MOLECULAR AND SUPRAMOLECULAR STRUCTURES AT THE INTERFACEs

Determination of the Flory–Huggins Parameter for a Pair of Polymer Units from AFM Data for Thin Films of Block Copolymers

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Abstract—The structures of thin films of the polystyrene–polybutadiene–polystyrene (SBS) and polystyrene–poly(methyl acrylate)–polystyrene (SMAS) triblock copolymers were studied. The film morphology was found to depend on the conditions of film formation. The average domain sizes of these films and the period of the lamellar structure of SMAS films were determined. The Flory–Huggins parameter was estimated for a pair of styrene and methyl acrylate units.

INTRODUCTION

Polymers have found extensive use in various fields of human life and activity: industry, agriculture, science, engineering, and all types of transport. Our everyday life cannot be imagined without employing a variety of polymer materials. Application of block copolymers can help to create novel materials with desired technological characteristics. Rapt attention is currently given to thin block-copolymer films and, in particular, microphase separation (MPS) in them because their use provides great scope for the creation of nanomaterials.

Block copolymers consist of two or more polymer chains (blocks) that differ in chemical composition (hereafter designated as A and B) and are linked by a covalent bond. If interactions between the units of similar blocks are more favorable than interactions between dissimilar blocks, then the system undergoes microphase separation: the blocks segregate to form individual phases ordered in some way. Microphase separation is determined by three main factors: degree of polymerization N; relative concentrations f_A and f_B of the units A and B, respectively (where $f_A = N_A/N$ and $f_A + f_B = 1$ [1]); and the Flory–Huggins parameter $\chi(A/B)$, which describes A–B interactions [2]:

$$\chi(A/B) = \frac{1}{k_B T}\left(\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right),$$

where ε_{AA}, ε_{BB}, and ε_{AB} are the energies of the A/A, B/B, and A/B contacts, respectively. The positive values of the Flory–Huggins parameter correspond to repulsion between the units and its negative values correspond to their mutual attraction. In most cases, χ is inversely proportional to the temperature; so mixing can be impossible at high temperatures and microphase separation can occur in the system at low temperatures.

Depending on the value of the product χN, one distinguishes between weak ($\chi N \sim 10$) and strong segregation of MPS ($\chi N \gg 1$). In the former case, the modulation of the density is low. Strong segregation gives rise to microstructures with pronounced boundaries; the thickness of the interfacial boundary $\Delta \ll D$ is much less than the D period of the structure. In this study, we consider only the cases of strong segregation since this mode of MPS is of the greatest interest for nanotechnological applications.

Apart from the main parameters, a number of additional factors determine the MPS structure. The MPS morphology largely depends on the prehistory of the preparation of block-copolymer films (from solution or from melt). Annealing of copolymer samples further changes the MPS morphology [3]. The block copolymers with the same chemical structure can differ substantially in morphology when films are prepared in different solvents (use of a general solvent or a selective solvent for one of the blocks). Moreover, by employing special solvents, one can obtain identical film morphologies for chemically dissimilar block copolymers.

An important problem in calculating the parameters of the MPS structure in block-copolymer films is determination of the Flory–Huggins parameter for a given

Table 1. The thicknesses of the SBS and SMAS films determined from AFM data

Sample	SBS	SMAS ([PS] : [PB] = 1 : 1)	SMAS ([PS] : [PB] = 1 : 2)
Thickness	60–90 nm	30–60 nm	30–60 nm

pair of polymer units. Most often, this parameter is calculated by the formula

$$\chi(A/B) \, = \, \frac{V}{RT}(\delta_A - \delta_B)^2,$$

where V is the molar volume of the polymer, R is the universal gas constant, T is the absolute temperature, and δ_A and δ_B are the solubility parameters of the polymers A and B, respectively.

The goal of this study was to experimentally determine the Flory–Huggins parameter for a pair of styrene and methyl acrylate units from processed AFM images of thin polystyrene–poly(methyl acrylate)–polystyrene films.

