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Microlayer and Glass Formation in Block Copolymers

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The present state of the theoretical and experimental studies on one of the possible types of phase transformations in block copolymers, namely microlayer formation, as well as the influence on the latter of vitrification is surveyed. It is shown that microlayer formation leads to the appearance of supermolecular structures whose parameters depend on the composition, temperature, and the number and length of the blocks; microlayer formation also determines the vitrification parameters, which can in their turn inhibit the microlayer formation. The mutual influence of microlayer and glass formation processes is discussed.
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I. INTRODUCTION

Block copolymers (BP) is the name usually given to substances whose linear macromolecules consist of fragments of homopolymers (blocks) linked covalently via their ends (Fig.1). Depending on the primary chain structure, the chemical structure of the monomer units, the length of the blocks, their number and distribution in the chain, and their flexibility, various phase transformations can take place in BP: separation into microphases in the melt, crystallisation (fusion), polymorphic transitions, liquid crystal ordering. Furthermore, the non-crystalline component is capable of vitrifying. The phase transformations in BP take place in many respects analogously to the phase transitions in mixtures, but the presence of a covalent bond between the components leads to a number of characteristic features, which differentiate BP as a separate class of multi-component systems.

This review is devoted to the consideration of one type of transformations in BP—microlayer formation—and its dependence on the primary structure of the macromolecule. The mutual influence of microlayer and glass formation processes is also discussed.

The study of phase transformations in BP is not only of purely theoretical interest but is also essential in connection with their possible application in the development of experimental techniques (neutron radiation monochromators, materials for microelectronics, and conductors several tens of angstroms in diameter), in medicine, and in industry (gas- and liquid-separating membranes, constructional materials). Since BP constitute the simplest models of a heteropolymer, the study of the phase transformations in them is also useful for the understanding of the processes occurring in biological structures (in particular, in cell membranes).

A BP constitutes a special case of a heteropolymer, i.e. a polymer made up of monomers having different chemical structures, and the description of the primary structure of an isolated heteropolymer macromolecule is analogous to the description of the structure of biopolymers.[1-7] We shall not dwell on the fundamental theoretical questions concerning the amount, complexity, and value of the information inherent in heteropolymers,[2,3,7] while questions relating to the selection and calculation of self-averaging quantities have already been discussed.[8,9] In the present review, we shall merely consider briefly the quantitative differences between the degrees of order in the intramolecular components,[10] such order influencing the parameters of the phase transformations. (The distribution of the intermolecular components characterises the feasibility of phase transformations at the intermolecular level and the difference between the structures of the macromolecules characterises their feasibility at the macroscopic level.)

The existing classification includes four types of linear synthetic heteropolymers: (1) periodic block copolymers; (2) statistical copolymers (SP), whose macromolecule is usually represented as one in which there is a non-ordered distribution of the monomers; (3) gradient (or conical) BP in which there is a SP block between two homopolymer blocks; (4) statistical BP in which the blocks are joined up statistically (a SP is a special case of such BP); the differences between the primary structures are specified by the methods and conditions of synthesis.

In the present review, the term block copolymer is understood (in contrast to the exact definition given previously) as a polymer whose linear chains are made up of blocks consisting of a continuous sequence of monomers of one kind, the average length of the blocks (with respect to the assembly of primary chain structures) being significantly greater than the standard deviation characterising the scatter of the blocks with respect to their lengths. We shall consider below only BP (type 1) and their blends, while blends of BP with homopolymers, statistical and gradient SP, as well as low-molecular-weight solvents are not included in the review.

II. SEPARATION INTO MICROPHASES IN THE MELT

A number of reviews have been devoted to the separation into different phases in BP melts.[11-19] However, in recent years much new information has been published, which permits a deeper understanding of the nature of this phenomenon. We shall therefore describe only briefly the information which has already become generally known and the main analysis will be devoted to studies carried out in recent years.

Like blends, BP are capable of separating into different phases. The fundamental difference between the phase separation in BP and the separation in blends consists in the fact that the characteristic size of the species and of the phase is of the order of several radii of inertia of the block and, depending on the length of the block, can

vary from several nanometers to several tens of nanometers. Separation into layers in BP occurs for dimensions of the phase species less than the length of the macromolecule and is an intramolecular process (Fig.1), so that it is referred to as microphase layer formation. Here one of the phases represents a monoconnected region (matrix) whilst the other constitutes a polyconnected region, i.e. one consisting of a large number of bounded domains, alternatively both phases can be polyconnected (alternating lamellae), or both phases can be monoconnected (interpenetrating phase networks).

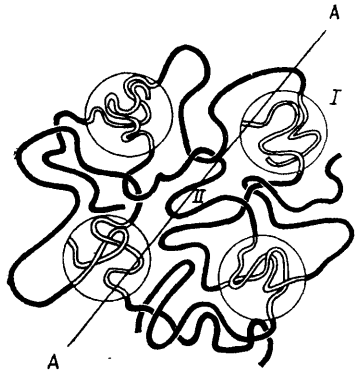


Figure 1. Schematic representation of the supermolecular structure of a periodic BP separated into pure microphases:[16] (I) phase consisting of spherical domains incorporating type 1 blocks; (II) phase constituting a monoconnected matrix consisting of type 2 blocks; $A-A$—straight line along which the concentration profile is determined.

Prolonged annealing leads to the improvement of the domain structure of the BP but does not entail the coalescence of the domains, as happens in blends. The improvement of the BP structure during annealing consists in the fact that in periodic BP the supermolecular structure (SMS), made up of domains having different relative positions, may become strictly regular, resembling the disposition of atoms at the crystal lattice sites of a crystal of a low-molecular-weight compound,[20,21] as a result of which such SMS is sometimes referred to as a supercrystal.[22] Thus one may say that microlayer formation in BP is analogous to separation into layers and supermolecular crystallisation.†

The phase state of BP is characterised by the spatial distribution of the concentrations of its components. The straight line passing through the BP ($A-A$ in Fig.1) determines the curve representing the distribution of concentration which is referred to as the concentration profile (Fig.2). The form of the profile, which can be characterised by its parameters, namely the amplitudes (phase compositions) Φ' and Φ'', the thicknesses of the domains T' and T'' and of the interfacial layer Δ, and the period D, depends in the general case on the temperature and the molecular weight distribution (MWD) of the blocks and also on the position of the straight line specified in space. We shall consider separately the influence of temperature and MWD on the parameters of the concentration profile and also on the symmetry of the SMS.

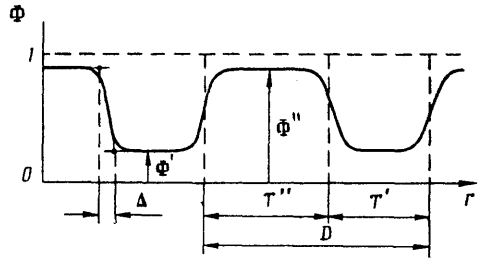


Figure 2. Second component concentration $\Phi = \Phi_2$ profile along a certain specified direction (r = distance); Φ' and Φ''—contents of the second component (concentration amplitudes) in phases I and II respectively; T' and T''—microphase thicknesses; D—SMS period; Δ—thickness of the interface.

1. Transition from the Non-ordered State to the State Separated into Microlayers

At sufficiently high temperatures or for sufficiently small lengths of the blocks r_1, the BP can exist in a single-phase (non-ordered) state. A decrease in temperature or an increase in r_1 should lead to a transition across the microphase separation boundary (MSB), provided, of course, that another phase transition or vitrification does not occur before that. In the general case, the MSB is represented by a curve in terms of the variables T, Φ_i, r_i or χ, Φ_i, r_i (χ is the Huggins interaction parameter, T the temperature, Φ_i the volume fraction of the ith component, and r_i the degree of polymerisation of the ith component block, and $i = 1-n_{ia}$, the number of intramolecular components).

Some of the qualitative features of the MSB are manifested when the method of geometrical thermodynamics is applied to the BP.[10,23-26] By analogy with blends, one can assume that, for a fixed composition of the BP, the compositions of the coexisting phases vary with temperature in conformity with the binodal curve in the temperature–composition plane. Since in binary periodic BP the intermolecular composition (the content of the second component) is defined by the formula

$$x \equiv x_2 = M_2/[a(n)M_1 + M_2] \qquad (1)$$

[M_1 and M_2 are the molecular weights of blocks 1 and 2 and $a(n)$ is a coefficient which depends on the number of blocks and, for branched BP, on the way in which unlike blocks are joined together], the construction of the temperature–composition diagram requires the variation of the molecular weight (MW), i.e. r_i, of the blocks, for example, by varying M_2 for a constant M_1. As for blends, a displacement and deformation of the binodal curve should then occur.

For a geometrical representation of the dependence of the position and form of the binodal curve on the MW, it is necessary to introduce a third coordinate (M_2) in addition to T and x, and M_1 should be regarded as a parameter (Fig.3). In the $T-x-M_2$ three-dimensional state, the binodal curve unfolds into the binodal surface

† BP separated into microphases are sometimes classified as lyophilic liquid crystals.[18]

and the composition defined by Eqn.(1) is represented geometrically by a curve in the $x-M_2$ plane. The MSB is then represented by a spatial curve defined by the intersection of the binodal surface with a curvilinear cylinder with the composition curve at its base. It is sometimes convenient to adopt as the MSB the projection of this curve onto the $T-x$ or $T-M_2$ plane. Such geometrical representation reveals that, firstly, the microlayer formation critical point for monodisperse BP is not displaced to the left of the maximum although it is located on the MSB; secondly, for certain relations governing the form of the binodal surface, which is determined by the nature of the components and the curvature of the composition curve, a second maximum can appear on the MSB, being located to the right of the maximum; thirdly, one cannot rule out the possibility of the existence of a single-phase state when M_2 increases very markedly.[23-26]

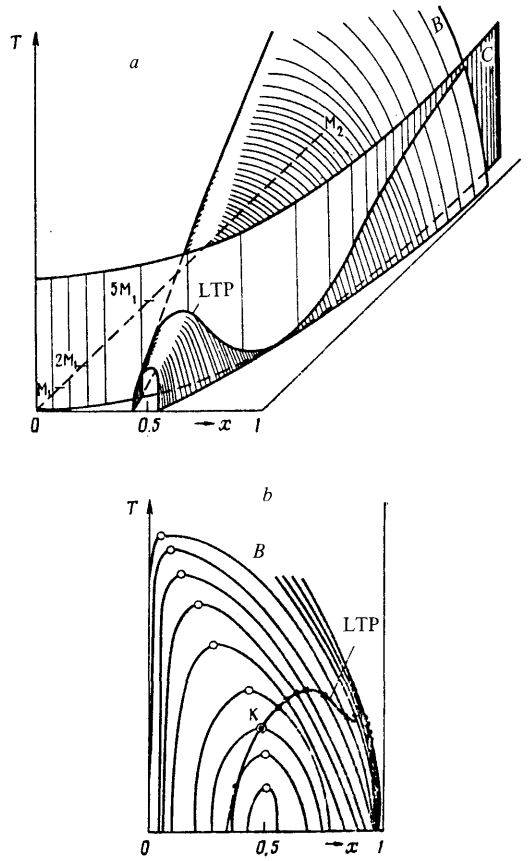


Figure 3. Construction of the locus of the turbidity points (LTP) for BP with M_1 = const. by the surface intersection method:[26] (a) three-dimensional representation in terms of the coordinates $T-x-M_2$ [B—binodal surface; C—curved cylinder, with generator parallel to the temperature axis, whose base is the overall composition curve $x = x(M_2)$]; (b) two-dimensional representation in the $T-x$ plane {B—family of binodal curves corresponding to different values of M_2 [with increase in M_2, the consolute point K (open circles) is displaced upwards]; LTP—projection of the three-dimensional LTP onto the $T-x$ plane}.

