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Structure and Properties of Block Copolymers of Polystyrene and Polybutadiene

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Recent studies of the structure and properties of block copolymers of polystyrene and polybutadiene are reviewed, with special emphasis on the effect of the structure and of the formation conditions for the samples on the interrelated physico-mechanical properties. Problems associated with the macro- and micro-layering of block copolymer solutions are examined in detail. Work on the analysis of block copolymer structures from measurements of sorption characteristics is reviewed in the light of an assumed relaxation mechanism for the sorption and swelling processes. The prospects of controlling the structure and properties of block copolymers are shown to be good.
The bibliography contains 190 references.

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I. INTRODUCTION

The literature on the structure and properties of block copolymers is now extensive. Some recent reviews[1-4] include work on the structure and properties of block copolymers published up to 1976: they deal mainly with thermoelastoplastics, i.e. systems in which fairly large flexible blocks of elastomers are chemically bound to equally large rigid blocks.

Thermoelastoplastics in the form of block copolymers are thought to be promising materials with a wide range of prospective applications in technology.[5] They are simple to prepare and not very different from ordinary plastics in the fabrication of components. The addition of block copolymers (for example, polystyrene/polybutadiene) of the styrene–butadiene–styrene type (SBS) to ordinary plastics polyethylene, polypropylene, polystyrene) improves their elasticity and raises their impact resistance. Yet the workability of the compositions remains almost the same as that of the initial plastics. The potential applications of block copolymers stem from the overall effect of these properties. The most substantial developments have been achieved for block copolymers of polystyrene and polybutadiene, and the present review will deal mainly with these systems.

Block copolymers (especially those based on polystyrene) have attracted sustained development because their practical applications are already considerable.[6-11] The rheological properties of block copolymers are complex, and they differ from those of the dispersed system and of homopolymers. These problems are specially reviewed in Ref. 12. Other review articles[13-16] discuss the morphology of block copolymers, their mechanical properties, and the dependence of their properties on composition and on the measurement conditions.

This review will examine in detail only the most recent results, published in the last few years, though reference to earlier work will be made, where necessary, to make the presentation more logical. No attempt will be made to deal with the historical aspects of the problem.

II. CONFORMATIONAL STATE OF MACROMOLECULES IN SOLUTIONS. EFFECT OF THE COMPOSITION OF THE SOLVENT MIXTURE. MICRO- AND MACRO-LAYERING OF BLOCK COPOLYMER SOLUTIONS

As was stated above, block copolymers consist of large fragments of one polymer chemically bound to fragments of another polymer. In the case of block copolymers of polystyrene and polybutadiene the central block is a fragment of a polybutadiene chain, and the two end blocks are polystyrene (this is the commonest structure, though other variants are possible).

The behaviour of block copolymers in solution was studied even in earlier work. The characteristic form of block copolymers produces specific structures even in dilute solutions, though some workers believe that theories developed for homopolymers[17-19] can be applied to block copolymers. It has been shown fairly convincingly that intramolecular phase separation often takes place in dilute solutions. As a result, micelles are formed, consisting of the block whose thermodynamic affinity for the solvent is lower, with a shell of the block whose thermodynamic affinity for the solvent is higher.[20-22] By varying the composition of the surrounding medium we can control the segregation of the blocks, as has been predicted theoretically.[23-25] The structure of the micelles can be varied by adding a selective precipitant, and this method has been used widely to control the properties of the resulting samples.[26-32] The introduction of a selective precipitant into a block copolymer solution causes coiling of one of the blocks and hence lowers the characteristic viscosity of the solution.[33-36]

Micro-layering in solutions of block copolymers and the mutual compatibility of the two blocks depend on the type of solvent, and on whether the solvent is a common solvent for both blocks or a selective solvent for one of them.[37] In the determination of the phase state of block copolymers in solution the most important consideration is the intermolecular interaction between the blocks and their interaction with the solvent. A change from dilute to concentrated solutions is not always possible: specific conditions

may be necessary. Thus for an equimolar ratio of the components in a copolymer of the ABA type this change is possible only in solvents selective towards the central block;[38] in other solvents phase separation takes place, with precipitation of the polymer.

Depending on the character of the intermolecular interaction between the like and the unlike blocks, the chains of block copolymers may take on different shapes.[39] Thus if the AA and BB interactions are negligible, and the AB interaction results in attraction between the segments, the chains are coiled into a tight ball. On the other hand in the case of mutual attraction between like blocks and mutual repulsion between unlike blocks we observe a collapse of the chains of a three-block copolymer.

Of course, the type of structure formation in block copolymers in solution depends not only on the concentration but also on the type of the solvent. If we use a solvent which is thermodynamically poor for the polybutadiene blocks (for example, ethyl acetate) the ternary block copolymer of polybutadiene and polystyrene in solution forms spherical or worm-like micelles whose core consists of polybutadiene blocks.[40]

As was mentioned above, in selective solvents the block copolymers form micelles consisting of a dense core (contributed by the less soluble component) and a shell, containing the more soluble component and therefore swelled by the solvent. The tendency of block copolymers to form micelles depends on their composition, on the molecular weight of the blocks, and on other factors. For block copolymers of polystyrene with polybutadiene the micelle formation process is conveniently studied in n-alkane solutions. A study[41] by light scattering and sedimentation methods has shown that depending on the molecular weight of the blocks, on the type of solvent, on the concentration of the polymer in solution, and on the temperature, the system can exist as a homogeneous solution and as a micellar structure, with possible transitions between the two states. The molecular weight of the polystyrene has the dominant effect on the type of structure formation in the solutions. If these blocks have a relatively small molecular weight (less than 10000) true solutions are formed in n-alkanes, but if their molecular weight is greater than 20000 only micellar solutions are formed. We note that the number of molecules in the micelle depends on the method of preparing the solution and on the molecular weight of the polystyrene blocks. Micelle formation in solutions of block copolymers of polystyrene and polybutadiene in selective solvents is discussed also in Ref. 42.

In work with solutions of block copolymers (in particular, ternary block copolymers of polystyrene and polybutadiene) it is important to allow for the special behaviour and for the instability of these substances. Thus an anomalous opalescence has been observed in solutions of this block copolymer in isopropyl acetate,[43] which is a selective solvent for polystyrene. The anomaly occurs in a narrow temperature range (37–35 °C): it is due to a change in light scattering caused by the formation of large particles under these conditions. The opalescence temperature decreases as the concentration of the solution is decreased, and micelles of normal size are formed. The formation of anomalously large micelles is an unstable process which can be observed over periods of several hours.

A metastable state was observed[44] in a detailed study of the viscosity of binary block copolymer solutions (polystyrene and polybutadiene) in solvents selective for the individual blocks as well as in mixtures of these solvents. Transitions from one type of micelle to the other were observed after changing the composition of the mixture (by gradually changing from a solvent selective for one of the blocks to a solvent selective for the other); the transition occurs through a region of metastability. This transition is accompanied by characteristic changes in the viscosity of the solution and in the selective sorption coefficient for one of the components of the mixture. All these properties depend on the molecular weight of the blocks of polystyrene and polybutadiene.

The association of block copolymers in selective solvents has been studied[45] with hydrogenated block copolymers of polystyrene and isoprene. At high concentrations of the selective solvent and low temperatures, compact monodispersed micelles were formed. At lower concentrations of the selective solvent and higher temperatures, the associations were larger and polydispersed.

The conformational state of block copolymers in dilute solutions has been analysed in a computer experiment,[46] applying the Monte Carlo method to a simple cubic lattice in which self-intersections were forbidden. The most significant conclusion[46] was that in ternary block copolymers the middle block has a higher swelling coefficient than in a homopolymer of the same structure. Furthermore the ternary block copolymer is larger than the equivalent binary block copolymer. These results were confirmed by experimental measurements of viscosity and light scattering in the same investigation.[46]

Various methods have been used to study micro-layering in solutions of block copolymers. One of these consists in determining the solubility parameters of the blocks of the copolymer and of the solvent.[47] This approach in many cases allows qualitative predictions of the phase state of the block copolymer–solvent system as a function of the chemical structure of the blocks and of the solvent molecules. An alternative approach relies on a theoretical analysis of the thermodynamics of the micelle formation processes and of phase separation in dilute solutions of block copolymers.[48]

The compatibility of the blocks in block copolymers may differ from that of the corresponding homopolymers. This effect is observed[49] in thermodynamic studies, for example in calculations of the free energy of mixing of the components. It is found that the homopolymers are less easily integrated than blocks of the same structure incorporated in a block copolymer.

