

Permeation and Diffusion of Gases in Styrene-Butadiene-Styrene Block Copolymers

Hisashi ODANI, Kazuo TAIRA, Norio NEMOTO,
and Michio KURATA*

Received May 22, 1975

The permeation and diffusion behavior for a series of inert gases in SBS block copolymers were studied in the temperature region from 25° to 120°C. The block copolymer samples having two different types of domain structures were prepared by careful solvent-casting and thermal treatments. The domain structures of the samples, assured by electron microscopic observation, are (a) polystyrene rods dispersed in polybutadiene matrix, and (b) alternating lamellae of styrene and butadiene components. The inert gases studied were helium, argon, krypton, xenon, and nitrogen. The permeability coefficient P was determined from the steady-state permeation rates and the diffusion coefficient D from the time-lag method. Fick's and Henry's law were accurately obeyed for all the systems over the temperature and pressure range studied. For all the systems studied the permeability coefficient P , or the diffusion coefficient D , for the copolymer samples were intermediate between those of homopolybutadiene and homopolystyrene. The coefficients P and D for the sample (a) were greater than those for the sample (b). It has been found that the observed values of P for these block copolymer samples are well explained in terms of a simple model consisted of parallel array of elements of the respective component homopolymers. From an examination of the selectivity for permeation to gases having different molecular size, however, it was suggested that permeation behavior of gases of greater molecular size through the sample (b), of lamellar-type structure, was influenced by interaction between the two different polymer phases. The trend was discussed in terms of a dependence of two impedance factors for permeation and diffusion, proposed by Michaels and Parker, on size of gas molecule. The temperature dependence of P , or D , in the temperature range 25° to 85°C was represented by the Arrhenius-type equation with constant activation energy for permeation, or diffusion. The dependence was interpreted by the fundamental relationship, suggested by Meares, between the entropy and the energy of activation. It has been inferred that, as far as the kinetic nature is concerned, the permeation and diffusion of gases in the SBS block copolymers are governed primarily by those in rubbery polybutadiene matrix.

INTRODUCTION

Diffusion and permeation processes of small penetrant molecules in and through polymer films, comprised of more than two components or phases, are of practical importance. Interest in the study of the processes has been mainly motivated by fields of application such as the technology of packaging materials and protective coatings, drying of polymeric films and fibers, and the use of heterophase polymer membranes in separation processes of gases and vapors, because many materials in common use are heterogeneous in structure. Knowledge of diffusion, permeation, and solution behavior is the basis for the successful manufacturing and usage of heterogeneous polymeric films as, for example, packaging materials or permselective membranes.

* 小谷 壽, 平 和雄, 根本紀夫, 倉田道夫: Laboratory of Polymer Solutions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

The study of the transport and solution processes also yield much information and insight into the polymer structures and molecular motions. The diffusion, permeation, and solution behavior of small penetrants such as simple gas molecules in a polymer film are sensitive to changes in the polymer microstructure on a scale comparable to the size of the penetrant molecule. The data which result from the studies with different types of penetrants reflect the various kinds of interactions which may occur between the penetrant and the polymer segments as the processes proceed in the film. The results of the studies with these "molecular probes," therefore, allow one to deduce the nature of certain changes in the polymer microstructure, molecular motions, and the interactions between penetrant molecules and polymer segments.

Since the earliest reports on the transport behavior of penetrants through heterogeneous macromolecular systems have already appeared at date back to the nineteen-twenties,¹⁾ a large amount of work, both experimental and theoretical, has been carried out in the past by using various types of heterogeneous polymeric materials. In certain special types of heterogeneous systems, such as laminates and composites containing dispersed phases, much progress has been made in the theoretical field during recent years. For example, complete expressions for the time lag expected from laminates were developed by Ash *et al.*²⁾ and others.³⁻⁵⁾ Also, in the case of composites containing dispersed impermeable phases of specific geometries and arrangements success has been attained in relating the permeability behavior of the composite system to that of the unfilled material. Excellent summaries of these theoretical studies can be found in a recent review by Barrer.⁶⁾

Outstanding among experimental investigations of diffusion and solution processes of gaseous penetrant molecules in heterophase polymers are the study of filled rubbers and that of semicrystalline polymers. Now there has been a great accumulation of important data on the subjects; in particular, due to van Amerongen,⁷⁾ and Barrer *et al.*⁸⁾ for the former system and to Michaels and his co-workers for the latter.⁹⁻¹²⁾ Rogers¹³⁾ and Barrer⁶⁾ have reviewed recent progress in the fields.

Despite of the fact that our understanding of the transport phenomena through heterogeneous polymeric materials has improved very much in recent years as described above, still many problems remain partly or completely unsolved and a number of difficulties in theoretical treatments and experiments have yet to be overcome. Let us consider, for instance, the diffusion and permeation behavior of a single penetrant species in a composite containing one dispersed permeable phase the transport process is complicated by the different modes of diffusion within each phase and by discontinuities across phase boundaries. Moreover, the nature of multiphase interface and interaction will modify considerably the process where the interface is of high area. Generally, even when all the information about the morphology of new heterophase system, such as geometry and arrangement of the dispersed phase, is available, it would still be very difficult to predict the properties of the system because these are not usually additive. Furthermore, in the case of the diffusion and permeation the simple laws of diffusion which are developed for homogeneous media are not applicable for systems more than two components,¹⁴⁾ and for only certain special systems the processes have been able to be treated within the framework of the usual Fick's law concepts, though the treatments are not strictly rigorous from the viewpoint of thermodynamics of irreversible processes. This situation is indeed the case for several examples referred to in the foregoing lines where various efforts have been made to modify or expand the existing equations.

The present paper describes permeation and diffusion behavior for a series of inert gases in carefully prepared samples of styrene-butadiene-styrene (SBS) block copolymers, where domain structure was assured by electron microscopic observation. Block copolymer solids can afford one of the most excellent examples of heterogeneous polymeric media. This is because polymers having chemically dissimilar segments are not compatible as a rule. Solvent-cast and annealed film samples of two types of fundamental domain structures were prepared: polystyrene rods dispersed in polybutadiene matrix and alternating lamellae of styrene and butadiene components. The purpose of this study is to examine how will be described permeation and diffusion processes of inert gases in SBS block copolymer solids having different types of domain structure in terms of those in the respective component homopolymers. It will be tested whether the simple two-phase model for the block copolymer, which has been shown widely applicable to explain various properties of block copolymer solids, is adequate to describe the observed permeation and diffusion behavior or not. If the behavior observed is not able to be compared well with that expected from the simple additivity of the properties of the constituents, the deviation will be interpreted by taking into consideration of effects due to the architecture of the block copolymer molecule, interactions between the different homopolymer subchain segments especially those at the multiphase interface, polymer microstructure, and molecular motions. In contrast to the fact that interest in morphology, mechanical properties, and structure-property relationships of block copolymers has increased remarkably in the past several years, little interest has been shown in the transport and solution processes of small penetrant molecules in block copolymer media. The only attempt, in which the observed diffusivity of simple gases in block copolymers of urethane with ester and ether has been compared with predictions of permeability theory for heterogeneous system, has been that of Ziegel.¹⁵⁾ In the report a model has been proposed, and the observed behavior has been explained qualitatively in terms of the model.

An ultimate objective of the work in this laboratory has been to provide a means of predicting the permeability and diffusivity of an arbitrary system of a penetrant and a heterogeneous polymeric medium from knowledge of properties of the component homopolymers and the penetrant in question with that of morphology of the polymeric medium concerned. Also, as a counterpart of the aspect of this investigation, the utility of the permeation and diffusion data in getting insight into polymer microstructure and molecular motions must not be overlooked. Analysis of permeation and diffusion processes of penetrants, which are used as molecular probes, together with determined transport properties in the component homopolymers will provide much useful information regarding polymer microstructure and molecular motions as well as that concerning polymer morphology of the heterogeneous polymeric media. Solution of inert gases, and transport and solution behavior of low-molecular-weight organic vapors in the block copolymer will be reported subsequently.

MORPHOLOGY OF SBS BLOCK COPOLYMERS

First, we will sketch the morphology of SBS block copolymers. For block copolymers containing polybutadiene or polyisoprene blocks, it is possible to view directly the microstructure by using the osmium tetroxide fixation and staining technique due to Kato.¹⁶⁾

By utilizing this technique, many electron microscopic investigations of polymer morphology have been done for styrene/butadiene and styrene/isoprene block copolymers.¹⁷⁻⁴⁰ These morphological studies have revealed that diene polymer and polystyrene blocks aggregate into distinct microphases, or domains, and that several different types of domain structures are observed depending upon block copolymer composition, molecular weight, distribution of blocks in the polymer, and method of sample preparation. The existence of three types of domain structures, spheres, cylinders, and lamellae, has been confirmed for block copolymers of styrene with diene component. In solvent-cast films of the block copolymers the change of the fractional composition of the two components determines mainly which of the three types of structures is formed for a given solvent.^{17,23,24,26,29,33,36,39,40} The dimensions, namely the diameters of the spheres or cylinders or distance between adjacent lamellae, cylinders, or spheres, are determined primarily by the length of the corresponding block segment.^{19,20,32,33,36,39}

For solvent-cast solids of block copolymers several theoretical treatments have been developed in an effort to analyze thermodynamically the process of microphase separation and the domain structures resulted therein. Kawai and his co-workers^{24,41} and others^{42,43} have shown that the shape and size of the domain are to be dependent of block copolymer composition, molecular weight, interaction between the corresponding homopolymers, solvent used for casting, and temperature of casting. The results of these studies, both theoretical and experimental, allow us to prepare heterogeneous polymeric films of desired domain structure by making suitable choice of block copolymer sample and/or pair of block copolymer and solvent.

EXPERIMENTAL

Materials

Block Copolymers

The styrene-butadiene-styrene (SBS) block copolymers used were commercial products by Shell Chemical Company and Phillips Petroleum Company under the trade names Kraton TR-1102 and Solprene 414, respectively. These block copolymers were precipitated twice from a 1% benzene solution with *iso*-propanol as non-solvent, and the precipitated polymer was dried *in vacuo* for more than a week at room temperature. The block copolymer samples, Kraton TR-1102 and Solprene 414, thus prepared are designated hereafter as R-1 and L-1, respectively.

Characterization of Block Copolymers

The copolymers were characterized by ultracentrifuge sedimentation, osmotic pressure, and ultraviolet and infrared spectra.

Sedimentation Pattern. For both samples sedimentation studies were carried out at 59,780 rpm with Spinco Model E ultracentrifuge employing the schlieren optics. The sedimentation pattern of a 5 g/l carbon tetrachloride solution of each sample was observed at 20°C, and the pattern exhibited a very sharp single peak. Judging from the observation it may be considered that no discernible amount of free polystyrene and diblock material is contained in the purified samples and that each copolymer sample has a narrow molecular weight distribution.