Microphase separation is possibly only in those heteropolymers in which the intermolecular components have been "mixed" along the chain to a sufficiently slight extent, i.e. the primary chain structure is closer to BP than to SP.[34] The conditions imposed on the primary BP structure to achieve microlayer formation have the form

$$\overline{R^2N^2}/\overline{N^2} > \overline{R_1^2N_1^2}/\overline{NN_1} + \overline{R_2^2N_2^2}/\overline{NN_2},$$
$$\overline{k_{12}}/\overline{N} < 2\,(\overline{N_1}/N)\,(\overline{N_2}/\overline{N}),$$

where $N_i(S)$ is the number of units of the ith kind in a macromolecule of type S, $N(S) = N_1(S) + N_2(S)$, $R_i^2(S)$ and $R^2(S)$ are the squares of the radii of inertia of the units of the ith kind of the macromolecule of S and of all the units respectively averaged with respect to the conformations, and $\overline{k}_{12}$ is the average number of bonds between unlike units (heterobonds) per macromolecule. The bars above the symbols denote averaging with respect to the molecular-structural distribution in the system: $\overline{A} = \sum_s n_s A(S)/\sum_s n_s$, where

n_s is the number of macromolecules of type S, which can be specified by their structural formula, per unit volume.

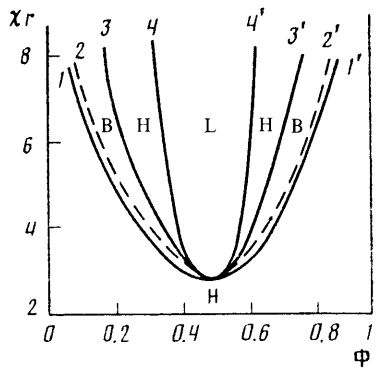


Figure 4. Phase diagram for a di-BP:[33,37] (1,1′) microphase separation boundary; (2) and (2′) spinodal curve; (3) and (3′) boundary corresponding to the transition from the body-centred cubic SMS (B) to the hexagonal SMS (H); (4) and (4′) boundary of the transition from the hexagonal SMS to the lamellar SMS (L); N—non-ordered phase.

For di-BP, the MSB has been calculated analytically both near the critical point[33] and at a distance from it.[37] These data supplement one another and make it possible to construct the complete phase diagram of the di-BP[37] (Fig.4). In a study,[33] based on Landau's theory of phase transitions, the free energy was defined by a series expansion in terms of powers of the order parameter $\psi(r)$:

$$\psi(\mathbf{r}) = \langle \delta\Phi_1(\mathbf{r}) \rangle \equiv \langle \Phi_1(\mathbf{r}) - \Phi_1 \rangle,$$

where $\Phi_1(\mathbf{r})$ is the ratio of the local density of type 1 monomers at the point $\mathbf{r}$ to the overall density of the monomers averaged with respect to the specimen (for a non-compressible system, Φ_1 corresponds to the concentration); the angular brackets denote averaging with respect to the Gibbs *ensemble*. The MSB was represented in the above study[33] by the dependence of χ' on composition. For $\Phi \neq 0.5$, the phase transition is a first-order transition, since the

order parameter varies abruptly.[33,37] For $\Phi = 0.5$, Landau's theory predicts a second-order transition, but at this point the concentration fluctuations with $|\mathbf{k}| \neq |\mathbf{k}^*|$, which can restore the first-order transition, should begin to play a role.[33] The above features of the thermodynamic behaviour of BP are associated with the fact that the spectrum of concentration fluctuations has a maximum at $k = k^*$, which is infinitely high on the spinodal curve. Several workers have noted simultaneously that fluctuations with $k^* \neq 0$ should grow in the vicinity of the spinodal curve.[33–36]

The range of temperatures and compositions where the BP is in the homogeneous state while blends of homopolymers with the same MW of the components have already separated into layers has been predicted theoretically.[33,38] This conclusion agrees with the results of experiments carried out on blends and polyblock BP.[39]

An important theoretical prediction is that the binodal and spinodal curves are close to one another,[33] which makes it possible to consider the influence of the primary structures of the macromolecules on the MSB as being the same as the influence on the spinodal curve, which is easier to calculate. The influence of the number of blocks and the way in which they are joined together and also of the polydispersity of the MW on the position of the spinodal curve has been examined.[34,40] The closeness of the spinodal curves for BP and homopolymers has been predicted and on the $T-x$ plane the spinodal curve for the BP lies below the spinodal curve for the blend, which agrees with conclusions reached in other studies.[33,38,39] An increase in the degree of asymmetry $s = r_1/(r_1 + r_2)$ of the tri-BP $A_{r_1}B_{r_2}A_{r_1}$ macromolecule and the increase in the number of blocks in periodic polyblock BP reduce the spinodal temperature T_{sp}.[34] A decrease in the fraction of long chains in a binary blend of monodisperse di-BP, differing in chain length, or in the polydispersity coefficient $P = r_w/r_n$ for a polydisperse BP also results in a smooth decrease in T_{sp} (increase in χ_{sp}).[40]

Hitherto, we have discussed the position and shape of the MSB itself, but BP have characteristic features also when the MSB is approached from the side of the single-phase region. It has been shown theoretically[41] and experimentally[42] that the "correlation hole" effect is observed in this region and leads to the appearance of a scattering maximum on the angular dependences of the intensities of X-rays and thermal neutrons. The value of k corresponding to the correlation hole has been predicted by the statistics of ideal chains. This effect is sensitive to the degree of polydispersity of the BP. The values of χ have been determined from the position of the scattering maximum by the method proposed by Leibler[33] and proved to depend on the composition in the region where they are low.

The prediction of the formation, as the MSB is approached from the side of the single-phase state, of a rarefied micelle gas, which becomes ordered only when its density increases, made[43] on the hypothesis of the mutual repulsion of the micelles, has been disproved[37] by demonstrating the existence of a region where the micelles attract one another. The formation of ordered structures made up of micelles should occur abruptly (first-order transition) without the formation of unified micelles. In order to reach a final conclusion, it is necessary to test experimentally the claims concerning the sign of the interaction of the micelles.

All the theoretical studies discussed in this review were performed on the assumption that there are no directed intermolecular interactions. However, the position and shape of the binodal surface for BP as well as for mixtures of low-molecular-weight liquids[27–30] must depend on the energy, direction, and degree of degeneracy of various intermolecular bonds, which may be formed both between the molecules of one component and between the molecules of different components. By analogy with mixtures, one can postulate that, when different types of intermolecular interactions are considered, the phase diagram for the BP may have a different lower consolute temperature and can contain loops, "compressed" loops, "compressed" domes, etc. On the other hand, covalent bonding can lead to additional changes in the phase diagram. The influence of directed intermolecular bonds on the shape of the MSB requires both theoretical and experimental study.

As a consequence of the complexity of the experimental investigation of the composition of the coexisting phases in microheterogeneous systems, no binodal curve for a real BP has been obtained hitherto. The optical methods and sample methods, employed to construct the binodal curves for these systems, are relatively ineffective or inapplicable. The low-angle X-ray and neutron scattering methods have been used so far only for the qualitative estimation of the segregation coefficient[31] but not for the quantitative measurement of the compositions of the coexisting phases. Apart from the diffraction methods, calibration relations between the glass point and the composition of the single-phase system[10,23–25] and also experimental $\chi(x,T)$ relations can be used to determine the phase composition.

2. The Symmetry and Repeat Period of the Supermolecular Structure

(a) The Influence of Temperature

It is known from early experimental data that the symmetry of the SMS varies as the intermolecular composition of the BP is varied.[18] The change in symmetry also as the temperature is altered has been predicted theoretically recently.[33,37] Semenov's theory[37] is valid in the region where $\chi_r \gg 1$, while Leibler's theory,[33] based on Landau's theory, is valid in the region where $(\chi_r)_{cr} = 2.62$. Thus the two theories supplement one another. With increase in χr (i.e. with decrease in temperature or with increase in the degree of polymerisation), a body-centred cubic SMS made up of spherical domains‡ should be formed immediately beyond the MSB and, under conditions such that $(\chi r)_1 > (\chi r)_{sp}$ [where $(\chi r)_{sp}$ represents the values of χr along the spinodal curve and $(\chi r)_1$ represents the values on the boundary corresponding to the transition from the body-centred to the hexagonal structure], is transformed into a hexagonal SMS made up of cylindrical domains; the latter is in its turn converted into a lamellar SMS for $\chi r = (\chi r)_2$ and then the structures are inverted, i.e. in the domains component 1 is replaced by component 2 and conversely (Fig.5). The transition from one type of SMS to another is a first-order phase transition. Although $(\chi r)_1 > (\chi r)_{sp}$, over a wide range of compositions ($0.2 < \Phi < 0.8$) these values are very close.

