

Hydrodynamically driven self-assembly of block copolymers studied by on-line small angle x-ray scattering

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ABSTRACT

New class of materials is taking advantage of self-organization at the molecular scale but also at the larger scale. For instance, the microphase separation of block copolymers induces local properties specific to each block. We are presenting in this paper the self-ordering of block copolymer solutions hydrodynamically controlled. We are coupling *in-situ* structural investigations with on-line rheometry. The fast data acquisition rate, down to the millisecond time scale, allows describing the mechanisms of macromolecular self-assembly at the early states, hence permitting the study of transients. The influence of hydrodynamic regimes on the microphase separated domain orientation, i.e. lamellae or cylinders will be shown. The enhancement of the level of self-assembly applied to film deposition will be discussed. The combination of structural and macroscopic information becomes a major asset to define the key parameters for film deposition technologies.

Keywords: block copolymer, rheology, synchrotron radiation, small angle x-ray scattering

1 INTRODUCTION

One of the most important evolution in the development of new class of materials is the way process engineering takes advantage not only from the molecular structure but also from its supramolecular organization. For instance, the key advantage of block copolymers onto statistic copolymers resides in the phase separation phenomenon and its related order-disorder transition. The large domains appearing during this phase separation are providing interesting and often contradictory properties to the final system e.g. soft touch but with high stiffness, separated glass transitions, etc... Microphase separated domains are often composed of anisotropically grown objects e.g. lamellae or cylinders and as such their distribution and orientation is sensitive to external fields - electrical, magnetic or hydrodynamic. By far the last represents the highest forces and for this it is widely used as an ordering mechanism for active processing.

We are presenting in this paper the ordering of hydrodynamically controlled block copolymers using a rheometer, coupled on-line to structural investigation by small angle x-ray scattering. This set-up already described elsewhere [1] permits to highlight the in-flow organization

in cylindrical geometry, by probing the velocity/vorticity plane, as well as out-of-flow organization by probing the gradient of velocity/vorticity plane. The observation of the two orientations helps to catch the mechanisms of organization and orientation of the microphase separated domains. In addition, we are taking advantage of the high flux of X-Rays delivered by ESRF: it permits to investigate the transients during the establishment of the flow down to time scale of the millisecond and it permits to use a specific design allowing the study of polymeric species in solution with low vapor pressure organic solvents or at temperature levels close to the boiling temperature. Such working conditions are simply not reachable in conventional x-ray cameras. By controlling the hydrodynamical field, it is possible to tune and even enhance the level of self-assembly. Parallely, the rheological behavior recorded *in-situ* emphasizes the structural analysis by its macroscopic approach.

By their complementarity, these two techniques of rheology and x-ray scattering are self-seeding the analysis of polymeric behavior under shear. The combination of these informations becomes a major advantage to define key parameters for film deposition technologies. It allows expecting major contribution of block copolymers in the design of nanosized structured devices if massive, collective and oriented properties are needed [2].

2 EXPERIMENTAL

The samples consist in block copolymer solutions with order-disorder transition temperature above room temperature. All observations were made at room temperature and therefore the samples are considered to be totally microphase separated. The samples were provided kindly through strong collaborations over Europe and as such are here deeply acknowledged. Various phases can be found, depending on the concentration, lamellae, cylinders or cylinders embedded in lamellae. The samples with their composition, characteristics and origins are listed in table 1. The films were elaborated from the SI and the SVT solutions, using the knife edge technique and has been left evaporated for 24hours prior to investigation. The speed of the knife was monitored. Thickness of the as deposited solution is of 0.3mm. A slow and a fast speed were used for film coating, 0.5 cm.s⁻¹ and 20 cm.s⁻¹, corresponding to shear rates of 15 s⁻¹ and 600 s⁻¹ respectively. The on-line rheometry were performed on the solutions using a RheoSAXS setup already described elsewhere [1]. The