Molecular Weight. The number-average molecular weights were determined with toluene solutions at 37.0°C. A Hewlett-Packard high-speed membrane osmometer, Model 503, was used.

Composition. The comonomer composition of each copolymer was determined by measuring the optical density of chloroform solutions at the polystyrene peaks at 262 nm and 269 nm using a Zeiss spectrophotometer, Model PMQ II. Matched quartz cells previously calibrated against optical density standards were employed for the measurements. The fraction by weight of polystyrene, m_s , can be determined by the following equations⁴⁴⁾

$$K = \frac{\text{optical density at 262 or 269 nm}}{\text{cell path length(cm)} \times \text{concn(g/l)}} \quad (1)$$

$$K = m_s K_s + (1 - m_s) K_B \quad (2)$$

Here, K_s and K_B are the specific extinction coefficients, at the particular wavelength, of polystyrene and polybutadiene respectively and K is the value for the copolymer. The values determined at both peaks coincided well with each other.

Isomer Content of Polybutadiene Block. The amount of *cis*-1,4, *trans*-1,4, and 1,2-vinyl isomers in polybutadienes can be determined by measuring the intensities of the particular bands of respective structures in infrared absorption spectrum. The infrared spectroscopic measurements were made with a Perkin Elmer spectrophotometer, Model 21, and solutions of the copolymer in carbon disulfide were employed. The method suggested by Silas *et al.*⁴⁵⁾ has been used to determine the isomer content of polybutadiene blocks. The content of the *trans*-1,4 isomer was calculated by analysis of a strong peak centered at 10.3 μm , and that of 1,2-vinyl isomer was determined by analysis of a band centered at 11.0 μm . Since styrene absorptions at 13.2 μm and 14.3 μm interfere with the broad band, 12.0–15.75 μm , of the *cis*-1,4-butadiene isomer, the *cis*-1,4 content was calculated by difference.

The results of the characterization of both copolymer samples are summarized in Table I.

Film Preparations. Films used in permeation measurements, and also in electron microscopic observations, were prepared by solvent casting. A benzene/*n*-heptane mixture, 8/2 by volume, and toluene were used as casting solvent for samples R-1 and L-1, respectively. Beecher *et al.*²²⁾ showed that electron micrograph of an SBS block copolymer, Kraton 101, cast from a benzene/*n*-heptane solution exhibited a butadiene-continuous

Table I. Characterization of SBS Block Copolymers

Sample Code	R-1	L-1	
Trade Name	Kraton TR-1102	Solprene 414	
M_n	68,000 (9,000-50,000-9,000) ^a	94,000 (19,000-56,000-19,000) ^a	
Wt. Fraction of Styrene	0.268	0.408	
Isomer Content of Polybutadiene Block, %	<i>cis</i> -1,4	37	30
	<i>trans</i> -1,4	54	58
	1,2-vinyl	9	12

^a Block lengths S-B-S in molecular weight units.

phase. The weight fraction of styrene of Kraton 101 has been reported as to be 0.28,²²⁾ or 0.30.⁴⁶⁾ These values are very close to that of R-1 determined in the present study (Table I). On the other hand, the alternating lamellar structure was observed in SBS block copolymer films, with molar fraction of styrene of 0.40 (corresponding to 0.56 by weight), cast from toluene solution.²³⁾ Also, quite the same domain structure was exhibited in an SIS block copolymer with about the same weight fraction of styrene component as that of the sample L-1. All solvents used were of GR grade, and no attempt was made to effect further purification.

Copolymer solutions of about 5%, after addition of 0.5% of 2,2-methylenebis(4-methyl-6-*tert*-butylphenol) as an antioxidant, were poured into a shallow dish, the bottom of which was just covered by freshly distilled and cleaned mercury. The dish was placed in a darkened desiccator, and controlled evaporation was achieved by simply adjusting pressure inside the desiccator with a suction pump. The evaporation procedures were performed in a fume cupboard at room temperature. Lewis and Price^{25,31,47)} and others^{19,26)} have found that higher rates of evaporation yield a rather disordered mixture of domains of irregular shape and regions of incomplete phase separation. Also it has been presumed that microphase separation of the block segments as the critical concentration in quasi-equilibrium state is responsible for the formation of a particular type of fundamental, and well-organized, domain structures.^{18,24,32,41)} The evaporation rate was therefore taken as rather slow, about 0.5 cm³/hr. The slow rate also helped to obtain films of uniform thickness. The final traces of solvent were removed by prolonged drying in a darkened vacuum oven at 25°C for at least a week. The sample films thus prepared were stored until use *in vacuo* in the dark at about -10°C. The film thickness was measured by means of a micrometer with a precision of about $\pm 2 \times 10^{-4}$ cm. The films used for permeation measurements were from 3.0×10^{-2} to 1.2×10^{-1} cm thick according to the sizes of inert gas molecule used in the measurements.

Inert Gases

Helium, argon, krypton, xenon, and nitrogen were used as penetrant. These inert gases were of research grade and supplied by Takachiho Kagakukogyo, Ltd. The purity of each gas quoted by the supplier, exceeded 99.995% by volume.

Methods

Electron Microscopy

The domain structure of the film specimens was investigated by transmission microscopy in a Hitachi HU-11D electron microscope. After embedding in an epoxy resin,⁴⁸⁾ the specimens were pre-sectioned, and were stained and fixed with osmium tetroxide. The specimens placed on a support film were allowed to stand about half an hour at room temperature over an approximately 1% aqueous solution of osmium tetroxide in a small, tightly closed glass vessel. The stained films were cooled with liquid nitrogen to approximately -150°C and cut by an LKB ultramicrotome to a thickness of about 35 nm. Sections were cut in two directions so as to determine the orientation characteristics of the domain structures—perpendicular and parallel to the film surface. Also, the electron microscopic observations were carried out with films treated three hours at 120°C, the

highest temperature of permeation measurements, *in vacuo*, and with films having been experienced a series of permeability measurements at various temperatures, and effects of the thermal treatment and seriated permeation measurements upon the domain structure were examined.

Permeability Measurements

Methods of determining the permeability of polymeric films as described in the literature are of two general types. In the first method, which is usually called the partition cell method, a change in pressure as penetrant permeates through the film under conditions of constant volume and temperature is measured without disturbing either the film or the apparatus. In the second method, on the other hand, is measured a change in volume, or weight, under constant temperature and pressure. Measurement of pressure change has the advantage that the determination of the permeability coefficient permits the simultaneous determination of the diffusion coefficient, while the other method does not permits this determination, and a separate measurement is required. In order to determine simultaneously the permeability and the diffusion coefficients of a given system from each measurement under both steady and non-steady state conditions the first type of method was employed in the present work.

Apparatus. The arrangement of the permeability apparatus used is shown schematically in Fig. 1. The apparatus consists of three parts: the high pressure part, the permeability cell, and the low pressure part, and is similar to that described by Szwarc and his co-workers.⁴⁹⁾

The high pressure part, which works as a gas supply on the ingoing side of the specimen film, is consisted of the gas supply *S* and the gas-supply manometer *M*. A desired

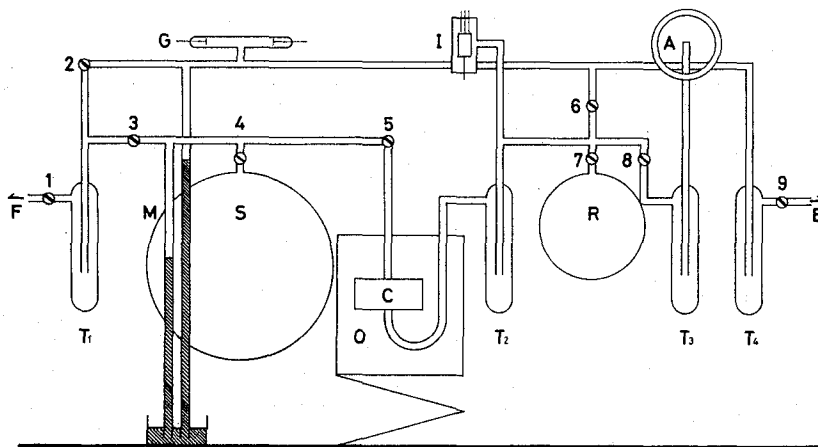


Fig. 1. Gas permeability apparatus.

S, gas supply. *M*, gas-supply manometer. *C*, permeability cell. *O*, oil thermostat. *I*, vacuum tube of ionization gauge. *R*, gas reservoir. *A*, rotary McLeod gauge. *G*, Geisler tube. *E*, to oil diffusion and vacuum pumps. *F*, to gas cylinder. *T*₁, gas-purification trap. *T*₂, mercury trap for vacuum tube of ionization gauge. *T*₃, mercury trap for rotary McLeod gauge. *T*₄, trap for oil diffusion pump. 1-9, stopcocks.

penetrant gas is introduced to this part from a gas cylinder through a gas-purification trap T_1 . The gas supply is a ten-liter flask, and is placed in an air thermostat controlled to $\pm 0.3^\circ\text{C}$. The greater volume of the gas supply helps to keep the pressure of penetrant on the ingoing side constant. The gas-supply manometer is a wide bore mercury manometer.

The design of the permeability cell C is shown in Fig. 2. It consists of two halves, both constructed of stainless steel and held together with six steel bolts. The film under test is placed in the lower half, supported from below by a piece of filter paper, which is held in turn by a drilled stainless steel plate. The exposed area of the test film is 11.34 cm^2 . A vacuum-tight closure is ensured by means of a fluoro elastomer O ring (Dainichi Electric Wire & Cable Co., Compd. no. 1312-70) and a mercury seal. The two holes through the upper half admit mercury to form the seal when the cell is assembled, and the junction of the two halves is covered by a piece of plastic electrical tape to prevent escape of mercury from the seal. The copper tubes are welded on to two halves of the cell. Each copper tube was connected to the glass tube by means of a carefully hand-ground joint, and Apiezon high vacuum grease was used at the joint. This grease made possible to perform permeation measurements in the whole range of temperature studied without any discernible leak. The permeability cell is immersed in the thermostated oil bath O . The temperature of the oil thermostat could be maintained with an accuracy of $\pm 0.2^\circ\text{C}$ in the temperature region 25° to 90°C . At higher temperatures, 95° to 120°C , the thermostat was controlled to $\pm 0.3^\circ\text{C}$.