Since in the region of the diagram between the binodal and spinodal curves the formation of a microphase structure is very slow, the body-centred cubic SMS should be metastable. This may serve as an explanation of the absence of direct observations of the body-centred cubic SMS much below the microlayer formation temperature; we may note that the absence of such observations can be

‡ In contrast to Semenov's[33] and Leibler's[37] theories, the theory of Helfand and Wasserman[47] predicts a transition to an SMS with a face-centred cubic lattice made up of spherical domains.

accounted for also by the high stability of the face-centred cubic SMS (see the last footnote). These hypotheses require experimental confirmation. It may be expected that body-centred cubic SMS are easier to observe for low and high values of Φ (for $\Phi < 0.2$ or $\Phi > 0.8$), since in this case the difference $(\chi r)_1 - (\chi r)_{sp}$ is considerable and the temperature range corresponding to the stability of such SMS expands significantly. When the blocks are highly incompatible ($\chi r_1 \gg 1$), the transition from the spherical SMS to the cylindrical SMS occurs at $\Phi_1 = 0.12$ and that from the cylindrical to the lamellar SMS takes place whence $\Phi_2 = 0.28$.[37] The sequence of the changes in the SMS as Φ is varied from χr = const. agrees with thoroughly established empirical data.[11,13,18]

The formation of a SMS of the supercritical type depends on the preparation conditions. A structure of the paracrystalline type is frequently formed in which there is only short-range order in the arrangement of the domains and long-range order is absent;[45] such structures generate a single diffuse ring on low-angle X-ray diffraction patterns. The X-ray diffraction pattern of the supercrystal is characterised by a rigorously symmetrical distribution of localised reflections up to fairly high orders.[20,21,46] With increase in annealing time above the glass points of the components, the SMS is improved, which increases the number of reflections and their sharpness.[21]

The transitions between different types of symmetry of the supercrystal have been poorly investigated experimentally, but a series of studies have been published recently[48-58] on the disappearance of the SMS with increase in temperature. Their main results are presented in Table 1. Most of the experiments were performed on the polystyrene–polyisoprene and polystyrene–polybutadiene BP; precautions were taken to eliminate thermal degradation, which is known, from studies on blends of homopolymers,[59-61] to be capable of modifying greatly the phase diagram. The principal finding, which agrees with the theory, is the disappearance of the SMS with increase in temperature and also with decrease in the MW (even at room temperature[62]). The authors explain the disappearance of the SMS either as the breakdown of the ordered SMS or as the mixing of the components.

The disruption of the SMS was accompanied by characteristics which can be divided into two types: (1) a decrease in the number of small-angle Bragg reflections without change in the long period; (2) a decrease in the number of reflections with increase in the long period by a factor greater than 2 before the disappearance of the SMS. A decrease in the long period has been noted only for lamellar supercrystals (not in all the experiments), while for other types of SMS the periodicity vanishes without change in the period. Studies on the kinetics of the thickening of the lamellae have shown that the weight of the latter increases with increase in temperature and with decrease in MW.[55] One can therefore postulate that in certain cases the long period increases during a time shorter than the duration of the experiment. Qualitatively this hypothesis has been confirmed by the sudden disappearance of the long period from BP with a low MW (Table 1). Within the framework of the existing ideas, it is not altogether understood why the thickening in lamellar supercrystals begins at approximately the same temperature regardless of the MW. In order to elucidate the nature of the disappearance of the ordered SMS, further experimental studies are essential.

Certain hypotheses, which have not been discussed hitherto, can be put forward concerning the influence of temperature on the concentration profile and symmetry of SMS. With increase in temperature, the difference $\Delta x = x'' - x'$ diminishes; this should be accompanied by a transition of the block from one phase to another.

Table 1. The influence of temperature on the parameters of the SMS of the block copolymers.

No.	Primary structure (10^{-3} MW)	x_2/P	SMS	Method	Type of temperature singularity	Refs.
1	PS-PI				weak l/p maximum at	[53]
	(51-47)	0.48/1.30	lamellae	SAXS	383 K and its marked growth in the range 453-523 K, after which it disappears	
2	PS-PI		PCP,	SAXS	there are no singularities	[52]
	(187-33)	0.15	PI spheres		in the range 293-453 K	
3	PS-PI			SAXS, EM	l/p disappears at 463 K; growth of l/p above 473 K	[55]
	(13.5-13.5)	0.5/1.25				
	(25.5-25.5)	0.5/1.20				
	(36-36)	0.5/1.15	lamellae			
	(49-49)	0.5/1.30				
4	PS-PB			SAXS	l/p disappears at	[50]
	(7-20)	0.75/1.04	PS spheres		~423 K	
5	PS-PEO					
	(14-20)	0.59/1.15	lamellae	SAXS, PM	l/p disappears at 433 K	[87]
	(22-10)	0.32/1.15	HEX, PEO cylinders		l/p disappears at 403 K	
	(22-53)	0.71/1.15	HEX, PS cylinders		l/p disappears at 308 K	
6	PS-PVTMS			PE	CPE maximum at 500 K	[166]
	(97-89)	0.52/–	–			
7	PS-PI-PS			DMA,	sharp fall of viscosity and	[48]
	(16-12-16)	0.38/–	lamellae	SAXS	of modulus of elasticity at 498 K, disappearance of l/p at 513 K	
8	PS-PI-PS			SAXS	disappearance of	[54]
	(8-35-8)	0.68/1.25	FCCP, PS cylinders		reflections at 426 K	
9	PS-PI-PS			SAXS	marked growth of l/p above 473 K	[55]
	(16-32-16)	0.5/1.30	lamellae			
10	PS-PB-PS			EM, DMA	disappearance of micro-heterogeneity between 398 and 463 K and fall of dynamic viscosity at 423 K	[49]
	(7-43-7)	0.77/–	HEX, PS cylinders			
11	PS-PB-PS			DSC	annealing at 563 K leads to disappearance of vitrification of PB	[51]
	(7-43-7)	0.77/–	ditto			
12	PS-PB-PS			SAXS	disappearance of l/p at 513 K	[50]
	(7-43-7)	0.75/–	BCCP, PS spheres			
13	PS-PB-PS			PE	CPE maximum at 400 K	[50]
	(10-55-10)	0.73/–	PS cylinders			
14	PS-PB-PS	0.55/–	–	PE	CPE maximum at 393 K	[167]

Notation: P = M_w/M_n = polydispersity coefficient, PS = polystyrene, PI = polyisoprene, PB = polybutadiene, PEO = poly(ethylene oxide), PVTMS = polyvinyltrimethylsiloxane, PCP = primitive cubic packing, FCCP = face-centred cubic packing, BCCP = body-centred cubic packing, SAXS = small-angle X-ray scattering, EM = electron microscopy, PM = polarisation microscopy, DMA = dynamic mechanical analysis, DSC = differential scanning calorimetry, PE = photoelasticity, CPE = coefficient of photoelasticity, l/p = long period observed for small X-ray and thermal neutron scattering angles, HEX = hexagonal packing.

Such transitions can occur via two pathways: (1) as a result of the rotation of the macromolecule by 180° about the junction between the blocks, so that blocks of different kinds change places simultaneously; (2) as a result of the "folding" of the macromolecule, i.e. a transition to another phase of only a block of one kind (in this instance the heterobond need not necessarily remain at the interface).§ The predominance of one mechanism over the other should

§This mechanism has also been proposed and examined in a recent communication.[63]

depend on temperature and on the primary structure of the macromolecule.

With increase in temperature, the amplitude of the elastic waves which have developed on the surfaces of the domains increases owing to the increase in the role of thermal fluctuations and the decrease in surface tension. These excitations can become collective and can lead to fluctuations in the form of the domains and to the fluctuation overlapping of neighbouring domains as a consequence of their relative proximity. The stability of the superlattice can therefore be diminished before the molecular mixing of the components take place. As a consequence of the decrease in stability, the long period disappears before the components are completely mixed. For this reason, it would be premature to combine the concepts of the fusion of the superlattice and mixing, as suggested by Leibler.[33]

The ordered SMS has a characteristic period which depends on the molecular parameters. Theory predicts the following expression for the period which is valid for three structures (spherical, cylindrical, and lamellar):

$$D = z a r^{2/3} \chi^{1/6},$$

where a is the effective radius of the inertia of one unit; $z = 3.5\Phi^{1/3}$ for the spherical domains, and $z = 4(3/\pi^2)^{1/3}$ for the lamellar SMS.[37] The $D \propto r^{2/3}$ relation for the lamellar structure has also been predicted by the scaling method.[64,65] However, the $D \propto r^{0.643}$ and $D \propto r$ relations have been predicted[66] for high and low MW respectively. We may note that the theory[66] is inapplicable at low MW, where the approximation of a thin interfacial layer, on which it is based, may not hold.

Table 2. The parameter β and the thicknesses of their interfacial layer Δ (at T = 293 K).

Primary structure	10^{-3} M/x_2, wt.%	P	SMS	Method	β	Δ, nm	Refs.
PS-PI	(21—102)/(0.39—0.60)	1.15	lamellae	SAXS	2/3	1.7—2.6	[67]
PS-PI	M_2:13—144/0.15	—	PCP, PI spheres	SAXS	2/3	1.8	[93]
PS-PI	M_1:93—232/0.25—0.80	1.20	variable	SAXS	—	2.9	[94]
PS-PI	8.5—205/0.50	1.22	lamellae	SAXS	0.79	<5.0	[62]
PS-PI	2.7—11/0.50	—	—	DSC	—	0.8—1.4	[13]
PS-PI			PI spheres		0.63		[93]
PS-PB	M_1:77—560, M_2:11—230/0.12—0.36	1.10	PB spheres, BCCP-paracryst.	SAXS	0.37	2.0—2	[91]
PS-PB	$M_1 = 80$, M_2=13/0.136	1.07	BCCP, PI spheres	SAXS	—	2.0	[92]
PS-PB	4—60/0.53—0.87	—	variable	EM, SAXS	0.58	—	[95]
PS-PB	$M_1 = 7$. $M_2 = 28/0.75$	—	PS spheres	SAXS	—	0.44	[53]
PS-PI-PS	M_1: 7.8; 14.5/0.85; 0.59	1.12	variable	SANS	—	2.9	[94]
PS-PI-PS	32.5—96/0.50	1.25	lamellae	SAXS	—	<5.0	[62]
PS-PB-PS	M_1 =7.8, M_2=43/0.75	—	PS spheres	SAXS	—	0.63	[53]
PI-PS-PI	59.9—134/0.50	1.30	lamellae	SAXS	—	<5.0	[62]

Notation: SANS = small-angle neutron scattering method; for the remaining notation, see the footnote to Table 1.

The experimental data compiled in Table 2 indicate the stepwise character of the variation of D in the experimental range of MW and an appreciable scatter of the results obtained by different workers. In the range of values of M from 2×10^4 to 2×10^5, the empirical relation $D = 0.024\ M^{2/3}$ has been obtained and is valid for di- and tri-BP[67] (it was assumed that $M_0 = M_A + \frac{1}{2}M_B$ for tri-BP of the ABA type). This relation agrees well with the theory developed by Semenov[37] and Zhulina and Birshtein[64,65] and somewhat less well with that of Helfand and Wasserman.[66]

(b) The Influence of the Molecular Weight Distribution

The studies on the symmetry and period of the SMS examined above refer to BP with a narrow MWD, which can be regarded as monodisperse to a first approximation. The influence of polydispersity on the period of the SMS has been studied theoretically.[34,40] A simple expression for the period has been obtained in the limiting case where the content of the type 1 component is low:[34]

$$D = (2\pi a/3)\,[3\,(r_{12}r_{1w} - 1)/2x\bar{\nu}^2]^{1/6},$$

where $r_{12} = \overline{r^3}/\overline{r_1^2}$, $r_{1w} = \overline{r_1^2}/\overline{r_1}$, and $\bar{\nu}$ is the average number of neighbours per short block. For di-BP and tri-BP of type 1—2—1, the parameter $\bar{\nu} = 1$ and D is a maximum, while for tri-BP of type 2—1—2, $\bar{\nu} = 2$ and D is a minimum with $D_{max}/D_{min} = 2$. The period diminishes with increase in the number of blocks in polyblock copolymers.