Many workers have analysed the micro-layering effect theoretically and tested their results experimentally. The theory proposed by Leary and Williams[50] was further developed by Pico and Williams:[51] it relates to systems in which the polymer is predominant and the solvent is present only in small amounts. It is shown that even if the solvent is good for both blocks the system can undergo micro-phase separation at high enough concentrations, as in the case of cooled melts. By assigning a geometrical shape to the domains consisting of blocks of either component the Gibbs free energy could be calculated. A comparison of these results with those for a random mixture of the components allowed the layering temperature of the system and its dependence on the volume fraction of the solvent to be determined. The lowest layering temperature is obtained when the solubility parameter of the solvent is equal to the half-sum of the solubility parameters of the blocks of which the copolymer is composed.

The proposed model was tested experimentally by light transmission and by rheological methods.[52] Plasticised samples of the block copolymer were used in light transmission measurements, and the frequency dependence of the dynamic viscosity of the same samples was measured over a wide temperature range. Dipentane (a good solvent for both types of block) was used as the plasticiser/solvent. At the layering temperature of the micro-blocks all the measured

characteristics show a sudden change, and therefore this temperature can be measured very accurately. The agreement between experiment and theory was good except when the micro-layering temperature was lower than the glass transition temperature of the polystyrene blocks.

Many studies of the rheological properties of block copolymer solutions have been reported.[53-55] If the chosen solvent is a good solvent for both blocks the rheological behaviour of the solution is the same as that of a homopolymer solution. In the presence of selective solvents, in which the solubility of one of the blocks is temperature-dependent, very different properties are observed.[53]

Similar results were reported from a study[54] of the rheological behaviour of concentrated solutions of block copolymers of polystyrene and polybutadiene, having a four-pointed star structure. When a solvent common to both blocks was used the rheological behaviour of the solutions was indistinguishable from that of homopolymer solutions. When the solvent was selective for one of the blocks the rheological results were difficult to reconcile with conventional views.

The work was later extended[55] to other solvents and other methods of studying rheological properties. The rheological behaviour of block copolymers in solutions can be explained by postulating a macroscopic network formed by the polystyrene domains in the solution. This network is unstable and can be broken down by mechanical stresses.[56] Intermolecular interaction, depending on the type of solvent and on its selectivity towards the blocks, can play a major role in these effects.

As was pointed out above, the type of structure of a block copolymer in solution depends on the concentration. The appearance of viscoelastic properties in these systems suggests[57] the formation of a continuous lamellar structure (arising from the polystyrene domains) at high concentrations. Below some limiting concentration the solution develops a network whose points consist of polystyrene domains. The solution becomes truly molecular only at high dilutions.

There are also reports[58] that block copolymers in solutin can exist in a mesomorphic state at high concentrations.

Various papers discuss the compatibility of block copolymers in solution with homopolymers having the same structure as one of the blocks. Thus the compatibility of polystyrene/polybutadiene block copolymers with a butadiene homopolymer in solution was determined viscometrically, and compared with the compatibility of polybutadiene with the random copolymer.[59] The latter was found to be more compatible with polybutadiene, the compatibility decreasing as the molecular weight of the block copolymer increases.

The second virial coefficient for block copolymers of polystyrene and polybutadiene and for mixtures of polystyrene and polybutadiene of the same composition was determined (in different solvents) by an osmometric method.[60] A difference between the second virial coefficients was detected for these systems, but the difference was decreased by raising the temperature and by increasing the proportion of polystyrene in the mixture. Structure formation by the block copolymers in solution was studied using the polarised luminescence method, and it was shown that globular, dumb-bell, and other structures can develop, depending on the type of solvent.[61]

Brief mention should be made of the special features of the fractionation of block copolymers. Fractionation methods applicable to block copolymers, including gel chromatography, precipitation chromatography, and fractional precipitation are discussed in Ref. 62. Compositional non-uniformity in block copolymers has been successfully analysed by gel-permeation chromatography.[63] The study of the molecular weight of block copolymers by gel chromatography is complicated by the special structure of these materials, which causes difficulties in the choice of solvent. A detailed discussion of these problems will be found in Ref. 64. The specific problems of the chromatographic separation of block copolymers on porous adsorbents are discussed in Ref. 65. The separation theory developed in that work[65] can identify the most favourable conditions for accurately separating a block copolymer according to the length of one of the blocks.

A convenient method for detecting compositional non-uniformity in block copolymers is centrifuging in a density gradient, obtained by using two solvents of different density. This technique allows the separation of fractions in which the concentration of polystyrene varies between very narrow limits.[66]

The molecular structure of block copolymers (i.e. the length and molecular-weight distribution of the blocks) can be controlled by introducing various lithium-organic compounds into the reaction mixture.[67] This process, too, is affected by the specific structure of the block copolymers, which differ substantially from those of homopolymers prepared under similar conditions.

To complete the description of the behaviour of block copolymers in solution we should note that the nature of the intermolecular interaction of the repeating units of different blocks, both with each other and with the solvent molecules, has been studied extensively in recent years. These interactions are very important in studies of the phase state of block copolymers in solution. Depending on the nature of the intermolecular interaction, which dictates the choice of a selective solvent or precipitant, dilute solutions can be replaced by concentrated solutions, the conformation of the chains in solution can be varied, and micellar structures in which the cores consist of blocks of either type can be obtained.

Another important aspect of the problem is the rheological behaviour of block copolymer solutions. In recent work on this topic the rheological behaviour of the solution (which depends on concentration) has been used to study the structure of block copolymers in solution. It is generally assumed that macroscopic networks whose nodes consist of domains of one of the blocks are formed in concentrated solutions. Concentration of the solution favours the formation of a lamellar structure, though in some cases the solution can show a mesomorphic structure. The macroscopic network can be broken down either by diluting the solution or by mechanical stresses. This approach can account for the rheological properties without postulating mechanical meshing of the chains in the solutions.

Thus block copolymers offer a convenient model system for studying the behaviour of polymer solutions, since they offer almost limitless possibilities of controlling the structure by varying the chemical arrangement of the blocks, their length and relative position, by varying the concentration of the solution, by using selective precipitants and solvents, etc. When solid samples are prepared from solutions of block copolymers all these aspects of their previous history can affect their structure and mechanical properties, as shown in the following Section.

III. STRUCTURE AND MECHANICAL PROPERTIES OF BLOCK COPOLYMERS IN THE SOLID STATE

The structure of block copolymers (and especially of block copolymers based on polystyrene and polybutadiene) was carefully studied even in the earliest work.[68-70] Structural

changes produced by increasing the content of polybutadiene phase in the polymer have been studied,[71] and various types of structure have been detected. At low concentrations of the polybutadiene fraction spherical domains are formed, dispersed in the polystyrene matrix, but at higher concentrations the polybutadiene forms cylindrical domains in a hexagonal packing arrangement. A further increase in the concentration of polybutadiene produces layer structures (alternating sheets of polybutadiene and polystyrene); the next stage is phase inversion, with cylindrical domains of polystyrene arranged in a polybutadiene matrix, and lastly the polystyrene domains become spherical at very high concentrations of polybutadiene (up to 80%).

The effect of the chemical structure of the blocks on the structure of binary block copolymers has been studied by low-angle X-ray scattering and by electron microscopy.[72] The thickness of the layers and of the layer structure in binary block copolymers increases if polystyrene is replaced by poly-α-methylstyrene or by poly-2-vinylnaphthalene (while keeping the molecular weight constant). The parameters of the layer structure are affected also by the thermodynamic properties of the solvents and by the concentration of the solutions.

The structure of block copolymers of polystyrene and polybutadiene has been studied[73] by varying the concentration of the vinyl component in the polybutadiene block from 10 to 60%. This change in chemical structure was shown to lower the degree of ordering of the system at the supermolecular level.

A theory which allows the size of the spherical domains to be calculated and their free energy to be estimated has been proposed.[74] This theory was tested by an experimental study of block copolymers of polystyrene and polybutadiene.

A thermodynamic analysis of a system composed of a block copolymer with cylindrical domains has been reported.[75] The size of the domains and the distance between them were calculated as a function of the composition of the block copolymer. Subsequently the thickness of the phase layers was also calculated.[76]

Various methods of studying the micro-phase separation of block copolymers in the solid state have been used, including X-ray structural analysis,[77] transmission electron microscopy,[78] and others.[79,80] Thus the nature of the domain structure in block copolymers of polystyrene and polybutadiene has been determined by low-angle X-ray diffraction and by transmission electron microscopy.[78] For polystyrene contents below 25% the films prepared from solutions in benzene (common solvent) and in cyclohexane (solvent specific to polybutadiene) contain spherical domains of polystyrene showing a high degree of segregation. Films prepared from solution in ethyl methyl ketone contain domains of polybutadiene dispersed in a polystyrene matrix.

