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Chain conformation of polybutadiene blocks in lamellar bidispersed microdomains as revealed by small-angle neutron scattering

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Abstract.— Polybutadiene-polystyrene diblock copolymer lamellar supercrystals developed by binary mixture of PS-PB block copolymers with different molecular weights have been studied by SANS on the diffractometer "Membrana-2". The dependence of the lattice spacing and the radii of gyration of PB chains on the molecular-weight parameters of a domain have been studied. It turned out that the conformation of PB chains is dependent on the concentration of surrounding short chains.

1. Introduction.

The present paper is devoted to the study of block copolymer chain conformations in binary mixtures of polystyrene-polybutadiene (PS-PB) diblock copolymers with different molecular weights by small-angle neutron scattering techniques. It is common knowledge that the perfect domain structures in a wide range of polydispersity and composition are developed by such kinds of mixtures [1]. Recently a mean-field theory has been proposed for structures of this kind [2]. In this theory bidispersed diblock copolymer chains grafted to a plane surface are examined. According to this theory the domain consists of two sublayers (Fig.1). In the lower sublayer the conformation of those parts of the long chains which are in the sublayer

occupied by short chains is similar to that of the short chains.

Fig.1. Structure of bidispersed domain.

Only those parts of the long chains which are in the the range $H_1 \leq z \leq H_2$ (where H_2 is the full layer height, H_1 is the height of short chains, z is the coordinate along the normal to the grafting surface) are perturbed due to spreading in the lateral directions.

2. Experimental.

The samples of the PS-PB diblock copolymers have been synthesized in the Institute of Macromolecular Compounds, Academy of Sciences of Russia. Their molecular parameters are given in Table 1.

Table 1

Molecular parameters of block copolymers

Polymer	fraction	$M_w \cdot 10^{-3}$		M_w/M_n	$M_p \cdot 10^{-3}$	
		PS	BC		PS	PB
1 PS-PB	0.65		108	1.04	68	38
2 PS-PB	0.61		312	1.06	184	119
3 PS-PB ^d	0.45		279	1.04	120	146

We intended to study the conformation of polybutadiene chains of the PS-PB^d component (PB^d is deuterated polybutadiene) in the diblock copolymer superlattice depending on the number of neighbouring PB chains having the low molecular mass ($M_p = 38 \cdot 10^3$). With

this end in view, the block copolymers 1 and 2 were mixed in the ratios 2:1 and 5:1 by the number of chains. Films were obtained by casting from toluene solutions on lavsan sublayer. The dry films with the thickness about 0.7 mm were cut in the stripes of 2 mm width and 60 mm length. These stripes have been packed as a pile of $2 \times 5 \times 60 \text{ mm}^3$. It was experimentally determined that BC 1, 2, 3 and their mixtures formed common lamellar structures with lamellae oriented parallel to the film surface [3].

Small-angle neutron scattering experiments have been performed on the "Membrana-2" instrument [4]. The wavelength of the incident neutron beam is $\bar{\lambda} = 2.3 \text{ \AA}$, the halfwidth of the spectrum is $\Delta\lambda/\bar{\lambda} = 0.10$.

The period of lamellar superstructure D was measured for all samples oriented parallel to the beam. To determine R_{gx} projection of PB chain we oriented films perpendicular to the beam (T-orientation). In this case we measured the scattering curves from the protonated sample (background) and from the sample containing 3% of deuterated PB chains (block copolymer 3), then the difference in the scattering curve has been obtained by subtracting these two signals.

3. Results and discussion.

The scattering intensity for deuterated PB chains was expressed in the Guinier law form:

$$I(Q) \sim I(0) \cdot \exp(-Q^2 R_{gx}^2), \quad (1)$$

where R_{gx} is the radius of gyration of the chain along x-direction, $Q = 4\pi \sin\theta/\lambda$, and 2θ is the scattering angle.

The data obtained are given in Table 2. The calculated value of the unperturbed R_{gx} for the PB^d block is 76 Å. The R_{gx} of the long chain can be expressed in the form $R_{gx,1}^2 = u_{gx,1}^2 + l_{gx,1}^2$, where $u_{gx,1}$ and $l_{gx,1}$ are the radii of gyration of the parts of the chain in the upper and lower sublayers, correspondingly, of the i-th mixture (see Tabl.2). The value $l_{gx,1} = 23 \text{ Å}$ was calculated on the basis of

Table 2

The period of lamellar structure D and R_{gx} -projections of radii of gyration of PB^d -chain for block copolymer mixtures of different composition.

Polymer	BC1	BC2	BC1:BC2 (2:1)	BC1:BC2 (5:1)
$\bar{D}, \text{\AA}$	465±15	905±20	775±15	695±15
$R_{gx,1}, \text{\AA}$	-	45.1±1.9	54.9±2.8	61.9±3.1

the theoretical model assuming Gaussian conformation for chains [3,5]. These values are the same for all mixtures studied. Consequently one can obtain: $u_{R_{gx},1}=39 \text{\AA}$, $u_{R_{gx},2}=50 \text{\AA}$ and $u_{R_{gx},3}=57 \text{\AA}$. The calculated value of the unperturbed upper part of the chain is $u_{R_{gx}}=69 \text{\AA}$. Thus the effect of lateral contraction of the chain in the domain structure is rather strong [5].

Now let us consider the variation of the period of the lamellar structure. As developed in the theory [2] the variation of D depending on the layer composition can be written as follows:

$$D = D_0 + 2q_2(H_0^{PS}\alpha_{PS} + H_0^{PB}\alpha_{PB}), \quad (2)$$

where D_0 is the period of initial monodispersed structure, H_0^{PS} , H_0^{PB} are the heights of initial monodispersed layers of PS and PB, α_{PS} and α_{PB} are the relative differences in chain lengths for PS and PB, $\alpha = (N_2 - N_1)/N_1$ (N_2 and N_1 are the polymerization degrees of short and long chains) and q_2 is the fraction of long chains in the layer. At the same time for homodispersed diblock copolymers [6]:

$$D = kM_n^{0.64}. \quad (3)$$

Here M_n is the number-average molecular weight of the BC. If the the bidispersed layer is considered as a layer of chains with the same molecular weight M_{eff} , we would calculate D using relation (3). In Fig.2 these dependences are given along with the experi-

mental one.

It is obvious that the changes in the real superlattices formed

Fig.2. The dependence of the superstructure period D on the composition of block copolymers.

by bidispersed mixtures are not well described either by the theories developed for homodispersed chains or by those developed for bidispersed systems when the layer is separated in two independent sublayers. We suggest an empirical relation of D on the composition of bidispersed layers which describes adequately the dependence obtained:

$$D = D_0 + kM_n^{1/3}, \quad (4)$$

here M_n is an effective molecular weight of the upper part of the layer. The dependence $D(q_2)$ calculated using (4) is given in Fig.2. This dependence corresponds to free (ungrafted) monodispersed chains in the circumstances where their density is constant.

Thus, we can formulate the following conclusions for real block copolymers on the basis of the data obtained. It is observed that the conformation of lower parts of the chains (see Fig.1) depends on neither the length nor the concentration of long chains. However, in the upper sublayer the conformation of those parts of long chains which occupy this sublayer is not consistent with theoretical predictions developed both for homo- and bidispersed chains. We conclude that intermolecular interactions between chains affect their conformation and these effects should be taken into account.

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