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The Structure and Properties of Block Copolymers and Their Solutions

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The characteristics of the microphase structure of block copolymers and the decisive role of the incompatibility of the components of the block copolymer in this structure are examined and the factors influencing the type of structure and the size of the structural elements are discussed. A close relation is demonstrated between the segregation processes in dilute solutions and micelle formation on concentrating the solution, on the one hand, and the colloidal properties of solutions of copolymers determined by micelle formation and the structures of the solid polymers, on the other. The mechanical and physical properties of block copolymers are considered mainly in relation to thermo-elastomers.
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I. INTRODUCTION

Block copolymers constitute a specific class of polymers, the main chains of the macromolecules of which consist of two or more sections (blocks) each of which is in its turn made up of many identical units. The macromolecule is usually constructed of blocks of different types, so that it exhibits diphilic properties: This type of structure (in contrast to statistical copolymers characterised by a random alternation of units) leads to a combination of heterogeneous properties (for example the occurrence of two glass points) and even to the summation instead of the averaging out of the properties of the homopolymers. By varying the molecular weights of the blocks and their ratios within wide limits and hence the structure of the block polymers, which is determined by these parameters, it is possible to obtain polymers with specified properties.

The possibility of such modification of polymers together with the grafting of one polymer on another was suggested for the first time by Mark[1] at the beginning of the 1950s and since then research in this field has been developing vigorously[2-6]. Mechanochemical and other methods for the synthesis of block copolymers were used initially[7]. The discovery of anionic polymerisation and "live" polymers[8,9], whereby it is possible to obtain rigorously unimolecular block with any required molecular weight and to combine them with one another, was of fundamental importance for the successful development of this field. The method has been widely used to synthesise two-block (AB) and three-block (ABA) copolymers with a wide variety of compositions, the majority of which have been listed by Fetters[10]. A highly regular molecular structure is essential for the creation of long-range supermolecular order, which determines, as will be shown below, the most valuable properties of block copolymers. The polycondensation method was later used to obtain many-block polymers[11-14], whose molecular structure is not, however, quite so regular and this leads to certain characteristic features of these block copolymers, which will be considered below.

It is noteworthy that (despite the limited number of factual data available at the time) Soviet investigators Kargin, Plate, and coworkers were the first to conclude as early as 1960 that the occurrence of two glass points of a block copolymer, characteristic of its components, and in general the independent behaviour of these components can be accounted for solely by aggregation processes and the segregation of each component in the form of microphases or microregions[15,16]. Subsequently these ideas were extensively developed[17-19].

The formation of a two-phase structure and the degree of layer formation are determined by the degree of incompatability of the components constituting the blocks. The properties of block polymers are to a large extent determined by the size, form, and relative disposition of its structural elements. Microlayer formation processes and the formation of a structure occur as a rule in the solution from which the block copolymer is obtained and the properties of the solid block copolymer are therefore determined by those of the solution and the thermodynamic properties of the solvent. In connection with the foregoing, we shall consider the following problems in this review: (1) relation between the microlayer formation process in block copolymers and the incompatibility of its components and comparison of the relation with layer formation in mixtures of polymers; (2) dependence of the conformation of the macromolecules of block copolymers in dilute solutions on the segregation process and the relative conformational and thermodynamic properties of block copolymers and statistical copolymers; (3) transition from intramolecular to intermolecular aggregation as the solution becomes more concentrated, the formation of micelles, and the consequent manifestation of colloidal properties by block copolymers and their solutions; (4) dependence of the type of structure of the block copolymer on a number of factors; the possibility of predicting this dependence by means of models designed on the basis of statistical thermodynamic theories; the influence of the structure of the block copolymer on its mechanical and physical properties.

II. CHARACTERISTICS OF THE MICROLAYER FORMATION PROCESS IN BLOCK COPOLYMERS

Having applied the Flory–Huggins theory of solutions [20], Scott obtained the following expression for the free energy of mixing of two polymers [21]:

$$\Delta G_{mix} = \frac{RTV}{V_r}\left(\frac{v_A}{x_A}\ln v_A + \frac{v_B}{x_B}\ln v_B + \chi_{AB} v_A v_B\right), \quad (1)$$

where V is the total volume of the system, V_r the volume per lattice site, v_A and v_B are the volume fractions of components A and B in the mixture, x_A and x_B the degrees of polymerisation of these components, and χ_{AB} is the interaction parameter, which is the fundamental characteristic of the miscibility of the components, i.e. their thermodynamic compatibility (or incompatibility).

The parameter χ_{AB} is frequently expressed in terms of Hildebrand's solubility parameters, which are listed in handbooks [22]:

$$\chi_{AB} = \frac{V_r}{RT}(\delta_A + \delta_B)^2, \quad (2)$$

where δ_A and δ_B are the solubility parameters of components A and B.

For critical conditions, corresponding to layer formation in the system, we have $\partial^2\Delta G_{mix}/\partial v_A^2 = \partial^3\Delta G_{mix}/\partial v_A^3 = 0$, and

$$(\chi_{AB})_{cr} = \frac{1}{2}\left[\frac{1}{x_A^{1/2}} + \frac{1}{x_B^{1/2}}\right]^2, \quad (3)$$

$$(v_A)_{cr} = \frac{x_B^{1/2}}{x_A^{1/2} + x_B^{1/2}}; \quad (v_B)_{cr} = \frac{x_A^{1/2}}{x_A^{1/2} + x_B^{1/2}}, \quad (4)$$

where $(v_A)_{cr}$ and $(v_B)_{cr}$ are critical layer-formation concentrations.

Eqn. (3) shows that χ_{AB} depends on the molecular weight of the polymer. A large value of the latter for polymers results in a corresponding value of χ_{AB}, which is always small, so that the majority of polymers should be incompatible. This has been confirmed experimentally: of the enormous number of pairs of polymers investigated, the majority of which (102 pairs) have been listed in a review [23], only a few pairs proved to be compatible; all others formed layers starting from a definite critical concentration [defined in terms of Eqn. (4)] over a shorter or a longer period [24]. The application of Scott's theory to ternary polymer A–polymer B–solvent systems showed that the incompatibility in mixtures diminishes significantly with increasing molecular weights of both polymers and is independent of the solvent; however, this postulate is valid only in the sense that polymers which form layers in one solvent also form layers in another. The critical concentration proved to be different in different solvents and the difference is manifested to a greater extent the bigger the role played in the polymers by specific interactions with the solvent.

Similar relations have also been observed for block copolymers [25,26]. Krause [27] examined the case of phase layer formation in block copolymers when all the A–B contacts have been disrupted under the condition of an average ratio of components A and B and identical molecular weights of all the molecules. She obtained the following expression for $(\chi_{AB})_{cr}$:

$$(\chi_{AB})_{cr} = -\frac{V_r}{V_A n_A v_B}\ln[(v_A)^{v_A}(v_B)^{v_B}], \quad (5)$$

where v_A and v_B are the volume fractions of components A and B, V_A is the molar volume of the A repeating unit, and n_A is the number of these units. Calculation of the compatibility of polymers having the same molecular weight and taken in the same proportions in the mixture and in the block copolymer enabled the author [27] to conclude that the two components are more incompatible in a block copolymer than in a mixture of polymers. This conflicted with other theoretical studies [28], but subsequently, when account was taken of the surface free energy at the boundary between the microphase regions, Krause also concluded [29] that layer formation in the mixture proceeds more readily than in the block copolymer. Furthermore, it was shown [29] that, for the same molecular weight of the block copolymer, the formation of layers becomes increasingly more difficult with increase of the number of blocks, owing to the increase of the surface energy and of the number of segments at the boundary of the microphases, which leads to a decrease of the freedom of their movement and of the total entropy.

As in mixtures of polymers, a better compatibility of components A and B in block copolymers is achieved in solvents whose affinities for each component are most similar, i.e. the incompatibility of the pair of polymers is determined by the selectivity of the solvent in relation to them [30]. An unusual feature of the microlayer formation process in block copolymers and their solutions, compared with macrolayer formation in solutions of mixtures of polymers, is the retention of the integrity of the block copolymer specimen (i.e. the impossibility of the formation of two layers in its solution) owing to the combination of heterogeneous blocks in the block copolymer macromolecules via covalent bonds.

We may note that the blocks of A and B may be regarded as individual components only when their thermal motions are mutually independent. This requires a sufficient length and flexibility of at least one of the blocks and a decrease of flexibility requires an increase of length, i.e. of the degree of polymerisation of the block. With decrease of the size of the block, boundary conditions play an increasing role.

III. CONFORMATIONS OF THE MACROMOLECULES OF BLOCK COPOLYMERS IN DILUTE SOLUTIONS

The fundamental conformational characteristics of the macromolecule in solution are the mean square distance between its ends and its unperturbed dimensions in a θ-solvent, while one of the parameters used to estimate the degree of interaction between the polymer and the solvent in dilute solutions is the degree of swelling of the coil. According to the Fixman–Stockmayer equation [31], the unperturbed dimensions of the macromolecule are related to the intrinsic viscosity by the expression

$$[\eta]M^{-1/2} = K_\theta + 0.51\Phi_0 B \cdot M^{1/2}, \quad (6)$$

where $K_\theta = \Phi_0(\overline{R}_0^2/M)^{3/2}$, $\Phi_0 = 2.68 \times 10^{23}$ is Flory's constant, $\overline{R}_0^2$ the mean square distance between the ends of the chain, $B = 2(1/2 - \chi)/V_1\rho^2 N_a$ the long-range interaction parameter, χ Flory's interaction parameter, M the molecular weight of the polymer, V_1 the molar volume of the solvent, ρ the density of the solvent, and N_a the Avogadro number.

For homopolymers, the slope of the plot of $[\eta]M^{1/2}$ against $M^{1/2}$ (i.e. the parameter B) is different in different solvents, but $K\theta$ (equal to the intercept which the plot makes on the ordinate axis), which characterises the θ-conditions, is a constant and is independent of the nature of the solvent. In statistical copolymers, $K\theta$ is not constant and does depend on the solvent, so that the

conditions for the compatibility of such polymers also depend on the solvent. In this connection, Dondos and Benoit note [32], that θ-conditions do not actually exist for statistical polymers. This is because of the hetero-contacts between groups A and B leading to a deviation from the Gaussian distribution and to a significant increase in the size of the chain compared with the corresponding homopolymers.