The formation of block copolymer structures depends on the width of the molecular weight distribution (MWD) of the chains in the blocks. If the distribution is similar in each block (either narrow, or wide) and the concentration of the components is the same, the phase structure will also be approximately the same.[81] On the other hand if the polystyrene blocks have a narrow MWD and the polybutadiene blocks have a wide MWD the structure of the block copolymer becomes similar to that of a sample with a narrow MWD of all the components and a lower polybutadiene content. For the opposite relationship of the MWD of the blocks the structure is again similar to that of a sample with a narrow MWD of all the components, but this time with a lower concentration of polystyrene.[82] Because of its dependence on the MWD distribution of the blocks the structure of the block copolymers affects the properties of the material. A wide MWD favours the formation of a lamellar structure, which lowers the tensile strength and increases elongation. Samples with a narrow MWD display Newtonian flow over a wider range of shear rates than samples with a wide MWD.[82]

Micro-layering is essential to the development of toughening in block copolymers. This type of layering appears only when the molecular weight of the blocks exceeds a critical value. For example, for the block copolymers of polystyrene and polybutadiene the critical molecular weight of the polystyrene fragments was found[83] to be 2500, and that of the polybutadiene fragments 6000. At lower molecular weights no micro-layering was detected, and the toughening effect of the rigid blocks was absent. Conversely, in mixtures of polymers layering occurs at much lower molecular weights: for example, in a mixture of polystyrene and polyisoprene layering is observed at a molecular weight of polystyrene of 500.[84]

Changes in structure of block copolymers of polystyrene and polybutadiene as a result of heat treatment have long been known.[85] Annealing at temperatures above the glass transition point of the rigid block leads to equilibration in only a few minutes, whereas many hours are needed to reach equilibrium at temperatures below the glass transition point of the rigid block, in spite of the high elasticity of the sample as a whole. At higher temperatures the intensity of the low-angle X-ray reflexions decreases, and still further increase in temperature suppresses the reflexions completely, but the low-angle diffraction properties are fully restored by lowering the temperature.[86] Thus heating causes a gradual suppression of the phase structure of the block copolymer and a transition into a homogeneous system. However, the size of the transition regions stays almost constant during heating, i.e. an intermixing of different blocks appears to take place. This process is reversible, and micro-layering is restored by cooling.

Thus at high temperatures a transition from a two-phase to a single-phase structure may take place. In the case of block copolymers of polystyrene and polybutadiene this transition is observed[87] at 140–150 °C. The rheological properties of the samples change at the same time: non-linear mechanical behaviour is replaced by a linear behaviour, with a substantial decrease in elasticity. The existence of a transition from non-linear to linear rheological behaviour at 150 °C, caused by the breakdown of a multi-phase structure and the formation of a single-phase structure, has been confirmed calorimetrically.[88]

The specific structure of the block copolymers and the type of aggregation of the blocks allow us to produce some unusual structures in these polymers by special methods. Thus if samples of block copolymers of polystyrene and polybutadiene are oriented and then annealed at a relatively high temperature (for example, at 155 °C for 18 h) an oriented macroscopic lattice is formed: this is suggested by low-angle X-ray diffraction and electron microscopy measurements,[89] which detected the formation of a macroscopic lattice of polybutadiene cylinders in a polystyrene matrix. This type of micro-phase separation influences the properties of the system.

Different methods of analysis of the structure of oriented block copolymers[90] have indicated the possibility of a mesomorphic structure for block copolymers in this state. The rigid domains can form either cylinders or lamellae, and within the domains the macromolecules can be coiled in a bundle, as shown by measurements of double refraction and i.r. dichroism.

Previous studies of the orientation of the structure elements in block copolymers by low-angle X-ray diffraction,

electron microscopy, and other methods have been supplemented[91] by a study of the depolarisation of scattered light (in the polystyrene/polyisoprene block copolymer system). The method can detect small changes caused by the orientation of structure elements in block copolymers.

We shall now turn to an analysis of the structure and of the mechanical properties of block copolymers. The early work[92-94] was aimed mainly at the behaviour of these materials under uniaxial elongation conditions; hysteresis phenomena were also examined. The optico-mechanical properties of block copolymers[95] have been studied, and a detailed study of relaxation processes in these materials has been reported.[96] In both these investigations[95,96] an attempt was made to interpret the results by the classical theory of high elasticity, the rigid polystyrene domains being treated as filler particles incorporated in a polybutadiene matrix and not effectively involved in the relaxation processes. Some attempts to apply the classical theory of high elasticity to these systems were successful, but the general validity of the theory has not been confirmed.

The mechanical properties of block copolymers are influenced by the type of solvent used to prepare film samples for measurement. The influence of the properties of the solvent (measured by the solubility parameter) on the tensile curves and on the limiting strength and deformation properties is discussed in Ref. 97. A marked effect of the thermodynamic affinity of the solvent for each of the blocks on the shape of the tensile curves was noted in samples of polystyrene/polybutadiene block copolymers of different composition. As was subsequently established, the properties of the solvent from which the films are cast determine the hysteresis of the mechanical properties.[98]

The effect of the type of solvent on the structure and mechanical properties of block copolymers of polystyrene with hydrogenated polyisoprene or hydrogenated polybutadiene has been studied extensively.[99] Increasing the affinity of the solvent for the polystyrene fragments causes a transition from spherical to cylindrical polystyrene domains, though a lamellar structure is also possible for the block copolymers of polystyrene with hydrogenated polybutadiene. Increasing the anisotropy of the rigid domains causes a transition from samples with properties similar to those of unfilled rubber to materials showing induced elasticity.

The fracture mechanism in styrene–diene ternary block copolymers depends on the conditions used in their preparation and orientation. It has been shown[100] that crack propagation under tension at right angles to the axis of the flexible fragments causes brittle fracture, whereas if the cracks are propagated in a direction parallel to the bundles of flexible fragments plastic fracture is observed. The fracture surface is different in the two cases.

The block structure of these copolymers (as opposed to the random distribution of the units in conventional copolymers) affects not only the limiting mechanical and other properties of the material but also its compressibility. For example, for identical compositions the specific volume and compressibility of the random copolymer of styrene and butadiene are greater than those of the block copolymer of polystyrene and polybutadiene.[101]

The presence of rigid domains in block copolymers suggests a model in which flexible chains are held between neighbouring pairs of rigid domains: this model shows neither deformation nor swelling.[102] It can be used to calculate the elastic modulus, the partial molar free energy of swelling, and the dependence of the stress on the strain. When examining the effect of the structure on the mechanical properties of block copolymers it is important to allow for the polydispersivity of the sample and its influence on these properties.

By fractionating samples of block copolymers of polystyrene and polybutadiene it was shown[103] that the elastic modulus calculated from the stress–strain plot is slightly higher for the narrow fractions than for the original samples.

The prospective applications made possible by the control of the properties of ternary block copolymers through changes in the chemical structure of the blocks are demonstrated in Ref. 104. In this work polymers based on styrene, α-methylstyrene, ethylene sulphide, etc. were used as the rigid end blocks, whereas the flexible central blocks were polymers based on isoprene, butadiene, hexamethylenetrisiloxane, etc. In block copolymers of polystyrene and polybutadiene an increase in concentration of polystyrene was found to increase the strength of the material, but not in block copolymers of polystyrene with polyisoprene. In general good strength is achieved by using a high enough molecular weight for the end (polystyrene) blocks: according to these authors[104] it should be greater than 6000.

Hydrogenation of block copolymers based on polystyrene and polybutadiene causes a change in the mechanical properties of the samples: an increase in elastic modulus, etc.[105] Block copolymers show changes in properties also under the influence of radiation, though these changes reflect the special structural features of the materials.[106] Increasing the concentration of polybutadiene fragments in the block copolymer makes the properties more sensitive to the radiation: the strength decreases, the hardness and stiffness increase, the thermal diffusivity increases, and the swelling tendency is affected. All these effects arise from the cross-linking of the polybutadiene blocks, which thus cease to be inert fillers and become active sites in the network.

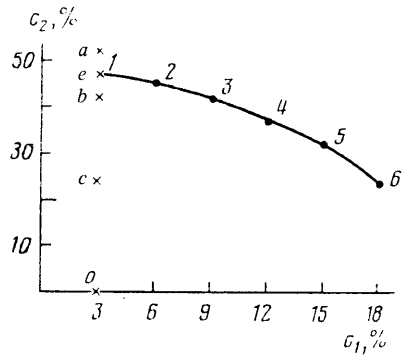


Figure 1. Nephelometric titration curve for solutions of the block copolymer of polystyrene and polybutadiene in benzene against iso-octane: c_1 is the concentration of polymer, c_2 is the concentration of iso-octane, *1–6* are compositions on the nephelometric titration curve, the crosses denote the compositions used to prepare the samples for these experiments.[115]

We should again stress the fact that changes in the structure of block copolymers produced by varying the type of solvent during film preparation can result in changes in properties as substantial as those produced by varying the chemical structure of the copolymer. The shape of the tensile curves is affected not only by the composition of the

block copolymer but also by the thermodynamic properties of the solvent from which the sample is cast.[107,108] Controlling the structure of the block copolymer by varying the composition of the solvent is a convenient method of minimising internal stresses in coatings.[109]

In studies of the adhesion strength of these materials the properties of the surface layers of block copolymers have been monitored by the changes in resonance frequency of a quartz prism on which a layer of polymer had been deposited. According to these experiments[110] an increase in the concentration of polystyrene decreases the number of bonds to the substrate and lowers the adhesive strength.

