



	Experiment title: Bottlebrush polymers in external shear flow	Experiment number: SC-1478
Beamline: ID02	Date of experiment: from: 18.05.04 to: 21.05.04	Date of report: 28.02.05
Shifts: 9	Local contact(s): Dr. Pierre Panine	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Silke Rathgeber* , Forschungszentrum Jülich, Institut für Festkörperforschung, D-42425 Jülich, Germany Tadeusz Pakula, Max Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz Krzysztof Matyjaszewski, Carnegie Mellon University, Department of Chemistry, Pittsburgh, PA 15213, USA.		

Report:

The aim of our experiments is to investigate the alignment (shear induced phase transitions) of stiff bottlebrush polymers in highly concentrated polymer solutions under shear flow.

Bottle-brush polymers are macromolecules with relatively long side chains densely grafted to a backbone in a regular manner. Interest in cylindrical comb polymer brushes is related to the possibility to form stiff cylindrical shape persistent structures based exclusively on intra-molecular excluded volume interactions. In melts of bottlebrush polymers thermotropic transitions between isotropic, nematic and smectic phases [1] were observed, whereas in solutions indications for lyotropic transitions between isotropic and nematic phases have been found [2].

The samples consist of a poly(alkyl methacrylate) backbone with poly(n-butyl) acrylate side chains attached to each backbone monomer in toluene solutions. Toluene is a good solvent for the backbone and side chain polymer. Architectural parameters varied are the number of segments comprising the backbone N_b and the side chains (N_s). Figure 1 shows form factors $P(q)$ obtained for brushes with different side chain length including the bare backbone by small-angle neutron (SANS) and static light scattering (SLS). The solid lines represent fits where the overall shape of the brush is modelled by a flexible cylinder with Gaussian or extended exponentially decaying radial density profile (for the sample with the shortest side chains only B1). The basic features of the model are sketched in Figure 2 which also shows the radial density profiles obtained for the different brushes. The scattering at high scattering vectors is dominated by the blob scattering and reflects the loose polymeric internal structure of the comb polymers. The brushes have a rather persistent

shape with a Kuhn length of about 70nm where, depending on the length of the backbone, only two to four segments build the overall, flexible cylinder. Depending on side chains length, the ratio of Kuhn length to cylinder diameter ranges from five to nine. For more details see [3].

In this first SAXS experiment we measured the samples under rest for various concentrations ranging from 5wt% up to 40wt%. In Figure 3 the measured intensity $I(q)$ is shown and not the structure factor $S(q)=I(q)/P(q)$ since the simple relationship does not hold at these high concentrations. However, the samples obviously exhibit lyotropic behaviour. At concentrations above 20wt% higher order peaks appear. From their location the appearance of a hexagonal (nematic) phase can be deduced. At concentrations above 35wt%, screening of the excluded volume interaction leads to a melting of the ordered structure.

We also have performed stress controlled SAXS shear experiments on a (1) isotropic sample and (2) on a pre-aligned (perpendicular to the flow direction) sample. For instance, in Figure 4 the rheological response of the pre-aligned sample is shown (taken online with the SAXS experiment). A minimum torque (1750 μNm) is necessary to flip the preferred direction of orientation into the flow direction. After a first spontaneous, elastic response the sample is shear thinning over a time interval of about two hours. The viscosity reduces by about two orders of magnitude. During the shear-thinning the system undergoes complex structural rearrangements (via intermediate metastable phases) which are first visible in radial direction and then after this process is completed in tangential direction. These transitions are partly accompanied by instabilities in the rheological response (marked by arrows in Figure 4). Unfortunately, due to a hard disk crash in combination with a corrupt back-up (tar) file the two-dimensional results of the experiment were lost.

Therefore, we applied for beam time to repeat these measurements. Further experiments on this interesting system can include: (1) variation of the concentration, (2) shear rate instead of stress controlled measurements (3) changing the aspect ratio by varying the side chain lengths and (4) variation of the cylinder flexibility by changing the backbone length.

References:

- [1] V.P. Shibaev, E.B. Barmatov, Y.J. Tao, R. Richardson, *Polymer Science Series A* **42**, 1086 (2000).
- [2] M. Wintermantel, K. Fischer, M. Gerle, R. Ries, M. Schmidt, K. Kajiwara, H. Urakawa, I. Wataoka, *Angew. Chem. Int. Ed.* **34**, 1472 (1995); Y. Tsukahara, Y. Ohta, K. Senoo, *Polymer* **36**, 3413 (1995).
- [3] S. Rathgeber, T. Pakula, A. Wilk, K. Matyjaszewski, K.L. Beers, *J. Chem. Phys.* in press (03/2005)

Figures:

- Figure 1: (top, left) Form factor of bottlebrush polymers with increasing side length.
- Figure 2: (bottom, left) Basic features of the model used to describe the SANS and SLS spectra and the derived radial density profiles.
- Figure 3: (top, right) SAXS spectra obtained for highly concentrated comb polymer solutions.
- Figure 4: (bottom, right) Rheological response of a pre-aligned sample to a step-wise increase of the applied torque.