The situation in block copolymers is different. It is known [20] that the following relations hold under θ-conditions with $\chi_{AB} = 0$ for a Gaussian conformation of a linear polymer chain consisting of two components:

$$\overline{R}^2_\theta = (\overline{R}^2_A)_\theta + (\overline{R}^2_B)_\theta \,, \tag{7}$$

$$[\eta]_\theta = [(x[\eta_A]_\theta)^{2/3} + \{(1-x)[\eta_B]_\theta\}^{2/3}]^{3/2} \,. \tag{8}$$

For $\chi_{AB} \neq 0$, these equations are valid when fairly long blocks A and B are completely separated in space, so that the Gaussian conformation holds for each [33]. This form of separation of heterogeneous blocks has been called segregation and the conformation itself, in which blocks A and B are separated in space and intramolecular heterocontact are reduced to a minimum, is called the segregated conformation.

Thus the more complete the segregation, the closer the chain size of the block copolymer to the sum of the sizes of the homopolymers making up these blocks. Under these conditions, the intrinsic viscosity of the block copolymer in effective solvents is intermediate between the intrinsic viscosities of the two homopolymers A and B, whose molecular weight is equal to that of the block copolymer; the θ-temperature, the degree of swelling of the coil, the second virial coefficient, and the precipitation point obtained when a precipitant is added to a solution of the block copolymer are also usually intermediate between the corresponding values for the homopolymers [25,33-54]†. In the absence of segregation, these quantities exceed the corresponding values for the two homopolymers. Comparison of the intrinsic viscosities and chain sizes calculated by Eqns. (7) and (8) with the experimental quantities indicates the degree of segregation in solution.

The segregation of block copolymers in solution was first pointed out by Burnett et al. [55] They showed that the thermodynamic and hydrodynamic parameters of the block copolymer macromolecule also depend on the ratio of the overall masses of the blocks. Plots of the θ-temperature, the entropic and energetic components of the free energy of solution, the intrinsic viscosity, and unperturbed size, and the swelling coefficient of the coil pass through a maximum as a function of the composition of the block copolymer, which corresponds to the component ratio A : B = 1 : 1. This behaviour was subsequently confirmed by other workers [56].

The majority of studies on the conformations of block copolymers were carried out using the same systems—two- and three-block copolymers of polystyrene and poly(methyl methacrylate) in different solvents without varying the component ratio, but the data obtained by different workers conflict; the intrinsic viscosity is consistent with Eqn. (8) in some cases, while in others it is greater or smaller than the calculated value. Thus, either owing to the different degrees of incompatibility of the blocks, manifested in the experiments of different workers, or owing to the quality of the given solvent (the incompatibility increases particularly when the solvent is selective with respect to one of the blocks [25,33,48]), or owing to the different molecular weights of the blocks or their ratio, the conformation of the molecule may be fully segregated, partly segregated, or pseudo-Gaussian, in which there is interpenetration of heterogeneous blocks [33, 45,52]. Froelich [38] showed that, under the conditions of complete separation, the chain length of the block copolymer is 15% greater than in the absence of segregation.

The fully segregated conformation of a two-block polymer can have the form of a "molecular micelle" [57], which comprises a nucleus, consisting of the coiled insoluble block surrounded by the soluble extensible block (Fig. 1*a*), or it has the shape of a loop [34], the size of which is smaller the longer the coiled block (Fig. 1*b*).

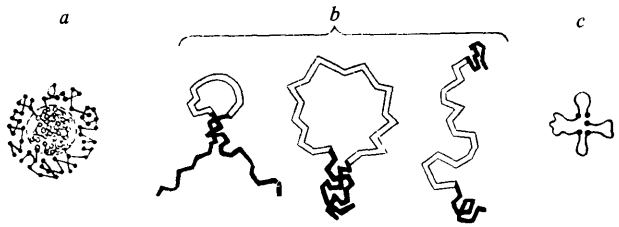


Figure 1. Various conformations of the aggregated macromolecule in solution: *a*) two-block copolymer—"molecular micelle" [77]; *b*) three-block copolymer with different block lengths—"loop" conformation (the insoluble block is indicated by the continuous line) [35]; *c*) a many-block copolymer—"bead" conformation (the circles indicate the insoluble blocks and the lines the soluble blocks) [58].

Bresler et al. [58] proposed a model for the segregation of many-block copolymers on the basis of the block copolymer of styrene and isoprene with a block ratio of 4 : 5 which they investigated. In an effective solvent, such a macromolecule obeys Gaussian statistics, while in a selective solvent the insoluble blocks are "precipitated" from solution, forming a rigid nucleus surrounded by the flexible "filaments" of the dissolved blocks. An example of such segregation is illustrated in Fig. 1*c*. Since, depending on the solvent employed, different blocks are "precipitated", the properties of the block copolymer obtained from solution depend significantly on the nature of the solvent. There has been yet another study on the properties of many-block polymers in dilute solutions [59]: the authors compared the block copolymers of styrene and isoprene with a rigorously constant molecular weight in which the number of blocks was varied from two to nine (with a corresponding change in the length of the blocks) in solution in toluene and its mixtures with methanol and iso-octane. It was found that the intrinsic viscosity increases with decrease of chain length and hence with increase of the number of blocks, since an increasing number of the latter "avoid" one another, which leads to an increase of the size of the macromolecule.

The same behaviour has been observed also when the properties of two- and three-block copolymers were

† It is noteworthy that the possibility of achieving θ-conditions [38-40,49] for all block copolymers is not evident and requires further investigation.

compared. Overall, the properties of their dilute solutions differ little, but the intrinsic viscosity of a three-block copolymer is frequently greater than that of a two-block copolymer having the same molecular weight; this indicates a less complete segregation in a three-block copolymer and is consistent with the theoretical conclusion that layer formation in a block copolymer is hindered with increase of the number of blocks (see above).

Measurements of intrinsic viscosities in dilute solutions of block copolymers also make it possible to estimate qualitatively the degree of incompatibility of their components. The application of the equations of statistical thermodynamics to solutions of polymers is known to be capable of yielding a relation between the hydrodynamic parameters of the macromolecule (i.e. the ratio of the intrinsic viscosities in the given solvent and in a θ-solvent), on the other hand, and quantities characterising the thermodynamic interaction of the polymer with the solvent, on the other[60]. Relations have been proposed for copolymer solutions which also include quantities characterising the interaction of the components with one another[61,62]. It was found that in many instances the theories developed for dilute solutions of homopolymers are also valid for solutions of block copolymers in a solvent which is effective in relation to both components. Deviations from these relations are associated with the action of selective solvents, which lead to a significant alteration of the conformations of the block copolymers.

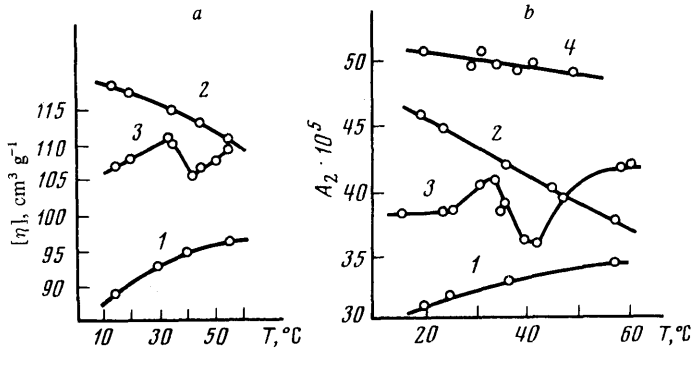


Figure 2. Dependence of the intrinsic viscosity (*a*) and the second virial coefficient (*b*) on temperature in homopolymers [poly(methyl methacrylate) (curves *1*) and polystyrene (curves *2*)], in a methyl methacrylate–styrene block copolymer (curves *3*), and in a statistical copolymer (curve *4*).[52,63]

The change in the conformation of the macromolecules of block copolymers with temperature, which is expressed in the temperature dependence of the intrinsic viscosity $[\eta]$ and of the second virial coefficient A_2 (determined by the light scattering method), characteristic of block copolymers alone, is of considerable interest. Fig. 2*a* shows that, with increase of temperature, the intrinsic viscosity of the copolymer increases initially to a maximum and then falls sharply, after which it again begins to increase. The nature of this variation is always the same, but the degree of the increase of the viscosity, the size of the peak, and the corresponding temperature depend significantly on the solvent and also on the ratio of the blocks and their molecular weights. All the observed transitions are fully reversible with respect to temperature. The peak is attributed to a conformational transition[45,52,63,64]. The segregated conformation exists below the transition temperature and the insignificant increase of viscosity is associated with the formation of a certain number of heterocontacts with increase of temperature, while the decrease of viscosity beyond the transition is due to the interpenetration of previously separated segments, which leads to a decrease of the volume of the macromolecule.

The validity of this treatment is confirmed, for example, by the fact that a film of a polystyrene–polyisoprene block copolymer, prepared below the transition temperature (i.e. when the segregated conformation of the copolymer obtains), has two glass points corresponding to the two separate blocks, while in a film prepared above the transition temperature, where the separation of the blocks is less pronounced, the glass point of polystyrene is appreciably displaced towards lower temperatures (the shift depends on the component ratio)[64]. The temperature of this conformational transition should be close to the glass point of the block copolymer, which is closely related to the degree of incompatibility of its components in the given solvent (i.e. the greater the incompatibility, the higher the glass point[33]). For example, it has been shown[32] that $\chi_{AB} = 0.031$ in benzene, 0.046 in tetrahydrofuran, and 0.053 in *p*-xylene for styrene–methyl methacrylate copolymers. The transition temperature of this block copolymer is smallest in benzene, where the incompatibility is a minimum. Urwin and Giralomo[64] believe that the transition temperature is near the θ-temperature of the copolymer and may be the most important characteristic of the block copolymer.

The temperature dependence of the second virial coefficient A_2 is analogous to that of the intrinsic viscosity, as can be seen from Fig. 2*b*, where data for a statistical copolymer and a block copolymer are also compared.