In the low pressure part, the glass tubing connects the outgoing side of the permeability cell to the mercury trap T_2 , the vacuum tube of ionization gauge I , and the gas

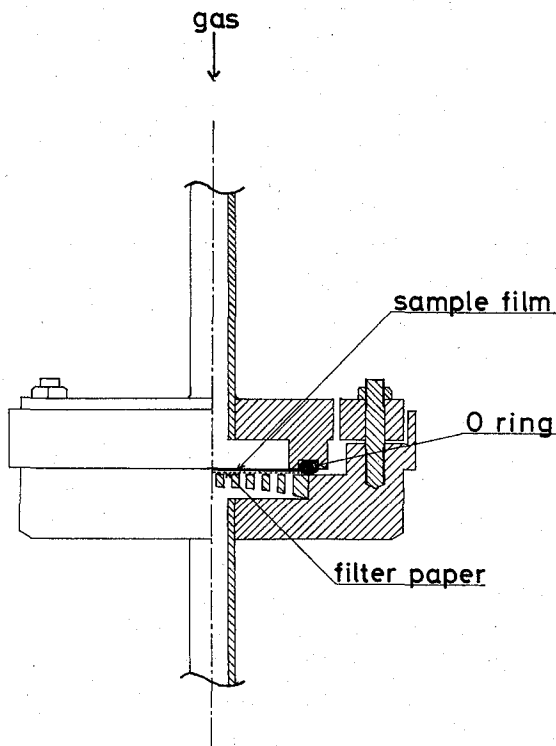


Fig. 2. Permeability cell.

reservoir R. Also the limb of the glass tubing line is connected to the rotary McLeod gauge A through the mercury trap T_3 . The ionization gauge, Tokuda Seisakusho, Ltd., Model HFT-III, was used in measurements of pressure change of permeated gas in the low pressure part. The rotary McLeod gauge was of the type developed by Axelbank,⁵⁰⁾ and was used to determine the volume received the permeated gas in the outgoing side of the test film and to calibrate the readings of the ionization gauge. The gas reservoir is connected to the line by a hand-ground joint, and the joint makes it possible to exchange a gas reservoir flask for another one of different volume. Though it is not shown in Fig. 1, this part is duplicated in the apparatus. Therefore, it is quite easy to vary the receiving volume according to the expected permeability of the system under test. That is, the receiving volume can be kept greater in measurements of higher permeation rates by employing two big flasks in this part. While, for penetrant of greater molecular size, and hence in measurements of lower permeation rate, the stopcock 7 is turned to the closed position. This helps much to speed the measurements by making the receiving volume very small. Three reservoir flasks of different volumes were provided for permeation measurements. The volume of the outgoing side which involves the mercury trap T_2 , the vacuum tube of ionization gauge, the gas reservoir, and the tubing connected them was determined from the known cut-off volume of the rotary McLeod gauge and the mercury trap T_3 by expansion experiments using helium.

Procedure. The test film is installed in the permeability cell, and the cell is then fixed to the glass tubings of the ingoing and the outgoing sides of the equipment with the ground joints. A gas supply of suitable volume for the measurements is also fixed to the glass tubing of the outgoing side with the ground glass joint. Special care was taken to prevent vacuum leak at these joints. The permeability cell is then immersed in the oil bath by raising the bath with a laboratory jack. After all stopcocks have been turned to the open position, the whole apparatus is out-gassed by prolonged pumping down to a pressure of about 10^{-6} mm of mercury. Pumping was continued until there was no increase in pressure on the rotary McLeod gauge for an hour after the stockcock 9 had been turned to the closed position.

Next, the sample film installed in the cell is annealed at a temperature 120°C for about three hours under high vacuum. During the annealing period it is expected that internal stresses, if exists, developed within the film during the process of film casting is released, and also that traces of casting solvent, which has still remained irrespective of prolonged vacuum drying at room temperature, will be removed thoroughly. The temperature of the annealing was decided so as to effect the release of the internal stresses without any change of the domain structure of the sample film under test. As will be described later, no detectable change in the domain structure was observed with films thus annealed. After the annealing treatment has been completed, the pumping of the whole system is continued until a satisfactory vacuum, about 10^{-6} mm of mercury, is maintained in the apparatus for at least two hours.

All stopcocks, except for the stopcocks 3 and 4, is then turned to the closed position, the desired penetrant gas is introduced into the high pressure part through the liquid nitrogen surrounded trap T_1 , and the stopcock 3 is turned to the closed position. Ingoing pressures from 1 to 40 cm of mercury were employed. The oil bath, in which the permeability cell is immersed, is controlled at the desired temperature.

At zero time a pressure of the gas is applied to the ingoing side (the upper side of the assembled cell as shown in Fig. 2) by turning the stopcock 5, and the increase of pressure in the outgoing side is observed by means of the ionization gauge as a function of time. The sensitivity of ionization gauge varies with gas species and correction of direct readings of the gauge is required. The correction factors for several inert gases have been determined by Dushman and Young.⁵¹⁾ In the apparatus used the correction factors determined by them were ensured to be applicable to readings on the ionization gauge with each gas studied from experiments using the rotary McLeod gauge as an absolute gauge. The ingoing pressure is read to 0.05 cm by observing the gas-supply manometer. The readings are repeated several times within each run. No substantial variation in the ingoing pressure was observed as the amount of gas permeated was very small and room temperature was controlled to $\pm 1^\circ\text{C}$.

Typical permeation curves are shown in Fig. 3. Measurements of the outgoing pressure are continued for at least three times the time of nonlinear portion of the permeation curve at the experimental temperature, and the steady state is established after between one and a half and two times the time.

The apparatus was evacuated between runs for at least 15 times the time corresponding to nonlinear portion of permeation curve. Measurements at different temperatures were usually made in the ascending order of temperature from 25°C with the interval of about

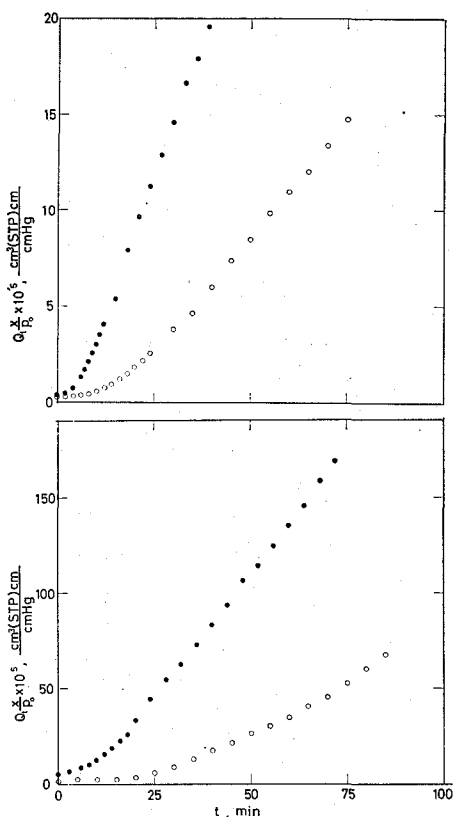


Fig. 3. Typical permeation curves at 30°C . SBS block copolymers: $\bullet$, R-1; $\circ$, L-1. Gases: upper, Argon; lower, Xenon.

10°C. The temperature was maintained constant for at least six hours before making measurements. In order to see if the sample film has been changed by repeated permeation measurements at various temperatures, observations at different temperatures were performed occasionally at random and the final observation was always made at the original temperature, 25°C. No hysteresis or time effects were observed under the conditions described above in the temperature region studied.

CALCULATIONS

The permeation of penetrant through a polymer film, which is free from cracks, pinholes, or other flaws, is governed by the coupled solution-diffusion mechanism. The penetrant molecules dissolve in the surface layer on the ingoing side of the film, diffuse through the film in response to the concentration gradient, and evaporate from the other surface on the outgoing side.

The mathematical theory of diffusion is based on the hypothesis that the rate of permeation J is proportional to the concentration gradient measured normal to the section, that is,

$$J = -D \frac{\partial C}{\partial x} \quad (3)$$

Here J is the amount of penetrant permeated during unit time through a surface of unit area normal to the direction of transfer, C the concentration of penetrant, x the space coordinate measured normal to the section, and D the diffusion coefficient. Equation (3) is commonly referred to as Fick's first law of diffusion. By considering the mass-balance of an element of volume, is derived the following diffusion equation, Fick's second law of diffusion;

$$\frac{\partial C}{\partial t} = \text{div} (D \text{ grad } C) \quad (4)$$

where t is time.

As described before, in the beginning of a permeation experiment the sample film is freed from penetrant. This condition is represented mathematically by

$$C=0 \quad (0 < x < X, t=0) \quad (5)$$

where X is the thickness of the film, and the origin of x is taken on one surface. At zero time of the experiment a constant pressure p_0 is suddenly established on the ingoing side of the film. The frequency of molecular impacts from the gas phase on to the film surface is enormous compared with the rate of diffusion of penetrant into the bulk of the polymer. Thus equilibrium is presumed to exist at every instant between the penetrant molecules in the gas phase and those in the surface layer of the film. The concentration at the surface on the ingoing side, therefore, is kept constant and written as follows by choosing the origin of x at the surface on the ingoing side;

$$C=C_0 \quad (x=0, t>0) \quad (6)$$

where C_0 denotes the equilibrium concentration corresponding to the given pressure p_0 . On the outgoing side pressure of the penetrant is always kept negligible compared with that

on the ingoing side. Accordingly the boundary condition at the surface on the outgoing side is given by

$$C=0 \quad (x=X, t>0) \quad (7).$$

When penetrant permeates through a thin polymer film, the film approximates to an infinite plane sheet across which the diffusion occurs effectively only in one direction x . Equation (4) then reduces to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (8),$$

if D is constant. After a time from the start of the experiment a steady state is reached in which the concentration remains constant at all points of the film. Then Eq. (8) becomes

$$\frac{d^2 C}{dx^2} = 0 \quad (9),$$

and on integrating with respect to x and introducing the conditions at $x=0$ and X we obtain

$$-\frac{C-C_0}{C_0} = \frac{x}{X} \quad (10).$$

Thus the steady-state permeation rate J_s is given by

$$J_s = D \frac{C_0}{X} \quad (11).$$

The equilibrium concentration C_0 is related to the ingoing pressure p_0 by an expression of the form

$$C_0 = S p_0 \quad (12)$$

where S is the solubility coefficient of the penetrant in the polymer. If Henry's law is obeyed, there is a linear relationship between concentration and pressure and S is a constant at constant temperature, so that we have

$$J_s = D S \frac{p_0}{X} \quad (13)$$

or

$$P \equiv D S = J_s \frac{X}{p_0} \quad (14).$$

The product $P \equiv D S$ is referred to as the permeability coefficient and is calculated as

$$P = \frac{\Delta Q}{\Delta t} \frac{X}{p_0 A} \quad (15)$$

where ΔQ is the amount of gas at STP which has permeated within the time interval Δt in the steady state of flow and A is the effective area of the film. The quantity $\Delta Q/\Delta t$ can be evaluated from the permeation curve (cf. Fig. 3). As mentioned before the volume V of the low pressure part (the outgoing side) is kept constant, so that the amount of gas permeated at STP is

$$\Delta Q = \Delta p \frac{V}{76} \frac{273}{T} \quad (16)$$

where Δp is the pressure increase, expressed in cm of mercury, on the outgoing side within the time Δt and T is the temperature of the low pressure part. Thus P is expressed in terms of change of the outgoing pressure with time in the steady state as

$$P = \frac{\Delta p}{\Delta t} \frac{V}{76} \frac{273}{T} \frac{X}{p_0 A} \quad (17)$$

and in units of $\text{cm}^3(\text{STP})\text{cm}/(\text{cm}^2\text{sec cm Hg})$ provided that A , V , X , and Δt are expressed in CGS unit, and p_0 and Δp in cm of mercury.