A smooth increase in the period D with increase in the fraction of long chains in the blend of two di-BP having different block lengths but identical intramolecular contents of the components and with increase in the polydispersity coefficient in di-BP having a Schultz—Zimm distribution has been predicted.[40]¶

The influence of polydispersity on the SMS has been studied experimentally in blends of two monodisperse BP with identical intermolecular components differing in the MW or in the number of blocks.[69] If a tri-BP with a cylindrical SMS is added to a di-BP having a lamellar SMS, then, for a low content of the former, the lamellar structure persists, its parameters varying with composition. This indicates the compatibility of blocks of one kind. In the region of average compositions, two macroscopic phases coexist, each being a saturated solution of one BP in the other and the geometrical parameters of the microphases do not change on dissolution. For high contents of the tri-BP, only a cylindrical structure is formed, its parameters depending on the composition.

If a di-BP with a low MW, in which there is no ordered SMS, is added to a tri-BP having a lamellar SMS, then, for a di-BP content up to 50%, the lamellar structure persists, undergoing only a smooth change in its period, and then sudden disordering takes place. This makes it possible to assign this transition to first-order transitions. Studies have also established that the blending takes place at a molecular level and not at the level of the lamellae.[69] It is noteworthy that the components of the blend were not rigorously monodisperse and that the polydispersity varied with composition.

Analysis of experimental data on BP blends having a lamellar SMS[70] has led to the following observations. Since the number of thermodynamic components in such blends is two, macroscopic separation of the liquid—liquid type can occur in them. The parameter of the interaction of BP of type α with BP of type β is defined by the formula[71]

$$\chi_{\alpha\beta} = \chi_{12}\,(\Phi_{1\alpha} - \Phi_{1\beta})^2 = \chi_{12}\,(\Phi_{2\alpha} - \Phi_{2\beta})^2,$$

¶ It has been noted[40] that the study of Leibler and Benoit[68] proved to be erroneous because of the use in the latter of number-average molecular weights.

where $\Phi_{1\alpha}$ and $\Phi_{2\alpha}$ are the volume fractions of blocks of the first and second kinds in the BP of the α and β types and χ_{12} is the parameter of the interaction between the polymers 1 and 2. Since $\Phi_{1\alpha} = \Phi_{1\beta}$ and $\Phi_{2\alpha} = \Phi_{2\beta}$ in the blends investigated, it follows that $\chi_{\alpha\beta} \to 0$. Consequently, in the absence of microphase separation, there is also no macrophase separation, which can occur only as a consequence of the microlayer formation in one of the BP. A mixture of substances which are compatible in the melt but separate into layers on crystallisation is a low-molecular-weight analogue of the BP blend.

With decrease in temperature or on evaporation of the solvent, the block copolymer α having a higher MW and hence a higher T_{cr}^{micro} than the copolymer β is the first to begin undergoing a phase separation. The copolymer β then acts as a solvent, reducing T_{cr}^{micro}. Presumably the equilibrium structure comprises either a mixture of lamellar domains with periods D_α and D_β (structure I)[70] or of lamellar domains with a period D_{mix} and $D_\beta < D_{mix} < D_\alpha$ (structure II).[40,70] In the first case domains and in the second molecules have been mixed. It has been suggested that structure I is stable, while structure II is metastable, since the chains in the latter are perturbed to a greater extent the greater the difference between the sizes of the chains, which increases the free energy. Structures I and II have been observed respectively for large and small differences between the MW of the block copolymers α and β.

If the rate of the microphase separation is lower than the rate of the translational diffusion of the block copolymers α and β, then the microlayer formation in α leads immediately to phase separation between α and β. On further cooling, β also undergoes microphase separation, which leads to structure I. On the other hand, if the rate of microphase layer formation is lower than the rate of translational diffusion, then there is insufficient time for β to diffuse and structure II results. In a study[73] where structure II was observed, it was postulated that it can be both metastable and can correspond to equilibrium, provided that the MW of α and β do not differ greatly.

(c) The Influence of the Number of Intramolecular Components

Hitherto we have discussed two-component BP. However, from both theoretical and practical points of view, BP with three and more components are of interest. A large number of three-component BP have been synthesised and partly investigated[74–86] but the structure has been apparently studied only for PS–PVMA†–PI.[83] Each block of this BP is segregated in "its own" domain, which leads to a three-phase periodic structure. Overall, the SMS consists of alternating PS and PVMA lamellae, while the PI domains are distributed regularly within the PVMA lamellae, forming a two-dimensional structure (Fig.5d).

The field of study concerned with the SMS of BP with three and more components separated into microphases, the theoretical and experimental investigation of all possible types of symmetry of the SMS, and of the forms of the domains is of current interest; the MSB in them has not been investigated at all.

3. The Size of the Domains

The size of the domains should depend primarily on the MW of the blocks and their temperature. The influence of temperature has not so far been investigated either theoretically or experimentally.

† Poly(vinyl methacrylate) (Editor of Translation).

The influence of the MW has been studied only under conditions remote from the MSB, but the domains have a narrow interfacial layer. Theories concerned with the calculation of parameters of the micro-domain structure such as the size of the domains and the thickness of the interfacial layer as well as their dependence on the MW are based on the reasonable assumption of a thin interfacial layer. These theories predict the sizes of the domains in di- and triblock BP, postulating the symmetry of the SMS: cubic with spherical domains,[47] hexagonal with cylindrical domains,[87] and lamellar.[66] The size of the domains has been recently calculated from first principles.[37] A critical survey of the dependences of the size of the domains on MW for $\chi r \gg 2$, i.e. far from the MSB, has been published[70] for di-BP.

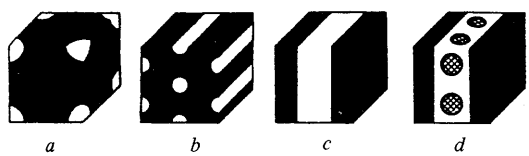


Figure 5. Types of symmetry of the ordered SMS of two- (a, b, and c) and three-component (type ABC) (d) BP:[18] (a) body-centred cubic packing of spheres of phase II in matrix of phase I; (b) hexagonal packing of cylinders of phase II in matrix of phase I; (c) alternating lamellae of phases I and II; (d) alternating lamellae of phases I (A blocks) and III (C blocks) with spherical domains of phase II (B blocks) within phase III.[83]

For spherical domains, the radius of the nucleus of the micelle in the ordered structure is described by the formula[37]

$$R = 2.18\, ar^{2/3}\Phi^{-1/3}\chi^{1/6}.$$

The predicted power dependence of R on the MW with a power exponent of 2/3 agrees with the dependence for lamellar domains,[64,65] the agreement with the conclusions reached by Helfand and Wasserman[66] is less satisfactory, and it differs markedly from the exponent 1/2 predicted by Meier.[96]

In a binary blend of binary BP with blocks having different MW, the thickness of the lamellae, formed by blocks of one kind mixed at the molecular level, is equal to the thickness of the lamellae formed in a BP having the number-average MW of the polymers α and β: $M_n = x_\alpha M_\alpha + x_\beta M_\beta$ (x_i is the number-average fraction of the polymer i). The power exponent in the relation between R and M_n is then 2/3.[70] Thus the size of the domains in BP blends is described by a power relation with the same exponent as in the pure BP. However, a different power exponent, namely 4/5, has also been obtained[69] for BP blends, so that it is necessary to revise these exponents taking into account the non-equilibrium nature of the SMS and the supercooling of the system relative to the MSB.

The degree of homogeneity of the lamellar domains with respect to size proved to be much greater than the homogeneity of the BP with respect to the MW. The degree of polydispersity with respect to the size of the domains is $D_w/D_n = 1.001$, whereas with respect to the MW it amounts to $M_w/M_n = 1.1$, which shows that the macromolecules are packed in domains and that the distribution of the latter with respect to size is much narrower than the MWD.[88]

It is noteworthy that structures with spherical and cylindrical domains have been less thoroughly investigated than the lamellar structures.

4. The Interfacial Layer

It is natural to suppose that, under conditions remote from the MSB, the thickness of the interfacial region is much smaller than the size of the domain. The theories developed in a number of studies[37,47,66,86,96] have been constructed on the basis of this hypothesis, which has been shown experimentally[105] to hold satisfactorily. These theories do not, however, yield an explicit analytical relation for the concentration profile of the block copolymer $\psi(r)$ in the form of a periodic function. We may note that for homopolymer blends, this relation has a form of the Kahn–Hilliard type:[102,103]

$$\psi(r) = \tanh(2r/a_1), \tag{2}$$

in which the thickness Δ of the interfacial layer can be defined as follows:

$$\Delta \equiv \left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\bigg|_{r=0}\right)^{-1} = a_1 = 2a_K/(6\chi)^{1/2} \tag{3}$$

where r is the distance from the interface and a_K the length of the Kuhn segment. Despite the fact that these expressions have been obtained for polymer blends, they have been frequently used also for the analysis of BP.

An expression for the concentration profile under conditions remote from the MSB, valid for lamellar BP and blends, has been obtained recently in an explicit form:[104]

$$\psi(r) = \frac{1-h}{2} F,$$

where $h(r) = k\,\mathrm{sn}(2r/a_1, k)$ is an elliptical Jacobi function with a modulus $k > 0$, a_1 the thickness of the interfacial layer specified by Eqn.(3), and F a complex function of elliptical integrals of the first and second kinds and of the Jacobi function which is independent of r. For $k \neq 1$, the function $h(r)$ is periodic with a period $4(2a_1)^{-1}D$, and, when $k = 1$, i.e. when $D \to \infty$, it is converted into the function (2).

To a first approximation, the thickness of the interface is

$$\Delta(k)/\Delta(1) = [1+2\varepsilon S_1(k)]/k, \tag{4}$$

where $S_1(k)$ is a function whose values lie in the range (0,1), which depends on χr, and ε is a small quantity. For blends, $\varepsilon = 0$ and $\Delta(1) = a_1$, i.e. Eqn.(3) is obtained. Block copolymers have a finite period ($k < 1$) and it follows from Eqn.(4) that they have a thicker interfacial layer.

The thickness of the interfacial layer under conditions remote from the MSB, measured in different studies (see Table 2, and also Henderson and Williams[98] and Shilov et al.[105]) is in the range from 4.4 to 30 Å. The scatter of its values is fairly large and may be associated both with the different ways of calculating the thicknesses from low-angle X-ray and neutron scattering data and with the non-equilibrium nature of the specimens. Various adjustable functions have been used[105] for the electron density profile, but the most realistic equation (4) has not so far been used for analysis.