When a precipitant is added to the solvent, i.e. when the quality of the latter is impaired, the transition temperature increases, in conformity with the ideas described above[52]. On the other hand, at a constant temperature, the addition of a precipitant (particularly one selective for one of the blocks) to a dilute solution of the block copolymer leads to a sharp decrease of the intrinsic viscosity[12,65–67], which is associated with the coiling of the insoluble blocks and their displacement to the interior of the macromolecule. It is of interest that, in solutions of polystyrene–poly(methyl methacrylate) block copolymers treated with a precipitant specific to poly(methyl methacrylate)[67], the same content of precipitant gives a lower intrinsic viscosity of the block copolymer regardless of its composition than the solution of poly(methyl methacrylate) alone. This demonstrates the decisive role of the blocks insoluble in the given system, which become coiled, and the independence of their behaviour of the presence of polystyrene blocks; they apparently form microgel particles in the soluble polystyrene. On the other hand, owing to the stronger interaction between the components as the concentration of the component which becomes insoluble following the addition of the precipitant is reduced, in a statistical copolymer the viscosity

increases with increase of the concentration of the precipitant—this is yet another manifestation of the difference between the conformations of block copolymers and statistical copolymers.

However, a decrease of the viscosities of both homopolymers and block copolymers is not observed in all solvent–precipitant mixtures. It has been shown [63] that this effect depends on the parameter χ_{12} of the interaction between the solvent and the precipitant: when $\chi_{12} > 0$, the addition of the precipitant causes a fall of the viscosity, while under conditions where $\chi_{12} < 0$, the addition of the precipitant results in an increase of the viscosity.

We shall consider yet another approach to mixtures of polymers and block copolymers. The solvent in which component B is dissolved behaves as a less effective solvent in relation to component A than the pure solvent itself owing to the incompatibility of these components. From this it follows that the intrinsic viscosity and the size of the macromolecule of A will decrease in the presence of component B. This has been confirmed by systematic studies on mixtures of polymers by viscometric and light scattering methods [68–73]. Such joint study of the solvent and component B as a single solvent for component A made it possible to apply the so called method of invisible species in order to determine the molecular weight of one of the components in the presence of the other: if the solvent and component B have the same refractive indices, the solution of component A in this mixture is optically a two-component system and light is scattered solely by component A, whose molecular size and weight can thus be determined by measuring the light scattering parameters. The aggregation of the system can be followed by the same procedure—from the change in the molecular weight of component A in the presence of component B. This method can also be used to determine the molecular weights of block copolymers.

In connection with the possibility of determining the molecular weight of a block copolymer by the light scattering method, we shall mention briefly the general approach to the estimation of the molecular weights and the microheterogeneity of copolymers proposed for the first time by Benoit and coworkers [74,75] and widely used by many investigators [76]. Since the increments in the refractive indices of the copolymer components are different, for a correct measurement of the molecular weight of the block copolymer it is necessary to know the increment of the refractive index in the given solvent for each component. The relation between the measured apparent molecular weight M_{app}, the true molecular weight of the block polymer M_W^{AB}, and the molecular weights of the individual blocks M_W^A and M_W^B is expressed by the following equation:

$$M_{app} = (\nu_A^2/\nu^2) M_w^A x + (\nu_B^2/\nu^2) M_w^B (1-x) + 2(\nu_A \nu_B/\nu^2) M_w^{AB}, \quad (9)$$

or the equivalent equation

$$M_{app} = M_w^{AB} + 2[(\nu_A - \nu_B)/\nu] P + [(\nu_A - \nu_B)/\nu]^2 Q, \quad (10)$$

where ν_A, ν_B, and ν are the increments in the refractive indices of the homopolymers A and B and of the block copolymer AB respectively, x is the weight fraction of component A, and P and Q are parameters characterising the inhomogeneity of the composition of the copolymer. By determining the molecular weight of the block copolymer in three different solvents, we obtain a system of three equations from which the values of M_W^{AB}, M_W^A, and M_W^B can be determined.

IV. COLLOIDAL PROPERTIES OF BLOCK COPOLYMERS AND THEIR SOLUTIONS

Gallot et al. [77] noted that the following cases of the dissolution of block copolymers in selective solvents are possible. If the soluble block is short or if its content in the copolymer is unduly low and its affinity for the solvent is insufficient, the block copolymer does not dissolve at all. If the degree of solvation of the soluble blocks and their number are sufficient for the dissolution of the polymer, the latter results either in a molecular dispersion (the solution is then completely transparent), or a polymolecular dispersion, or a micellar solution. The molecular dispersion corresponds to solution of the "macromolecular micelles" mentioned above; a coiled insoluble block in such a solution is fully surrounded by a shell of the uncoiled soluble block, which prevents it from coming into contact with other insoluble blocks. With increase of the concentration of the polymer, intermolecular contacts arise between the insoluble blocks and, when combined, the latter give rise to a lyophobic nucleus surrounded by fairly flexible lyophilic blocks (Fig. 3*a*), i.e. micelles analogous to soap micelles in aqueous solutions are formed. Thus, at moderate concentrations, solutions of block copolymers are typically colloidal.

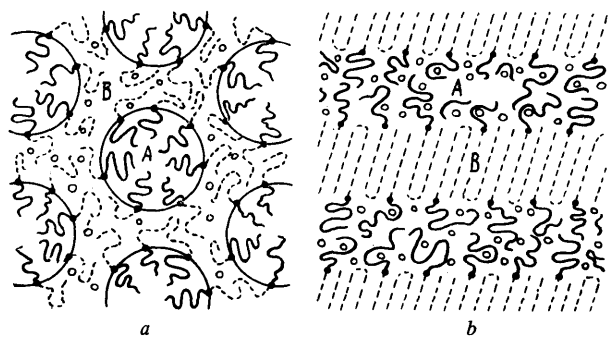


Figure 3. Types of colloidal micelles of block copolymers. The influence of the solvent on the type of micelles of a styrene (A)–ethylene oxide (B) block copolymer; solvent: *a*) nitromethane; *b*) dibutyl phthalate (the solvent molecules are shown as circles) [98].

A very important consequence of the micellar nature of solutions of block copolymers is the possibility of varying the type of micelles, i.e. the composition of the nucleus and the shell, by selecting various precipitants. Thus Merrett showed for the first time [78,79], in relation to a graft copolymer of natural rubber and poly(methyl methacrylate), that it is possible to obtain a "hard" or "soft" form of the polymer by inducing the formation of micelles and the subsequent precipitation of either poly(methyl methacrylate) or the rubber. Virtually at the same time, Korotkov [9] and Bresler [58] obtained analogous results for a styrene–isoprene block copolymer. Such studies were frequently carried out subsequently [80–82] and established the possibility of varying within wide limits the properties of objects obtained from solutions, by altering the nature of the binary solvent.

The critical concentration for micelle formation (CCM) depends on the chemical structure and the number of blocks in the polymer, the phase state, the molecular weight, and the quantitative ratio of the blocks as well as the thermodynamic properties of the solvent in relation to the polymer [77,83-86].

The selectivity of the solvent is usually achieved by adding a θ-solvent which is effective for both components or a substance which does not dissolve one of the blocks [83]. For example CCM for styrene–butadiene block polymers in toluene amounts to 9%, [84] while after the addition of ethanol to dioxan in the same block copolymer micelles are formed starting from a concentration of 1%. [83] CCM and its dependence on the nature of the solvent are closely related to the degree of segregation of the macromolecules of block copolymers in dilute solutions in various solvents: the more pronounced the segregation in the given solvent, the lower the value of CCM in the latter.

In order to assess micelle formation, light scattering measurements are used in the first place [87-91] as well as viscosity and diffusion measurements, the determination on their bases of the ratio of the hydrodynamic particle radii [83,87] and the study of sedimentation in an ultracentrifuge [89]. The characteristic variation of the intensity of the scattered light during micelle formation as the temperature is altered is seen in Fig. 4. A molecular solution is formed at 65°C in a block copolymer of polystyrene and polyisoprene with a block ratio of 1 : 3 in n-decane, which is a selective solvent for polyisoprene; when it is cooled to 55–40°C, the intensity of the scattered light increases sharply, indicating the appearance of large scattering particles and a further increase of their dimensions, while below 25°C the scattering intensity is again constant and corresponds to the establishment of a stable micellar solution [88].

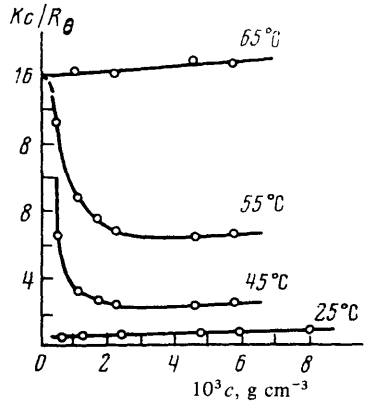


Figure 4. Dependence of the light scattering intensity $R\theta$ in a solution of a polystyrene–polyisoprene block copolymer on temperature and concentration [87].

The molecular weight of the micelles is usually greater by two orders of magnitude than that of the individual macromolecules (10^6 in the example under consideration compared with 10^4), but their radius of inertia is extremely small (~200 Å) which demonstrates their compact nature. This is also indicated by the intrinsic viscosity and the Huggins constant [83]. The weight fraction of the micelles in solution increases with increase of the polymer concentration and impairment of the quality of the solvent, but their molecular weight remains constant under these conditions [83].

A characteristic property of micellar solutions of block copolymers is their similarity to lyotropic liquid crystals. The manifestation of this phenomenon involves the double refraction [84,91,92], optical anisotropy [91], and rainbow colours [84,93] of such solutions. Vanzo showed that below CCM (to which a light transmittance maximum corresponds), the solution is colourless, while above CCM it acquires various colours, which depend on the concentration (ranging from pale blue to green and pink) [84]. In 1% solutions of the polystyrene–poly(ethylene oxide) block copolymer in solvents selective with respect to both blocks, the Kerr effect is observed [75]. All these characteristics indicate the formation in moderately concentrated solutions of block copolymers having specific ordered structures which do not exist in solutions of homopolymers.