shear geometry used was of Searle type, made of concentric cylinders, in x-ray transparent very thin aluminum (0.1mm). The sample is then sheared by the relative motion of the inner cylinder. The difference in diameter between the 2 cylinders is of 2 mm so the thickness of the sample was 1 mm. By shifting the rheometer in front of the beam, we investigated in-flow and perpendicular-to-flow structuration. The THF based samples were studied with a particular external geometry limiting the evaporation. The X-ray scattering experiments were performed at the ID2 beamline, European Synchrotron Radiation Facility (ESRF), Grenoble, France [3]. The detection is achieved by a x-ray intensified Thomson tube optically coupled to a FReLoN CCD camera. The detector is placed in a evacuated pipe and was remotely moved from the sample at various sample-to-detector distance from 3 to 10 m. The incident X-ray wavelength (λ) was 1 Å and the scattering intensity $I(q)$ is normalised to absolute scale using a secondary standard. The scattering vector q is defined as $q=(4\pi/\lambda)\sin(\theta/2)$, θ being the scattering angle. A beam size of $0.3 \times 0.3 \mu\text{m}^2$ was used for dry film investigation and $0.1 \times 0.1 \mu\text{m}^2$ for RheoSAXS experiments. The quantification of the domain alignment is achieved by the calculation of the order parameter P_2 can be calculated for each q by integrating the $I_q(\varphi)$ over azimuthal angle φ from 0 to 2π :

$$P_2 = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (1)$$

with

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{2\pi} d\varphi (I_q(\varphi) \cos^2(\varphi) \sin(\varphi))}{\int_0^{2\pi} d\varphi (I_q(\varphi) \sin(\varphi))} \quad (2)$$

Hence, the value of P_2 will vary from 0 to 1 for a system that aligns along $0-\pi$ axis, with $P_2=1$ as perfect alignment parallel to π axis. For alignment along $\pi/2-3\pi/2$ axis, the value of P_2 will range from 0 to -0.5, with $P_2=-0.5$ as perfect alignment parallel to $\pi/2$ axis.

3 RESULTS AND DISCUSSION

This section is divided in 2 parts, one for the on-line rheometry of block copolymer solutions and the other one for the investigation of dry films. In both case we will discuss the self-assembly ability of these systems and how hydrodynamical field affects the ordering.

3.1 On-line rheometry of solutions

In the past, we have studied various solutions of diblock and triblock copolymer, of various concentrations and therefore of various microstructures were found, following well the Landau mean field theory developed by L. Leibler [4]. However, the systems below the order-disorder transition (ODT) were very sensitive to the mechanical stress and the history of manipulation and strong anisotropic scattering pattern were obtained, reflecting the strong inhomogeneity orientation of the each microphase. Subsequently started the idea to control and monitor the mechanical stress applied to the sample and the best tool for such control is a rheometer. Usually, insertion of the solution in the shear cell already affects the orientation, favouring the formation of domains but principle it is possible to erase the mechanical history either by letting the system relax a long time or by going through the ODT using thermal control. Figure 1 depicts one example of shear rate sensitive system, SBM solution in toluene. This system, provided by M. Cloitre, exhibits a lamellar microphase separation, with a typical repetition distance in the solution of about 60 nm. Once any prior mechanical history is erased (here by letting the system relax several minutes), we apply a continuous motion to the inner cylinder. We found that depending on the shear rate applied, the lamellar phase is orienting parallel or perpendicular to the shear cell. More precisely, one can define the normal \mathbf{N} to the planes constituted by the lamellae. In a Searle geometry, the flow is characterized

Name	Components block fraction, Mn (in kg/mol)	Weight fraction	Solvent	Expected morphology	Collaborating team Contact person, Institute, Country
SBM triblock	styrene, butadiene, methyl methacrylate 11:19:70, 70	30%	Toluene	Lamellae	M. Cloitre, ESPCI, FRANCE
SVT triblock	styrene, vinyl pyridine, methyl methacrylate 16:21:63, 128	40%	THF	Core-shell cylinder	A. Böker, Uni. Bayreuth, Germany
SI diblock	Styrene Isoprene 50:50, 80	45%	Toluene	Lamellae	A. Böker, Uni. Bayreuth, Germany

Table 1: List of the samples used in this study.

