

Properties of Cylindrical Brush Polymers

Bin Zhang,¹ Karl Fischer,¹ Franziska Gröhn,² J. S. Pedersen,³
Manfred Schmidt,^{1,*} *mschmidt@uni-mainz.de

¹Institute of Physical Chemistry, University of Mainz, 55099 Mainz, Germany,

²Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany,

³Department of Chemistry and iNANO Interdisciplinary Nanoscience Center, University of Aarhus, 8000 Aarhus, Denmark.

Introduction

Flexible polymers with densely grafted side chains adopt the shape of cylindrical brush polymers,¹ because the steric repulsion of the side chains overcomes the entropic restoring force of the main chain. Published results on the conformation of such macromolecules in terms of the main chain stiffness, l_k , and cylinder length, L , are quite contradictory.²⁻⁶ In the present contribution these quantities were determined by combined light scattering and neutron scattering on samples with varying side chain length.

Experimental

The synthesis of cylindrical brush polymers with polystyrene side chains and a methacrylic main chain is described elsewhere.⁷ Light scattering and small angle neutron scattering (SANS) was performed in a good solvent (toluene) and in a poor solvent of the side chains (cyclohexane). After standard manipulation of the measured intensities the SANS-data were shifted onto the LS-curves, in order to obtain absolute intensities. The combined LS-SANS data were analyzed in terms of the Pedersen-Schurtenberger model⁸ in order to extract the chain stiffness in terms of the Kuhn statistical segment length, l_k , the contour or cylinder length, L_m , and the cross-sectional radius of gyration, R_{gc} .

Results and discussion

In Fig. 1 the Pedersen-Schurtenberger fit to the combined LS-SANS data is shown. The fit matches the data perfectly well.

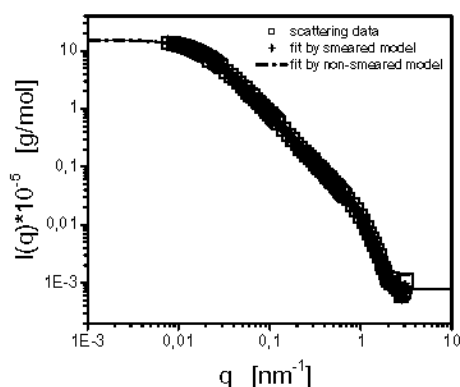


Figure 1. LS-SANS data for the sample with 6 styrene units per side chain, measured in toluene

Whereas l_k and R_{gc} can be determined at small but finite concentration, the cylinder length is strongly concentration dependent due to the non-zero second virial coefficient. Therefore the cylinder length was determined by the $c = 0$ extrapolated light scattering curve which is keeping l_k from the Pedersen-Schurtenberger fit fixed.

In Fig. 2 and 3 the Kuhn length, l_k , and the cylinder length per main chain monomer, l_m , are plotted versus side chain length. The Kuhn length is found to increase with increasing side chain molar mass. The increase is stronger for the samples measured in toluene as compared to the poor solvent cyclohexane, as expected.

The cylinder length per main chain monomer is found to be independent of side chain length for both, toluene and cyclohexane. However, $l_m = 0.207$ nm in cyclohexane is significantly smaller than $l_m = 0.241$ nm in toluene, i. e. the cylinder significantly shrinks for poor solvent of the side chains.

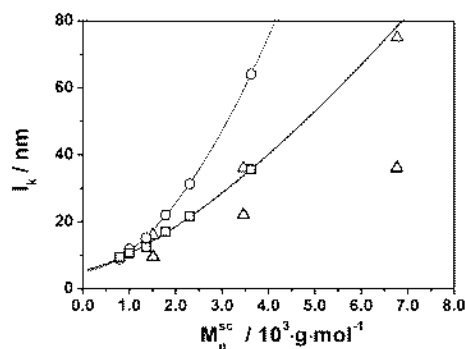


Figure 2. Kuhn length as function of side chain molar mass for samples measured in D8-toluene (red circles, this work; red triangles, ref. 12-16) and for the samples measured in cyclohexane (black squares, this work; black triangles, ref. 12 -16). The lines represent the respective fits according to eq. 11 (data of this work, only).

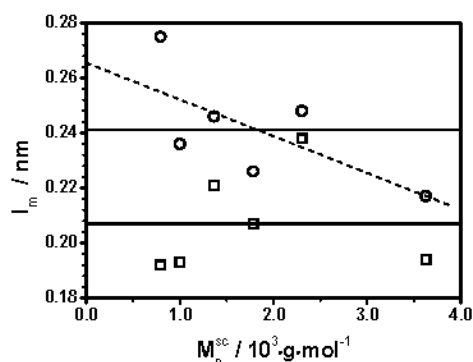


Figure 3. Cylinder length per monomer as function of side chain molar mass for the samples measured in D8-toluene (red circles) and in D12-cyclohexane (black squares) as determined by Holtzer analysis as explained in the text. The full lines indicate the mean values of $l_m = 0.241$ nm and of $l_m = 0.207$ nm, respectively, the dotted red line represents a least square fit to the red circles.

References

- [1] Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwara, K.; Tsukahara, Y. *Macromolecules* **1996**, *29*, 978.
- [2] Fischer, K.; Schmidt, M. *Macromol. Rapid Commun.* **2001**, *22*, 787.
- [3] Terao, K.; Takeo, Y.; Tazaki, M.; Nakamura, Y. *Polymer Journal* **1999**, *31*, 193.
- [4] Terao, K.; Nakamura, Y.; Norisuye, T. *Macromolecules* **1999**, *32*, 711.
- [5] Gerle, M.; Fischer, K.; Müller, A.H.E.; Schmidt, M.; Sheiko, S.S.; Prokhorova, S.; Möller, M. *Macromolecules* **1999**, *32*, 2629.
- [6] Rathgeber, S.; Pakula, T.; Wilk, A.; Matyjaszewski, K.; Beers, K. *L. J. Chem. Phys.* **2005**, *122*, 12490.
- [7] Zhang, B.; Zhang, S.; Okrasa, L.; Pakula, T.; Stephan, T.; M. Schmidt *Polymer* **2004**, *45*, 4009.
- [8] Pedersen, J. S.; Schurtenberger, P. *Macromolecules* **1996**, *29*, 7602.