These microheterogeneous highly ordered structures were investigated in particular detail by Skoulious and coworkers for polystyrene–polyvinylpyrrolidinone (both components are amorphous) [92,94-97] and polystyrene–poly(ethylene oxide) or polystyrene–poly(propylene oxide) (one of the components crystallises) [97-107] block copolymers. At certain concentrations in selective solvents, these systems form gels, which the authors referred to as mesomorphic phases characterised by a high degree of order. The structure of these gels depends on the nature of the solvent and the concentration of the block copolymer. For example, in nitromethane, which is a solvent for poly(ethylene oxide) but does not dissolve polystyrene, the insoluble phase forms discrete structural elements in the form of cylinders in a continuous dispersion medium consisting of a solution of poly(ethylene oxide) blocks in nitromethane (Fig. 3*a*). In dibutyl phthalate, which dissolves polystyrene but not poly(ethylene oxide), the crystallising poly(ethylene oxide) forms structural elements in the form of plates in a solution of polystyrene in dibutyl phthalate (Fig. 3*b*). We shall consider the structures of these gels in greater detail below in connection with the general characteristics of structure formation in block copolymers. On solidifying the block copolymer, by evaporating the solvent, the structural elements or micelles involved in an ordered arrangement remain dispersed in the dispersion medium or matrix consisting of soluble blocks. These micelles have the same compositions, constituting regions of a microheterogeneous system with interfaces, which are, however, linked by chemical bonds with the continuous dispersion medium. In order to indicate their difference from the usual phase particles and the usual micelles, these "micelles" can be called microphase regions. In the non-Soviet literature, the term "domain" is used for this purpose.

The wide variety of the colloidal properties of solutions of block copolymers is also manifested by their emulsifying action in oil–water systems, by the increase of the mutual compatibility of the homopolymers, by the stabilisation of organic latexes, etc. [108-118] The compatibility of block copolymers with homopolymers having the same structures as the blocks constituting the block copolymer and the acquisition of some compatibility in the presence of block copolymers by polymers which are usually incompatible are due to a kind of solubilisation, i.e. the dissolution of the homopolymer in the corresponding "micelle" of the block copolymer. Riess et al. [108] and

subsequently other workers[109,110] suggested that the transparency of the resulting films be used as a criterion of the compatibility of the systems obtained. These data can be conveniently represented graphically on triangular diagrams in which the transparency of the film is plotted against the composition of the ternary systems block copolymer (with a specific block ratio)–homopolymer A–homopolymer B. It was found that, for a ratio of blocks A and B in the block copolymer of 80:20 or 20:80, there is no solubilisation at all; it occurs when the amounts of the blocks are more similar and is a maximum for the 50:50 ratio[108].

This procedure can be used to increase the compatibility of only those homopolymers whose molecular weight is lower than that of the corresponding blocks, which is important for solubilisation. Furthermore, solubilisation is more pronounced, the most distinct the segregation of the micelles in the solution of the block copolymer[111]. For example, polyisoprene is solubilised in polyisoprene micelles and its solubilisation therefore occurs for the compositions of the block copolymer in the solvents or their mixtures which promote the segregation of the polyisoprene micelles in the block copolymer. Polystyrene is solubilised most effectively under conditions where polystyrene blocks are segregated as a discrete phase; it has been shown that up to 30% of polystyrene may be solubilised[111]. Despite the turbidity of the solubilised solutions, they are extremely stable[111].

If the molecular weight of the homopolymer exceeds that of the corresponding block, it is not solubilised and may be dispersed in the continuous phase, but after a time it is separated in the form of a gel[112]. The size of the spherical regions of the block copolymer where solubilisation takes place increases and they are frequently converted into an elliptical form[111]. It has been shown by the light scattering method that, although the molecular weight of the mixed micelles of the styrene–isoprene block copolymer and a styrene homopolymer increases from 10^6 for the block copolymer to 10^{10}, their size increases comparatively little and does not exceed 300 Å.[111]

The same solubilisation phenomenon has been observed by the low-angle X-ray scattering method[113]. It has been shown that it is common for structures of any type—not only spherical but also cylindrical and lamellar (see below), and in all cases the size of the structural elements of the block copolymer increases on solubilisation and in many instances there is a change in the conformation of the block copolymer macromolecule. Homopolymer molecules become ordered under these conditions, like the blocks of the block copolymer, and a case has been described[113] where homopolystyrene with a molecular weight of 60 000 is solubilised, apparently as a result of a change in the conformation of the homopolymer molecules on solubilisation in a polystyrene block with a molecular weight of 40 000.

It is noteworthy that the increase of the compatibility of the polymers is observed only in the presence of block copolymers; neither statistical nor graft copolymers give rise to this effect. According to Molau and Wittbroadt[86], this effect cannot be regarded as a true increase of compatibility; it is purely colloidal in nature and is associated with the formation of a finer dispersion of one phase in the other.

A thermodynamic study by Unoue and coworkers[109,110] showed that, when CCM is found outside the binodal curve separating the region of the homogeneous solution from the region corresponding to its separation into layers comprising solutions of the block copolymer and the homopolymer, solubilisation occurs and the resulting solution is homogeneous; on the other hand, when CCM is found within the binodal curve, layer formation occurs even before a film is produced from the solution and there is no solubilisation.

Block copolymers are used as emulsifying agents both in order to obtain emulsions of high-molecular-weight substances in organic solvents and to prepare emulsions of low-molecular-weight substances. The first case includes emulsions obtained on polymerisation of a monomer in which a polymer of another type is soluble[114-117]. This entails the formation of a homopolymer and a graft or block copolymer, which prevents the separation of the two polymers into layers and promotes the formation initially of an emulsion of the polymer in the monomer (for example, of natural rubber in styrene), which then becomes fixed after the polymerisation of styrene. One such example is impact-resistant polystyrene, obtained by this procedure, in which natural rubber particles are dispersed in solid polystyrene.

The emulsifying effect of the polystyrene–poly(ethylene oxide) block copolymer on the water–toluene system has been investigated[118] and it has been shown that 1% of the block copolymer is sufficient for the formation of the emulsion, that the most stable emulsions are obtained in the region of phase reversal, and that a three-block copolymer makes it possible to emulsify a larger amount of toluene in water than does a two-block copolymer.

Thus it follows from the foregoing that the colloidal properties of solutions of block copolymers are manifested starting from extremely low concentrations of the latter. Such colloidal nature of the block copolymer solutions make it possible, on the one hand, to employ them in many specific applications and, on the other, it constitutes the basis for the formation of the structures of solid block copolymers obtained from these solutions.

V. THE TYPES OF STRUCTURES OF BLOCK COPOLYMERS AND THE FACTORS INFLUENCING THEM

The structure of solid block copolymers, which can be of three main types (spherical, cylindrical, or lamellar phase formations), constitutes an extremely unusual manifestation of the supermolecular organisation, which is characteristic of polymers in general—not only in the crystalline but also in the amorphous state. As a result of the fairly considerable length of the block, whose macromolecules are homogeneous, the structural elements with interfaces formed under conditions where the blocks are incompatible are not only homogeneous with respect to size but are also arranged in a very regular manner. Despite the amorphous nature of the components constituting the block copolymer, its structure is therefore in most cases characterised by long-range order and the presence of a lattice with long periods, which is usually characteristic of single crystals only; spherical structural elements are packed in a cubic lattice, cylindrical elements are in a hexagonal lattice, and plates are arranged parallel to one another in the plane of the film[119-123]. Similar instances of the presence of long-range order in non-crystalline materials are also known for certain non-polymeric systems: soaps, minerals[124], latexes[125], silica gel[126], etc. The detection of such order in block copolymers, where the microheterogeneity of the system leads to a distinct two-phase state, and the study of the characteristics of such structure formation are therefore of great interest.

The principal methods for the investigation of the structures of block copolymers are electron microscopy [127-132] and low-angle scattering of X-rays [133-139]. A distinct representation of the structure of electron microscope photographs is achieved by shading thin films of block copolymers containing double bonds with the aid of OsO_4 vapour in order to increase the difference between the electron densities of the microphases [140]. If the experimental conditions are such that the electron photomicrographs of thin films show structural elements in only one plane, then the volume fraction of these aggregates can be calculated from their shape and distribution. On the basis of the conditions governing the packing of the aggregates, the volume fractions of different types of structures are defined by the following relations [121]:

$$\varphi_{sph} = 0.74\left(\frac{D_{sph}}{A_{sph}}\right)^3, \quad (11)$$

$$\varphi_{cyl} = 0.91\left(\frac{D_{cyl}}{A_{cyl}}\right)^2, \quad (12)$$

$$\varphi_{lam} = \frac{D_{lam}}{A_{lam}}, \quad (13)$$

where D is the size and A the distance between the aggregates. The volume fractions calculated in this way agree well with the results of the chemical analysis of the block copolymer.

The method of low-angle X-ray scattering makes it possible to determine the average dimensions and the distribution of the numerous aggregates. Its advantage is that it permits the study of the structure of films in the presence of a solvent and when the temperature is varied. The quantitative assessment of the structure and of the type of packing by this method is based on a comparison of experimental scattering diffractometer traces with scattering by various model structures for which formulae have been proposed [134,137,139]. Each type of structure is characterised by a definite number of reflections and a definite distance between them. Thus diffractometer traces with five or seven reflections, the reciprocals of the Bragg radii of which are in the ratios $1:2:3:4:5:6:7$, correspond to lamellar structures; the ratios of the reciprocal radii $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ correspond to hexagonal packing of cylinders and the ratios $1:\sqrt{2}:\sqrt{3}:\sqrt{4}$ correspond to cubic packing of spheres. In order to reveal these structures more effectively, Keller extruded specimens of the block copolymers. Extrusion leads to the formation in amorphous block copolymers of structures with a particularly high degree of order, usually encountered only in single crystals and therefore referred to as supercrystals [141,142]. The results of both methods discussed above are usually in good agreement [130,132,138]. The size of the structural elements may be determined also from the scattering of polarised light [143]. The dimensions of the structural elements vary from 60 to 1000 Å as a function of the structure of the block copolymer and the conditions under which it is obtained, but usually they are in the range 200–300 Å. [119,120,130,137]

The type of structure of the block copolymer depends on many factors: on the ratio of the blocks in the copolymer, on the molecular weight of the blocks, on the concentration of the copolymer in solution, on the nature of the solvent, and on the temperature conditions under which the specimen is obtained. The dependence of the structure on the component ratio is clearly illustrated in the styrene–butadiene block copolymers obtained from an effective solvent (toluene) [119]. With increase of the weight fraction of butadiene from 20 to 80%, five types of structures, illustrated in Fig. 5, are observed: spherical polybutadiene domains dispersed in the polystyrene matrix; hexagonally distributed cylindrical polybutadiene domains in the polystyrene matrix; layer structures consisting of alternating polystyrene and polybutadiene plates (or lamellae) in the region where the concentrations of both types of block are similar and where phase reversal takes place; on further increase of the concentration of polybutadiene, the latter forms a continuous phase in which cylindrical polystyrene domains are dispersed and, when the concentration of polystyrene is lowered further, its domains become spherical. Similar structures have been detected also in other systems [138,144,146].