EXPERIMENTAL

Objects of Investigations

We studied polystyrene–polybutadiene–polystyrene (SBS) and polystyrene–poly(methyl acrylate)–polystyrene (SMAS) triblock copolymers. Polystyrene–polybutadiene–polystyrene belongs to a thoroughly studied class of block copolymers. Distinct microphase separation and its mechanical characteristics makes it an ideal object for AFM studies in the contact mode and for verification of the scope of the theories chosen for the calculation of the Flory–Huggins parameters.

According to the presumed properties, SMAS is a "soft" sample and can be examined only in the resonance mode. The chosen relative contents of polystyrene in the SMAS and SBS copolymers allowed investigations of both the lamellar structure and the domain structures of two types ("soft" domains in a hard matrix and "hard" domains in a soft matrix).

The polystyrene content of SBS samples was 85 wt %. The weight-average molecular weight was $\langle M_w \rangle$ = 100000. The polydispersity of the block copolymers under study was 1.03 to 1.04.

SMAS was prepared by free-radical pseudoliving polymerization. We studied two series of samples: with M_n = 75 000 ([PS] : [PMA] = 1 : 2) and with M_n = 30000 ([PS] : [PMA] = 1 : 1; PS : PMA = 16000 : 14000). The polydispersity was 1.4 to 1.5.

Preparation of SBS Films

Thin films were prepared from a 1% solution of the polymer in toluene by direct adsorption at freshly cleaved mica. To find conditions for the formation of the most stable MPS structure, films were obtained in different ways:

(1) rapid evaporation of the solvent in open air (~1 min);

(2) slow evaporation of the solvent in the saturated vapor of toluene (~24 h);

(3) slow evaporation of the solvent in the saturated vapor of toluene followed by annealing at 110°C for 1, 2, and 4 h.

Thin SBS films for TEM studies were prepared from a 1% solution of the polymer in toluene. Films were formed on the water surface and then transferred to TEM grids.

Preparation of SMAS Films

Thin films were prepared from a 1% solution of the polymer in chloroform by direct adsorption at freshly cleaved mica. The solvent was removed in the saturated vapor of chloroform.

Methods of Investigations

AFM measurements were carried out on a Nanoscope-IIIa instrument (Digital Instruments, USA). TEM studies were performed on a LEO 912AB instrument (Carl Zeiss, Germany). AFM and TEM images were processed with the FemtoScan Online software (OOO NPP Tsentr Perspektivnykh Tekhnologii, Moscow). The average domain size and the period of the lamellar MPS structure were calculated using the previously developed algorithms [4].

Determination of Film Thicknesses by Atomic Force Microscopy

Film thicknesses were determined by combined AFM studies in the contact and resonance modes. The contact mode with strong cantilever forces was used to remove block-copolymer films from the mica surface in the scanned range. Then we scanned a larger area and estimated the film thickness from a height difference between the film surface and the cleaned mica surface (Fig. 1). The data obtained are given in Table 1.

Transmission Electron Microscopy

Before TEM studies, SBS films were kept in the vapor of OsO_4 to make the double bond in the block copolymer more contrasting in TEM images, thus highlighting the polybutadiene phase. We obtained photomicrographs of SBS films with a relative polystyrene content of 85%.