So far our discussion has been confined to the effect of the structure of the block copolymers on the limiting strength and deformation properties. Let us now examine the relaxation properties of block copolymers under static conditions.

The structure of block copolymers makes these materials specially suitable for studies of the mechanical properties of two-phase systems. The effects of physical ageing on the relaxation properties of block copolymers of polystyrene and polybutadiene have been studied, and the dependence of the time to reach equilibrium on the duration of the annealing treatment has been determined.[111,112] The prediction of the behaviour of polymers under creep conditions from stress relaxation data has been demonstrated[113] for block copolymers of polystyrene and polybutadiene. The strongly non-linear viscoelastic behaviour of these materials is noteworthy.

The most detailed studies of the relaxation properties of block copolymers of polystyrene and polybutadiene are reported in Refs.114 and 115. The samples used in this work contained between 30 and 62% of polystyrene, and they had a wide range of properties. As was stated above, these block copolymers are a convenient medium for the study of the effect of polymer structure on the viscoelastic behaviour of the sample. The structure of these copolymers can be easily changed during the preparation of films from solutions by varying the composition of the solvent, which can be either a mixture of a solvent and a selective precipitant for one of the blocks or a homogeneous solvent with different solubility parameters for the two blocks. The solvent most commonly used in this work is benzene,[114,115] while iso-octane has been used as a selective precipitant for polystyrene blocks. A nephelometric titration curve was used to determine the composition of the solvent medium (Fig.1). The region below the curve corresponds to true solutions, the region above the curve to dispersions. The points in Fig.1 give the composition of the solvent medium used in the preparation of samples of block copolymer film.

The stress relaxation curves for block copolymer films prepared from solvent media of different composition were also determined in the same investigation.[114,115] The measurements were made in the strain region between 5 and 600% at temperatures between −30 and +80 °C. It was found that the addition of a selective precipitant for polystyrene

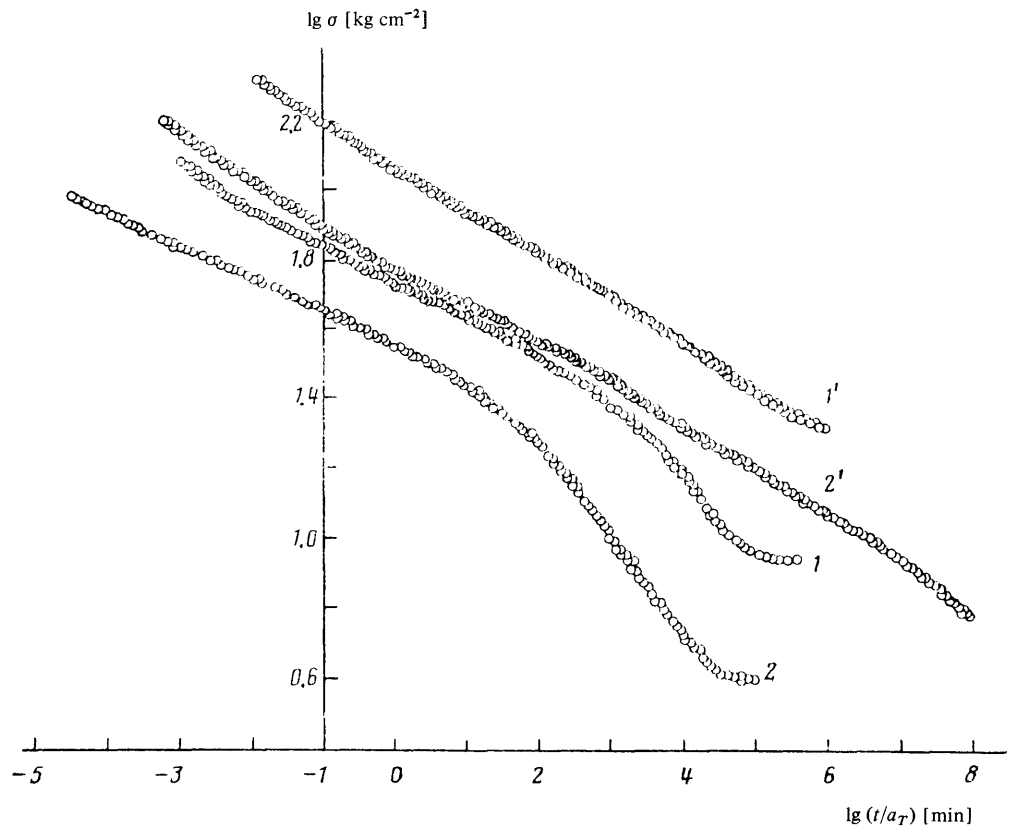


Figure 2. Generalised relaxation curves for deformations by 10% (*1*, *2*) and by 400% (*1'*, *2'*): *1*) and *1'*) are for samples formed from solution, *2*) and *2'*) for samples formed from a dispersion[115] (a_T is the shift factor).

blocks accelerates the stress relaxation, and at the same time the equilibrium elastic modulus is lowered, the effects being observed at all temperatures. Irrespective of the initial concentration of the block copolymer in the mixture of solvent and precipitant, the films formed from a true solution show a much greater equilibrium elastic modulus and relaxation time than films prepared from dispersions.[115] A sharp decrease in equilibrium modulus and in relaxation time can be induced by forming the film from a mixture of solvent and precipitant of composition close to the phase separation curve but on the true solution side.

Fig. 2 shows, as an example, the generalised relaxation curves for films prepared from a solution (point "0" in Fig. 1) and from a dispersion (point "a" in Fig. 1). The generalised curves were obtained by shifting the stress relaxation curves along the lg t axis. The generalised curves for samples prepared from dispersions are invariably found in the region of lower stresses than those for samples prepared from solutions. This may be due to coiling of the polystyrene blocks as a result of the addition of a selective precipitant, with formation of a compact structure which does not contribute so effectively to the relaxation process.

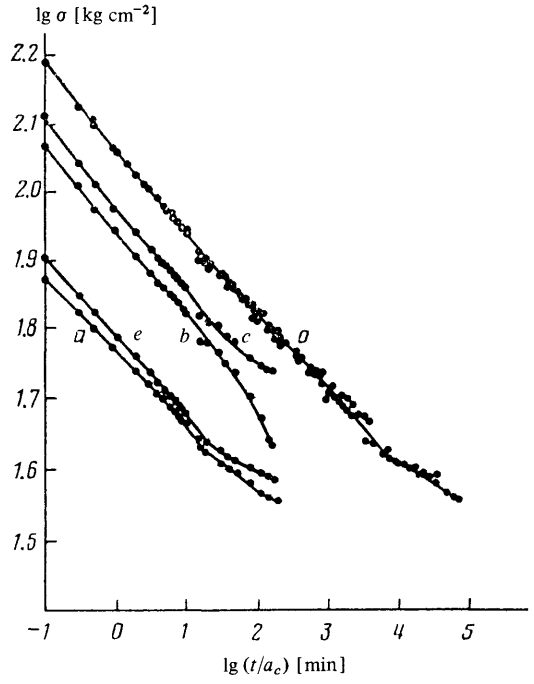


Figure 3. Initial and generalised stress relaxation curves for films prepared at different concentrations of the selective precipitant, ε = 400%, curves numbered as in Fig. 1.[115]

This conclusion is consistent also with the relaxation curves for samples prepared from media with different concentrations of the selective precipitant. These curves can be reduced to a single curve, shown in Fig. 3, by a shift along the lg t axis. In this case the reduced parameter is not the temperature but the concentration of selective precipitant. The plot of the logarithm of the shift factor lg a_c against $(c - c_0)$, where c is the concentration of the selective precipitant and c_0 is the concentration used in the reduction, has the characteristic shape shown in Fig. 4, indicating the presence of a narrow range of concentrations of the precipitant in which the relaxation processes are strongly accelerated. In the case of this particular block copolymer (containing 62% of polystyrene) the critical concentration of precipitant is 45%.

