Macromol. Symp. ***149,*** *257–262 (2000)*

STRUCTURES OF P(S-BLOCK-BMA) DIBLOCK COPOLYMERS IN THIN FILMS

D. W. Schubert

GKSS Research Centre, Max- Planck- Strasse, 21502 Geesthacht, Germany

Summary: Symmetrical diblock copolymers (P(S(D)-b-nBMA)) of deuterated poly(styrene) (PS(D)) and poly(nbutylmethacrylate) (PnBMA) were investigated by neutron reflectometry with respect to periodicity and interfacial width. Four different molecular weight P(S(D)-b-nBMA) samples were used to prepare thin films by spin coating on glass substrates. Two of the samples were in the intermediate segregated state. The other two samples were in the bulk disordered state, however, due to thin film geometry a surface and substrate induced ordering could be revealed. Utilizing the respective theories (Matsen and Bates for intermediate segregated samples and Fredrickson for a surface and substrate induced ordering), the product of interaction parameter χ and chain length N was calculated. Taking account for the different molecular weights, an interaction parameter was obtained which is the same for all of the four samples, within the experimental error. Using the strong segregation theory from Semenov to calculate χ for the intermediate segregated samples, the interaction parameters for the four samples are not consistent.

Introduction

Block copolymers offer a wide range of application due to their different microstructures controlling the macroscopic properties such as fracture behaviour 1). Varying the block lengths the morphology can be tailored to specific use. It has been recognised that the interface between adjacent microphases has also an impact on macroscopic properties.

In particular it has been shown recently1) that the large interface width a_I of 8 nm in a diblock copolymer P(S-block-nBMA) of polystyrene (PS) and poly(nbutylmethacrylate) (PnBMA) compared to a diblock of PS and polyisoprene with a_I =2 nm 2), exhibits extra - ordinary mechanical properties. The reason for the large interface width in P(S-block-nBMA) might be due to the fact that the interaction parameter χ for styrene and nBMA is relatively small 3), approximately 0.01. Therefore an investigated block copolymer with a total molecular weight of 248kg/mol is in the intermediate segregated regime (ISR)4). It is the purpose of this work to reveal the interfacial width and interaction parameter of P(S-block-nBMA) in the ISR. Neutron reflectometry (NR) is used to analyse the lamellar structure of symmetrical P(S-block-nBMA)

CCC 1022-1360/00/$ 17.50+.50/0

diblock copolymers in thin films, where the PS block is deuterated. Different molecular weight diblock copolymer samples are investigated. This task is of importance to clarify the validity of a recent theoretical treatment from Matsen and Bates5) dealing with block copolymer morphology and interfacial width in ISR. To confirm these experimental studies, samples in the bulk disordered phase are additionally under consideration. Due to thin film samples, also in this case a lamellar structure is formed which can be analysed by NR6) and corresponding χN values are accessible.

Experimental

Poly(styrene-block-nbutylmethacrylate) diblock copolymers were prepared by anionic polymerisation. This procedure yields well-defined block lengths and narrow molecular weight distributions. Molecular characteristics are shown in table 1. Molecular weight and distribution were determined by gel permeation chromatography. NMR was used to determine the composition of block copolymers. Chain lengths N are calculated from molecular weight respectively, where an error of 10% is taken into account. For the thin film preparation the block copolymers were dissolved in toluene at a concentration of typically 35 g/l. Subsequently films were spin coated7) on 10 x 10 cm^2 float glass plates as substrate at a typical spinning speed between 1000 and 2000 rpm to obtain clear films after annealing 8). If the film thickness does not consist to the lamellae periodicity islands occur at the surface and yield turbid films.

sample	1	2	3	4
Mw (kg/mol)	248	148	72	46
Mw / Mn	1.05	1.07	1.05	1.05
ϕ_{PS} block	0.51	0.5	0.5	0.5
N	1953 ± 195	1165 ± 117	567 ± 57	362 ± 36

Table 1. Molecular characteristics of used P(S(D)-block-nBMA) samples.

For NR experiments the films were quenched to room temperature after annealing for two weeks at 151°, respectively. Measurements were carried out using TOREMA II at GKSS Research Centre, Geesthacht, with a fixed wave length of 0.43 nm, and a position sensitive gas detector. The angle of incidence was varied from 0.2 to 1.2 ° and the reflection was measured. The analysis of specular reflectivity curve yields information on the neutron refractive index and composition profile perpendicular to the surface4,9). The interface between adjacent microphases is described by a hyperbolic tangent profile [6,9,10)]. Using a matrix formalism the reflectivity of the planar structure was calculated [9,11)].

Results and Discussion

A typical neutron reflection curve of an ordered sample is shown in Figure 1 using material 2. Clearly the highly ordered structure is evident by Bragg peaks originated by 6 lamellae.