The influence of this equilibrium on the thickness of the interface has been investigated in relation to BP with spherical domains.[106] The thickness of the interface in a specimen prepared under non-equilibrium conditions (at a temperature below the glass point of one of the components) and then heated above the glass point diminishes exponentially, tending to the limiting values 7.5 Å (the relaxation time is ~60 h). The diameter of the domains then changes little.

The equilibrium thickness determined from experiments on annealed specimens is more than twice smaller than the value calculated by Eqn.(3). The following possible causes of this discrepancy have been quoted:[106] (1) systematic errors in the calculation from low-angle X-ray scattering data to which the greatest contribution may come from the density fluctuations within the domains which has not been taken into account; (2) the inadequate accuracy of the determination of the quantities χ and a in Eqn.(3); (3) the unsuitability of Eqn.(3) at temperatures where one of the components has been converted into a glass. In our view, we may note yet another cause, namely the lack of validity of the application of Eqn.(3), obtained for blends, to BP.

Comparison of the thicknesses of the interfacial layer with the sizes of the domains shows that their ratio does not usually exceed 0.1, which indicates the validity of this intervening layer approximation under conditions remote from the MSB. Nevertheless, the volume fraction of the substance in the interfacial layer can reach considerable values (up to 30%).

Henderson and Williams[99,100] put forward and developed the hypothesis of the asymmetry of the concentration profile in the interface. However, since this hypothesis was based on the temperature variations of viscoelastic quantities, it may reflect the temperature asymmetry and not the spatial asymmetry. At any rate, the hypothesis requires experimental confirmation.

Hitherto we have considered the behaviour of the concentration profile under conditions remote from the MSB. The distribution of concentration in the form of a periodic profile has been obtained on the basis of Landau's theory near the consolute point:[107]

$$\psi(r) = \psi_m(t, k)\sin[r/\delta(t, k)], \tag{5}$$

which is similar to that illustrated in Fig.2. The parameters of this function are defined by the relation

$$\psi_m(t, k) = \psi_0[|t|k^2/(1+k^2)]^{1/2},$$
$$\delta(t, k) = \Delta_0[(1+k^2)/|t|]^{1/2},$$

where $t = T - T_{cr}$, while ψ_0 and Δ_0 are expressed in terms of the coefficients of the Landau expansion. The modulus k is determined by specifying the period $D = 4K(k)$, where $K(k)$ is the total elliptical integral of the first kind.

According to Eqn.(3), the thickness of the interfacial layer is given by

$$\Delta(k, t) = \Delta_0(1+k^2)/|t|k.$$

For a fixed period D, the amplitude of the profile $\psi_m(t) \propto |t|^{1/2}$ and the thickness $\Delta(t) \propto |t|^{-1}$ as the consolute point is approached. For a specified t, the increase in the period ($k \to 1$) converts Eqn.(5) into an expression analogous to Eqn.(2), while the decrease in the period ($k \to 0$) leads to the expression

$$\psi(r) = \psi_0 k|t|\sin(r/\delta).$$

The relation

$$\Delta(k)/\Delta_{min} = (1+k^2)/2k,$$

where $\Delta_{min} = 2\Delta_0|t|$ predicts an increase in the thickness of the interfacial layer with decrease in the period (on passing from a blend to the BP) and the amplitude ratio

$$\psi_m/\psi_m^{max} = [2k^2/(1+k^2)]^{1/2}$$

indicates a decrease in the miscibility of the components in the bulk of the phases on passing from the BP to the blend. This theory is applicable to the range of not unduly low MW of the blocks, which entails an increase in the upper consolute temperature (UCT) and hence is responsible for the difficulty of the experimental test.

The influence of temperature on the thickness of the interfacial layer has been investigated for BP in which the disappearance of the periodic SMS was observed.[50] An increase in temperature did not alter the thickness of the interfacial layer. Such qualitative discrepancy with the theory can be explained either by the fact that the composition differs from the critical composition or by the appearance of a cooperative surface instability (see above), which was not taken into account in the theory.

5. The Chain Conformations in the Domains

The interface should exclude some of the possible conformations of the block and the radius of inertia of the blocks should therefore differ from the radius of inertia of chains of the same length in the absence of an interface. So far only a small number of studies have been devoted to the elucidation of these differences and also of the degree of overlap of neighbouring coils. There are contradictions between ideas concerning the degree of interpenetration of coils of one kind in the direction normal to the surface of the lamella. Some workers conclude that there is slight interpenetration of the coils, so that double layers are produced (Fig.6),[62] while others conclude that they overlap to a marked extent.[70] In the direction parallel to the surface of the lamella, neighbouring coils overlap markedly[67] and are compressed. This compression is accompanied by the swelling of the coils along the normal to the surface, so that the overall radius of inertia remains virtually unchanged.[90]

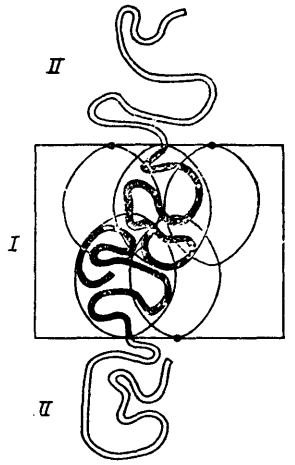


Figure 6. The relative disposition of coils of different blocks in a di-BP within the lamellae: (I) lamellae comprising type I blocks; (II) lamellae comprising type II blocks.

A change in the radius of inertia of the chains relative to the radius of inertia of the corresponding homopolymers have not been observed in the spherical domains.[91] The radius of the domains and their packing are then approximately the same as predicted by Vallance and Cooper.[86] Under non-equilibrium conditions, which frequently obtain in BP with a high MW obtained from a solvent, the macromolecules have significantly greater radii of inertia and the size of the domains at high BP concentrations and/or low temperatures diminishes in accordance with the law $D \propto \Phi_{BP}^{-\gamma}$, where γ = 1/3 for spherical domains, 1/2 for cylindrical domains, and 1 for lamellae.

The average area of the interface per chain (between neighbouring chemical cross-links joining the blocks along the interface), S/N, where N is the number of chains passing through the interface, is described by the following empirical scaling law for both narrowly dispersed BP and their blends:

$$S/N \propto M_n^{1-\beta}, \tag{6}$$

where the exponent β = 2/3. We may note that, among all the types of average molecular weights (M_n, M_w, M_z), M_n leads to the best adjustment of the relation. A relation of type (6) with an exponent of 1/3 is applicable to both lamellar[70] and spherical[91] domains.

6. The Grain Size

An ordered inter-domain structure is limited by the grain size, which is of the order of several microns. The grain boundaries are two-dimensional defects analogous to the boundaries of a crystallite in polycrystalline substances and of magnetic or electrical domains in ferromagnetic and ferroelectric materials. Rod-shaped grains have been observed in BP with lamellar and cylindrical domains, the grains being distributed at random relative to one another.[110,111] These anisotropic grains are strained and are surrounded by cavities and inclusions. It has been suggested that the stresses arise during the evaporation of the solvent.

The optical axis of the grain is parallel to the axis of the cylindrical domains and can be directed either parallel or at an angle to the axis of the rod-shaped grain. Single supercrystals exhibit double refraction associated with the difference between the refractive indices of the microphases.[112,113] If the optical axis is at an angle to the rod, then, on heating, it becomes parallel to the latter owing to the relaxation of the elastomer phase and the rotation of the cylinders.[112] The size and shape of the grains have been investigated by the low-angle scattering of depolarised light, which depends on the anisotropy of the shape and boundaries of the grains.[110,114] The domains do not contribute to the scattering, since their size (300 to 500 Å) is much smaller than the wavelength. The scattering by mechanical stresses is negligible. Apart from the defects of the type of grain boundaries, defects of the type of dislocations have also been observed.

Using special methods, it is possible to obtain macroscopically anisotropic specimens,[21] which are sometimes called single supercrystals by analogy with single crystals. There exist three methods for obtaining them: (1) by the shear flow of the melt,[21,115] (2) by extrusion,[116] and (3) by casting from a solution with a high boiling point of the solvent.[117]

7. Kinetics of Microlayer Formation

The kinetics of separation into microphases (in the abrupt transition from the single-phase state to the region where two-phase states are stable) in BP should be in general analogous to the kinetics of

the separation into macrophase layers in mixtures, although it should have its characteristic features. However, despite the vigorous studies on the kinetics of separation of blends (as regards homopolymer blends, see, for example, Refs.118–131), the separation of BP melts into layers has been little investigated.

The early stages of the spinodal decomposition have been investigated theoretically in a study[34] where it was shown that periodic (with a period $L_0 = 2\pi/k_0$) inhomogeneities form a train with a length l ($l \gg L_0$), which increases in accordance with the diffusion law

$$l^2(t) \propto l_0^2(t)/\tau(k_0, \Delta T),$$

where l_0 is the length of the train under the conditions of slight supercooling, while the amplitude of the inhomogeneity increases exponentially. The period L approaches L_0 after a time. These theoretical predictions have not so far been confirmed experimentally.

The experimental study of the kinetics of the appearance of the structure is complicated by the need to use powerful sources of X-ray (including synchrotron) radiation or neutron radiation, which make it possible to reduce significantly the exposure time.