The change in the length and number of blocks (from two to four) for the same component ratio does not lead to a significant change in the structure [119]. As a rule, in

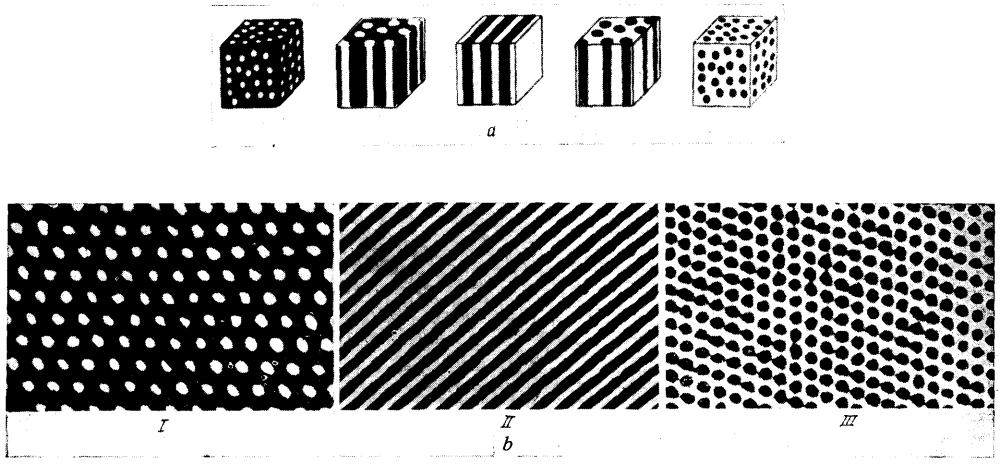


Figure 5. Types of structures of block copolymers as a function of the ratio of the blocks: *a*) schematic representation; *b*) electron microscope photographs of styrene–butadiene block copolymers containing different percentages of polystyrene [145]: I) 28.3; II) 61; III) 69.5.

the middle range of compositions of block copolymers obtained from solution in toluene (which is an effective solvent for polystyrene and polydienes), these block copolymers form alternating lamellar structures; from other solvents, less distinct structures of the "islands in a matrix" type are obtained[92]. The resulting structure is insensitive to temperature changes in the range 20° to 60°C.[105]

A specific feature of block copolymers is that the type of solvent plays just as important a role in the formation of their structure as the composition of the polymer. By a suitable choice of selective solvents, it is possible to achieve phase reversal for the same composition of the block copolymer, i.e. as already stated above, blocks which are insoluble in the given solvent are "precipitated" as a discrete phase[78-82], which has a sharp effect on the properties of the block copolymer.

A large series of studies designed to determine the structures of block copolymers in solution has been carried out by Skoulious, Gallot, and coworkers, mainly by the low-angle X-ray scattering method[147-152]. One structural dimension—the distance between the structural elements—can be determined directly from X-ray diffractometer traces; the size of the structural elements (the diameter of the sphere or cylinder and the thickness of the layer in the plate occupied by each block) can be calculated from the measured distance, the polymer concentration in the solution, the ratio of the blocks in the polymer, and the densities of the blocks and the solvent. For the hexagonal packing of cylinders, two versions of such structure are possible: either the cylinders are formed by the block insoluble in the given solvent and the continuous medium consists of the soluble block together with the solvent or the cylinders are filled by the solvent together with the soluble block and the continuous medium consists of the insoluble block.

The study of the dependence of the size of the cylinders (and other structural elements) on solvent concentration and on the molecular weights of the blocks helps to establish which specific type of structure obtains. As the solvent is varied, the structure is reversed. The concentration of the solvent has different effects on the structure for different block copolymers. The formation of a distinct ordered liquid-crystal structure, i.e. the mesomorphic gel already mentioned, proceeds from a polymer concentration of 40–60%, while at a lower concentration there is no structure at all. On further alteration of solvent concentration, either only the dimensions of the structural elements and of the distances between them change (in different directions determined by the solvent selectivity) or the very type of structure is altered. Thus cylindrical structures have been detected in polystyrene–polyvinylpyrrolidinone block copolymers with a polymer concentration of 70%, while at a higher concentration lamellar structures were found. When the monomer is used as the solvent and is subsequently polymerised, it is possible to obtain solid polymeric systems with a fixed highly ordered structure of the gel or the solution at any stage during its concentration. In such systems, it is more convenient to investigate by electron microscopy the block copolymer structure obtained on passing from a solution to the solid state than in films obtained from solutions at different concentrations by evaporating the solvent. It has been shown by this method that, regardless of the polymer concentration in the initial solution (between 0.8 and 10%), the same structure is observed in films of the styrene–isoprene block copolymer obtained from toluene[153], which enabled the authors to regard it as the equilibrium structure produced at the critical concentration for micelle formation.

Kinetic phenomena play a major role in the formation of the structure of block copolymers[121,154]. Thus an increase of the molecular weight of the block copolymer leads to a decreased regularity of its structure and to an increase of the distances between the structural elements as a consequence of the increased viscosity of the solution, which hinders the attainment of a state of equilibrium[122]. The temperature and the rate of removal of the solvent on formation of the film are just as important. When the solvent is removed rapidly, the size and distribution of the microphase regions in the film are insufficiently homogeneous and are far from equilibrium. The films formed from solution are therefore annealed at temperatures above the glass points of both blocks, the structure being rearranged during the annealing process[122,154,156]. Under these conditions, the distance between the domains decreases and the plates frequently become thicker. On the other hand, annealing at a temperature somewhat below the glass point frequently leads to some breakdown of order in the structure and the appearance of an intermediate phase[153,155]. Extremely interesting data concerning the dependence of the time required for the attainment of the equilibrium degree of order in an SBS (styrene–butadiene–styrene) block copolymer on the annealing temperature have been published[122]:

Annealing temp., °C	Time, min
120	5
110	25
90	180
80	1800
70	3600

It is significant that this temperature dependence of the rate of rearrangement of the structural elements of polystyrene is similar to the temperature dependence of the viscosity of polystyrene near the glass point.

In certain cases, particularly when one of the components of the block copolymer is crystallisable, the nature of the structure formed depends also on the temperature at which the film is formed from solution. For example, films of the polythiacyclobutane–polyisoprene–polythiacyclobutane block copolymer[157] obtained at room temperature are isotropic, while a highly regular hexagonal packing of cylinders at right angles to the plane of the film is observed in the films obtained at 60°C, which is clearly manifested in their mechanical properties. This is associated with the kinetics of the crystallisation of polythiocyclobutane and the superposition of two processes: liquid microlayer formation, which is usual for block copolymers, and the formation of a crystalline phase.

Owing to the complexity of the structure of the block copolymers, there is a possibility of different types of phase equilibria in polymer–solvent systems.

Phase diagrams of two types have been described in the literature: (1) those characterising the transition from the liquid-crystal (highly ordered) state to an isotropic (structureless) solution and (2) those characterising the compatibility of the components and the liquid layer formation in the system polymer–selective solvent for the first block–selective solvent for the second block or in the system first block–second block–solvent. When a crystallisable block is present in the block copolymer, the regions corresponding to the appearance (disappearance) of the crystalline phase are indicated on phase diagrams of both types. Diagrams of the first type have been obtained by French investigators (Gallot, Douy, and

Gervais)[158-162] by plotting the temperature of the disappearance of the liquid-crystal (and crystalline) phase (determined by scanning calorimetry) against solvent concentration. Fig. 6*a* illustrates an example of this type of diagram for the polystyrene–poly(ethylene oxide) block copolymer, which is characterised by the presence of regions corresponding to the existence of a crystalline lamellar poly(ethylene oxide) phase [the form of the chains in the latter is analogous to pure crystalline poly(ethylene oxide)], an amorphous lamellar phase, and isotropic solution. Investigations showed that the nature of the blocks in the polymer determines the number of mesophases and the nature of the solvent determines the region where they are stable (i.e. the greater the affinity of the solvent for the polymer, the greater the reduction of the transition temperature caused by it).

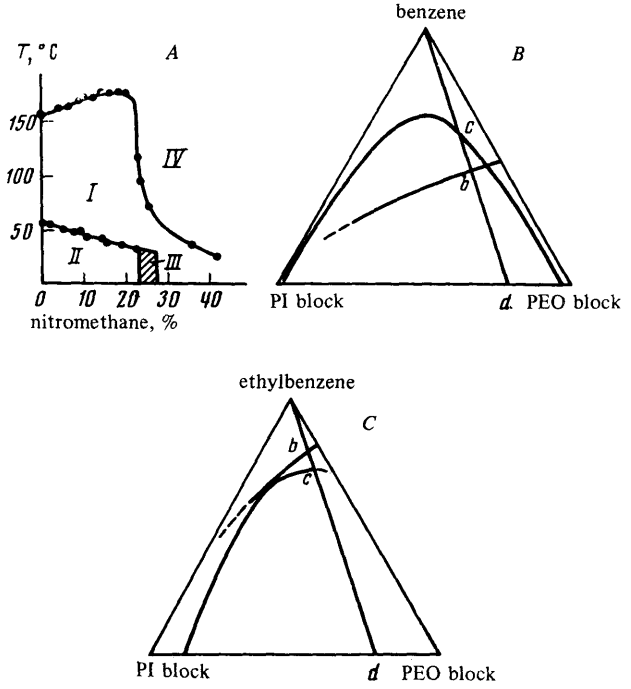


Figure 6. Phase diagram for polystyrene–poly(ethylene oxide) block copolymers (A)[162] [I) lamellar amorphous structure; II) lamellar crystalline structure; III) transitional region between them; IV) isotropic solution] and a polyisoprene (PI) and poly(ethylene oxide) (PEO) block copolymer in benzene (B) and ethylbenzene (C); curve *c* represents CCM for the block copolymer with the composition *d* and curve *b* represents the critical concentration for the crystallisation of the block copolymer having the same composition[144].