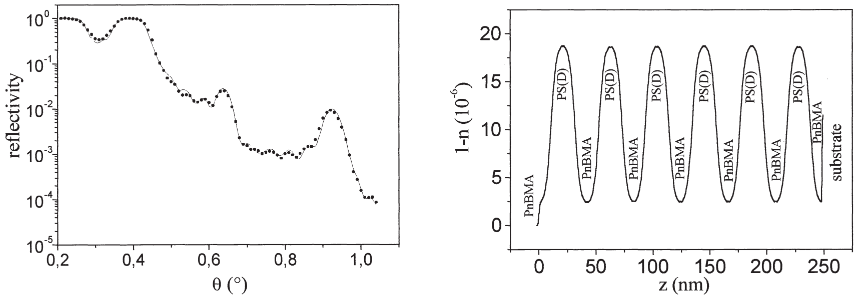

Fig. 1: Reflection curve (left) of P(S(D)-block-nBMA) M_w=148 kg/mol. Dots are the measured reflectivity and solid line corresponds to best fit utilising the refractive index profile shown right. Maximum error in reflectivity is less than the size of the dots.

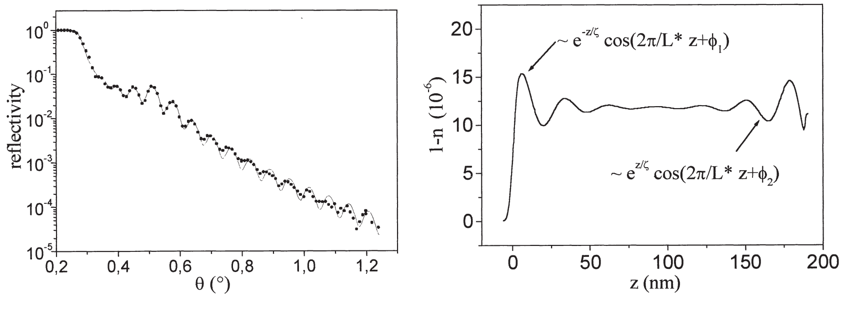

Fig. 2: Reflection curve (left) of P(S(D)-block-nBMA) M_w=72 kg/mol. Dots are the measured reflectivity and solid line corresponds to best fit utilising the refractive index profile shown right given by a damped cosine modulation. Maximum error in reflectivity is less than the size of the dots.

In contrast, samples of much less molecular weight are prepared to be in the bulk disordered regime. For example, a typical reflection curve of a film from material 3 after annealing is shown in Figure 2, dominated by interference pattern from a single layer. However, a weak broad peak is underlying in the range of 0.5 to 1.0° due to a surface and substrate induced ordering. This ordering is predicted by the theory of Fredrickson[12)] for thin films of symmetric diblock copolymers in bulk disordered state. The driving force is a difference in energies of the two block materials at surface and substrate[8)]. The details of predicted damped cosine modulation depend, however, on bulk properties the segment length b and $N\chi$ value with respect to periodicity L and decay length ξ.

From fitting the experimental reflection curves the following results are obtained.

material	interface width a_I (nm)	decay length ξ (nm)	periodicity L (nm)
1	9.2 ± 0.2	-	61.03 ± 0.02
2	8.4 ± 0.2	-	41.40 ± 0.02
3	-	21 ± 2	28 ± 2
4	-	6 ± 2	25 ± 2

Table 2: Results of the neutron reflection experiments using thin films of P(S(D)-nBMA) diblock copolymers with molecular weights of 248, 148, 72 and 46 kg/mol, respectively.

In order to understand the results for the samples in ISR with respect to interfacial width and periodicity the recent work of Matsen and Bates[5)] is taken into account. Matsen and Bates calculated interfacial width and periodicity normalized to $bN^{1/2}$ as a function of χN. To eliminate the segment length b, the relation a_I/L is used (see figure 3) to calculated χN from original Matsen- Bates data, similar to the work of Scherble et al [13)]. Additionally a_I/L is calculated using the strong segreation theory from Semenov[14)]. To determine χN values for the scenario of bulk disordered samples (46 and 72 kg/mol) the relation L/ξ, calculated from Fredricksons theory is used to circumvent the unknown segment length.