From the start of the permeation experiment and prior to the establishment of the steady state, both the rate of flow and the concentration at any point of the sample film vary with time. When D is constant, the amount of penetrant Q_t which passes through the film in time t under the conditions of Eqs. (5), (6), and (7) is given by

$$\frac{Q_t}{XC_0} = \frac{Dt}{X^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{X^2}\right) \quad (18)$$

At t goes to infinity, the steady state is approached and the exponential terms become negligibly small, so that the graph of Q_t against t tends to a line

$$Q_t = \frac{DC_0}{X} \left(t - \frac{X^2}{6D}\right) \quad (19)$$

The behavior can be seen in Fig. 3. The line has an intercept θ on the time axis given by

$$\theta = \frac{X^2}{6D} \quad (20)$$

The quantity θ is called the time lag for permeation. When θ and X are expressed in sec and cm, respectively, then D has dimensions cm^2/sec . Thus both values of P and D can be determined simultaneously from each permeation experiment.

Since P is defined as the product DS (Eq. (14)), the solubility coefficient S can be calculated as the quotient P/D . The solubility coefficients evaluated indirectly by this method will be reported in a subsequent paper together with those measured directly by using the desorption method.

RESULTS

Electron Microscopy

Figure 4(a) shows the electron micrograph of an ultrathin section of the block copolymer sample R-1, cast from the benzene/*n*-heptane solution and cut normal to the film surface. The dark regions in the micrograph represent the polybutadiene phase stained selectively by osmium tetroxide, and the light regions the polystyrene phase. Micrographs of the same sample film sectioned in the plane of film quite resembled to that shown in Fig. 4(a).

The polystyrene phase in the film is essentially the form of randomly oriented bundles of curved fibrils. Moreover, in parts of the figure, is observed the polystyrene domains of discrete spheres, in the lower right quadrant of the figure, and ellipsoids, at the left. In the former region, it can be seen that the polystyrene domains set in comparatively regular

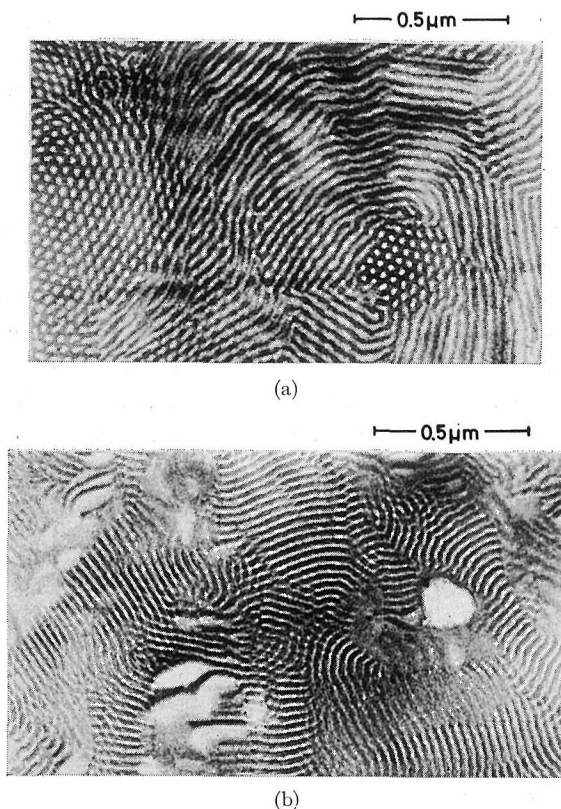


Fig. 4. Electron micrographs of ultra thin sections cut normal to the surface of films: (a) Film of sample R-1 cast from benzene/*n*-heptane solution; (b) Film of sample L-1 cast from toluene solution.

hexagonal array in the polybutadiene matrix. These features rule out a lamellar structure provided that the films are characterized by a single morphology. Accordingly it may be concluded that in the sample film R-1, cast from the benzene/*n*-heptane solution, the polystyrene phases agglomerate into a rod and the rod assemblies regularly to form a bundle with a certain crosssection area. Similar domain structure has been observed for an SBS block copolymer of 30 wt. % styrene cast from toluene and carbon tetrachloride solutions.³⁵⁾ The average values of the radius of the polystyrene rod, R_r , and the spacing between adjacent rods, D_r , are about 9 and 19 nm, respectively (Fig. 7(a)).

As mentioned above, electron micrographs of parallel sections did not alter appreciably from those of normal sections. Thus it appears that the bundles of polystyrene rods arrange at random in the film. Whether these bundles are relatively long or short cannot be decided from the limited two dimensional information provided by the electron micrographs. From examination of several micrographs of both the normal and the parallel sections, however, it may be inferred that the length of the bundles is rather short. Also it may be suggested that the highly ordered arrays of uniform polystyrene rods, embedded in the polybutadiene matrix, form a grain texture, presumably shape of the grain is prolate ellipsoid, in the bulk of the film. Though grain boundaries are vaguely defined in micrographs, the size of grains vary from about 0.3 to 0.7 μm . The existence of the grain texture

in solvent-cast films has been revealed from light scattering experiments⁵²⁾ or small angle X-ray scattering analysis.⁵³⁾ Also, local heterogeneity of the domain structure has been discussed basing upon kinetic considerations of the process of film casting.⁵⁴⁾

The electron micrograph of the film of sample L-1 cast from toluene solution is shown in Fig. 4(b). The micrograph was observed for ultrathin, normal section of the sample film, and the pattern of parallel sections resembled to that of the normal one. Clearly, the morphology of the film of L-1 cast from toluene is characterized by lamellae, and the orientation of the lamellae is at random in the film. The thickness of the polystyrene lamella is about 10 nm and the distance between two consecutive lamellae is about 17 nm (Fig. 7(b)). As in the case of the sample film R-1, the grain texture, which is constituted of piled alternating lamellae of polystyrene and polybutadiene, was again discernible in electron micrographs. The size of the grain was estimated roughly as to be about 0.5 μm . Judging from random orientation of zebra patterns of alternating stripes in the micrograph Fig. 4(b), the grains, or in other words nodule-like higher-order structures of piled lamellae, appear to be arranged randomly to the film surface.

For the both samples R-1 and L-1 electron micrographs of sample films treated three hours at 120°C exhibited essentially the same pattern as described in the foregoing lines. This was also the case with films having been experienced a series of permeability experiments within the temperature range studied. This indicates that the characteristics of each domain structure are not influenced by the thermal treatment or seriated permeation experiments.

Permeation and Diffusion

Typical permeation curves have already been exhibited in the previous section. Reference to Fig. 3 indicates that for the both gases permeation rates through the sample film R-1 are higher than those through the film L-1. This is always the case in the whole region of temperature for all gases studied. In permeation of helium through the both copolymer films the diffusion coefficient is so great, no time lag was observable, the steady-state curve passed through the origin and only the permeability coefficient P was obtainable.

The dependence of P on the ingoing pressure p_0 was examined, and no dependence was observed under the experimental conditions. Also it was found that the observed values of P for sample films of various thicknesses were reproducible within about 10%. This suggests that the domain structures of the copolymer films do not alter with varying thicknesses provided that fairly slow evaporation rate was employed in the preparation procedure of sample films.

In contrast to the permeability coefficient, examination of dependence of the diffusion coefficient D on p_0 or on film thickness could not be performed over so wide range as that of P . This is mainly due to the fact that values of D can not be determined precisely from very short time lags. To overcome the difficulty it is essential either to prepare films of great thickness or to extend range measurable of the outgoing pressure. However, the both were limited by the experimental conditions. Though the present experiments were restricted within rather narrow range the observed values of D exhibited no substantial dependence on p_0 and film thickness.

In the temperature region below 85°C, which is in the vicinity of the glass transition

temperatures of polystyrene blocks, T_{gs} , in the block copolymer samples R-1 and L-1,* the error in determining P was on average $\pm 10\%$. Diffusion coefficients were reproducible within about $\pm 15\%$ in this region of temperature. Above 85°C , however, determination of P and D became less accurate and scatters of results sometimes exceeded 150% , especially at temperatures higher than 100°C . This may be considered as due to primarily the softening and great thermal expansion of sample films in the higher temperature region. In what follows, therefore, the permeation and diffusion behavior at higher temperatures will be discussed only in qualitative manner.

The temperature dependence of the permeability coefficient for each gas is shown in Figs. 5(a) to (e). As indicated in the figures by straight lines the temperature dependence of P in the temperature region lower than about 85°C can be expressed by the Arrhenius-type equation

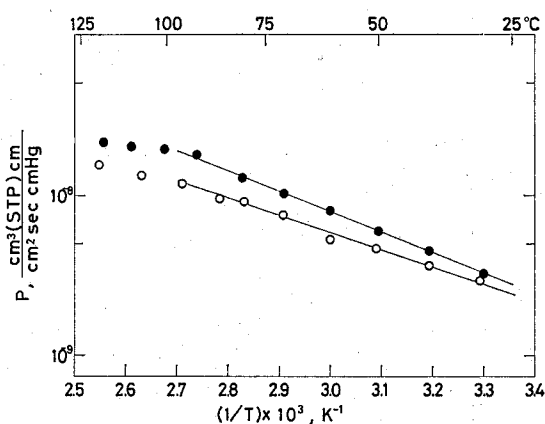


Fig. 5(a). Temperature dependence of permeability coefficient P . SBS block copolymers: ●, R-1; ○, L-1. Gas: Helium.

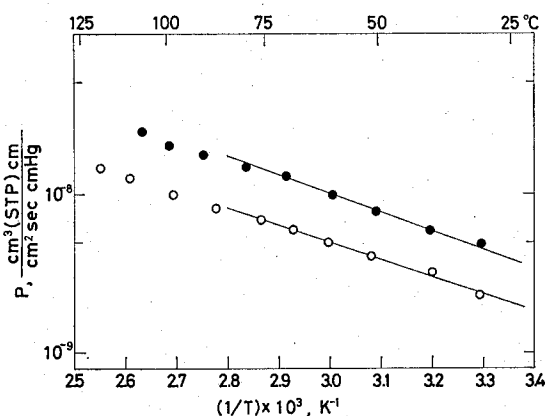


Fig. 5(b). Argon.

* According to the relationship between the glass transition temperature and the molecular weight, which is established for narrow molecular-weight-distribution polystyrene by differential scanning calorimetry,⁵⁵⁾ the values of T_{gs} are estimated to be 83° and 95°C for R-1 and L-1, respectively.