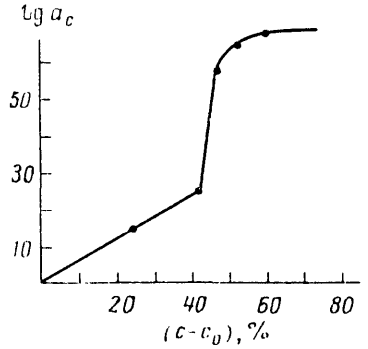


Figure 4. Plot of lg a_c against $(c - c_0)$.[115]

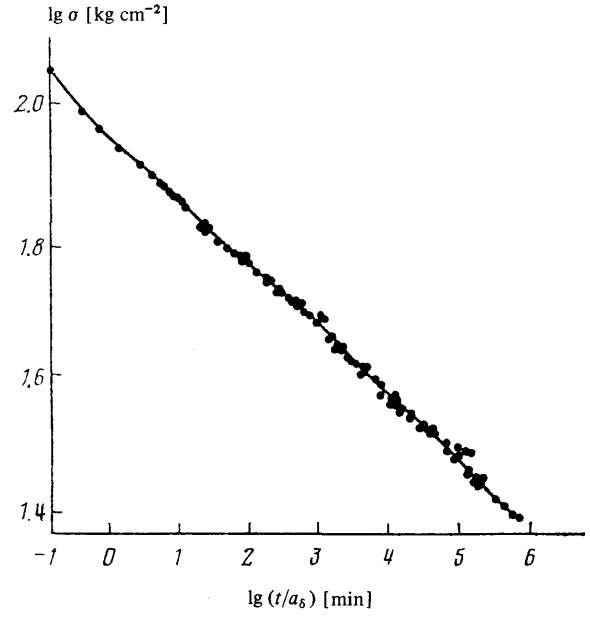


Figure 5. Generalised stress relaxation curve for samples formed from different solvents (ε = 10%).[115]

The relaxation properties of a block copolymer can also be controlled by preparing samples from solvents with different solubility parameters δ. The initial and the generalised relaxation curves for samples prepared from solvents with different values of δ are shown in Fig. 5. Increasing the δ value of the solvent to a value equal to or greater than the characteristic value for the polystyrene blocks causes a

marked increase in the relaxing and the equilibrium stresses. Hence by changing the solvent medium we can substantially affect the relaxation properties of block copolymers, and we can lower, or raise, the strength of the equilibrium stresses, i.e. we can control the degree of completion of the relaxation process.

To generalise this conclusion the relaxation curves (corresponding to different values of δ) were shifted along the $\lg t$ axis to merge into the previously obtained generalised curve (see Fig. 5). The dependence of the shift factor $\lg a_\delta$ on $(\delta_0 - \delta)$ is shown in Fig. 6, where δ_0 is the solubility parameter for dioxan. As the solubility parameter δ increases, the shift factor decreases.

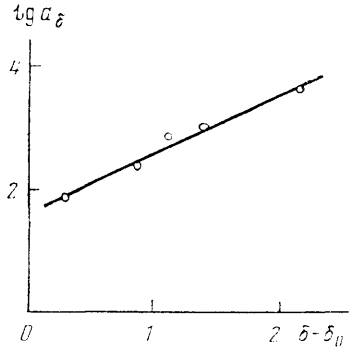


Figure 6. Plot of the shift factor $\lg a_\delta$ against $(\delta - \delta_0)$.[115]

Thus the study[114,115] of the mechanical (relaxation) behaviour of block copolymers has revealed extensive prospects for controlling the relaxation properties of these materials, depending on the previous history of the formation of the film samples from solution. Obviously, studies of the relaxation properties allow us to reach definite conclusions as to the activity of the rigid particles formed by the polystyrene domains which act as a strength-enhancing filler.

The durability and creep properties of polystyrene and polybutadiene block copolymers under conditions of uniaxial tension are discussed in several papers.[116–118] Both reversible and irreversible deformation is observed in the creep process, and the durability is decreased by an expression which is characteristic of rubber. The activation energies of the fracture, creep, and viscous flow processes are identical, suggesting that all three processes take place by the same mechanism (involving the breakdown of the domain structure).

The relaxation properties of block copolymers have been studied also in melts. The relaxation of the stresses in a melt of the block copolymer of polystyrene and polybutadiene after stopping the deformation has been measured.[119] It was found that the stress decays not to zero (as in linear elastomers based on homopolymers) but to some final value which is greater, the shorter the deformation time of the melt. Hence the evidence for a network structure is present also in the melt. The existence of a final stress was detected also in a study[120] of stress relaxation in block copolymers at relatively high temperatures. This behaviour of block copolymers under conditions of stress relaxation in the melt is attributed to the formation of star-shaped structures after the initial breakdown of the domain structure originally present in the melt by the action of the shear deformations.[121]

The relaxation properties of block copolymers under conditions of dynamic mechanical interaction have been studied in depth. We shall not dwell on any particular investigation, but we shall merely point out that in addition to the strengthening effect of the rigid blocks we find two maxima in the temperature dependence of the slope of the mechanical losses[122–125] for many of these copolymers. There is also a change in the temperature dependence of the shift factor, detected by applying the temperature–time superposition principle to the analysis of the experimental results.[126,127] Deviations from the usual dependence, described by the Williams–Landel–Ferry equation, are observed at temperatures above the glass transition temperature of the polystyrene phase of the block copolymer of polystyrene and polybutadiene.

As in the case of the parameters of the static mechanical properties, the type of solvent used in the preparation of the sample has an important effect on the results of dynamic mechanical tests. Thus the dependence of the dynamic mechanical properties of films of a ternary block copolymer of polystyrene, polyethylene, and polybutene on the solubility parameter of the solvent used in casting the film has been studied.[128] Because of the better dispersion of the polystyrene domains and of the possibility of contacts between these domains the use of a good solvent causes a large increase in the accumulation modulus of the system. If a poor solvent is used the polystyrene blocks are isolated and cannot form mutual contacts: as a result, the relaxation of the stresses is rapid, and the accumulation modulus decreases.

The structure of block copolymers and the tendency of their fragments to aggregate lead to an unusual effect of the rate (or frequency) of the mechanical interaction and of the temperature, and also of the magnitude of the mechanical stress, on the dynamic mechanical properties of the samples. Thus at low shear rates the block copolymers of polystyrene and polybutadiene behave as dispersed systems showing marked thixotropy.[129] At high shear rates the viscoelastic behaviour of these systems is determined mainly by the polybutadiene matrix. Similar effects are observed at high shear stresses. The viscoelastic properties of block copolymers of polystyrene and polybutadiene at low temperatures are similar to those of rubber. At high temperatures (above the glass transition temperature of the polystyrene fragments) even low-amplitude deformations produce a small amount of viscous flow in spite of the substantial residual aggregation of the polystyrene blocks mentioned above.

A similar study by a different method is reported in Ref. 130. The samples were block copolymers of polystyrene and polybutadiene in which the molecular weight of the polystyrene blocks was much lower than that of the polybutadiene fragments. Measurements of the dynamic shear modulus and of the dynamic viscosity over a wide range of temperature showed that the temperature–time superposition principle applies in these systems, the temperature dependence of the dynamic viscosity dropping sharply at 142 °C (in the low-frequency region). At high frequencies a different behaviour is observed. From these results the authors concluded[130] that a critical temperature exists for block copolymers at which the domains formed by the rigid blocks begin to collapse and the material becomes more homogeneous.

Detailed studies of the dynamic mechanical properties of ternary block copolymers of the ABA type of different chemical structure have been reported.[131] The end blocks

were polystyrene, and the central block was polybutadiene, polyisoprene, polydimethylsiloxane, etc. Most of the work was carried out at temperatures above the glass transition temperatures of both blocks. The main difference between the mechanical behaviour of the block copolymers and of the homopolymers is a higher value of the dynamic viscosity, due to the aggregation of the polystyrene domains. This aggregation is found even at temperatures above the glass transition temperature of polystyrene. The aggregation is less evident in block copolymers containing polyisoprene as the central block. An analysis of the dynamic mechanical behaviour of these systems has shown that differences between the solubility parameter for the central block and for the end blocks play a major role.

The dynamic mechanical behaviour of block copolymers of polystyrene with polybutadiene, hydrogenated polybutadiene, polyisoprene, hydrogenated polyisoprene, and polydimethylsiloxane has been fully analysed.[132] Both binary and ternary block copolymers were studied. The work was aimed mainly[132] at demonstrating the influence of the molecular weight distribution of the block copolymers on the relaxation transitions. Two relaxation transitions were observed, corresponding to the devitrification of the two phases, and the temperatures of these transitions were shown to depend on the type of molecular weight distribution. The high-temperature transition takes place at a lower temperature than in homo-polystyrene.

The relaxation properties of block copolymers have been studied not only by dynamic mechanical methods but also by various other physical methods: dielectric, i.r. spectroscopic, etc. Careful attention is currently paid in studies of the dielectric properties of polymers to processes associated with the boundaries of structural formations. In this respect block copolymers are specially interesting, because they are micro-heterogeneous systems. A theoretical and experimental study[133] of dielectric relaxation has shown that at low frequencies the experiment is adequately described by the theory, though allowance is needed for both the bulk concentration of components and the type of supermolecular structure in the calculation of the dielectric parameters.