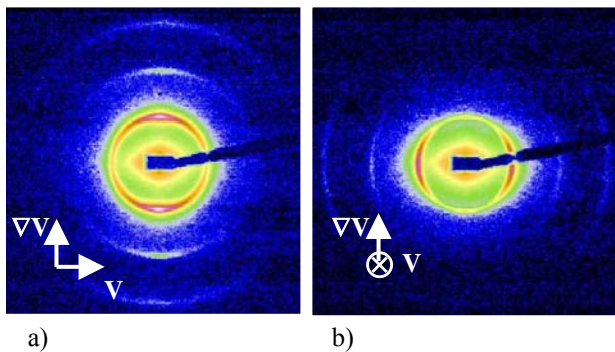


Figure 1 : Dependence of the lamellar orientation of SBM upon shear rate. a) Below critical shear rate, the lamellae are perpendicular to the wall of the shear cell. b) Above critical shear rate, the lamellae are parallel to the wall of the shear cell. Arrows indicate direction of flow and vorticity, \mathbf{V} and $\nabla\mathbf{V}$ resp.

by 3 vectors : the velocity \mathbf{V} along the flow direction, the gradient of velocity $\Delta\mathbf{V}$, oriented along the radius of the shearing cylinders and finally the vorticity direction $\nabla\mathbf{V}$ representing the vector product of \mathbf{V} by $\Delta\mathbf{V}$, oriented parallel to the axis of the shearing cylinders. The direction of these vectors is indicated on the patterns. This critical shear rate is in the range of 50s^{-1} and has been recognized to be the signature of the relaxation time of the chain, in the frame of the Rouse model and its related free-draining limit [5]. Indeed, more intuitively, if the shear rate is low enough, then the chain has the time to relax, hence the lamellae remains perpendicular to the shear wall (\mathbf{N} is parallel to the main axis of shearing cylinder). If the shear rates increases enough that the sollicitation period is shorter than the relaxation time of the chain, then the microstructure flips parallel to the shearing walls (\mathbf{N} is then along the radius). It can be explained by the minimization of friction energy in the flow field : the orientation of the lamellae parallel to the shear will be favorable as long as the extended configuration of the chain is kept. Indeed, upon cessation of shear, the lamellae orientation randomizes slowly. Hence, we tried to freeze this hydrodynamically induced orientation. For this purpose, we chose the concentrated systems SI and SVT (see table 1) to elaborate films that entrap oriented domains.

3.2 Dry films

A. Böker and co-workers, kindly providing the systems SI and SVT, were studying in particular the orientation of the lamellar phase and of the cylinders by the mean of an external electrical field [6,7]. The main advantage of electrical field over other alignment procedures is that it can be applied, in principle, at distance without inducing perturbation. However, this methodology is time consuming as well as complicate to scale up. Additionally, the low coupling efficiency of electric field leads to

solutions with very high voltage. As a reason, mechanical field is generally chosen to process alignment under shear in bulk polymer, fibers or films. Nevertheless, mechanical alignment generally leads to relatively distorted monodomains formation and the main reason can be found in the low control of the mechanical stress applied during the processing. As depicted on the figure 2, it is possible to generate nicely ordered monodomain over large distances (few $300 \times 300 \text{ mm}^3$) with very low distortion, providing the mechanical stress and strain rate are controlled. As described in [7], the formation of dry films usually distort the orientation and this last property depends on the casting methods or influence of the surfaces upon drying etc..., the [200] reflection disappearance within the peak broadening being an indicator of this distortion. We are reporting here from this simple example that a control on the stress applied on the copolymer solution during the film deposition is necessary. We are discussing here after the 2 systems SI and SVT separately. The orientation of microphase, lamellae (SI sample) and core-shell (SVT sample) is frozen by the evaporation of the solvent and subsequent rapid increase of the viscosity of the film. We will see the impact of this latter parameter in the next paragraph.

In the case of SVT "Fast" fig. 2 top right, the core-shell cylinder structure is clearly distinguished by indexing the peaks in the sequence $1:\sqrt{3}:2:\sqrt{7}$ which corresponds to