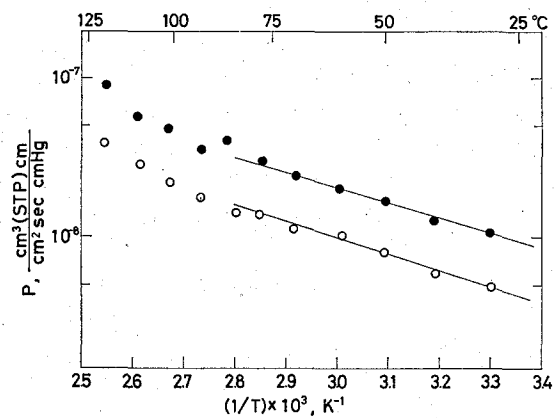


Fig. 5(c). Krypton.

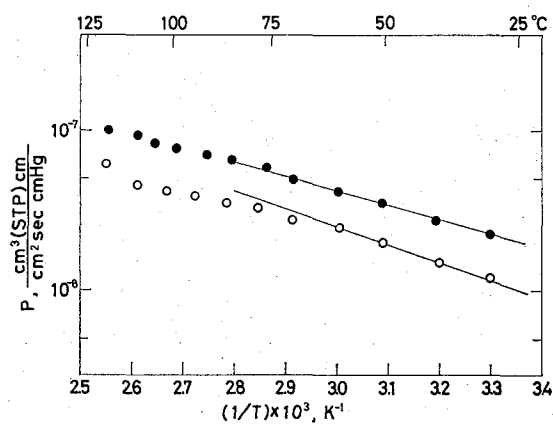


Fig. 5(d). Xenon.

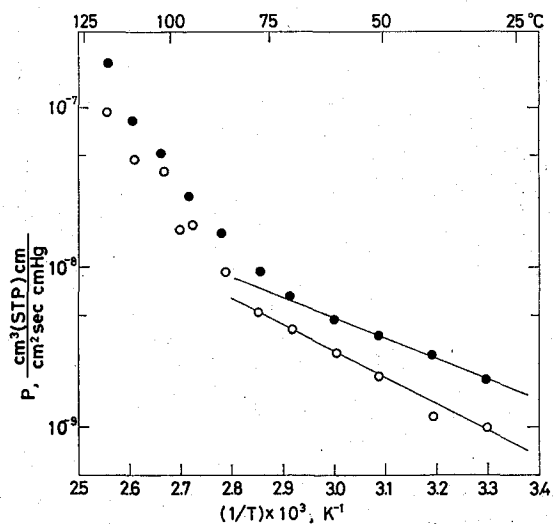


Fig. 5(e). Nitrogen.

$$P = P_0 \exp(-E_P/RT) \quad (21).$$

Here P_0 is the temperature-independent inherent permeability coefficient (or pre-exponential factor), E_P is the activation energy for permeation equal to the sum of the apparent activation energy for diffusion and the heat of solution and RT has its usual meaning. In the temperature region above T_{gs} , however, results deviate from the linear relationship at lower temperatures. In particular deviations for nitrogen are remarkable. The reason for this trend is not known to us at present.

Figures 6(a) to (d) show the Arrhenius plots of the diffusion coefficients. Though results somewhat scatter compared with the corresponding plots of P , the temperature dependence of D is well expressed again by the Arrhenius-type equation with constant E_D , that is,

$$D = D_0 \exp(-E_D/RT) \quad (22).$$

Here D_0 is the temperature-independent inherent diffusion coefficient (or pre-exponential factor) and E_D is the apparent activation energy for diffusion. Values of E_D and D_0

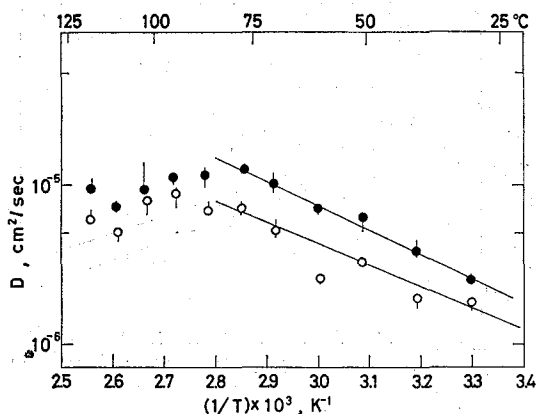


Fig. 6(a). Temperature dependence of diffusion coefficient D .
SBS block copolymers: ●, R-1; ○, L-1. Gas: Argon.

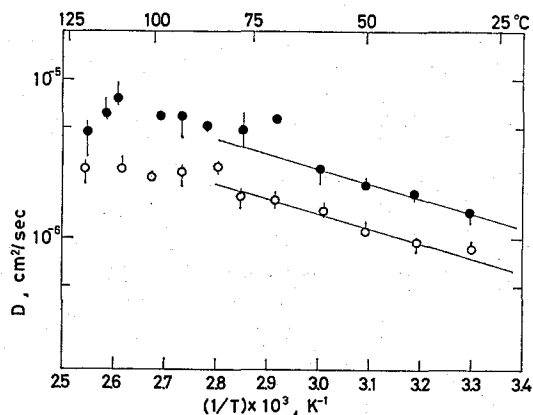


Fig. 6(b). Krypton.

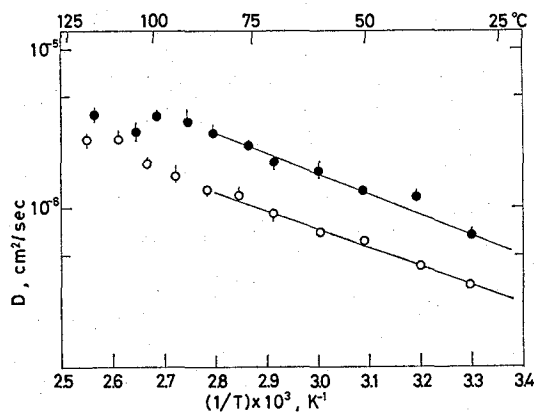


Fig. 6(c). Xenon.

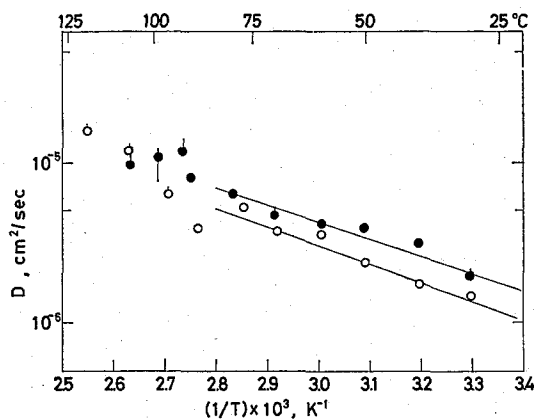


Fig. 6(d). Nitrogen.

Table II. Apparent Activation Energies for Permeation and Diffusion, and Inherent Diffusion Coefficients

Gas	R-1			L-1		
	E_P KJ/mol	E_D KJ/mol	D_0 cm²/sec	E_P KJ/mol	E_D KJ/mol	D_0 cm²/sec
He	25.1			20.9		
Ar	22.2	20.5	6.34×10^{-8}	20.5	22.6	9.87×10^{-8}
Kr	18.0	18.0	1.85×10^{-8}	19.7	18.0	2.33×10^{-8}
Xe	17.2	25.1	1.20×10^{-2}	21.3	22.2	2.17×10^{-8}
N ₂	24.3	29.3	2.65×10^{-1}	31.8	25.9	4.74×10^{-2}

in the temperature region below T_{gs} evaluated by using Eq. (22) are given in Table II together with those of E_P .

DISCUSSION

Fundamental Domain Structures and Molecular Arrangements

As described previously, the domain structures of the two block copolymer samples R-1 and L-1 may be represented respectively by two different types of fundamental domain structures; that is, rodlike domains of polystyrene dispersed in a matrix of polybutadiene and alternating lamellar structure of styrene and butadiene components. The results are in agreement with generally observed scheme of systematic change in types of fundamental domain structures of the styrene/diene block copolymers with increasing styrene content.^{18,24,26,29,32,33,35} When binary ABA type block copolymers are organized into these domain structures, all of the junction points of the block chains must be arranged at the interface between the two phases. The two types of the domain structures observed and possible molecular arrangements within the domains are illustrated schematically in Fig. 7. In the figure are given data of domain size for the rodlike and the lamellar domains, evaluated from electron microscope examination. From these data we can calculate volume fractions of the respective block chains. The volume fractions of styrene component v_s calculated from the domain sizes shown in Fig. 7 are respectively 0.21 and 0.37 for the samples R-1 and L-1. The values of v_s can also be evaluated from the weight fraction of styrene m_s by the relation

$$v_s = \frac{m_s/\rho_s}{m_s/\rho_s + m_B/\rho_B} \quad (23),$$

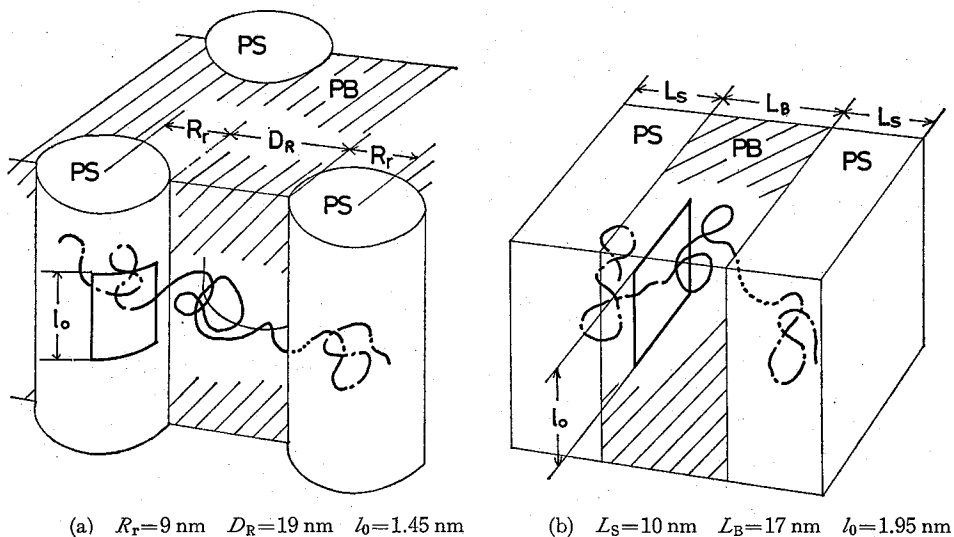


Fig. 7. Schematic representations of elements of two types of domain structure, molecular orientations within the elements, sizes of the domain, and effectively occupied area per interfacial S-B junction: (a) R-1, rods of styrene component in a matrix of butadiene component; (b) L-1, alternating lamellar arrangement of the two components.

where m_B is the weight fraction of butadiene and ρ_S and ρ_B are the densities of polystyrene and polybutadiene respectively. The corresponding expression for the volume fraction of butadiene component is

$$v_B = \frac{m_B/\rho_B}{m_S/\rho_S + m_B/\rho_B} \quad (24).$$

The values of v_S for the two SBS block copolymer samples were calculated from m_S by assuming ρ_S and ρ_B to be respectively 1.05 and 0.90, and obtained 0.24 and 0.37 for R-1 and L-1, respectively. These values are well compared with those calculated from the domain dimensions.

