Experimental report

23/02/2016

Proposal:	**9-11-1723**	**Council:**	10/2014
Title:	Polymer brush extradigitation		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: Polystyrene brush on a silicon substrate
Polystyrene solution

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	13/07/2015	16/07/2015

Abstract:

We shall study the kinetics of polymer brush interaction with dissolved free chains. First, we increase the free chain density (by evaporating the solvent) and measure the interpenetration time by NR. Second, we reverse the process by decreasing the free chain density (pour new solvent), and measure the extradigitation time. The thermodynamic driving force is identical in the two cases, but we have strong theoretical and experimental evidence that the time taken is different.
This kind of measurement has never been published before. The outcome would help us understand our earlier results in shear experiments, as well as contribute to the fundamentals of brush physics.

Experimental Report for NIST:14676 and ILL:9-11-1723,TEST-2003

1. Experimental

The Neutron Reflectivity measurements were performed at the NG7 horizontal reflectometer at NIST using a home-build cone-and-plate shear device[**1**] and on the FIGARO reflectometer at ILL using a commercial cone-plate rheometer [**2**]. The measurements at NIST were performed with a monochromatic beam of 4.75 Å wavelength with a wavelength resolution of 4%. The beam size was fixed to result in a fixed footprint of 35x35 mm^2 on the sample with a angular resolution of 2% $\Delta\theta/\theta$. At ILL a white beam was used providing 2-20 Å wavelengths and three reflection angles of $0.8°, 1.4°$ and $2.6°$ were used to cover the full q-range in TOF mode [**3**]. The wavelength resolution was set to 7.4% and the beam footprint was fixed at 35*30 mm^2 with 2% angular divergence.
All brushes were prepared by ATRP. Mn is obtained from the GPC measurements of free polymer chains grown in the solution at the same time when the grafted chains are growing from the initiator immobilized on the substrate. It has already been shown that for ATRP, NMP and RAFT synthesis techniques the molecular weight and polydispersity of grafted and free chains grown at the same time in the same polymerization solution are very close to each other. They found that the difference is usually less than 5% relative to the measured molecular weight [1. Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques, Macromolecules 1998, 31, 5934.

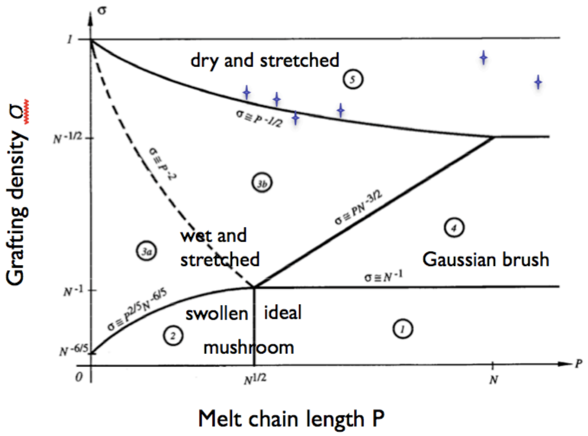
2. Husseman, M.; Malmstrm, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. Controlled Synthesis of Polymer Brushes by Living Free Radical Polymerization Techniques, Macromolecules 1999, 32, 1424.

3. Baum, M.; Brittain, W. J. Synthesis of Polymer Brushes on Silicate Substrates via Reversible Addition Fragmentation Chain Transfer Technique, Macromolecules 2002, 35, 610.]. Thus we calculate theoretical molecular weight(Mn,th) from the conversion ratio and molar quantities of reactants.

2. Conclusion

2.1. Static case and diffusion kinetics. In summary, we have studied a large set of high density PS brush/melt interfaces which are not accessible by "grafting to"-techniques. Figure 1 shows their location in the phase diagram anticipated in literature [**4**].

The measured density profiles corroborate the phase diagram although probably not all samples can be thought of being in equilibrium. One particular interesting case is the comparison of the 9 nm hPS brush and the 18 nm dPS brush both in contact with



	σ	N	P
PS on dPS55	0.3	546	582
PS on dPS18	0.13	460	27
dPS on hPS45	0.26	523	20
dPS on hPS30	0.26	354	20
dPS on hPS10	0.26	84	20
dPS on hPS20	0.24	171	535

Figure 1. Phase diagram of a polymer brush in a polymer melt matrix taken from [**4**]. The systems studied here are marked by blue crosses and tabled on the right.

a low molecular weight PS melt: Although the dry thickness of the protonated brush is thinner its density profile in contact with the melt shows a clear dry part, whereas the thicker deuterated brush is completely wet when brought in contact with the melt. This is correctly predicted by the phase diagram given the difference in grafting denisty of the two systems. This means that the statistical segment length $a = 0.67\,\mathrm{nm}$ of PS brushes as proposed in [**5**] is correct. The glass transition temperature (T_g) of grafted PS was reported to be at least $25°C$ above T_g [**6**] which implies that the experiments were performed around T_g for the brush and explains the slow diffusion/relaxation times.

2.2. Sheared samples. No influence of shear on the brush structure could be observed for the cases where the temperature control was well behaved. Excessive shear degrades the brush as we have reported earlier [**7**].

References

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