Transitions resulting from molecular mobility in the interphase regions have also been detected by the positron annihilation method.[134]

Transition in block copolymers and in their solutions are reliably observed ultrasonically, using the form of the adsorption and the velocity of the ultrasound.[135] Two transitions, corresponding to the devitrification of the polybutadiene and polystyrene phases, were observed in the initial block copolymers. The same transitions were observed in the swelled samples, but in this case the transitions were shifted towards lower temperatures. In solutions high-frequency attenuation is enhanced, due to the presence of micellar formations. The study of the acoustic properties of block copolymers of polystyrene and polybutadiene has shown[135] that the glass transition temperature (which is related to the polybutadiene phase) depends on the concentration of the polystyrene component and on the method of preparation of the sample. Extruded samples show a characteristic increase in glass transition temperature.

The relaxation properties of block copolymers have also been studied by thermally stimulated current and thermoluminescence methods.[137]

In general, each of the components of a block copolymer can influence the glass transition temperature of the other component, which depends on the length of the block. An analysis of this effect[138] has clarified the dependence of the glass transition temperature of the polystyrene component on the length of the polystyrene block. The second components of the block copolymers were polyisoprene and polydimethylsiloxane blocks, whose compatibilities with polystyrene are different. Nevertheless the decrease in glass transition temperature caused by a decrease in the length of the polystyrene block was about the same in the two cases. This suggests that the change in glass transition temperature is not always determined by the level of compatibility and may also depend on other factors (for example, internal stresses).

The relaxation properties of block copolymers have also been studied (as was mentioned above) by i.r. spectroscopy.[139] The micro-heterogeneous structure of the block copolymers results in a non-monotonic decrease in optical density with increase in temperature.

A detailed analysis of relaxation transitions in block copolymers of polystyrene and polybutadiene has been carried out by a dilatometric method.[140] The character of the transitions was found to depend not only on the molecular weight and composition of the block copolymer but also on the previous thermal history of the sample. Thus in samples containing 44 wt.% of polystyrene the transitions were observed at 0.87 T_g and (0.92–0.95)T_g. Heating the samples to 40 °C causes these transitions to disappear, and annealing at 55 °C induces a new transition at $T = 0.90T_g$. All these effects have been ascribed[140] to ordering of the inter-phase regions during annealing.

It is interesting to compare the dilatometric characteristics of block copolymers with those of mechanical mixtures of homopolymers having the same composition.[141] Whereas several transitions are detected at temperatures below the glass transition temperature of polystyrene, no relaxation processes are observed in mixtures of polystyrene and polybutadiene.

Several papers discuss the rheological behaviour of block copolymers, which is important for optimising the technological processing of these materials. The special rheological behaviour of block copolymers is ascribed[142] to the formation of a stable physical network and to the possibility of transition to the highly elastic state at high shear rates (of course, this refers to a melt of the block copolymer at high temperature). During the technological treatment of block copolymers of the SKS type, the only changes are a slight swelling and a small shrinkage.

The rheological properties of ternary block copolymers of polystyrene and polybutadiene have been compared with those of polybutadiene rubber.[143] The most significant result was that the block copolymer shows a non-linear dependence of the logarithm of the viscosity on the reciprocal temperature, which cannot be described by the conventional relations which apply to homopolymers.

The rheological behaviour of ternary block copolymers has been described by a model[144] in which the interfacial layer between the matrix and the domains embedded in it plays the main role in controlling the rheological properties. The effect of structure on non-Newtonian flow, phase inversion, etc. can be described by introducing three segmental friction coefficients.

The rheological behaviour in the pre-stationary region of the deformation of block copolymers of polystyrene and polybutadiene has been studied.[145] These systems are characterised by an anomalous dependence of the limiting shear strength on the shear rate: under these conditions an important role is played by orientation effects.

Considerable effort is being devoted to the development of micro- and macroheterogeneous systems free from the brittleness found in the homopolymers which form the rigid domains in block copolymers. A recent review[146]

of this topic discusses, in addition to the traditional methods of preparing block copolymers and their mixtures with homopolymers, some original approaches such as polymerisation of the monomer from one of the blocks in a solution of the complete block copolymer. Of course, this method applies to the formation of composite materials, which can also be prepared by other methods.

As was stated above, block copolymers offer very attractive possibilities of controlling the properties of synthetic materials. Even more important prospects of controlling the structure and properties of these materials are created by mixing block copolymers with homopolymers of various structures. Whereas in block copolymers we observe micro-phase separation of the system and phase inversion, in the case of mixtures of a block copolymer with homopolymers having the same structure as the fragments of the block copolymer we find both micro- and macro-layering.[147] The nature of the phase separation depends mainly on the difference in molecular weight between the homopolymer and the corresponding blocks, and also on the composition of the components of the mixture. If the molecular weight of the homopolymer is approximately equal to (or smaller than) the molecular weight of the corresponding block the homopolymer dissolves in the blocks of the copolymer. In the opposite case we observe macro-layering, and the homopolymer forms a separate phase, while the corresponding blocks of the copolymer distribute themselves at the boundary of this phase. In the first case (micro-heterogeneity) the specific impact viscosity stays low. The best result was obtained[147] for a micro-heterogeneous system in which the particles of the copolymer are dispersed in the polystyrene matrix.

As we have already pointed out, mixtures of block copolymers with homopolymers having a constitution analogous to that of the corresponding blocks are being intensively studied at present. The properties of these systems are sensitively dependent on the micro-domain structure of the block copolymers and on their deformation mechanism.[148] One possible mechanism is the formation of micro-cracks under tension in the rigid domains in the block copolymer (for example, in the polystyrene domains), which requires a large expenditure of energy. Another mechanism consists in the formation of a macroscopic neck in the rigid component of the block copolymer: this mechanism has been confirmed in samples with a micellar structure. A successful combination of a block copolymer and a homopolymer should produce a system with impact-resisting and other useful properties. Thus the rheological behaviour of mixtures of polystyrene and ternary block copolymers of polystyrene and polybutadiene under shear conditions is typical of mixtures of incompatible polymers, the addition of a small amount of the block copolymer to the polystyrene causing an increase in the viscosity and the elasticity of the melt.[149]

The structure and the dynamic mechanical properties of mixtures consisting of the normal block copolymer of polystyrene and polybutadiene (SBS type) and of a branched block copolymer have been studied.[150] The mixtures were prepared in a way which kept the concentration of polystyrene constant (75%) but allowed the block length to be varied. The structure of the samples can be controlled during preparation so as to vary not only the mechanical properties and their anisotropy, but also the glass transition temperature of the rubber-like component embedded in the polystyrene matrix. In general the use of mixtures of block copolymers offers very wide prospects of controlling their structure: samples containing structure elements varying from spherical to rod-like have been obtained in this way.

Macro-heterogeneous compositions based on block copolymers of polystyrene and polybutadiene of the SBS type and containing prescribed amounts of polystyrene as a filler can be prepared by the pressure casting method.[151] Optical and microscopic studies have shown that the addition of polystyrene leads to phase layering of the system. Composite materials based on block copolymers are conveniently prepared by using rollers or rubber mixers. Changes in composites based on thermoelastoplastics and polystyrene have been studied by a thermomechanical method and by hydrostatic weighing.[152]

Ternary block copolymers have been mixed with binary block copolymers in order to control their physical and mechanical properties.[153]

Composite materials can also be prepared by adding various fillers to block copolymers (for example, technical carbon). The effective density of nodes in the three-dimensional network of block copolymers of polystyrene and polybutadiene has been shown to increase with the concentration of technical carbon added to the block copolymer.[154] Increasing the dispersion of the filler has the same effect.

Block copolymers have been used to prepare vulcanisates by cross-linking hexachloro-*p*-xylene in the presence of metal oxides.[155]. The presence of these oxides allows the formation of coordination and adsorption bonds, which raise the strength of the vulcanisates. The relaxation properties of these materials have also been studied,[155] and shown to be controllable through changes in the characteristics of the bonds.

We shall conclude this discussion by reviewing the work on structural changes in block copolymers during deformation. Both direct structural methods and thermodynamic approaches have been used in this analysis.