If the phase separation is so perfect as illustrated in the schematic diagram, Fig. 7, the effectively occupied area per chain block, and hence the inter-chain distance, may be evaluated from the average sizes of the domains and the average block molecular weights.^{23,31,32,53} For the rodlike domain the number of polystyrene chains in a rods, of the radius R_r and the length l , is given by $l\pi R_r^2 \rho_S N / M_s$, where N is Avogadro's number and M_s the styrene block molecular weight. Since the surface area of the rod is $2\pi R_r l$, the occupied area of an interfacial S-B junction S_R is given by the following expression

$$S_R = \frac{2\pi R_r l}{l\pi R_r^2 \rho_S N / M_s} = \frac{2M_s}{R_r \rho_S N} \quad (25).$$

For the lamellar domain, the number of polystyrene chains existing in a styrene lamella of the volume $S' L_s / 2$ is $S' L_s \rho_S N / 2 M_s$, and hence the occupied area of interfacial S-B junction S_L is given by

$$S_L = \frac{S'}{S' L_s \rho_S N / (2M_s)} = \frac{2M_s}{L_s \rho_S N} \quad (26).$$

Here, S' and L_s are the interfacial area and thickness of styrene lamella, respectively. The values of S_R and S_L calculated using the above equations are 2.10 and 3.80 nm², respectively. The average inter-chain distance l_0 for each type of domain structures was calculated from these values. Values of 1.45 and 1.95 nm were obtained for rodlike and lamellar domains, respectively. It is noted that these values are somewhat greater than the values of the inter-chain distance of amorphous homopolystyrene in glassy and rubbery states, <1 nm. The latter was estimated from X-ray diffraction analysis.⁵⁶

Permeation and Diffusion

At first, the effect of the configuration in each polymer block chain upon permeation and diffusion behavior will be discussed briefly. Van Amerongen has reported that vinyl groups attached to polybutadiene chain have a lowering effect on diffusivity for penetrant.^{7c} The diffusivity of *cis*-1,4 polybutadiene was considerably higher than emulsion polymerized polybutadiene in which 1,2-vinyl isomer content was about 19%. Accordingly, if the content of isomers, especially that of 1,2-vinyl isomer, in polybutadiene block chains differs to a certain extent among SBS block copolymers, the structural difference may considerably affect permeation and diffusion properties of the copolymers. As has been shown in Table I, there is little difference in the content of 1,2-vinyl isomer between our two block copolymer samples, R-1 and L-1. Also, the contents of other isomers, *cis*-1,4 and *trans*-1,4, do not differ appreciably from each other. Furthermore,

Permeation and Diffusion of Gases in SBS Block Copolymers

Table III. Permeability Coefficients at 25°C for the Inert Gases through SBS Block Copolymers, Polystyrene,^a and Polybutadiene.^b P in cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{ sec cmHg})$.

Gas	SBS Block Copolymer		Polystyrene	Polybutadiene
	R-1	L-1		
He	2.82×10^{-9}	2.45×10^{-9}	1.56×10^{-9}	3.3×10^{-9}
Ar	3.90×10^{-9}	2.16×10^{-9}	1.00×10^{-10}	4.1×10^{-9}
Kr	9.38×10^{-9}	4.32×10^{-9}	3.49×10^{-11}	
Xe	2.01×10^{-8}	1.00×10^{-8}		
N ₂	1.70×10^{-9}	7.66×10^{-10}	1.0×10^{-10}	1.9×10^{-9}

^a Data for He, Ar, and Kr obtained in our laboratory with annealed films of narrow molecular-weight-distribution polystyrene, and that for N₂ from Ref. 57.

^b Literature values from Ref. 57.

the possibility of existence of crystalline regions in polybutadiene phase of the copolymer films may be excluded since the *trans*-1,4 isomer contents of our samples, 54 and 58% (cf. Table I), are not so high as that of crystallizable polybutadiene, >75%.

Concerning polystyrene block chains of the copolymer, variations in local molecular structure and/or chain packing density, which are due to differences in contents of stereo-isomers in the polymer chain, may be reflected in the permeation and diffusion behavior of penetrant. Since both copolymer samples were prepared by the anionic polymerization technique, it may be expected that the stereo-isomer contents of the two samples are practically the same with each other. Therefore, for the two block copolymer samples any difference observed in permeation and diffusion behavior may be concluded as to be almost exclusively attributable to the domain structure, that is either rodlike or lamellar, of the respective films.

Generally the permeability coefficient for penetrant through a blend of two polymeric materials is intermediate between those through the components.* Table III compares the permeability coefficients in permeation of inert gases at 25°C for the two SBS block copolymer films with those for the component polymers, polystyrene and polybutadiene. The figures in the table clearly indicate that the general trend is also the case for the block copolymer system. Quite the similar behavior can be seen in Table IV, in which the diffusion coefficients for inert gases in the SBS block copolymers are compared with those in the component polymers.

For an understanding of these behavior, first we will analyze the permeation through the block copolymer films in terms of a simple model. In the model, as shown in Fig. 8, a film is consisted of parallel array of elements of the respective component homopolymers, and the elements are placed perpendicular to the film surface. The concentration of penetrant, C , referred to unit volume of the block copolymer may be composed additively of the contributions of the film elements, that is

$$C = v_B C_B + v_S C_S \quad (27).$$

Here C_B and C_S are respectively the concentration of penetrant in polybutadiene and

* Examples for blend of two elastomers have been referred to in the review by van Amerongen.⁷⁰⁾

Table IV. Diffusion Coefficients at 25°C for the Inert Gases in SBS Block Copolymers, Polystyrene,^a and Polybutadiene.^b D in cm²/sec

Gas	SBS Block Copolymer		Polystyrene	Polybutadiene
	R-1	L-1		
He			2.62×10^{-6}	1.6×10^{-5}
Ar	1.75×10^{-6}	1.14×10^{-6}	5.79×10^{-8}	4.1×10^{-6}
Kr	1.26×10^{-6}	6.22×10^{-7}	1.45×10^{-8}	
Xe	5.62×10^{-7}	2.82×10^{-7}		
N ₂	2.10×10^{-6}	1.43×10^{-6}	1.0×10^{-7}	3.0×10^{-6}

^a Data for He, Ar, and Kr obtained in our laboratory with annealed films of narrow molecular-weight-distribution polystyrene, and that for N₂ from Ref. 57.

^b Literature values from Ref. 57.

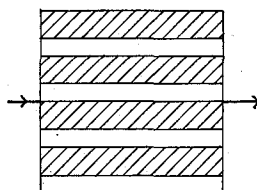


Fig. 8. The parallel model for the permeation of inert gases through the SBS block copolymers.

polystyrene elements, both referred to unit volume of the polymer. If Henry's law governs the solution of penetrant in each element, then

$$p_0 = \frac{C_B}{S_B} = \frac{C_S}{S_S} \quad (28),$$

where S_B and S_S denote the Henry's law solubility coefficients of the penetrant in polybutadiene and polystyrene, respectively. It follows that

$$S_{app} \equiv \frac{C}{p_0} = v_B S_B + v_S S_S \quad (29),$$

and

$$C = \left(v_B + v_S \frac{S_S}{S_B} \right) C_B \quad (30),$$

here S_{app} is the apparent Henry's law solubility coefficient of the composite film.

For flow in the steady state one may write

$$J = v_B J_B + v_S J_S \quad (31),$$

where J_B and J_S are steady-state flows in polybutadiene and polystyrene elements, respectively. By virtue of Fick's first law of diffusion (Eq. (3)), J_B and J_S are expressed respectively by

$$J_B = -D_B \frac{\partial C_B}{\partial x} \quad \text{and} \quad J_S = -D_S \frac{\partial C_S}{\partial x} \quad (32),$$

where D_B and D_S are diffusion coefficients of polybutadiene and polystyrene, respectively. Thus Eq. (31) may be written as

$$-D_{app} \frac{\partial C}{\partial x} = -v_B D_B \frac{\partial C_B}{\partial x} - v_S D_S \frac{\partial C_S}{\partial x} \quad (33)$$

where D_{app} represents the apparent diffusion coefficient for the penetrant in the composite film. If all the diffusion coefficients are independent of concentration, from Eqs. (28), (30), and (33)

$$D_{app} = \frac{v_B D_B S_B + v_S D_S S_S}{v_B S_B + v_S S_S} \quad (34).$$

Since the apparent overall permeability coefficient, P_{app} , of the composite is defined by $P_{app} = D_{app} S_{app}$, we may obtain the expression for P_{app} in terms of permeability coefficients of each component, P_B and P_S , respectively for polybutadiene and polystyrene, that is

$$P_{app} = v_B D_B S_B + v_S D_S S_S = v_B P_B + v_S P_S \quad (35).$$

For the permeation of helium through the composite film, it is seen from Table III that diffusion coefficients in both component polymers do not differ practically from each other. Therefore, we calculated the apparent overall permeability coefficient by using Eq. (35).

However, in the case of permeation of argon or nitrogen, one may neglect the second term on the right hand side of Eq. (31), because the values of D_B are fairly greater than those of D_S (cf. Table IV). Then the expression for D_{app} becomes

$$D_{app} = \frac{v_B S_B}{v_B S_B + v_S S_S} D_B \quad (36),$$

and it follows that

$$P_{app} = v_B P_B \quad (37).$$

The values of P_{app} for argon and nitrogen were calculated by using this equation.

In Table V the values of the apparent overall permeability coefficient thus calculated

Table V. Comparison of Calculated and Experimental Values of Permeability Coefficients at 25°C.^a

Gas	R-1		L-1		
	P_{app}	P	P_{app}	P'_{app}	P
	calcd by the parallel model	exptl	calcd by the parallel model	calcd by the series model	exptl
He	2.8	2.8	2.6	2.2	2.5
Ar	3.0	3.9	2.5	0.39	2.2
Kr		9.4		0.13	4.3
N ₂	1.4	1.7	1.2	0.26	0.77

^a Expressed as 10^{-9} cm³ (STP) cm/(cm² sec cm Hg).

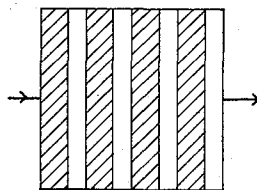


Fig. 9. The series model for the permeation of inert gases through the SBS block copolymer L-1.

are compared with the observed values for the block copolymer films. The agreement in helium permeation is excellent for both types of film, and those in permeation of argon and nitrogen are also fairly good. The results indicate that irrespective of the difference in the types of the domain structure the permeation of the inert gases in each phase of component polymers of the block copolymer is independent of each other and also there is no substantial flow through regions of phase boundary provided that each phase separates distinctly in the block copolymer solid.