The ternary diagrams illustrated in Figs. 6*b* and 6*c* for the poly(ethylene oxide) (PEO)–polyisoprene (PI) block copolymers in two selective solvents are an example of diagrams of the second type[144]. Fig. 6 shows that in benzene, an effective solvent for PEO, the critical concentration of the latter at which it crystallises (point *c*) is much higher than the critical concentration for micelle formation at which the phases are separated into layers (point *b*), while in ethylbenzene, a poor solvent, the opposite situation obtains. Accordingly, crystallisation in the effective solvent for PEO takes place after microlayer formation and therefore has little effect on the structure of the block copolymer, while in the poor solvent crystallisation precedes microlayer formation and determines the structure of the block copolymer. For example, fibrils of almost the same shape and thickness as in the crystallisation of pure polytetrahydrofuran are observed in the block copolymer of styrene and crystallisable polytetrahydrofuran[163]. The nature of the kinetic curves for the crystallisation of polytetrahydrofuran in the block copolymers remains the same, but, with increase of the content of the amorphous component, the crystallisation of the crystallisable component is retarded; the degree of crystallinity and the melting point decrease monotonically with decrease of the fraction of the crystallisable component in the block copolymer.

The study of the kinetics of the crystallisation of polystyrene–poly(ethylene oxide) block copolymers from dilute solutions, carried out by both structural methods and by dilatometric and calorimetric methods[164-169], showed that both the nature of the crystallisation and the morphology of the crystalline formations in the block copolymers correspond to those of pure PEO. The same behaviour was confirmed for block copolymers containing crystallisable polyphenylenesiloxanes[170,171] and polyurethanes[172]. However, a decrease of the size of the block below a definite limit and an increase of the content of the solvent lead to the disappearance of the ability of the block to crystallise[168]. For example, poly(ethylene oxide) with a molecular weight in the range 1000–20 000 does not crystallise in the block copolymer of poly(ethylene oxide) and polycarbonate[11].

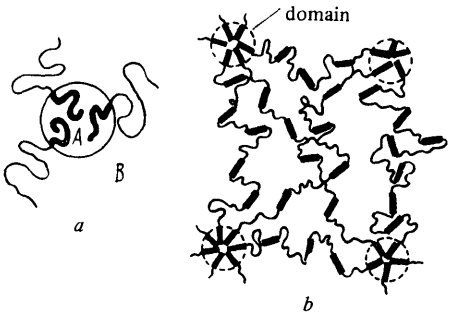


Figure 7. Models of the structure of block copolymers: *a*) Meier's model[28]; *b*) LeGrand's model for a polycarbonate–polydimethylsiloxane many-block copolymer[223].

The influence of the above factors on the type of structures formed can be treated theoretically by applying statistical thermodynamics to various selected models. This approach makes it possible to predict the type of structures arising under different conditions. Thus, in Meier's theory[28,173,174], attention is concentrated on the uniform filling of space by blocks in order to achieve a uniform density within the domains. In his model, which is illustrated in Fig. 7*a*, all the units A are distributed within the domain, while all the units B are outside it. Since contacts between heterogeneous units occur only at

the boundaries of the domains, the author estimated exactly the limits to the configurational entropy corresponding to the domain morphology. Using the general diffusion equation of statistical thermodynamics, he calculated the probability of the distribution of chains within the domain as function of their size and hence obtained the stable size of the domain corresponding to a conventionally uniform density. This stable size depends on the shape of the domain and amounted to $1.33\alpha\ KM^{1/2}$ for spheres, $1.00\alpha\ KM^{1/2}$ for cylinders, and $1.40\alpha\ KM^{1/2}$ for plates (where M is the molecular weight of the polymer forming the domain, K a constant relating the unperturbed dimensions of the polymer to the molecular weight, and α a parameter characterising the degree of perturbation of the chains). Thus, in order to maintain the conditions for a uniform density, the distance between the ends of the chains must differ from that for a Gaussian coil. The observed relation between the size of the domain and the size of the macromolecule was confirmed experimentally by low-angle X-ray scattering in polystyrene–polybutadiene–polystyrene block copolymers [130,175,176].

Subsequently Meier expressed the free energy of the above system as the sum of three components: the surface energy, the enthalpy of formation of the domains, and the change in entropy owing to volume restrictions and elastic deformations of the A and B blocks. By minimising the free energy, taking into account the shape of the domains, he obtained the conditions for microlayer formation and morphological transitions from one shape of the domain to another, expressed in terms of the dimensions of the blocks and their ratio.

The critical size of the polystyrene block thus obtained for the polystyrene–polybutadiene block copolymer proved to be greater by a factor of 2–2.25 than the critical molecular weight determined experimentally for macrolayer formation in mixtures of the same polymers. After introducing simplifying assumptions, Fedors [176] found that the minimum molecular weights of the blocks for which incompatibility is manifested amount to 2500 for polystyrene and 6000 for polybutadiene. The estimation of these quantities plays a major role in block copolymers of the ABA type, since the stabilising effect of the rigid component is shown only as a consequence of microlayer formation, i.e. when the dimensions of the blocks exceed the critical values indicated.

The critical dimensions of the blocks depend significantly on the nature of the polymer and on the affinity of the polymers for one another. Thus in polydimethylsiloxane–polysulphone block copolymers, incompatibility begins to be manifested starting from a molecular weight of polydimethylsiloxane of 2000, [80,178] while in polycarbonate–polydimethylsiloxane block copolymers it appears starting from a molecular weight of 875. [179] Furthermore, the size of the block should exceed the size of the segment for each polymer, determined by the condition that the glass point ceases to depend on the molecular weight. According to Kanig [177], this value is 12 000 for polystyrene. The greater of the two quantities—the size of the segment and the critical molecular weight for microlayer formation—determines the minimum size of the block which can be usefully employed in a block copolymer. For a given component ratio in the block copolymer, determined by the volume fraction Φ_A of one of the components, which is related to the molecular weights M_A and M_B and the densities ρ_A and ρ_B of the blocks by the expression

$$\Phi_A = \frac{2M_A\rho_B}{2M_A\rho_B + M_B\rho_A}, \qquad (14)$$

the selected molecular weight of one of the blocks determines the molecular weight of the second block.

Inoue and coworkers [153,180] expressed the surface free energy of formation of microphase regions in terms of their geometrical dimensions, their volume fraction (for different shapes of these regions—spherical, cylindrical, and lamellar), and the parameters of the interaction of the blocks with the solvent. The total free energy consists of the surface free energy and a term related to the entropy change:

$$G_{sph} = 6V_A^{2/3}(1/D_{sph})\ \Delta W + {}^3/_2 kTN\left\{\frac{D_{sph}^2}{4}\left[\frac{(1-V_A^{1/3})^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^{2/3}}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (15)$$

$$G_{cyl} = 4V_A^{1/2}(1/D_{cyl})\ \Delta W + {}^3/_2 kTN\left\{\frac{D_{cyl}^2}{4}\left[\frac{(1-V_A^{1/2})^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^{2/3}}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (16)$$

$$G_{lam} = 2(1/L)\ \Delta W + ({}^3/_2) kTN\left\{\frac{L^2}{4}\left[\frac{(1-V_A)^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^2}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (17)$$

where L_{sph} and D_{cyl} are the diameters of the sphere and the cylinder, L is the length of the plate, ΔW the energy of the surface contact per unit surface, V_A the volume fraction of the domain occupied by block A, σ_A and σ_B are the swelling parameters of the blocks characterising the ratio of their mean square distances in solution and in the free state (i.e. the interaction of the polymer with the solvent), n_A and n_B the degrees of polymerisation of the blocks, and a_A and a_B the sizes of the blocks.

Since the first terms on the right-hand sides of Eqns. (15)–(17) lead to a decrease of free energy and the second terms lead to its increase with increased geometrical size of the microphase region, the dependence of the free energy on the size of the microphase region is characterised by a minimum corresponding to a specific size of the region. The presence of this minimum shows that the microphase separation is thermodynamically the most stable process, in contrast to macroscopic phase separation in mixtures characterised by zero free energy of mixing. Since microphase regions having mainly the shape corresponding to the smallest relative free energy minimum are formed for the given weight fraction of block A, it follows (as can be seen in Fig. 8) that, with increase of the weight fraction of block A, there should be a transition from spherical to cylindrical and then to lamellar forms, which, as stated above, has been confirmed by numerous experimental data. The weight fraction of block A, corresponding to the transition from one type of structure to another, is found to depend on σ_A/σ_B, i.e. on the relative solvating capacity of the solvent in relation to each type of block, or on the selectivity of the solvent.

The size of the microphase region corresponding to the free energy minimum is expressed by the product of the surface tension and a function of three quantities: the degree of polymerisation of block A, its weight fraction, and the parameter σ_A. The concentration of the block copolymer in solution is not included among these parameters and therefore has little influence on the size of the microphase region. Two- and three-block polymers are characterised by identical thermodynamic features; the only difference is that in three-block polymers account must be taken of the possibility of a different disposition of the ends of the chain on the surfaces of the microphase regions (the two ends of the middle block may be located at the boundaries of the same or different regions). The size of the structural elements in three-block copolymers should be greater, other conditions being equal, than in two-block copolymers.

As the block structure becomes more pronounced, the conditions for the free energy minimum are significantly complicated, because microlayer formation does not go to completion (see Section II) which entails a less ordered form and distribution of the aggregates and in general a less distinct heterogeneous structure [176,181]. A similar theoretical examination of the transition temperatures in a three-block styrene–butadiene copolymer has been carried out [170,171] on the basis of approximately the same model for different types of structure and under different structure formation conditions. These temperatures proved to be in good agreement with the transition temperatures determined experimentally under the same conditions by scanning calorimetry, by turbidity measurements, and by electron microscopy.

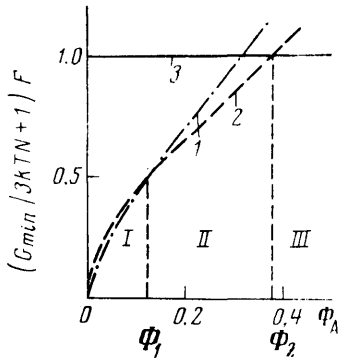


Figure 8. Dependence of the minimum in the free energy for layer formation on the composition of the block copolymer for spherical (line *1*), cylindrical (line *2*), and lamellar (line *3*) structures [153]; $F = (8/3)^{1/3}[(na^2\sigma_A^2)^{1/3}/\gamma^2]$, where a is the size of block A, n the degree of polymerisation of block A, σ_A the swelling parameter of block A, and γ the surface tension. The Roman numerals denote the regions corresponding to the existence of the lamellar (I), cylindrical (II), and spherical (III) formations.