A detailed study of the structural changes accompanying the deformation of block copolymers of polystyrene and polybutadiene is reported in Ref. 156. In the first elongation cycle the dependence of the stress on the deformation has the characteristic shape found in glassy polymers (the concentration of polystyrene was 48%). In a repeated elongation cycle the stress–strain relationship is typical of elastomers. The reason for these changes is that the first elongation causes breakdown of the initial lamellar structure to give small particles, so that the sample is converted into a polybutadiene matrix filled with dispersed particles. After a rest period the sample tends to revert to its initial structure, and heat treatment at 59 °C (which is well below the glass transition temperature of polystyrene) restores the initial structure almost completely. This effect suggests[156] the presence of a substantial inter-phase layer containing both polystyrene and polybutadiene blocks: this structure could cause a decrease in the glass transition temperature of polystyrene. However, in the absence of dynamic mechanical data the suggested mechanism[156] can only be tentative.

Electron microscopy and low-angle X-ray diffraction methods have been used to study the structural changes accompanying the transition from the "hard" to the rubbery state during mechanical elongation of block copolymers of polystyrene and polybutadiene and of their mixtures with polystyrene.[157–159] The results are similar to those discussed above: regular deformation of the lamellae is observed in the initial stages of elongation (up to 5%), then the lamellae undergo shear, fracture, reorientation, and collapse successively, and in the last stages of collapse a structure with polystyrene domains uniformly distributed in the polybutadiene matrix is produced.

A similar result was obtained in a study of the deformability of block copolymers of polystyrene and

polybutadiene containing different amounts of polystyrene.[160] The polybutadiene blocks contained fragments with *cis*- and *trans*- structures. The breakdown of the domain structure of the block copolymer and its dispersion in the polybutadiene matrix were again observed; annealing restored the initial structure and properties.

The break-up of the cylindrical domain structure formed by polystyrene blocks is observed most clearly during elongation of the block copolymers in the direction of the cylinder axis.[161] The same behaviour is observed in rheological studies.[161] In the presence of a small mechanical stress the domain structure of the block copolymer is preserved, but above some critical stress the giant networks formed by the domains begin to collapse. This produces a break in the plot of shear stress against shear rate. When the domain structure is fully broken down the viscosity of the block copolymer is described by the normal flow curves, and the temperature dependence of the viscosity by the Williams–Landel–Ferry equation.

The simultaneous application of small-amplitude dynamic deformations and large static deformations produces a mechanical loss peak at the point where the initial structure of the block copolymer is broken down by the static deformation.[163] Under these conditions the height of the peak increases with time, because the breakdown of the initial structure affects increasingly deep layers. The destruction of the initial structure of the block copolymer is accompanied by the formation of an oriented structure as a result of the development of large highly elastic deformations in the polybutadiene matrix.[164]

The deformation behaviour of block copolymers of polystyrene and polybutadiene (SBS type) has been studied[165] with allowance for the anisotropy of the structure of the material. Samples having a structure of the "single crystal" type were studied, i.e. samples in which the cylinders consisting of polystyrene domains were packed in a parallel arrangement in the polybutadiene matrix. As a result, the deformation behaviour in extension was different in directions parallel to and perpendicular to the cylinder axes. Under extension at right angles to the cylinder axes the cylinders (being hexagonally close packed) undergo affine deformations, like the sample as a whole. This deformation is reversible, but when it exceeds 10% we observe a well defined irreversibility attributed to the formation and development of cracks in the sample. In parallel deformation the fluidity limit is reached at low elongations, and the Mullins–Patrikeev effect is clearly shown. After a period of rest (especially with annealing) the sample becomes more elastic, and the effect can be explained by the dispersion of the cylinders after the first elongation and their re-establishment after the rest period. Thus the system displays thixotropic properties.

Structural changes during the deformation of isotropic and of oriented polymers have been compared.[166] In oriented samples, having an initial structure of the single crystal type, deformation in a direction perpendicular to the cylinder axes initially distorts the crystalline arrangement and then produces bends in the crystal (at the weakest points). The crystals (in the shape of a flat zig-zag) are deformed at the bends during subsequent extension. On the other hand if the deformation is applied in a direction parallel to the cylinder axes it causes the cylinders to break into residues about 1000 Å long. Under these conditions, and for small elongations, the orientation of the initial structure elements (for example, the cylinders) is retained, since the elongation is achieved by the deformation of the highly elastic matrix.[167]

The detailed thermodynamics of the deformation and fracture processes of block copolymers of polystyrene and polybutadiene have been investigated for systems containing 40–50% of the polystyrene phase, and the special features of the thixotropic processes in the solid phase, whose rate is strongly temperature-dependent, have been studied.[168–171] An analysis of the energy balance of the softening processes using a high-precision calorimeter showed that the softening caused by deformation depends on the break-up of the polystyrene phase, especially during the initial stages of the process, and that the process is accompanied by an increase in the internal energy of the sample. During the thixotropic recovery period the stored energy is dissipated, and the recovery process itself (as stated above) is strongly temperature-dependent: it goes to completion in a few seconds at 100 °C, as opposed to 5–10 days at room temperature.

The deformation calorimetry method has been used to show that at high deformations the increase in stress is due to the acceptance of the load by the polystyrene domains, and to the deformation of these domains, and not to the limited extensibility of the polybutadiene chains. On the whole, the morphology of the polystyrene phase is the main controlling factor in the deformation behaviour of block copolymers of polystyrene and polybutadiene.

The changes in lamellar structure caused by the elongation of block copolymers of polystyrene and polybutadiene, and their elimination by annealing, have been studied thermodynamically.[172] The thermodynamic properties of the materials were calculated theoretically by introducing an approximation[173] in which the space between the domains is assumed to be much narrower than the domains themselves. With this assumption the free energy could be calculated as the sum of the following quantities: the energy associated with the surface tension, the energy associated with the topology of the blocks at the interface, and the change in entropy. In this case the entropy decreases, since the samples should have a uniform density over the entire volume. By calculating the free energy of the system and minimising it a theoretical estimate of the periodicity and of the disposition of the domains could be obtained.

The influence of structure on various properties (hardness, strength, thermo-mechanical characteristics) has been studied with star-shaped block copolymers of polystyrene and polybutadiene.[174] The main effort was devoted to a comparison of the initial properties with those of deformed samples. As in other work it was found[174] that in the first experiment the star-shaped block copolymers exhibited the phenomenon of induced elasticity: the effect was more clearly marked than in linear thermoelastoplastics (20% higher than the Shore hardness). At the second deformation the polymer becomes more elastic, but its initial structure and properties can be restored by annealing. These phenomena are attributed[174] to the formation of an interfacial transition layer consisting of polystyrene bridges, which are broken during the first deformation cycle.

The properties of block copolymers have been studied[175] at relatively low temperatures and their structural transitions have been examined in depth.

Thus the main areas of research on the structure and properties of block copolymers in the solid state are the application of the latest physical methods for studying structures (low-angle X-ray diffraction, transmission electron microscopy, thermodynamic analysis, positron annihilation, ultrasonics, etc.), and also wide-ranging rheological studies covering large changes in temperature, stress, and deformation rate. Two series of papers on the latter topic deserve special mention. One series[116–118] deals

with the rheological behaviour of block copolymers under uniaxial elongation conditions. This work highlights the single mechanism common to fracture, creep, and viscous flow processes in block copolymers, involving the collapse of the initial domain structure. The other series of papers describes a study of the mechanical behaviour of these materials by deformation calorimetry, which has demonstrated the fundamental effect of the domains formed by the rigid blocks on the shape of the tensile curve.

To review the thermodynamic approaches to the analysis of block copolymer structures we must stress the problem of determining the parameters of the effective network by using the expressions of the classical theory of high elasticity. In principle the size of the fragment between the points of the network M_C can be determined if the equilibrium elastic modulus E_∞ is known. In the earlier work the quantity M_C had been found to coincide in many cases with the molecular weight of the flexible (for example, polybutadiene) blocks. It is important to establish the correct way of determining the equilibrium elastic modulus in the case of a block copolymer. We know that in lattices with chemically defined nodes the equilibrium stress (elastic modulus) can be determined from the stress relaxation curve, but the relaxation process should not only have gone to completion at the given temperature (for a given deformation) but the stress should also have been allowed to reach its equilibrium value after upward and downward temperature excursions. In block copolymers the nodes of the network are the domains formed by the rigid blocks, and an increase in temperature can cause softening of the nodes and substantial changes in the relaxing stress. Therefore the correct determination of the equilibrium stress in block copolymers remains an open problem, though experimental data convincingly demonstrate[114,115] the important influence of the rigid domains on the rheological properties and show that these domains do not act as an inert filler but take an active part in the formation of the set of relaxation properties of block copolymers, including those observed in studies by the swelling method.

IV. DETERMINATION OF THE STRUCTURE OF BLOCK COPOLYMERS BY THE SWELLING METHOD

The swelling (or sorption) method has been used to determine the structure of block copolymers in two variants. Firstly, the effective length of the flexible (for example, polybutadiene) blocks has been determined, and secondly the method has been used to study the structural changes accompanying the swelling, and the influence of the method of preparation and of the previous thermal history of the sample on its sorption characteristics.