There exists the possibility, in principle, of studying the kinetics of microlayer formation by simpler methods, when the components are capable of vitrifying. Such systems can be quenched at various stages of the phase separation and a change in the phase state can be investigated from vitrification parameters, which depend on the amplitude and size of the fluctuations. The increase in the heat capacity jump on vitrification with increase in the phase separation time has been observed by this method.[10,24] In the first instant, there was no jump, which is most probably due to the large scatter of the period and the low amplitudes of the fluctuations. After the appearance of the jump, its width changes insignificantly, which shows that fluctuations with a small scatter of the period contribute to the vitrification jump. The heat capacity jump, corresponding to the second phase, has not been observed either because of the small amount of the phase (it has not been recorded also in the phase separation of blends of homopolymers)[131] or owing to the small size of the phase (it has been shown[163] that, when the size of the particles of the phase is less than 60–70 Å, its vitrification is not recorded). However, in other experiments cooling in the postulated single-phase state leads to the observation of the two vitrifications, although one of them is highly diffuse.[51]

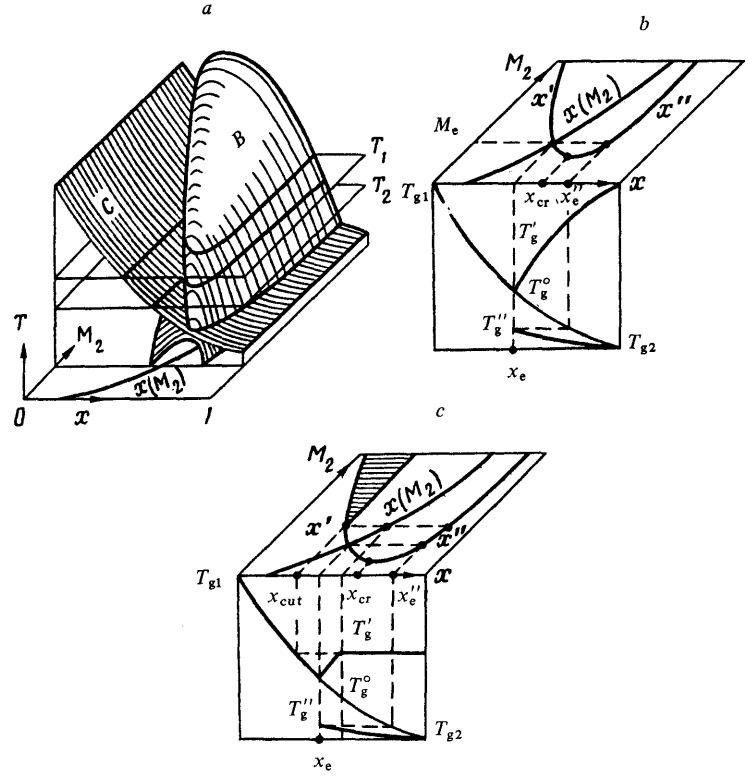


Figure 7. Construction of the vitrification diagrams for BP with M_1 = const. by the surface intersection method:[10] (a) three-dimensional representation of the surfaces in terms of the coordinates $T-x-M_2$ [B— binodal surface; C— vitrification surface for a single phase system (VSSS); $x(M_2)$—overall composition curve; T_1 and T_2—planes corresponding to the temperatures T_1 and T_2]; (b) section through the surfaces by the T_1 plane and the corresponding VD (x' and x''—compositions of the coexisting phases; x_{cr}—critical composition; x_e, M_e—the point at which the composition curve enters the region under the binodal surface; x_e''—the composition of the second phase at the point of entry; T_{g1} and T_{g2}—glass points of the pure components; T_g^0—VCSS; T_g' and T_g''—glass points of phases I and II respectively); (c) section through the surfaces by the T_2 plane ($T_2 < T_1$) and the VD corresponding to the section (x_{cut}—cut-off composition).

The kinetics of the disappearance of the SMS after a sharp increase in temperature have been investigated for PS–BP di-BP with $M_n = 5.2 \times 10^4$ and $\chi_{PS} = 0.30$ (to reduce the temperature of the transition to the BP, 60% of solvent was introduced).[132,133] Microdissolution occurred rapidly (after ~30 s) and accelerated on raising the final temperature. The scattering curve in the final stage corresponded to scattering by a homogeneous BP melt with a broad and weak maximum due to the effect of the correlation hole.

III. MUTUAL INFLUENCE OF MICROLAYER AND GLASS FORMATION

Separation into microlayers and glass formation exert a mutual influence on one another. On the one hand, microlayer formation determines the vitrification of the system if the phase state of the material does not change on cooling to the vitreous state. On the other hand, vitrification can be influenced in microlayer formation if during its occurrence one of the phases can vitrify, which leads to the deviation of the phase state from equilibrium.

The vitrification of BP is determined by parameters of the concentration profile (in the more general case, the density profile) such as the amplitude of the profile, the size of the domains, and the width of the intermediate layer. For different coefficients of the thermal expansion of the phases, the SMS should play a role. The commonest method of investigation of vitrification involves the construction of plots of T_g against the MW of a fixed composition or the construction of plots of T_g against composition for a fixed length of one of the blocks (usually the rigid block, i.e. one with a higher glass point T_{g1}). In relations of this kind, not one but several of the above parameters of the concentration profile contribute to T_g. The estimation of the contributions of different parameters requires special consideration in each case. The direct problem involves in this instance the study of vitrification in systems with a known concentration profile and is still at the beginning of its solution. The converse problem is usually solved: conclusions concerning the different parameters of the profile are reached from the vitrification investigated.

1. Vitrification in Block Copolymers which have Undergone Microphase Separation at Temperatures above the Glass Points of the Components

We shall assume that the systems have a binodal curve with a UCT which lies above the T_g of both components. On transition of the system from the single-phase state to the region of stable two-phase states, at temperatures above the T_g of both components, vitrification does not influence the phase separation and the system can, in principle, reach the state of equilibrium. Subsequent quenching from the phase separation temperature (annealing temperature) freezes (as a consequence of vitrification) the structure of the liquid corrsponding to a definite temperature. By quenching the melt from a specific point in the phase diagram, it is possible to compare the vitrification parameters at the given point on the $T-x$ phase diagram.

(a) Vitrification Diagrams (VD)

As already mentioned, the influence of phase composition on the temperatures of the transitions to the BP can be conveniently represented in terms of the $T-x-M_2$ variables for a fixed M_1. We shall consider initially the behaviour of the glass points on varying the composition of the BP annealed at a temperature T_1 (to which corresponds the T_1 plane in Fig.7a). Before the composition curve enters the region underneath the binodal surface, the system remains in the single-phase state and its single glass point should obey the relations characteristic of T_g for single-phase systems comprising two components. The glass point T_g in this composition range may be described by different semiempirical formulae obtained for SP and homopolymer blends,[135–138] which are also suitable for single-phase BP.[139]

When the composition curve enters the region under the binodal surface, a second phase appears, to which corresponds a second glass point. Depending on whether the composition curve enters from the left or from the right relative to the consolute point, either low-temperature or high-temperature vitrification will occur abruptly on the T_g–composition diagram (VD) (Fig.7b). On further increase in the length of the flexible component, the glass points of both phases should move away from one another, since the separation range $x''-x'$ increases. For this reason, a dip should be observed in the upper branch, whose minimum should be located at the point corresponding to the onset of phase separation. The first and second derivatives should change abruptly at this point.[10,24] For very large lengths of the flexible blocks, the composition curve can emerge from the region underneath the binodal surface and the upper T_g' branch then terminates.

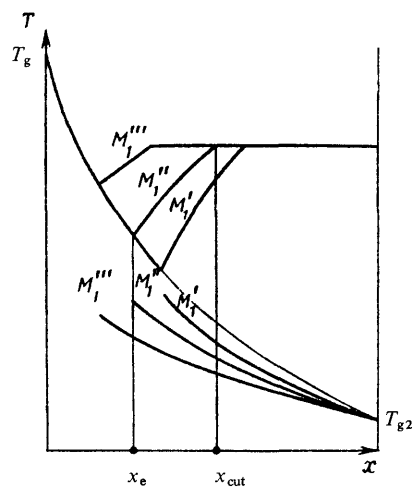


Figure 8. The influence of M_1 on the form of the vitrification diagram (the increase in the number of primes in the designations of the curves denotes an increase in M_1); x_{cut}—cut-off composition; x—content of the second component.[10]

With decrease in the phase separation temperature, the branches on the VD should move apart and the bifurcation point should shift towards lower contents of the flexible component. The increase in M_1 for a fixed phase separation temperature is analogous to a decrease in temperature for a fixed M_1 (Fig.8).

The type of VD predicted by the methods of topological thermodynamics has been observed experimentally for polyblock[39,84,140] (Figs.9a and 9b) and di- and tri-block[141] (Fig.9c) BP. For a low

content of the flexible component, a single vitrification is observed and the T_g of the BP varies in accordance with the same law as that governing SP (this has been tested both by measurements on SP and by calculations using the corresponding formulae). Thus, in the above composition region, the BP considered can be regarded as single-phase. The decrease in T_g depends not only on the content of the flexible component but also on the MW and the primary structure of the BP (di- or tri-block or star-shaped).[141] In BP with specific intermolecular bonds, an increase in M_1 for the same composition entails a decrease in T_g.[39,140] The decrease in T_g to the MSB amounts to several tens of degrees according to some data[141] and reaches 130 K according to others.[140]

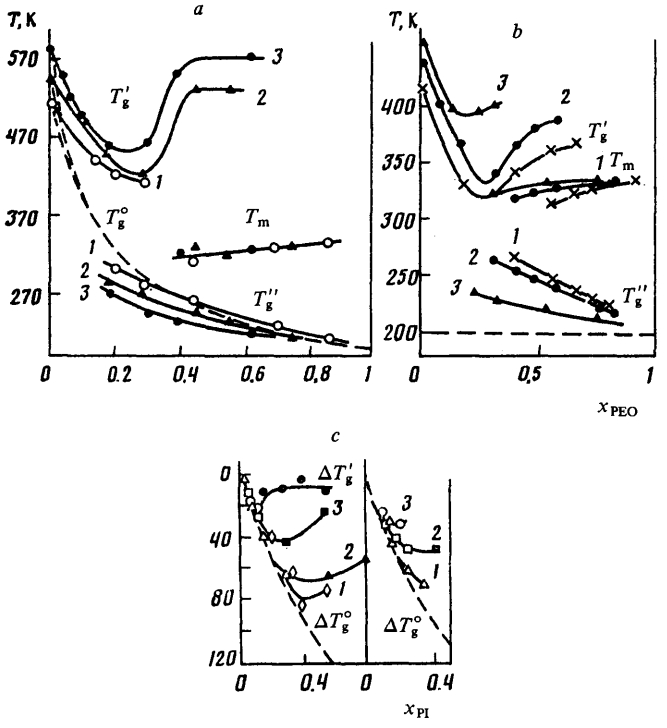


Figure 9. Experimental vitrification diagrams for BP (the increase in the number of the curve corresponds to an increase in M_1): (a) $(PA-PEO)_n$[39] (T_m—melting point); (b) $(PASO-PEO)_n$;[84] (c) PS–PI (on the left), PS–PI–PS (on the right);[141] $\Delta T_g' = T_{g1} - T_g'$; $\Delta T_g^0 = T_{g1} - T_g^0$ (the open and filled symbols denote single-phase and two-phase states respectively); x—the weight content of the component with a low glass point.

The second region—the region before the onset of phase separation—is characterised by a deviation of T_g' from the T_g of SP and by the appearance of a second transition to a vitreous state (T_g''). In some cases, the onset of the deviation coincides approximately with the appearance of the second transition,[39,84] while in others the second transition appears after the start of the deviation.[141,143] An attempt has been made to explain the latter finding by the presence of a large fraction of interfacial layers, which is unlikely. The increments in the compositions of the components were not always sufficiently small. For this reason, one cannot determine exactly the start of the appearance of the second vitrification and the form of the dip in the upper branch, although there is no doubt about the existence of the dip. A decrease in M_1 shifts the MSB towards higher values of x and increases the depth of the dip in the upper branch, which is consistent with the predictions by the geometrical method. The width of the heat capacity jump then increases.[141] After its abrupt appearance, the temperature T_g'' initially differs markedly from T_{g2}, but approaches the latter as x increases. We may note that for the BP discussed, the vitrification curve for single-phase systems (VCSS) is concave and for this reason the addition of the rigid component to the phase with a high content of the flexible component results in an appreciably smaller change in the T_g for the phase than the introduction of the same amount of the flexible component into the rigid phase. It is therefore difficult to observe the deviation of T_g'' from T_{g2}.