Thus it follows from the above that a theoretical treatment involving statistical thermodynamics makes it possible to predict all the main properties of block copolymers (see also Refs. 153, 184, 185).

VI. RELATION BETWEEN THE STRUCTURE OF BLOCK POLYMERS AND THEIR MECHANICAL AND PHYSICAL PROPERTIES

The vast majority of the published studies on the mechanical and other physical properties of block copolymers refer to two- and three-block copolymers of polystyrene with elastomers because, as already mentioned above, three-block copolymers of this class, in which the elastomeric (polybutadiene, polyisoprene) block is located between two blocks of the thermoplastic polymer, for example polystyrene, have found important practical applications as thermoelastoplastic materials [143,186–189]. The mechanical and physical properties of the block copolymer are determined by those of the continuous phase. The microphase regions in polystyrene, which consist of particles of the filler dispersed in the continuous elastomer matrix whatever the disposition of the blocks, tend to increase the strength of the elastomer [177]. However, only in polystyrene–elastomer–polystyrene block copolymers do the polystyrene domains serve simultaneously as nodes of a three-dimensional network between which the elastomeric blocks making up the matrix are deformed. Such polymers are therefore much stronger and less brittle than polymers of the elastomer–polystyrene–elastomer type having the same composition [17,123,143]. This makes it possible to obtain non-vulcanised rubbers with a fairly considerable strength, whose mechanical properties and the temperature range where they can be usefully employed are determined by the degree of microlayer formation, the perfection of the microphase structure of the block copolymer, and the glass points of the corresponding homopolymers. Above a definite polystyrene content, phase reversal takes place, which leads to a transition from thermoelastoplastic to thermoplastic polymers accompanied by a sharp increase of strength and the loss of viscoelasticity. Thermoelastoplastic properties have also been observed in other three-block copolymers, for example poly(ethylene sulphide)–polyisoprene [190] and polyster–poly(methyl methacrylate) [191] copolymers.

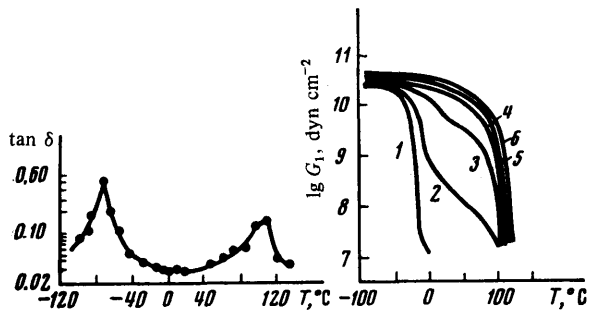


Figure 9. Temperature variation of tan δ (*a*) [195] and the dynamic modulus of elasticity (*b*) [198] for a polystyrene–polybutadiene block copolymer; percentage of polystyrene by volume: 1) 0; 2) 20; 3) 42; 4) 60; 5) 80; 6) 100.

The most characteristic property of block copolymers, which follows from their separation into individual microphases, is the presence of two glass points, reflecting the individual properties of each block. These two glass points are usually revealed by two maxima on plots of the temperature dependence of the mechanical [192–197] losses and two corresponding transitions on plots of the dynamic modulus against temperature [198–205]. The transition temperatures in block copolymers are also determined by differential thermal analysis and by scanning calorimetry [183]. There are block copolymers in which the glass points correspond fairly exactly to those of each component. Thus two loss peaks, at −80° and +100°C, are observed in the polybutadiene–polystyrene block copolymer (Fig. 9*a*), the polybutadiene glass point being independent of the composition and arrangement of the blocks [195]. Similar properties have been observed also for the polydimethylsiloxane and polyarylate block copolymers [14]. At the

same time the loss and dynamic modulus peaks depend on the composition of the block copolymer, starting from a definite fraction of polystyrene [192]. Fig. 9*b* illustrates the temperature dependence of the modulus of elasticity for styrene–butadiene block copolymers of different compositions. Evidently, at a fixed temperature the modulus varies sharply in the range of compositions corresponding to phase reversal.

However, complete microphase layer formation is by no means always observed and in many-block polycondensation copolymers is normally absent. Owing to the interpenetration of the blocks at the microphase interfaces, the glass points in the block copolymer are in most cases somewhat displaced: the glass point of the low-temperature block is higher and that of the high-temperature block is lower than for the pure components, the shift depending on the composition of the block copolymer. Whereas the glass point of the low-temperature, usually viscoelastic block, which in many cases constitutes a continuous matrix, usually changes by only several degrees (for example, the glass point of polydimethylsiloxane in the block copolymers of the latter with polysulphone [178], polycarbonate [179], and poly-α-methylstyrene [206]), that of the high-temperature rigid block frequently decreases sharply (by many tens of degrees) with increase in the concentration of the second component (for example, the glass point of polysulphone in its block copolymers with polydimethylsiloxane [178]). In this respect, the polyblock polydimethylsiloxane–polyarylate copolymer is an exception, probably as a consequence of the marked incompatibility of the components. Only one glass point is frequently observed in the block copolymer, diminishing significantly with increase of the content of the low-temperature block [207-209]. This usually occurs in block copolymers where there is no microlayer formation owing to the mobility of both blocks (at a temperature below the glass points of both homopolymers) and the system consists of a single phase [210,211]. In those cases where the degree of interpenetration of the blocks is fairly considerable in systems with layer formation, a third, intermediate phase is produced, as in mixtures of polymers, this being indicated by the appearance of an intermediate maximum on the plot of the temperature variation of the tangent of the loss angle [212]. The existence of an intermediate phase in the majority of block copolymers is indicated by an increasing amount of data [213-217]; according to various estimates, its thickness is 13–15 Å and the ratio of the difference between the radii of the sphere surrounding this domain and of the domain itself, i.e. the thickness of the intermediate layer, to the radius of the domain is 0.1–0.2. [212]

In certain block copolymers, mainly polycondensation copolymers, the properties of the individual components are not manifested at all and, when the composition is altered, there is a gradual transition from the properties of one component to that of the other. Thus, whereas the double refraction arising on deformation of a thermoelastoplastic specimen, for example in a styrene–butadiene block copolymer, is determined by the elastic polybutadiene matrix and increases with increasing polystyrene content (as a result of the formation and orientation of an elastic network of polystyrene domains [217-222]), in the polydimethylsiloxane–polycarbonate block copolymer the optical stress coefficient is intermediate between the corresponding values for the pure components [223]. A model has been proposed for this block copolymer, according to which the intermediate phase is not concentrated around discrete microphase regions and its presence is manifested by the fact that some of the polycarbonate blocks are segregated into individual microregions, while others form part of the continuous matrix, alternating with dimethylsiloxane blocks (Fig. 7*b*). Models and equations (proposed for the theory of two-phase systems consisting of spheres immersed in a continuous matrix), whereby the fraction of each component in the continuous and discrete phases of homopolymers and block copolymers can be determined from the moduli of elasticity or stress corresponding to the transformation of the material into an elongated shape with a constriction (neck) (or some other parameter), have been used by Robeson et al. [80] Faucher [224] calculated the moduli of elasticity of block copolymers from the volume fractions of the components alone without taking into account the presence of microphases and the calculated data agreed fairly satisfactorily with experiment.

The presence of an intermediate phase is also revealed by relaxation phenomena in block copolymers. The experimental dependence of the relaxation of stress has been described satisfactorily [225-229] from the standpoint of the superposition of several relaxation mechanisms—mechanisms characteristic of homopolymers as well as additional mechanisms. One of the latter is associated with the simultaneous movement of the elastic and plastic segments at the grain boundaries, i.e. the boundaries of the microphase regions. The segments of the soft component become less mobile in this intermediate region, while those of the rigid component become more mobile, the molecular order in the segment being the same as in statistical copolymers. Another, additional relaxation mechanism is associated with the flow of the entire block copolymer after the fusion of the domains. The constants for these relaxation mechanisms depend on the component ratio in the block copolymer.

The microheterogeneity and the operation of several relaxation mechanisms lead to numerous transitions in block copolymers and cause the principle of the temperature–time superposition to be inapplicable [230]. It has been shown for a three-block thermoelastoplastic styrene–butadiene copolymer [231] that, below a specific temperature, where the polystyrene microregions play the role of an inert filler in the elastomer, both relaxation and creep obey a reduction formula with constants close to those of polybutadiene; above the polystyrene glass point, a reduction formula is again valid, but this time with constants close to those of polystyrene; between these temperatures, the temperature dependence of the relaxation times and hence of the reduction factor is quite different, which indicates the operation of a new relaxation mechanism. Creep in block copolymers is manifested to a greater extent the lower the degree of order in the microregions [232].

Despite the distinct microheterogeneity of block copolymers, one of their specific properties is a high degree of transparency, which distinguishes them from mixtures of polymers and which is caused by the limited size of the microregions (as pointed out above, their diameter does not exceed the length of the polystyrene block and reaches 200–300 Å) and by their regular arrangement [188,221,222].

One of the most characteristic mechanical properties of polymers is the relation between stress and elongation, characterising the modulus of elasticity, the characteristics of the deformation of the system, and its strength. A specific feature of block copolymers is that the nature of the plots of stress against elongation depends mainly on the ratio of the blocks. The size of the individual blocks and the molecular weight of the block copolymer have

comparatively little influence on its mechanical properties. With increased content of polystyrene, there is a transition from the properties of the pure elastomer to those of pure polystyrene, which is clearly shown in Fig. 10*a*.

