

3.3.2 The alignment diagram

The results of the oscillation experiments have been mapped as a function of temperature, strain amplitude and frequency (see Fig. 3.3). Dimensionless temperatures (\( T/T_{opt} \)) and frequencies (\( \omega/\omega_c \)) are used to combine results obtained from PEP-block-PEE and PS-block-PI copolymers. The rheological difference between these two diblock copolymers is the mechanical contrast between the blocks. For the PS-block-PI copolymer, the mechanical contrast is large, as the PS block is rigid and the PI block is soft. Thus, this diblock copolymer will have a different response to the applied flow than PEP-block-PEE, which has mechanically similar blocks. Although other types of diblock copolymers have been studied, they will not be discussed here.
The alignment diagram of both diblock copolymers shows four regions, three regions of parallel alignment (A, C and D) and one region of perpendicular alignment (B). Boundary regions, where biaxial alignments and flipping of the orientation with strain amplitude are found, separate regions B and C, and regions C and D. The third alignment type, transverse, never proved to be stable, but was found en route to parallel alignment in region D (see section 3.4).

The critical frequency $\omega_c$ is located near the boundary between region B and C. This indicates an expected change in the alignment mechanism going from B to C. In region B, the (domains of) lamellae play a role in the orientation mechanism, whereas in region C local chain conformations determine the orientation behavior. At frequencies faster than the conformational relaxations of the chains, the deformation couples to more local dynamics and differences between the types of lamellar layers are probed. This is believed to be the crossover from region C to D. In region D, the more rigid PS-layers act as hard plates in a liquid of PI-layers, resulting in parallel alignment. In analogy to $\omega_c$, $\omega_d$ is assumed to be located at the boundary between region A and B, again indicating an expected change in the orientation mechanism upon crossing the boundary. This is a way of defining $\omega_d$ since determining it experimentally has proven to be very difficult as discussed in section 3.3.1.

### 3.3.3 Orientation trajectories

The pathways towards final alignment in each region consist of a cascade of processes, as the character of the orientation process slowly changes with time. Qualitatively, this change can be rationalized as a consequence of the coarsening of the domain structure and the change in orientation distribution of the lamellae. As an example, Fig. 3.4 displays the shear and loss moduli as a function of time during the orientation process of one of our systems, to be discussed in detail in Chapter 4. Initially, there is a sharp decrease in both moduli followed by a leveling off.

Prior to the oscillation, the material has a poorly organized, polydomain structure and contains a large number of defects, such as kink bands and focal conics, as was visualized by TEM. The randomly oriented grains are not uniform in shape; they size up from only two lamellae up to tens of lamellae. The majority of
the domains appear “pebbly” and only a small fraction of the sample has clearly defined lamellae exhibiting planar interfaces. Kornfield and coworkers investigated the evolution of the microstructure in regions B, C and D of Fig. 3.3 using TEM, birefringence and SAXS (see Figs. 3.5 and 3.6). They suggested to divide up the region of high frequency parallel alignment into two regions (C and D) on the basis of the different trajectories at $\omega > \omega_c$ and $\omega \gg \omega_c$. Figs. 3.5 and 3.6 summarize their results.

In region B, the final perpendicular alignment passes through a biaxial perpendicular/parallel alignment. In the initial fast process, regions with well-defined lamellae are formed out of poorly organized regions. In point 1) in Fig. 3.5a, the material contains parallel and perpendicular aligned lamellae, and everything in between. The amount of transverse aligned lamellae is strongly reduced. In point 2) the scattering due to perpendicular aligned lamellae is strongly enhanced, indicating a growth in the perpendicular population at the expense of the parallel population. TEM still shows a large amount of defects and poorly organized regions, even though the average domain size has increased. As the slow process continues, the perpendicular alignment is further enhanced and simultaneously other orientations are slowly eliminated, finally resulting in two sharp SAXS intensity maximums in the 3-direction in F). The birefringence in F) is large and positive, also indicating perpendicular alignment.
Figure 3.5. Different trajectories in regions B and C for a PS(10k)-block-PI(10k) co-polymer obtained from ref11 (a and b). For each region, one optical trace is shown. SAXS data were recorded in the tangential direction along different points in time: I) initial unaligned state, 1) middle of the fast process, 2) transition from a fast to slow process, 3) middle of the slow process, F) final well-aligned state.
In region C, in the early stages the distribution of perpendicular oriented lamellae increases more strongly than that of transverse aligned lamellae, as indicated by the increase in birefringence in Fig. 3.5b.6,11 Going from point 1) to 2), the parallel distribution is strongly enhanced, whereas the transverse distribution decreases. The perpendicular orientation has also increased, as indicated by the maximum in the birefringence at this point. TEM shows the material to consist of parallel and perpendicular orientations and everything in between.9 In the following slow process, the perpendicular orientations are slowly eliminated and a strong parallel alignment develops. The resulting birefringence slowly decreases to zero.