In the third region (with a high content of the flexible component), two T_g, differing from T_g^0, are observed, which indicates the existence of two amorphous phases. In this composition region, T_g' either approaches T_g for the corresponding homopolymers[39,141] or reaches a limiting value without attaining T_{g1}.[84] In the latter case, microphase separation is apparently inhibited by the vitrification of the rigid phase (cf. subsection 2 below).

The close correspondence between the forms of the VD predicted by the method of topological thermodynamics, which is based on the hypothesis that T_g depends solely on the phase composition, and the experimental VD as well as the large difference $T_g' - T_{g1}$ (up to 130 K) permit the conclusion that the change in the glass points of the BP indicated is responsible for the change in the amplitudes of the concentration profile as the composition is varied. The behaviour of T_g on crossing the MSB has been explained[141] by the presence of a large fraction of the interfacial layer, which appears to be inadequately justified.

(b) Vitrification in the Two-Phase Region in the Vicinity of the MSB

In the experimental studies examined above, the composition and MW ranges investigated included the MSB. The behaviour of the glass point as the microlayer formation boundary is approached from the side of the two-phase region has not been more thoroughly investigated, although the proximity to the boundary is not always clear because the position of the boundary itself is frequently unknown. It has been noted in many cases that, as the MSB is approached by reducing the MW of the blocks, T_g' falls and T_g'' increases (Table 3). Under these conditions, T_g' diminishes faster than T_g for the corresponding homopolymer. Extrapolation of T_g' and T_g'' to di-BP[108] and poly-BP[104] for a constant composition (decrease in the MW of the blocks in the former case and with increase in the number of blocks, keeping the overall MW constant, in the latter) leads to the intersection of the branches at the point which coincides with the T_g for the SP having the same composition.

Although the fact that the glass points approach one another is not open to doubt, there is as yet no unambiguous explanation for it. This is because the decrease in the MW of the block entails a decrease in the size of the domain and can lead simultaneously to a change in the phase composition and in the thickness of the interfacial layer and also in the MSB. The displacement of T_g is therefore attributed to a series of phenomena: (1) the increase in the content of the interfacial regions;[141,144,145] (2) the increase in the surface/volume ratio owing to the change in the SMS;[153] (3) the

intensification of the dynamic interaction of the flexible and rigid blocks which leads to joint segmental motion;[108] (4) the effect of interfacial tension between the microphases;[161,162] (5) the increase in the average free volume of the vitreous phase under the influence of the mixing near the interface;[153] (6) the change in phase composition.[39,84] We believe that the mechanisms (3) and (6) are the most probable.

In the study of vitrification and of the influence on the latter of the parameters of the concentration profile, it is essential to know the phase state of the melt, since BP are frequently obtained by cooling the melt, which is accompanied by the freezing of its structure. In most studies on vitrification in BP, the phase state of the melt at temperatures above T_{g1} remained unknown. The investigation[134] in which the transition of the BP, tentatively from a two-phase state to a single-phase state,[49] was observed from the change in the viscosity of the melt and electron microscope data is important for this reason. After annealing above the temperature of the postulated transition to the single-phase state and subsequent quenching, very diffuse vitrification of the rigid phase is observed, so that it proved impossible to determine where this process begins. On the other hand, the vitrification of the flexible phase occurred at the same temperature as in the slowly cooled specimens. The values of ΔC_{p1} and the width of the vitrification range of the rigid phase decrease with decrease in the cooling rate, although the heat capacity jump remains more than a factor of two greater than in the corresponding homopolymer. These data apparently indicate a higher content of the flexible sigments in the rigid phase, although, despite the higher degree of mixing, the BP nevertheless remain in the two-phase state after annealing above the transition temperature and subsequent quenching. The existence of a two-phase structure can be associated both with the higher rate of layer formation on cooling in the single-phase state and with the existence of a microheterogeneity at temperatures above the rheological transition temperature (see the discussion of the cooperative capillary instability of the SMS with retention of the two-phase structure in subsection 2 of Section I above). Nor can one rule out also that the diffuse nature of the vitrification is associated with the influence of vitrification on the phase separation (see below).

(c) Vitrification in the Far Two-Phase Region

Apart from the increase in T_g'' with increase in the length of the flexible block, its decrease has also been observed in the two-phase region[155–160] (Table 3). Depending on the nature of the blocks, the decrements in the glass point $T_g'' = T_g'' - T_g^{homo}$ reached 19 K,[155] 15 K,[158] 13 K,[156,157] and 10 K.[160,161] The study of the SMS showed that such decrease is observed only for compositions such that the flexible phase constitutes closed inclusions in a vitreous matrix.[155,157] This led to the reasonable conclusion that the decrease in T_g'' is associated with the difference between the thermal expansion coefficients of the inclusions and the matrix. As a result of the covalent bonds between the flexible chains and the skeleton, the volume of the flexible inclusions cannot diminish on cooling the melt to the extent that they would have decreased in the absence of the skeleton (matrix). This should lead to a "negative pressure", extending the flexible domain. Estimates carried out for a spherical BP domain within a PS matrix from the formula[155]

$$\sigma_i = 2(\alpha_i - \alpha_m)E_iE_m\Delta T/[6E_m(1-2\mu_i) + 3E_i(1-\mu_m)]$$

Table 3. The behaviour of the glass points of the block copolymers when the parameters of the primary structure of the macromolecule are varied.

No.	Primary structure	Type of relation plotted	Position relative to the MSB	SMS	Character of variation of T_g	Method of study	Refs.
1	$(PA-PEO)_n$	$T_g(x)$, $T_g(M_2)$, M_1 = const	on either side	variable	Fig.9*a*	DSC	[39]
2	$(PASO-PEO)_n$	$T_g(x)$, M_1 = const	ditto		Fig.9*b*	DSC	[84]
3	PS-PI, PS-PI-PS	$T_g(x)$, M_1 = const	»	*	Fig.9*c*	DSC	[141]
4	$(PTMP-PDMS)_n$	$T_g(M_1)$, x = const	»	*	merging of T_g' and T_g'' with decrease in M_1	DMA	[147]
5	PS-PI	$T_g(M_1)$, $x = 0.5$	in two-phase region	lamellae	mutual approach of T_g' and T_g'' with decrease in M_1	DSC, NMR	[108]
6	PS-PB, PS-PI, PS-PEO	$T_g'(M_1)$	ditto	*	ditto	DSC	[150—152]
7	$(PS-PB)_n$, PS-PB-PS	$T_g(n)$, x, M_0 = const	»	lamellae	mutual approach of T_g' and T_g'' with increase in n	DMA	[144]
8	PS-PB-PS, PB-PS-PB, PS-PI-PS	$T_g(M_1)$, x = const	»	»	mutual approach of T_g' and T_g'' with decrease in M_1	DMA	[145]
9	PS-PDMS	$T_g'(M_1)$, $T_g(M_2)$	»	variable	ditto	DSC	[148, 149]
10	PS-PMS, PMS-PS-PMS, PS latexes		in remote two-phase region	*	T_g' and T_g'' remain unchanged	DSC	[154]
11	PS-PB, PS-PB + homo-PS	$T_g''(M_0)$, $T_g''(R_{sph})$	in two-phase region	variable	T_g'' decreases on formation of spherical domains	DMA	[155]
12	$(PCUS-PDMS)_n$	T_g''	ditto	*	decrease in T_g''	DMA	[156, 157]
13	PC-PDMS	$T_g''(M_1)$	ditto	*	decrease in T_g''	DMA	[164]
14	PPSO-PDMS	$T_g''(x_2)$, M_1 = const	»	variable	decrease in T_g'' with decrease in x_2	DSC	[158]

Notation. PA = polyarylate, PASO = poly(arylene sulphoxide), PDMS = polydimethylsiloxane, PMS = polymethylstyrene, PC = polycarbonate, PCUS = polycarbonate with terminal urethane groups, PPSO = polyphenylsilsesquioxane, and PTMP = polytetramethyl-*p*-silphenylenesiloxane.

* The supermolecular structure was not investigated.

(subscript i refers to the inclusion and m to the matrix; σ_i is the thermal stress developed within the highly elastic domain, α the thermal expansion coefficient, E the modulus of elongation, and μ the Poisson coefficient) lead to a negative pressure of 78 MPa. The decrease in T_g, calculated from the relation $dT_g/dp = 0.24$ K MPa^{-1} and equal to 18.7 K, agrees well with the experimental value.

After a time, the free volume should be lost from the inclusion as a result of the relaxation of the vitreous matrix (the compaction of the specimen), which diminishes the hydrostatic extension of the flexible inclusion with which the observed decrease $\Delta T_g''$ is apparently associated. However, one should note that thermal stresses should apparently act not only on the spherical flexible domains but also always when the rigid phase forms a monoconnected region, i.e. the matrix. In particular, they should act also on cylindrical flexible domains. It may be that a decrease in T_g'', which begins already when the content of the rigid block is $\sim 50\%$, is associated with this factor.[156,158] The relaxation time of the free volume owing to the rearrangement of the matrix should decrease with increase in the content of the flexible block.

It is remarkable that T_g'' depends on the MW of the flexible block and not on the size of the domains, the decrease in MW resulting in a fall of $\Delta T_g''$.[155] Although this has been explained[155] by the decomposition of the flexible blocks, which tends to lower the thermal strain, this hypothesis requires proof.

Generally speaking, thermal stresses should alter T_g'' not only far from the phase separation boundary (where a rigid matrix still persists) but also in its vicinity, provided that the composition curve enters the region under the binodal surface far from the consolute point. The phase compositions and hence the thermal expansion coefficients will then differ greatly, which will lead to an effect by the rigid matrix on the flexible inclusions.

The behaviour of T_g'' in the remote two-phase region permits the following conclusions. The identity of T_g'' for the BP with a long rigid block and T_g'' for the homopolymer having the same MW in the range of MW where T_g of the homopolymer still depends on the MW is not consistent with the concept of the free volume of the terminal units, since the free volumes of the BP and the homopolymer should differ significantly.[148,155,164] This permitted the logical hypothesis[164] that the flexible segments attached to the end of the rigid block are so mobile that they can transmit their mobility to the rigid block, which should thus behave as if it had a free end. This idea agrees with the conclusion[108] that the disposition of the rigid block in the tri-BP macromolecule (at the centre or at the ends) does not influence T_g.[108,152] However, we may note that, in contrast to Kanbur's study,[164] where the decrease in M_2 for x = const. did not alter T_g', the decrease in M_2 from M_1 = const. in the study of Levin et al.[157] lead to a decrease in T_g'.