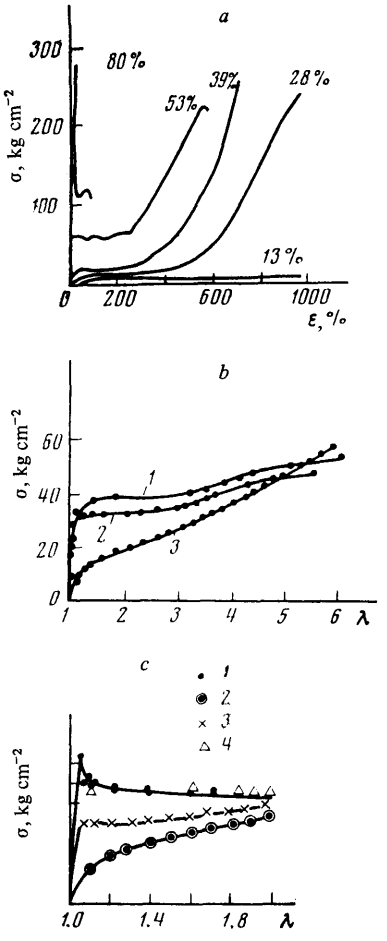


Figure 10. Dependence of the stress on deformation in films of SBS block copolymers having different compositions (*a*) [188], cast from different solvents (*b*) [236], and subjected to re-extension and annealing (*c*) [196];
a) for different polystyrene contents shown by the numerals against the curves;
b) [1) from ethyl methyl ketone; 2) from toluene; 3) from heptane];
c) [1) first extension; 2) repeated extension; 3) annealing for 8 min; 4) annealing for 41 days; λ is the relative elongation equal to the ratio of the final and initial lengths of the specimen].

This transition and the increased modulus of elasticity of the block copolymer are particularly marked when the content and the molecular weight of polystyrene are such that it is segregated as a separate phase [188], which depends to a considerable degree, as mentioned above, on the quality of the solvent, determining the conditions governing the incompatibility of the components. It follows from the results of Hendus et al. [130] that this happens in the presence of 50% of polystyrene in the polystyrene–polybutadiene system obtained from a solvent which is effective for both components. In films obtained from selective solvents, this phenomenon occurs in the presence of a much lower content of polystyrene.

The mechanical properties of block copolymers depend very significantly on the solvent from which the film has been cast [196,235–240]. The general rule is that the properties of the block copolymer approach those of the block in relation to which the given solvent is selective [80]. For example, Fig. 10*b* shows [241] that the properties of the film obtained from heptane, which is a selective solvent for isoprene, are typical for an elastomer, whereas the film obtained from ethyl methyl ketone, which is a selective solvent for polystyrene, has properties characteristic of polystyrene. In this case, this is manifested by the modulus of elasticity and the nature of the deformation, while the tensile stresses and deformations of the polymer are similar. In polysulphone–polydimethylsiloxane block copolymers obtained from various solvents, the strength varies from 130 to 220 kgf cm^{-2} and the deformation is in the range from 310 to 517%. [80,165] The solvent has a particularly marked influence on polydimethylsiloxane–polyarylate block copolymers, while the deformation with rupture on passing from chloroform to a chloroform–hexane or chloroform–toluene mixture increases by a factor >3 (from 120 to 400%) with a comparatively small decrease of strength [242].

Thus, owing to the change in the conformation of the macromolecule and in the structure of the block copolymer when the quality of the solvent in relation to each block is altered, one can achieve in the general case, without altering the composition of the block copolymer, a transition from "rigid" systems to "soft" systems and conversely. In connection with the discussion of the influence of the solvent, it is interesting to note that, when the film is placed in a selective solvent where the entire block copolymer does not dissolve but merely swells vigorously, there is a significant increase in the elasticity of the film after subsequent drying and a simultaneous decrease in its strength (for example, the deformation of the polymethylsiloxane–polysulphone block copolymer increases from 410 to 970% after swelling in carbon tetrachloride, while its strength diminishes from 220 to 150 kgf cm^{-2}). [178]

The presence of a quasi-network in thermoelastoplastic materials leads to additional characteristics of their mechanical properties. One of their manifestations is different forms of the plots of the stress against elongation for primary and secondary deformation [196]. Primary deformation is characterised by the development of a neck, of the type characteristic of the plastic component of the block copolymer; on repeated deformation, when the rigid structure formed by the network of polystyrene microregions has been disrupted, the extension curve is typical of an elastomer. After a long time, particularly when the specimen is annealed at an elevated temperature, the plot recovers its initial form (Fig. 10*c*), which indicates the restoration of the network structure. Annealing also leads to the disappearance of the apparent residual deformations from the block copolymer [176].

Another characteristic feature of the mechanical properties of thermoelastoplastic materials consists in the dependence of the nature of the deformation on its extent. For small deformations, the system behaves as a "soft" system, i.e. only the elastic block is deformed, while the

rigid domains are either not deformed at all or undergo an extremely insignificant extension; for large deformations, the system becomes "rigid", i.e. the rigid blocks undergo plastic deformation, which leads to the disruption of the network nodes. As a result, the system again becomes "soft" for still larger deformations, i.e. is purely viscoelastic [188].

The rate of relaxation processes in block copolymers is lower than in statistical copolymers [243,244]. It is independent of temperature and deformation up to certain values of the latter, but, on further increase of these parameters and of the stress, the rate increases owing to the disruption and plastic flow of the polystyrene domains. The gradual disruption of the network nodes with increase in the degree of deformation also affects the linear increase of the optical stress coefficient with increase of deformation [208]. This effect is very small for homopolymers (non-cross-linked polybutadiene and polystyrene) and reaches its maximum value in the presence of a polystyrene content such that its domains create most effectively a network ensuring a rubber-like state of the system [209]. The size of the elastic block M_c between the nodes of the quasi-network under consideration can be calculated using the statistical theory of viscoelasticity [20], applying this theory [245] with allowance for the dependence of the stress on the volume fraction of the filler, or using the Flory–Rehner theory [20], from the swelling of the block copolymer in the solvent interacting solely with the elastic matrix. However, one should note that the value of M_c determined in this way is significantly smaller than the actual length of the elastic block. The possibility of applying the Flory–Rehner equation on swelling of block copolymers has not been demonstrated unambiguously [157,196,235], in particular it has been questioned in a theoretical study [247] where a significant dependence not only of the magnitude but also of the nature of the swelling on the shape of the structural elements in the block copolymer was demonstrated. The final solution of this problem requires further study.

The two-phase structure of the block copolymer is retained up to temperatures much above the glass point of polystyrene. This results in a maximum on the curve relating the viscosity of the melt to the composition of the block copolymer in the presence of the polystyrene content for which the network structure is most marked below the glass point [244]. However, this structure is shown much more clearly above the glass point; this is readily seen from the fact that at 100°C the moduli of elasticity of the block copolymer and the statistical copolymer having the same composition are identical, but on cooling the modulus of elasticity of the block copolymer increases sharply. The presence of a two-phase structure in the block copolymer melt is manifested by the existence of two different states of the melt, distinguished by the activation energy for viscous flow, which at 100°C is closer to the activation energy for polystyrene and at 200°C is closer to that for polybutadiene, this being associated with the onset of the flow of polystyrene domains above 120°C. [188,244] Hence it follows that the viscosity of the melts of block copolymers is extremely sensitive to a change of temperature: when the latter is raised from 80° to 180°C, the viscosity falls from 10^{10} to 10^5 P. In contrast to the deformation properties of solid block copolymers, the viscosity of the melt depends very strongly on the molecular weights of the blocks and the entire block copolymer and to a lesser extent on its composition [244]. The viscosities of block copolymers can be measured not only above but also below the glass point; their finite values at 25°C indicate a fairly high degree of instability of the polystyrene domains.

The flow of block copolymers is non-Newtonian [248]. It has been shown [244] that the flow curves depend on the number and arrangement of the blocks for the same molecular weight of the polystyrene–polybutadiene block copolymer, namely the viscosity corresponding to the same stress decreases in the sequence SBS > SB > BSB, the differences being greater the lower the temperature. The dependence of the viscosity on stress in SBS is weaker than for other block copolymers, since the elastomeric blocks in this substance are clamped between the network nodes, but, for stresses exceeding 10^6 dyn cm^{-2}, the temperature dependence of the viscosity is manifested to the greatest extent in this polymer. The influence of stress on the viscosity and rate of relaxation is of the same type and is related to the disruption of the polystyrene microregions.

Specific rheological characteristics are also shown in concentrated solutions [249–251] and gels of block copolymers. The gels are formed either on swelling of the block copolymers in selective solvents or following the addition of a selective precipitant to a solution of the block copolymer in an effective solvent. Apart from the polystyrene–poly(ethylene oxide) gels already described (see Section V), the following systems have been obtained: poly(methyl methacrylate)–polyacrylonitrile–chloroform; starch–polystyrene–water; poly(methyl methacrylate)–poly(vinylidene chloride)–benzene; polytetrafluoroethylene–poly(methyl methacrylate)–chloroform [81]. In the second method, the addition of the precipitant causes increased aggregation of the insoluble blocks, which leads to the formation of a continuous network in solution in the case of three- and many-block copolymers. In this type of structure formation process, there is a sharp increase of viscosity, in contrast to solutions of homopolymers and statistical copolymers, where the viscosity diminishes after the addition of the precipitant [252]. Solutions of polystyrene–polybutadiene block copolymers in n-decane exhibit a Newtonian viscosity up to a concentration of 30%. When they are treated with decalin, the non-Newtonian viscosity is shown at decreasing concentrations, a maximum appears on the curves relating the stress to time for a constant rate of shear, characteristic of the gel-like state, a limiting shear stress appears, the elasticity increases, and the system becomes thixotropic [253]. Analogous changes have been observed also in a many block polydimethylsiloxane–polyarylate copolymer.

One of the important physical properties of block copolymers is their permeability to gases, which depends, like mechanical properties, on the composition of the block copolymer and changes sharply in the region of phase reversal [254]. This makes it possible to combine the effective permeability of one homopolymer and the mechanical properties of another for a definite composition of the block copolymer. Such materials are extremely promising for use as gas-separating membranes.

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The above data demonstrate the exceptionally unusual structures and properties of the polymeric materials formed by macromolecules consisting of two or more blocks. The properties of solutions and gels of block copolymers are no less interesting.

These unusual combinations of properties are already used in engineering and give rise to the prospect of an extremely wide variety of applications of polymers of this

class. The most interesting and important practical application of block copolymers involves their use as thermoelastoplastic materials, whereby one may obtain cast articles with adequate strength from non-vulcanised rubbers. The wide-scale employment of thermoelastoplastic materials is delayed by their low thermal stability, determined by the glass point of polystyrene, which gives rise to the problem of finding the optimum chemical structure of the block copolymer. Other technical applications of block copolymers include their use as the so called pluronics—(rubbers based on polyethylene–polypropylene block copolymers having the properties of surfactants), as well as the use of block copolymers to increase the miscibility of homopolymers, to increase the stability of emulsions of both low- and high-molecular-weight compounds, as gas-separating membranes, and for many other purposes.

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