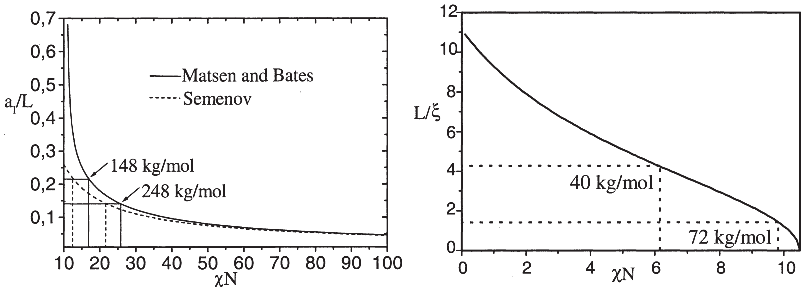

Fig. 3: (left) From Matsen - Bates and Semenov theory calculated a_I/L relation to determine $N\chi$ for 148 and 248 kg/mol weight samples respectively. (right) Relation L/ξ as a function of χN calculated from Fredrickson theory to determine $N\chi$ for 46 and 72 kg/mol weight samples.

material	1 (248 kg/mol)		2 (148 kg/mol)		3 (72 kg/mol)	4 (46 kg/mol)
	M. -B.	Semenov	M. - B.	Semenov		
$N\chi$	26.0 ± 1.0	21.5 ± 1.0	16.8 ± 0.4	12.5 ± 0.5	9.8 ± 0.4	6.2 ± 1.4
χ	0.0133 ± 0.0014	0.0110 ± 0.0012	0.0144 ± 0.0015	0.0107 ± 0.0011	0.0173 ± 0.0019	0.0171 ± 0.0042

Table 3: $N\chi$ values obtained from Matsen - Bates, Semenov and Fredrickson theories, respectively. χ values are thus calculated, taking into account for the different chain lengths.

For comparing the χ values given in table 3, a graphical representation (Fig. 4) is used. Also shown is the range of χ obtained from small - angle neutron scattering experiments (SANS) using several molecular weight samples P(S(D)-b-nBMA) in the bulk disordered state1,15). Figure 4 shows clearly that the results are in nice accordance using Matsen - Bates and Fredrickson theories. In particular, the χ values from NR experiments on thin films fit excellent to results obtained from SANS on bulk samples. Therefore capillary wave contributions to the interfacial width seems to be negligible for the present system, because much bigger interfacial widths would be calculated using the corresponding equation14). Another important point is that the χ values using Semenovs14) theory are not consistent with the others as shown in Figure 4. This might be a consequence of the fact that Semenovs theory is just valid for strong segregated block copolymers $N\chi > 100$. Finally, this study verifies the Matsen - Bates theory.

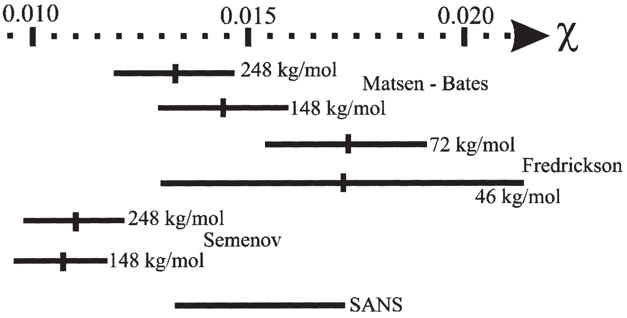

Fig. 4: Graphical representation of $\chi_{S/nBMA}$ values for P(S(D)-b-nBMA) diblock copolymers.

References

1. R. Weidisch, M. Stamm, D. W. Schubert, M. Arnold, H. Budde, S. Höring, *Macromolecules*, **32**, 3405 (1999)
2. T. Hashimoto, M. Shibbayama, H. Kawai, *Macromolecules*, **13**, 1237 (1980)
3. D. W. Schubert, V. Abetz, M. Stamm, T. Hack, W. Siol, *Macromol.,* **28**, 2519 (1995)
4. D. W. Schubert, R. Weidisch, M. Stamm, G. H. Michler, *Macromol.*, **31**, 3743 (1998)
5. M. W. Matsen, F. S. Bates, *Macromolecules*, **29**, 1091 (1996)
6. T. P. Russell, S. H. Anastasiadis, A. Menelle, G. P. Felcher, S. K. Satija, *Macromolecules*, **24**, 1575 (1991)
7. D. W. Schubert, *Polymer Bulletin*, **38**, 177 (1997)
8. relevant for sample 1 and 2, D. W. Schubert to be published elsewhere
9. M. Stamm, D. W. Schubert, *Ann. Rev. Mater. Sci.*, **25**, 325 (1995)
10. E. Helfand, A. M. Sapse, *J. Chem. Phys.*, **62**, 1327 (1975)
11. J. Lekner, *Theory of Reflection*, Martinus Nijhoff, Dordrecht (1987)
12. G. H. Fredrickson, *Macromolecules*, **20**, 2535 (1987)
13. J. Scherble, B. Stark, B. Stühn, J. Kressler, D. W. Schubert, H. Budde, S. Höring, P.Simon, M. Stamm, *Macromolecules*, **32**, 1859 (1999)
14. A. N. Semenov, *Macromolecules*, **26**, 6617 (1993)
15. R. Weidisch, D. W. Schubert, M. Stamm, P. Staron, in preparation