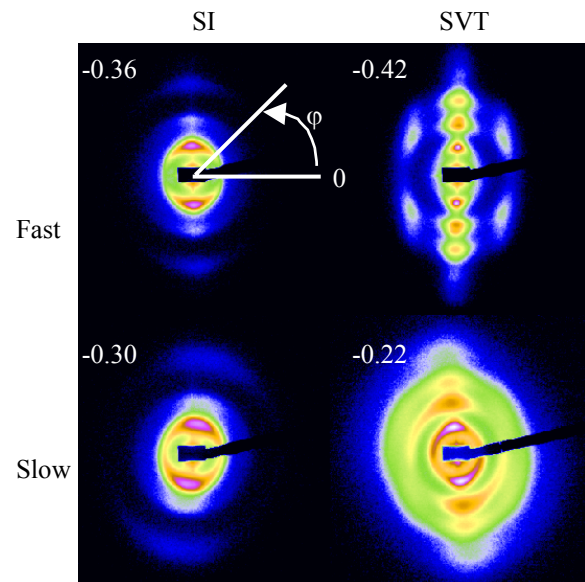


Figure 2: Influence of film deposition speed on the orientation of microphase separated domains. Shear flow induced by the knife is oriented from left to right. SI (left) samples are lamellar, lamellae being perpendicular to film surface with normal oriented perpendicular to shear flow. SVT (right) system consists in core-shell cylinders, oriented along the shear flow direction, parallel to the film surface. Top part corresponds to 15 s^{-1} and bottom part to 600 s^{-1} . P_2 parameter value from [100] peak is given inset.

the reflections [100], [110], [200] and [210]. This denotes a near perfect orientation, and confirmed quantitatively by the value of P_2 calculated for the [100] reflection, reaching the very high value of -0.42 , close to the theoretical limit of -0.5 . In contrast, on the bottom right of fig. 2, the [200] peak (SVT "Slow") is hardly distinguishable. Nevertheless, the P_2 value of -0.22 denotes a strong alignment of the cylinders along the flow but with domains strongly textured, characterized by the "flame trace" exhibited at the peak positions.

The case of the SI sample is very intriguing because even at low shear rate the lamellae are oriented perpendicular to the film surface, that is to say its normal \mathbf{N} is in the plane of the film, perpendicular to the flow. We saw in §3.1 that in some case, effect of shear rate may flip the lamellae from perpendicular to parallel to the shear planes. However, this effect has never been reported to our knowledge on diblock systems and at so low shear rate. The ordering effect induced by the flow is less important on these samples than for SVT and it can be attributed to the combination of lower viscosity with lower evaporation rate. Therefore, the oriented chains are reorienting faster and have more time as the solvent evaporate slowly. Hence, the speed of evaporation is also a crucial point that should be noted as a key parameter in freezing highly oriented systems. We conclude from this point that optimum shear rate and applied stress need be to determined for each type of copolymer solution, and be an alternative route to the formation of large oriented monodomain.

4 CONCLUSIONS

As a conclusion, the author would like to emphasize the key role of rheometry and online microstructure characterization also called RheoSAXS as a usefull tool to simulate flow regimes of a soft material under processing conditions. It allows in particular to discover optimum mechanical deformation regimes. The ability of scanning

rapidly through extended deformation ranges, shear rates or frequency dependent deformations is enlightening the effect of hydrodynamical field in the orientation of macromolecules. Recalling that the rheometer can work in stress-control as well as in rate-control, we can compare the order parameter obtained on identical systems from stress-controlled VS shear rate controlled experiments. It appeared recently that considering the stress field instead of velocity field would be an asset in processing.

The last example opens new horizons in controlling the organization of block copolymer over wide distances (several hundreds of microns) within a simple manner. The combination of high evaporation rate combined with the use of adapted mechanical film deposition leads to mono-oriented microphase separated domains. The aim of film deposition and subsequent orientation for application in nanotechnology i.e. lithography, nanosensors, nanoarrays etc... being to obtain large area of controlled morphologies, we expect that the stress control of the applied force field to be a new route for high efficiency and low cost nanostructured materials.

REFERENCES

- [1] P. Panine, M. Gradzielski and T. Narayanan, *Rev. Sci. Instrum.* 74, 4, 2451-2455, 2003
- [2] E. Schäffer, T. Turn-Albrecht, T. P. Russel and U. Steiner, *Nature*, 403, 874-877, 2000.
- [3] T. Narayanan, O. Diat, and P. Boesecke, *Nucl. Instrum. Methods Phys. Res. A*, 467-468, 1005-1009, 2001.
- [4] L. Leibler, *Macromolecules* 1980, 13, 1602-1617
- [5] G. R. Strobl, "The Physics of Polymers, 2nd Ed." Springer, NY, 1997.
- [6] A. Böker, H. Elbs, H. Hänsel, A. Knoll, S. Ludwigs, H. Zettl, A. V. Zvelindovsky, G. J. A. Sevink, V. Urban, V. Abetz, A. H. E. Muller and G. Krausch *Macromolecules*, 36, 8078-8087, 2003
- [7] S. Ludwigs, A. Böker, V. Abetz, A. H.E. Müller and G. Krausch *Polymer* 44 (2003) 6815-6823