RESULTS AND DISCUSSION

Using the contact mode, we obtained AFM images of SBS films. Even a prolonged scan with strong cantilever forces changes the film morphology only slightly. We scanned a series of SBS films prepared under different conditions. The most stable MPS structure was found in the films formed in the saturated vapor of the
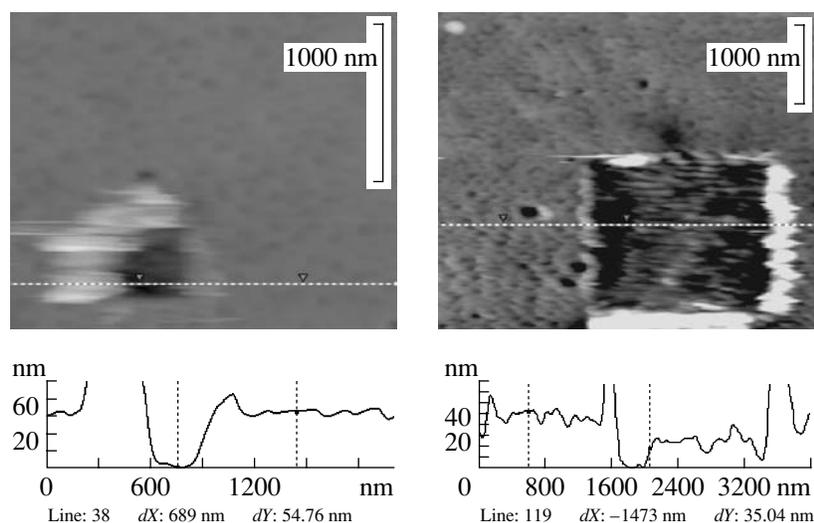
Fig. 1. AFM images of the SBS (left) and SMAS films (right) with the areas from which the polymer is removed. The cross section of the surface is shown at the bottom.
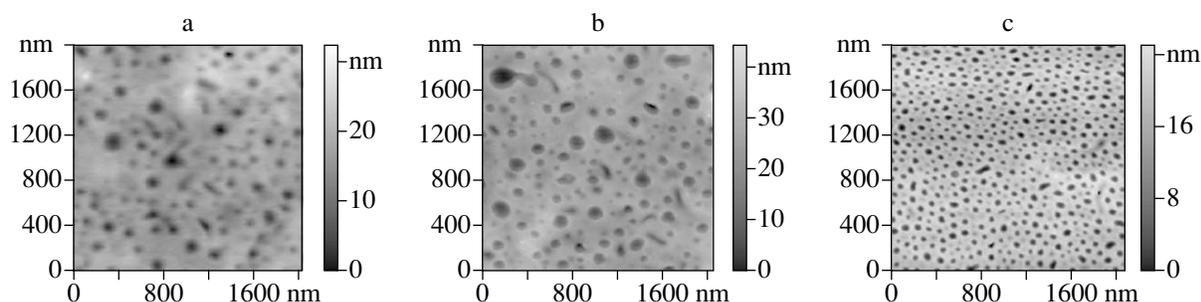
Fig. 2. AFM images of the SBS films obtained under different conditions: (a) rapid evaporation of the solvent, (b) slow evaporation of the solvent in the saturated vapor of toluene, and (c) slow evaporation of the solvent followed by annealing at 110°C for 2 h.

solvent and annealed for 2 h (Fig. 2). Further annealing did not change the film morphology any more. All the SBS films described below were obtained in the saturated vapor of the solvent with subsequent 2-h annealing.

The AFM images of thin SMAS films obtained in the resonance mode are shown in Fig. 3. In the films with $M_n = 75\,000$ ([PS] : [PMA] = 1 : 2), the microphase separation has a domain structure. In the films with $M_n = 30\,000$ ([PS] : [PMA] = 1 : 1), the microphase separation has a lamellar structure. The AFM images were processed with the use of the previously developed algorithms for calculating the average domain sizes and the period of the lamellar structure. The average size of polybutadiene domains in SBS films was $d = 40 \pm 17$ nm. The average size of poly(methyl acrylate) domains in SMAS films was $d = 27 \pm 5$ nm. The period of the lamellar structure was $D = 45 \pm 5$ nm.

The TEM images show areas with single domains without overlaps (Fig. 4a) and areas with many double overlaps (Fig. 4b) but reveal no areas with triple over-
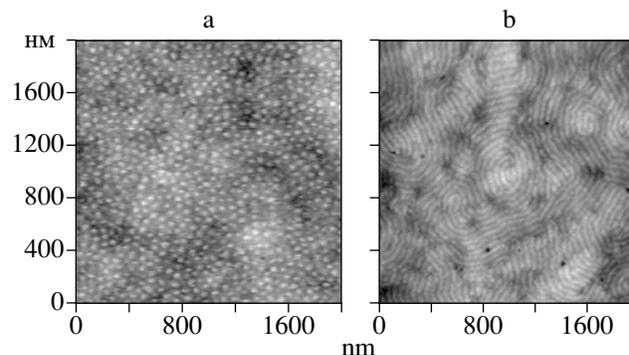
Fig. 3. AFM images of the SMAS films for [PS] : [PMA] = 1 : 2 (domain structure, left) and [PS] : [PMA] = 1 : 1 (lamellar structure, right).