Finally, in region D, the birefringence becomes negative in the fast process, indicative of an enhancement of the transverse orientation (see Fig. 3.6). In the slow process, the birefringence slowly increases again to zero; the final alignment is parallel. Similar to regions B and C, two alignments and all the orientations in between are initially enhanced in the fast process, out of which the metastable alignment is eliminated in the slow process. Regions of poorly ordered lamellae transform into regions of well-ordered lamellae.9 SAXS in point 1) shows the biaxial parallel / transverse orientation, showing the perpendicular orientation to be unstable here. The transverse alignment is metastable as the SAXS intensity maximums corresponding to transverse alignment continuously decrease in the slow process.6,9,11
TEM shows that in case of aligned samples, the lamellae are well defined, and that the grain size has increased. Single-grain samples have not been produced, showing that even in a macroscopically aligned sample, defects occur. This is also indicated by SAXS, which shows narrow intensity distributions in the points F) in Fig. 3.5 and Fig. 3.6. The theoretical delta peak, which is expected for a single grain sample, has not been found at all.

### 3.3.4 Interplay of time, frequency and strain amplitude

Prolonged oscillatory flow using low strain amplitudes gave similar results as short oscillatory flow using higher amplitudes. This implies a functional dependence between the oscillation time and the strain amplitude. Gupta et al. showed that the effect of strain amplitude in the fast process could be modeled as a third power law in region B and a fifth power law in region C for a PS(10k)-block-PI(10k) copolymer. Hence, the underlying mechanisms are distinctly different in each region. The slow process, however, could only be modeled in region C, namely as a third power law in the strain amplitude. Thus, a single dimensionless time is not sufficient to describe the alignment kinetics in a single trajectory, let alone the whole alignment diagram.

According to Wiesner and coworkers, it is not the strain amplitude that determines the orientation processes, but the combination of strain and frequency. They showed that a certain threshold value of the strain amplitude, ranging between 5 to 50 %, should be crossed in order to obtain perpendicular alignment in region B. Furthermore, double flipping of orientation occurred from parallel to perpendicular to parallel alignment in region C. Based on this they proposed an alternative alignment diagram, where the strain amplitude $\gamma$ is plotted against the frequency. Lines of constant shear rate, i.e., constant $\gamma \omega$, separate the different alignment regions. Kornfield and coworkers located the flipping phenomena in the boundary regions between regions A and B, and B and C in Fig. 3.3, where orientation mechanisms along different trajectories are competing.
3.3.5 Alignment mechanisms

The orientation mechanisms in each region in Fig. 3.3 are not well understood yet. Many authors have proposed mechanisms, such as “defect migration”, “selective melting”, “selective creation”, “selective elimination”, “grain rotation”, and “rocking of lamellae”.3-7,10,12-15,18-26,29,42,47,54,55 These mechanisms all fail to explain why one alignment is preferred in each region and why biaxial alignments can occur.

The key to understanding the orientation mechanism is to know which relaxation processes take place in each region. For example in region A the frequency is smaller than $\omega_0$, indicating that the chains and the lamellae are fully relaxed. Thus, oscillation only deforms the domains and disturbs the defects between them. Birefringence suggested that an irreversible “rocking of grains” led to a parallel alignment for PEP-block-PEE copolymers.14 In region B $\omega > \omega > \omega_0$, the oscillations couple to the lamellae.11 Here, a “selective melting” mechanisms was proposed,12,29 in which lamellae, which are not oriented with their normal along the 3-direction in Fig. 3.1, were supposed to disorder and re-order with their normal in the desired direction. Although the formation of well-defined lamellae out of poorly organized regions is covered by this mechanism, it is not capable of explaining why in the initial fast process two alignments are enhanced. Therefore, a “selective creation - selective elimination” process was suggested by Chen et al.,9,10 without going into much detail about the actual behavior of the lamellae under oscillatory shear flow. In regions C and D, $\omega > \omega$, the chain conformation is distorted and more local relaxation dynamics play a role. Here, the mechanical contrast plays a role especially in region D. One block acts as a hard plate in a liquid of the other, resulting in parallel alignment. Symmetry arguments can explain why transverse and parallel alignments are enhanced in region D, but not why they are created.11

3.4 Conclusion

The study of the macroscopic alignment of lamellar diblock copolymers, in particular PEP-block-PEE and PS-block-PI, has led to an overall mapping of the orientation with frequency, strain amplitude and temperature (see Fig. 3.3). At
frequencies below $\omega_d$, below which the relaxation of the lamellar domains becomes important, parallel alignment was found. For intermediate frequencies ($\omega_c > \omega > \omega_d$) both aligned perpendicular. Increasing the frequency above $\omega_c$, the chain distortion plays a role. Two trajectories were found en route to the final parallel alignment, suggesting two different frequency regimes. Here, no alignment was found for PEP-block-PEE copolymers, likely due to the small mechanical contrast between the blocks. PS-block-PI copolymers aligned parallel.

The trajectories en route to alignment show that in the initial fast process, where $G'$ and $G''$ show a strong decrease with oscillation time, two of the three alignments are enhanced. Simultaneously, poorly ordered domains transform into well-defined lamellae. In the following slow process, one alignment is further enhanced and all others are eliminated. The mechanisms underlying the trajectories are not well understood. A combination of several mechanisms is required to describe the trajectories and discriminate between the alignments. The mechanisms do not take the rheological differences between the different diblock copolymers studied into account, other than in the concept of mechanical contrast between the blocks.

### 3.5 References