Several procedurally important aspects must be included in the analysis of block copolymer structures by the sorption method.[176] The first is the dependence on the thickness of the sample of the diffusion coefficient D determined from sorption and desorption data. For example, the parameter D increases from 10^{-8} to 30×10^{-8} cm^2 s^{-1} as the thickness of a film of the block copolymer of polystyrene and polybutadiene is increased from 50 to 300 μm.[176] The second special feature is the dependence of D on the type of substrate used to prepare the film. Lastly, annealing of the sample also tends to increase the value of D.

There have been many attempts to determine the length of the elastic block from data on the swelling behaviour. In all this work swelling was allowed to take place in a solvent which is selective towards the elastic blocks. In some cases satisfactory agreement between calculated and experimental lengths of the elastic block (for example, polybutadiene) was obtained,[177,178] but in other cases the discrepancy was serious.[179–181]

The Flory–Huggins interaction parameters have been determined by sorption measurements for styrene–butadiene copolymers of different composition.[182] In these determinations, it is important to remember that the segmental mobility of the polybutadiene blocks in the copolymers is smaller than the chain mobility in the initial polybutadiene.[183] This is not surprising, since the transport process is obstructed by the polystyrene domains, which are impervious to the solvent vapour.

The changes in structure of ternary block copolymers during swelling and desorption, and the re-establishment of the initial structure by annealing, have been studied by the low-angle light scattering method.[184] Rods of the polystyrene blocks oriented at different angles retain their orientation during swelling in iso-octane, but changes are observed after evaporation of the solvent. This behaviour is characteristic of block copolymers of polystyrene and polybutadiene, but not of the analogous copolymers of polystyrene and polyisoprene.

The effect of the solvent used to cast the block copolymer samples on the sorption and desorption of *p*-aminoazobenzene has been studied. The differences in structure of the block copolymer resulting from changes in the type of solvent (for example, phase inversion) are reflected by changes in the diffusion coefficient and in the temperature dependence of the rate of desorption. The large increase in the rate of desorption at higher temperatures is attributed to devitrification of the polystyrene phase[185] because of the changes in the glass transition temperature of polystyrene as a function of the type of solvent used in the preparation of the film.

The properties of block copolymers of polystyrene and polybutadiene in film form depend on the substrate used in the preparation of the sample. This dependence is clearly seen in experiments on the sorption of cyclohexane vapour in film samples deposited on glass, Teflon, or mercury. The rate of approach to sorption equilibrium is determined by the type of substrate used. Films prepared on solid substrates develop internal stresses which are thought[186] to influence the packing density of the macromolecules and hence the diffusion coefficient. However, we should note that the mechanical stress itself can affect the diffusion coefficient through its influence on the relaxation time (see below).

In another paper from the same laboratory[187] the effect of the structure of block copolymers of polystyrene and polybutadiene on the sorption curves and on D is discussed for a sample containing 25% of polystyrene. The sorbate was iso-octane. The structure of the samples was varied by using different substrates (glass, mercury, Teflon) for film preparation, and also by varying the thickness of the films. The diffusion coefficient was found to depend on the size and on the number of the polystyrene domains in the block copolymer. Therefore the sorption experiments are an effective method for the analysis of the structural changes in block copolymers.

A detailed study[188] of the relaxation mechanism of the swelling of polymers, which determined the kinetics of the process, is relevant in this context. It is assumed that the diffusion of low-molecular liquids or vapours in polymers is determined not only by the penetration of the sorbate molecules into the pores of the polymer but also (and to a large extent) by conformational rearrangements of the macromolecules, i.e. by the relaxation phenomena which accompany the diffusion process. Under these conditions we observe degeneracy of the long relaxation times. The

suggestion that the swelling of polymers is related to conformational rearrangements in the macromolecules and to the degeneracy of long relaxation times was first put forward in Ref. 189. It has since been confirmed by calculations and experiments.[188]

The more recent work[188] is based on a mathematical model of the process in which the viscoelastic polymer medium responds to interactions with the sorbate molecules. The associated model of the viscoelastic body consists of two Aleksandrov–Lazurkin elements connected in parallel; this model was used in calculations of stress relaxation and creep processes for these materials.

The same workers[188] had previously introduced the concept of a time-dependent diffusion coefficient, and had obtained a solution of the differential equation for Fick's second law in which the diffusion coefficient is expressed in terms of Einstein's system of equations for the Brownian motion (which includes the velocity of the diffusing species). Having determined this velocity from the proposed model the authors[188] found the time dependence of the diffusion coefficient and used it to calculate the dependence of the mass of the diffusing species on time by the expression

$$\frac{M(t)}{M(\infty)} = A_1(1 - e^{-t/\theta_2^*}) + A_2(1 - e^{-t/\theta_4^*})$$

where θ_2^* and θ_4^* are the characteristic times of the relaxation, A_1 and A_2 are constants related to the parameter of the model, and $M(t)$ and $M(\infty)$ are the time-dependent and the final mass of the diffusing species respectively. Experimental data[188] for the block copolymer of polystyrene and polybutadiene are described reasonably well by this expression if two time lags are used. The calculated values of $M(t)$ are accurately consistent with the experimental kinetic sorption curves (Fig. 7). The formation of maxima and minima on the kinetic sorption curves was also analysed.[188] It was found that these mass oscillations can be ascribed to standing waves formed in the cylindrical cavity of a McBain balance at some pressures of vapour, the waves being diffuse rather than elastic in nature.

Other measurements of the sorption kinetics of the vapours of various liquids by block copolymers of polystyrene and polybutadiene have also been reported.[188] The equations were found to give an accurate description of the kinetics of the process, and the time lags determined from sorption data agreed reasonably well with the relaxation times obtained in independent stress relaxation experiments.

Relaxation experiments carried out in a medium of the sorbate[188] confirmed the assumption that the penetration of sorbate into the polymer causes degeneracy of the long relaxation times. All these results indicate that the relaxation mechanism associated with the swelling of the polymers is the main determining factor in the sorption process.

A statistical analysis of the behaviour of block copolymers during swelling, allowing for the conformation of the chains connecting the domains, has also been described.[190]

Thus the sorption process, which is accompanied by a large change in volume (i.e. by swelling), is closely bound to the relaxation processes involving conformational rearrangements of the macromolecules. These rearrangements are responsible

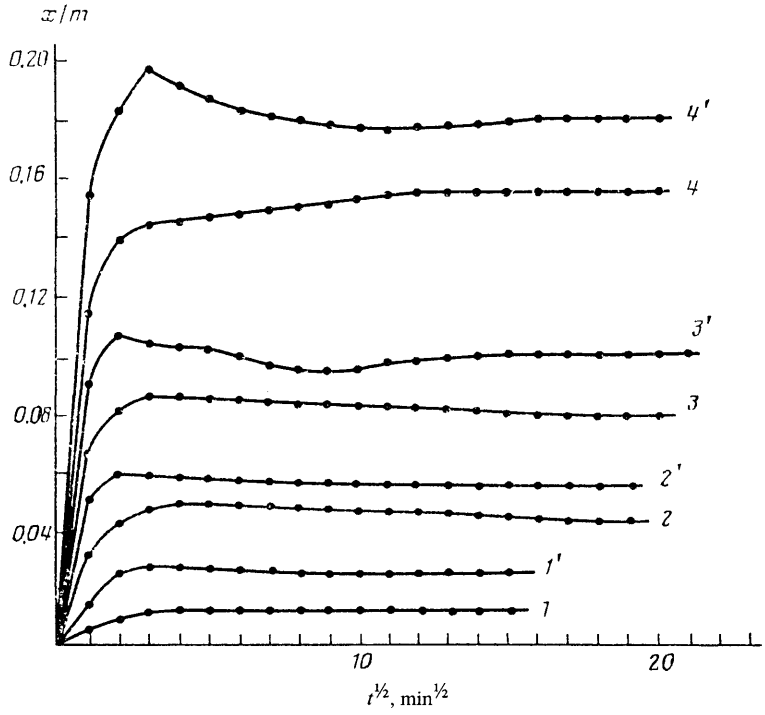


Figure 7. Kinetic curves for the sorption of iso-octane vapour on a block copolymer of polystyrene and polybutadiene containing 30% of polystyrene blocks. The ratio p/p_S is: *1*) and *1'*) 0.2, *2*) and *2'*) 0.4, *3*) and *3'*) 0.6, *4*) and *4'*) 0.8. Numbers without primes and with primes correspond to samples prepared from solution and from dispersion respectively[188] (x/m is the increase in weight of the sample caused by sorption, p/p_S is the relative vapour pressure of the solvent).

for the time-dependence of the diffusion coefficient. Allowing for this time-dependence gives an accurate description of the swelling kinetics and explains many other features of the process.

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