laps of domains. The average domain size was determined from the TEM images with single domains ($d = 31 \pm 6$ nm). The thickness of SBS films was estimated at 50 to 100 nm (one to two domain diameters) from the TEM images with double overlaps.

a   b
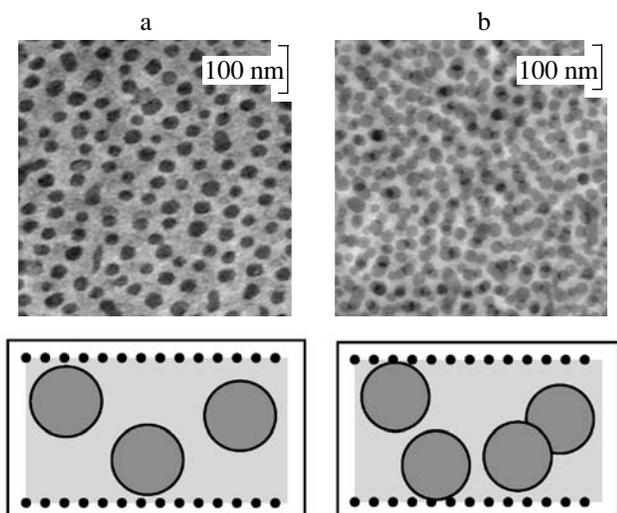
Fig. 4. TEM images of different areas of the SBS film (top) and the theoretical models of domain arrangement (bottom).

Theoretical Calculations of the MPS Parameters

Using the measured average domain sizes and the period of the lamellar structure, one can calculate the quantities that determine the MPS structure (e.g., the Flory–Huggins parameter).

In [5], a theoretical approach to the calculation of the period of the lamellar structure and the domain sizes in block copolymers has been described. It is assumed that (1) the numbers of segments in the blocks are equal, (2) the sizes of segments in A and B are equal, and (3) the contact points of blocks A and B are within a narrow layer. The energy of interaction of units A and B is a surface energy since the units are in contact only near the interface. The Gibbs energy components are the energy of interaction of the units and the extension energy of the blocks. The characteristic period of the MPS structure is calculated by the formula $L = c\,a\,N^{2/3}\chi^{1/}$, where a is the length of the Kuhn segment in either block, N is the number of segments in either block, χ is the Flory–Huggins parameter that describes the interaction between the units A and B, and c is a coefficient dependent on the MPS structure. For instance, c is 4.36 for the domain diameter and $c = 8(3/\pi^2)^{1/3}$ for the period of the lamellar structure.

Table 2. Kuhn segment (a), number of the monomer units in the segment (S), and the relative molecular mass of the monomer unit (M_m)

Polymer	a, nm	S	M_m
Polystyrene	2.00 [6]	7.9 [6]	104
Polybutadiene	0.69 [7]	4.3	54
Poly(methyl acrylate)	2.00	7.9	86

Theoretical Determination of the Sizes of Polybutadiene Domains in SBS Films

To verify the estimates predicted by this theory, we calculated the sizes of polybutadiene domains in SBS films. The parameters of either block in the macromolecules under study we need for theoretical calculations are given in Table 2.

Because the molecular weight of the whole macromolecule is $M_n = 100000$ and the relative weight fraction of polystyrene is $f_{PS} = 0.85$, then the molecular weights of the dissimilar blocks are $M_{nPS} = 85000$ and $M_{nPB} = 15000$. The domain size is given by the formula $d = 4.36\,a\,N_{ПБ}^{2/3}\chi^{1/6}$. The Flory–Huggins parameter for a pair of polystyrene and polybutadiene units is $\chi(PS/PB) = 0.045$ [8]. The number of polystyrene units in the macromolecule is

$$N_{ПБ} = \frac{M_{nPS}}{S_{PS}M_{mPS}} = 64.6.$$

Thus, the domain size is $d = 4.36 \times 0.69$ nm $\times (64.6)^{2/3} \times 0.045^{1/6} = 31$ nm.