As has been shown in Fig. 4(b), the domain structure of the sample film L-1 is distinctly the lamellar type. Therefore, it would be worthwhile to treat the permeation of inert gases through the sample film L-1 in terms of another simple model for polymer laminates. The gas permeability of a multilayer membrane as indicated for two component systems by a model shown in Fig. 9, in which a series array of distinct alternating layers of the two component polymers is placed parallel to the membrane surface, has been studied both theoretically and experimentally by many researchers. In the steady state of permeation the apparent overall permeability coefficient, P'_{app} , of the multilayer composed of polybutadiene and polystyrene layers can be expressed by ^{1,3,6,7c,13,58}

$$\frac{1}{P'_{app}} = \frac{v_B}{P_B} + \frac{v_S}{P_S} \quad (38).$$

Recalling that for argon or nitrogen $D_B \gg D_S$ and the difference between S_B and S_S is as small as by a factor less than about two, we may neglect the first term on the right hand side of Eq. (38). Then the equation reduces to

$$P'_{app} = \frac{P_S}{v_S} \quad (39).$$

For the calculation of values of P'_{app} we used respectively Eqs. (38) and (39) for permeation of helium and that of argon or nitrogen. The results are given in the fourth column of Table V. Values of permeability coefficient predicted by the series model are somewhat lower than those determined from experiments, and discrepancies become greater with increasing the size of the penetrant molecule. Also it is noted that agreement of predicted values with experimental data is worse with the series model than with the former parallel model. This would be interpreted as a result of random orientation of the domain structures of the lamellar type within the film L-1, and hence the barrier effect of low permeability polystyrene layers may be considered not so great as polymer laminates though the separation of the two microphases is fairly good as indicated in the electron micrographs of the film.

The fact that the permeation behavior of the inert gases through the block copolymer films could be well represented by the simple parallel model appears to imply that effect of the polystyrene domains, of rodlike or lamellar shape, in restricting polymer chain mobility in the adjacent polybutadiene domains would be absent in the permeation process concerned. If this is the case the permeation characteristics of the homopolybutadiene may be preserved in the polybutadiene domains. Also it may be expected that with the copolymer films the selectivity for permeation to gases having different molecular size will be practically the same as that with pure polybutadiene, since the permeation behavior through the copolymer films is governed primarily by that through the polybutadiene domains. In other words, the ratios of the permeability coefficients for any gas pair with the copolymer samples should be the same as that with polybutadiene.

Because for polybutadiene data of the permeability coefficient available are limited to three gases at present (Table III), the selectivity ratios of the block copolymers were compared only for permeation of helium, argon, and nitrogen. The results given in Table VI show that values of the ratio for the sample R-1 are very close to those for homopolybutadiene. While for the sample L-1 it can be seen that the ratios are all greater than those for pure polybutadiene. Furthermore, by comparing the ratios He/Ar and He/N₂ it appears that the discrepancy in the ratio to helium would become greater with increasing molecular size of the partner gas molecule. Therefore, it may be inferred that a certain lowering effect on permeability due to the restriction imposed upon the polymer chain would exist in the polybutadiene layers of the sample L-1.

Before discussing further the results, we should quote another factor which is important to interpret the permeation behavior in the heterogeneous polymer system. The factor, τ , commonly called the "tortuosity factor," accounts for the reduction in diffusion coefficient due to the necessity of penetrant molecules to bypass less permeable, or almost impermeable, polystyrene domains and move through the polybutadiene matrix. The situations in the sample films R-1 and L-1 may be represented by models illustrated schematically in Fig. 10(a) and (b), respectively. In the latter the domain structure of the alternating lamellar type is approximated by the structure that polystyrene plates of great surface area are dispersed in polybutadiene matrix.

For heterogeneous systems, in which impermeable particles are assumed to be uniformly and completely dispersed in the polymer medium, the tortuosity factor τ can be evaluated from the knowledge of the geometry of the two-phase system. In our sample films, the fairly low diffusivity, and hence the fairly low permeability of polystyrene, may allow one to treat the polystyrene domains as impermeable phase. For the sample

Table VI. Selectivity Ratios of the Permeability Coefficients for the Gas Pairs Indicated at 25°C

Polymer	Selectivity Ratios		
	He/Ar	He/N ₂	Ar/N ₂
R-1	0.72	1.6 ₆	2.2 ₉
L-1	1.1 ₃	3.2 ₀	2.8 ₂
Polybutadiene	0.80	1.7 ₄	2.1 ₆

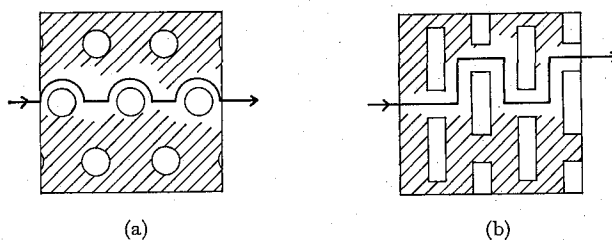


Fig. 10. Model for the path of a diffusing molecule through the SBS block copolymers. (a) R-1, polystyrene rods dispersed in polybutadiene matrix; (b) L-1, polystyrene plates dispersed in polybutadiene matrix.

R-1, the average spacing between the adjacent polystyrene rods, 19 nm, is much greater than the diameters of the inert gases concerned, less than 1 nm, and a contribution of each polystyrene rod to the tortuous diffusion paths can be estimated as being independent of the existence of other rods in the polybutadiene matrix. In terms of a model illustrated in Fig. 11(a), the tortuous path that a diffusing penetrant molecule should travel (thick line in the figure) is distorted in the plane normal to the axis of the rod by the following factor relative to the direct path (thin dotted line), that is

$$\frac{4r^2 \int_0^r \frac{1}{r} \cos^{-1} \frac{r-x}{r} dx}{4 \int_0^r \sqrt{r^2 - x^2} dx} = \frac{4}{\pi} \quad (40)$$

where r is the radius of the rod. In the steady state the diffusing molecule may travel to minimize the tortuous path as indicated by a thick line in Fig. 11(b). Since the polystyrene rods are arranged randomly to the film surface, we can obtain the expression for τ by a simple averaging process with the help of Fig. 11(b) as

$$\tau = 1 + \sqrt{\frac{3}{2}} \left(\frac{4}{\pi} - 1 \right) v_{SR} \quad (41),$$

where the subscript _R denotes the sample R-1. Using the value of v_{SR} calculated by Eq. (24), τ for the R-1 sample was obtained as 1.087. The value of τ can be evaluated alter-

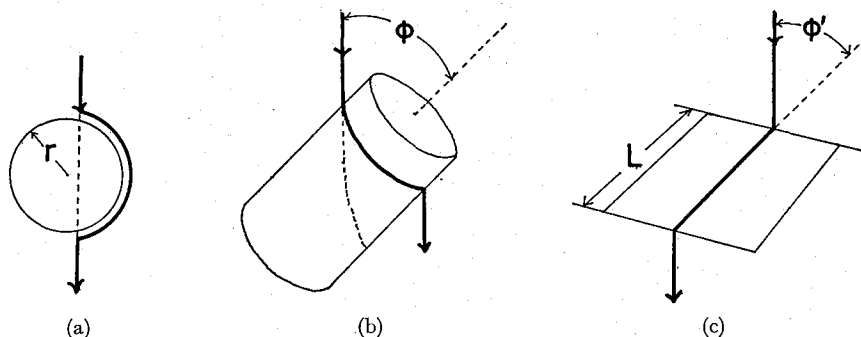


Fig. 11. Models for calculating the tortuosity factor τ in the permeation of inert gases through the SBS block copolymers. (a) and (b) R-1; (c) L-1.

natively by making the analogy between electrical conductivity and gas permeability. The value of τ was calculated as 1.086 by using the expression given by Barrer and others.^{8b)} The value can be compared well with that calculated above.

For the sample L-1 in view of the schematic diagram shown in Fig. 11(c), the factor to account for the tortuous path is

$$\tau' = \frac{L}{L \cos \phi'} \quad (42).$$

As described before, the arrangement of the polystyrene lamellae referred to the direction normal to the film surface is quite at random. Accordingly, by averaging with respect to ϕ' , the tortuosity factor can be evaluated as $\sqrt{3/2}=1.225$.

By taking account of the two effects, *i.e.* the reduction in mobility of the polybutadiene chains and the tortuous diffusion paths, due to the presence of almost impermeable domains of polystyrene, the permeability coefficient for homopolybutadiene P_B may be considered to be represented as follows in the block copolymer films, that is

$$P_B^* = \frac{P_B}{\tau\beta} \quad (43),$$

where P_B^* denotes the permeability coefficient for gas permeation through the polybutadiene phase in the copolymer. This equation is quite analogous to that has been proposed by Michaels and Parker to interpret the sorption and flow behavior of various gases in polyethylene.⁹⁾ In their treatment β is called the "chain-immobilization factor," and $1/\beta$ represents the fractional reduction in diffusivity attributable to restriction of chain movement in the amorphous phase of polyethylene. The values of P_B^* may be calculated by using the relation given in Eq. (35), which has been derived from the assumption that contributions from the each polymer component to the total permeability are simply additive. The product $\tau\beta$ thus evaluated is given in Table VII.

The values of $\tau\beta$ for the sample R-1 are close to unity. Therefore, in the R-1 film both τ and β may be considered as to be nearly equal to unity, and concerning the tortuosity factor this is in harmony with the result of model calculation given above. The values of the product $\tau\beta$ for the sample L-1, on the other hand, are all greater than unity. In part the results may be explained in terms of the somewhat greater value of τ for L-1, 1.225, which was evaluated with the model shown in Fig. 11(c). Nevertheless, an explanation would be required for the greater value of the product for nitrogen. The results, together with those of the selectivity ratios given in Table VI, may be interpreted tempo-

Table VII. Estimated Product of the Tortuosity Factor, τ , and the Chain-Immobilization Factor, β , at 25°C

Gas	$\tau\beta$	
	R-1	L-1
He	1.0 ₀	1.1 ₀
Ar	0.7 ₉	1.2 ₁
N ₂	0.8 ₃	1.5 ₃

rarily as that β might increase with increasing the size of penetrant molecule, since the thicknesses of polybutadiene layers in the sample L-1 are fairly greater than the diameters of gases and the factor τ is considered to not vary much with the size of gas molecule.