Comparison of the behaviour of T_g' in a series of BP, where the rigid block was the same and different components were selected as the flexible block, showed that, at a remove from the phase separation boundary, T_g' is independent of the chemical nature of the flexible block and of the BP composition.[148–152] The chemical nature and the MW of the flexible block influenced T_g' only when the MW and the composition were close to the MSB.[152] From this, one may conclude that, since the compatibility of different oligomers with the rigid oligomer varies, under conditions remote from the phase separation boundary there is no blending whatever of unlike segments in the vitreous microphase.

The width of the jumps in the BP thermal conductivity is greater than for the corresponding homopolymers and only the upper part of the vitrification region with T_g'' broadens in the direction of higher temperatures (up to 32 K) and only the lower part of the vitrification region with T_g' broadens towards lower temperatures (down to 26 K). A decrease in the content of the rigid block, accompanied by a decrease in the size of the inclusions of the rigid phase, led to the broadening of the vitrification region on the low-temperature side as far as 43 K.[154] The width of the vitrification region of the flexible phase as a function of the specific surface of the interface fits on a single curve for all the systems investigated regardless of the nature of the interface (i.e. for both BP and latexes), which has led to the conclusion that the width is determined solely by the area of the interface. The widening becomes appreciable for a specific surface of $\sim 10^4$ m^2 kg^{-1}, which corresponds to a microphase whose size is 0.5 μm. From this it follows, in particular, that in homogeneous BP the vitrification range should be the same as in homopolymers. It has been suggested[154] that an increase in the temperature of the upper boundary of the vitrification region is caused by the fact that the two vitreous phases are separated by a solid interface. It was not appropriate to take into consideration the thickness of the interfacial layer, which should be very small in the remote two-phase region, for the explanation of the broadening of the vitrification region.

Thus the above analysis of the data and ideas available at the present time on the vitrification of BP undergoing microphase separation at temperatures above T_{g1} permit the following conclusions. In the region of the single-phase state, T_g obeys the relations valid for SP. In the region of the transition through the MSB, the glass point of one of the phases deviates from the relation describing SP and a second transition to a vitreous state appears. In the two-phase region near MSB, the T_g of the rigid phase is usually below the T_g of the corresponding homopolymer and the T_g of the flexible phase is above it. Both these effects can be explained either by an increase in the similarity of the phase compositions as the phase separation boundary is approached or by the dynamic interaction of the linked blocks. As the boundary is approached, $\Delta C_p'$ decreases while $\Delta C_p''$ increases, the width of the vitrification region in the rigid phase increasing. However, the treatment of the changes in the intensity and width of the transitions is not unambiguous and requires further study.

In the remote two-phase region, both glass points agree with the T_g of the corresponding homopolymers and the heat capacity jumps correspond to the contents of the components, but the width of the jumps is as a rule greater than for the homopolymers. The widening of the range corresponding to the low-temperature vitrification is directed towards higher temperatures, while the corresponding widening of the high-temperature vitrification is directed towards lower temperatures. This can be explained by the presence of an interface, the widening becoming more pronounced with increase in the specific area of the interface. It may be that this effect contributes also to the widening in the region of the MSB. In the composition range where the flexible phase represents a polyconnected region, a decrease in the T_g of the flexible phase compared with the corresponding homopolymer is observed. This decrease is associated with the stretching hydrostatic pressure, which is exerted by the rigid matrix on the domains comprising flexible covalently bound chains and is associated with the difference between the thermal expansion coefficients of the domain and the matrix.

It appears essential at the present time to investigate quantitatively the vitrification in BP whose phase state and SMS have been characterised not only in the region between the glass points of the components but also in the melt. The study of the vitrification in

the region of MSB taking into account the kinetics of phase separation appears especially important. Furthermore, it is essential to devise a theory of the vitrification of BP in all the regions of the phase diagram.

2. Vitrification in Block Copolymers Undergoing Microlayer Separation at Temperatures between the T_g of the Components (the Influence of Vitrification on Microlayer Formation)

If the phase separation temperature is below the boundary temperature T_b, determined by the intersection of binodal curve with the VCSS (Fig.10), then the fluctuation concentrations develop until their amplitude in the half-period with a large content of the rigid component reaches the cut-off value x_{cut} at which the glass point for this half-period, having increased, becomes equal to the phase separation temperature.[10,24] Thus the microphase with a high content of the rigid component passes to the vitreous state before the attainment of equilibrium as regards composition. This effect should shorten the separation range in the phase diagram and in the VD.

The influence of vitrification on the phase separation has been observed experimentally.[10,24] After the system has passed from the single-phase to the two-phase region, the thermogram does not show initially any anomalies. This is apparently associated with the fact that in the initial instant there are only smooth concentration fluctuations with a large scatter of periods, which leads to the pronounced spreading of the transition to the vitreous state. A small thermal conductivity jump then appears and grows as a function of time, while the temperature corresponding to the point of inflection (T_g) increases monotonically (Fig.11). With decrease in the phase separation temperature (T_{ps}), the glass point, determined after annealing for 1 h, decreases linearly by more than 100 K with a slope close to unity, which corresponds to the predictions of the geometrical method. No other factor, apart from the change in the phase composition can apparently shift T_g by more than 100 K. The analogy between the freezing of the phase separation as a result of vitrification and the self-inhibition of the hardening reaction of network polymers is noteworthy.

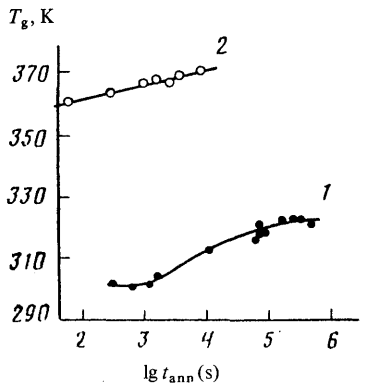


Figure 11. Dependence of T_g' on the annealing time in the PA–PEO BP:[10] (1) T_{ann} = 290 K; T_{ann} = 350 K.

The geometrical analysis based on the consideration of the intersections of the binodal surface, the vitrification surface for a single phase system (VSSS), and the temperature plane (T-plane), permits the construction of all possible types of T_g–composition and T_g–MW relations in the BP in the case where vitrification influences the phase separation.[10,24] This analysis presupposes that T_g depends solely on the phase composition. As an example, Fig.7a illustrates the mutual intersection of the binodal surface, the VSSS, and the T-plane. So long as the composition curve does not intersect the curve of the coexisting compositions, the system remains in the single-phase state. In this region, T_g should vary in accordance with the law for a single-phase system. If the composition x_e at which the composition curve joins the coexisting phases curve is greater than x_{cut}, then, after the start of phase separation, the difference between the phase compositions will increase and the glass points will therefore diverge. However, as soon as the composition of the phase with a high content of the rigid component reaches x_{cut}, it ceases to change on further alteration of the overall composition.

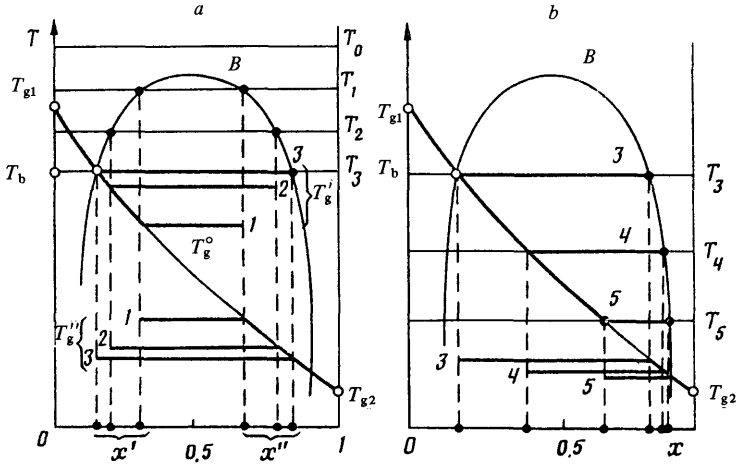


Figure 10. Construction of VD for blends in the case where the binodal curve and the VCSS are superimposed.[10] B—binodal curve; T_g^0—VCSS; T_b—boundary temperature; x' and x''—compositions of the coexisting phases; the numbers of the VD branches correspond to the subscripts of the T_i: (a) $T_i > T_b$; (b) $T_i < T_b$.

The upper branch in the VD beyond the cut-off composition should become horizontal (Fig.7).

The decrease in T_{ps} should reduce x_e and should increase x_{cut}, as a result of which the bifurcation point in the VD should shift towards lower values of x and and the horizontal plateau should be displaced towards lower temperatures. When the temperature falls so much that x_e becomes smaller or equal to x_{cut}, the bifurcation point should shift towards higher values of x and the dip in the upper branch should disappear. The plateau should again be displaced downwards as a linear function of T_{ps}. The increase in M_1 influences the form of the BP analogously to the decrease in temperature. All the possible forms of the VD, reflecting the influence of vitrification on the phase separation in BP, have been published.[10] VD, whose form is analogous to those discussed above, have been observed experimentally.[39,84,140,141] The attainment of a plateau below T_{g1} has been established most reliably by Godovskii et al.[84]

The above discussion shows that in the two-phase region, T_g for the rigid phase can be reduced owing to the presence of an excess of the flexible component in this phase. Since in the study of vitrification the BP was heated only slightly above T_{g1} in the vast majority of instances, the difference between the non-equilibrium and equilibrium compositions should diminish with increase in M_1 because the UCT then shifts towards higher temperatures and the equilibrium compositions approach the vertical axes. The decrease in T_g' with decrease in M_1 is apparently associated with this factor.

The study of the superposition of the layer formation and vitrification processes in BP and polymer blends has only just begun and detailed investigation of this problem is needed because such superposition is frequently encountered in practice.

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The above discussion on the microlayer and glass formation in block copolymers shows that in real systems these processes frequently superimpose and influence one another. For this reason, not only a detailed investigation of each separately but also of their mutual superposition and influence is needed. Despite the evident advances in the study of the mechanism of microlayer formation, we are still at the beginning of the path leading to the investigation of processes leading to microheterogeneity in BP. The influence of the MWD and of the number of blocks on microlayer formation, the microlayer formation kinetics, the transitions from one SMS to another, and the superposition of microlayer formation and vitrification have been studied inadequately. The importance of this field follows from the prospect that BP may be employed for technical purposes and also from the fact that BP constitute the simplest synthetic heteropolymers with a more or less ordered primary structure and serve as the first support of the bridge connecting synthetic and biological polymers. Specific synthesis of heteropolymers with an ordered primary structure will undoubtedly lead in the future to the complete construction of this bridge. The phase and microphase transformations in biological objects, which are multicomponent mixtures of heteropolymers and low-molecular-weight substances from the molecular point of view, apparently play an important role in the existence and evolution of living organisms.

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