This theoretical estimate of the average domain size agrees well with the experimental values (Table 3).

Theoretical Determination of the Flory–Huggins Parameter [chi](PS/PMA) for the Polystyrene–Poly(methyl acrylate) Interaction

No $\chi(PS/PMA)$ value for a pair of polystyrene and poly(methyl acrylate) units is available. However, this quantity can be estimated from the developed theoretical approaches [5] and the experimental values of the average domain size and the period of the lamellar structure in SMAS films.

Calculation of the Domain Structure

The molecular weights of the dissimilar blocks are $M_{nPS} = 25000$ and $M_{nPB} = 50000$. The domain size is given by the formula $d = 4.36\,a\,N_{PS}^{2/3}\chi^{1/6}$, where a is the length of the Kuhn segment in domain-forming units, N is the number of segments in either block, and χ is the Flory–Huggins parameter that describes the interaction between polystyrene and poly(methyl acrylate) units. The number of polystyrene units in the macromolecule is

$$N_{ПC} = M_{nPS}/(S_{PS}M_{mPS}) = 30.4.$$

To obtain the variance of N_{PS}^6, we raised the set of domain diameters to the sixth power and calculated, from the resulting bar chart, the average N_{PS}^6 value and its variance: $d^6 = (1.13–10.74) \times 10^8$ nm^6. Thus,

$$\chi(PS/PMA) = \frac{d_{PS}^6}{(4.36aM_{mPS})^6 N_{PS}^4} = (0.3–3) \times 10^{-3}.$$

Table 3. Theoretical and experimental average domain sizes (from AFM and TEM data)

AFM	TEM	Theory
40 ± 17 nm	31 ± 6 nm	31 nm

Calculation of the Lamellar Structure

The molecular weights of the dissimilar blocks are $M_{nPS} = 16000$ and $M_{nPMA} = 14000$. The period of the lamellar structure is given by the formula $D = 8(3/\pi^2)^{1/3}aN^{2/3}\chi^{1/6}$. The total number of units in the macromolecule is $N = N_{PS} + N_{PMA} = 40$. The period of the lamellar structure is $D = 45 \pm 5$ nm. Thus,

$$\chi(PC/PMA) = \left(\frac{D}{8(3/\pi^2)^{1/3}aN^{2/3}}\right)^6$$

$$= \frac{D^6}{8^6\left(\frac{3}{\pi^2}\right)^2 a^6 N^4} = (1-4) \times 10^{-3}.$$

The values of the Flory–Huggins parameter calculated from the domain and lamellar structures are consistent.

The pair of polystyrene and poly(methyl methacrylate) (PMMA) units is chemically most close to the polystyrene–poly(methyl acrylate) pair under study. The Flory–Huggins parameter $\chi(PS/PMMA)$ is 4.4×10^{-3} [8]. The $\chi(PS/PMA)$ values we obtained here are lower than $\chi(PS/PMMA)$; therefore, the effective repulsive forces between polystyrene and poly(methyl methacrylate) units are higher than those in a polystyrene–poly(methyl acrylate) pair.

This behavior of the Flory–Huggins parameter can be explained by two effects:

(1) the monomer units of poly(methyl methacrylate) are more hydrophobic than those of poly(methyl acrylate) and, consequently, the repulsive forces between them and the hydrophobic units of polystyrene are higher;

(2) the repulsive forces are additionally contributed by the polarization of polystyrene units under the action of adjacent units. The polarization effect of poly(methyl acrylate) on polystyrene units is stronger than that of poly(methyl methacrylate).

CONCLUSION

Hence, we revealed microphase separation in films of the polystyrene–poly(methyl acrylate)–polystyrene triblock copolymer with different relative concentrations of polystyrene. We found that the conditions for film formation influence the film morphology. We calculated the period of the lamellar structure and the domain sizes of these films. We were the first to estimate the Flory–Huggins parameter for a pair of polystyrene and poly(methyl acrylate) units: $\chi(PS/PMA) = (1-4) \times 10^{-3}$.

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