From the definition of the factors τ and β , the product $\tau\beta$ can also be evaluated from the diffusion coefficient. However, the literature values of pure polybutadiene are limited only to argon and nitrogen, and also unfortunately the values of diffusion coefficient for helium to the block copolymer samples have not been measured in the present study. At present, measurements of the permeability coefficients of various inert gases through homopolybutadiene samples, in which the isomer contents are nearly equal to those of polybutadiene block chains of the present copolymer samples, are in progress at our laboratory together with measurements of the diffusion coefficients of helium in the both copolymer samples. Therefore, we will reserve our conclusion concerning the two impedance factors in the block copolymer system until a forthcoming report will be published.

The results given in Table IV show that the values of D decrease with increasing the molecular diameters of the inert gases, except for that for nitrogen. This implies that the diffusion process of the system concerned is governed by the activated diffusion mechanism. A fundamental relationship between the entropy and the energy of activation has been demonstrated by Meares.⁵⁹⁾ The application of the theory of absolute reaction rates to diffusion⁶⁰⁾ gives

$$D = e\lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{E_D}{RT}\right) \quad (44)$$

where ΔS^* is the entropy of activation associated with a mole of unit diffusion acts, λ the unit distance travelled, and e , k , and h have their usual meanings. Comparison with Eq. (22) shows

$$D_0 = e\lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \quad (45)$$

Meares has considered that diffusion takes place along a cylindrical volume of $\pi d^2\lambda/4$,

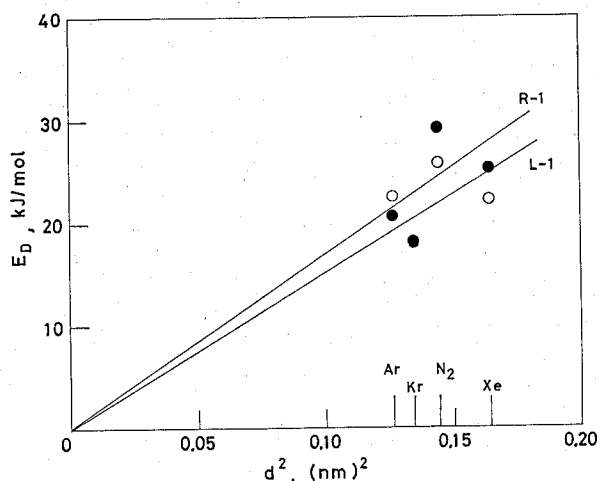


Fig. 12. Plots of activation energy for diffusion *vs.* square of gas diameter. SBS block copolymers: ●, R-1; ○, L-1.

where d is the diameter of the gas molecule, and that the activation energy for diffusion may be equated to the product of the cohesive energy density of the polymer, E_c , and the volume of the path of unit diffusion step; that is

$$E_D = \frac{\pi}{4} d^2 \lambda N E_c \quad (46).$$

The plots of E_D against d^2 , from gas viscosity data,⁶¹⁾ are exhibited in Fig. 12. It is seen that fairly linear relations from origin are obtained for the both block copolymers. If it is assumed again that the diffusion behavior of the gas molecules through the polybutadiene phase is primarily responsible for the total diffusion behavior through the copolymer films, then using the value of E_c for polybutadiene we may estimate the mean length of diffusional jump, λ_m , for the respective block copolymer samples. The value of E_c for polybutadiene was evaluated as to be 272 J/cm^3 from the solubility parameter of the polymer.⁶²⁾ The values of λ_m thus estimated are 1.4 and 1.2 nm for the sample films

Table VIII. Entropies of Activation for Diffusion at 25°C. ΔS^* in $\text{J}/(\text{mol } K)$

Gas	ΔS^*	
	R-1	L-1
Ar	-33.1	-26.8
Kr	-43.5	-38.9
Xe	-27.6	-39.3
N ₂	-1.8	-13.8

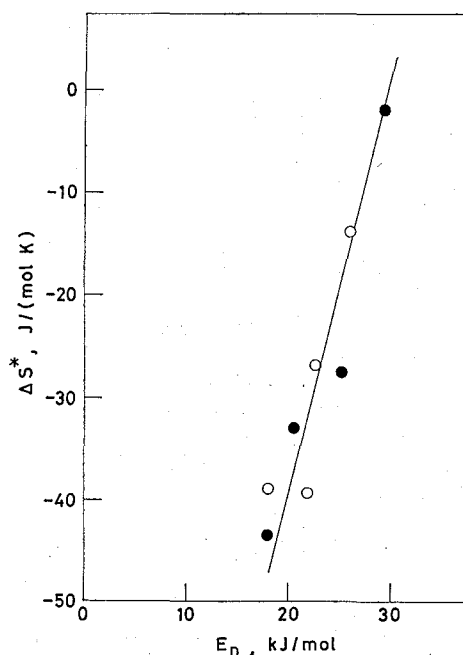


Fig. 13. Linear relation between energy and entropy of activation for diffusion.
SBS block copolymers : ●, R-1; ○, L-1.

R-1 and L-1, respectively. Somewhat smaller value of λ_m for the L-1 sample seems to harmonize well with greater values of β for the greater gas molecules, discussed in the foregoing lines.

The values of ΔS^* are then calculated from D_0 at 25°C by using Eq. (45). The results are given in Table VIII. The linear dependence of ΔS^* on E_D has been predicted by Barrer for a process in which the activation energy is shared between a number of degrees of freedom in a zone of activation.⁶³ The linear relationship between ΔS^* and E_D for the present systems is clearly indicated by the plots shown in Fig. 13. The fulfillment of this condition, which is valid for viscous flow in liquids and diffusion in polymers in the rubbery state, is considered as another rather convincing demonstration that the permeation and diffusion behavior in the block copolymer samples is governed mostly by that in the rubbery polybutadiene matrix at least the kinetic nature of the process is concerned. Also, the results appear to lend a support to the view that the transport behavior of the respective domains, being separated distinctly, may be well represented additively the independent contributions from each domain, though some secondary effect due to the interaction between the domains may be inferred.

ACKNOWLEDGMENTS

The authors thank Professor H. Kawai for taking the electron micrographs. Thanks are also tendered to Mr. H. Kimura of Shell Chemical Company, Tokyo and Mr. S. Azemoto of Phillips Petroleum International, Ltd., Tokyo for supplying us with SBS block copolymers Kraton TR-1102 and Solprene 414, respectively.

REFERENCES

- (1) (a) H. Daynes, *Proc. Roy. Soc. (London), Ser. A*, **97**, 286 (1920); (b) M. Bergmann and S. Ludewig, *J. Soc. Leather Trades' Chemists*, **13**, 279 (1929).
- (2) (a) R. Ash, R. M. Barrer, and J. Petropoulos, *Brit. J. Appl. Phys.*, **14**, 854 (1963); (b) R. Ash, R. M. Barrer, and D. G. Palmer, *ibid.*, **16**, 873 (1965).
- (3) J. A. Barrie, J. D. Levine, A. S. Michaels, and P. Wong, *Trans. Faraday Soc.*, **59**, 869 (1963).
- (4) J. H. Petropoulos and P. P. Roussis, *J. Chem. Phys.*, **51**, 1332 (1969).
- (5) H. L. Frisch and S. Prager, *ibid.*, **54**, 1451 (1971).
- (6) R. M. Barrer in "Diffusion in Polymers," J. Crank and G. S. Park Eds., Academic Press, London and New York, 1968, Chap. 6. References to more recent work can be found in G. E. Bell and J. Crank, *J. Chem. Soc., Faraday Trans. II*, **70**, 1259 (1974).
- (7) G. J. van Amerongen, (a) *Rev. Gen. Caoutchouc*, **21**, 50 (1944); (b) *Kautschuk Gummi*, **7**, WT 132 (1954); (c) *Rubber Chem. Technol.*, **37**, 1065 (1964).
- (8) (a) R. M. Barrer, J. A. Barrie, and N. K. Raman, *Polymer*, **3**, 605 (1962); (b) R. M. Barrer, J. A. Barrie, and M. G. Rogers, *J. Polym. Sci., Part A*, **1**, 2565 (1963); (c) R. M. Barrer and H. T. Chio, *ibid.*, *Part C*, No. **10**, 111 (1965).
- (9) A. S. Michaels and R. B. Parker, Jr., *J. Polym. Sci.*, **41**, 53 (1959).
- (10) A. S. Michaels and H. J. Bixler, (a) *ibid.*, **50**, 393 (1961); (b) *ibid.*, **50**, 413 (1961).
- (11) A. S. Michaels, W. R. Vieth, and J. A. Barrie, (a) *J. Appl. Phys.*, **34**, 1 (1963); (b) *ibid.*, **34**, 13 (1963).
- (12) H. J. Bixler, A. S. Michaels, and M. Salame, *J. Polym. Sci., Part A*, **1**, 895 (1963).
- (13) C. E. Rogers in "Physics and Chemistry of the Organic Solid State," Vol. 2, D. Fox, M. L. Labes, and A. Weissberger Eds., John Wiley & Sons, Inc., New York, 1965, Chap. 6.
- (14) H. Fujita, *Fortschr. Hochpolymer-Forsch.*, **3**, 1 (1961).

- (15) K. D. Ziegel, *J. Macromol. Sci.-Phys.*, **B5**, 11 (1971).
- (16) K. Kato, *J. Polym. Sci., Part B*, **4**, 35 (1966); *Polym. Eng. Sci.*, **7**, 38 (1967).
- (17) H. Hendus, K.-H. Illers, and E. Ropte, *Kolloid-Z. Z. Polym.*, **216-217**, 110 (1967).
- (18) T. Inoue, T. Soen, H. Kawai, M. Fukatsu, and M. Kurata, *J. Polym. Sci., Part B*, **6**, 75 (1968).
- (19) E. B. Bradford and E. Vanzo, *ibid.*, *Part A-1*, **6**, 1661 (1968).
- (20) M. Matsuo, T. Ueno, H. Horino, S. Chujyo, and H. Asai, *Polymer*, **9**, 425 (1968).
- (21) E. J. Fischer, *J. Macromol. Sci.-Chem.*, **A2**, 1285 (1968).
- (22) J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci., Part C*, No. **26**, 117 (1969).
- (23) M. Matsuo, S. Sagae, and H. Asai, *Polymer*, **10**, 79 (1969).
- (24) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *J. Polym. Sci., Part A-2*, **7**, 1283 (1969).
- (25) R. P. Lewis and C. Price, *Nature*, **223**, 494 (1969).
- (26) G. Kämpf, M. Hoffmann, and H. Krömer, *Ber. Bunsenges. Phys. Chem.*, **74**, 851 (1970).
- (27) J. Dlugosz, A. Keller, and E. Pedemonte, *Kolloid-Z. Z. Polym.*, **242**, 1125 (1970).
- (28) E. B. Bradford in "Colloidal and Morphological Behavior of Block and Graft Copolymers," G. E. Molau Ed., Plenum Press, New York and London, 1971, pp. 21-31.
- (29) A. Douy and B. Gallot, (a) *C. R. Acad. Sci., Ser. C*, **272**, 440 (1971); (b) *Mol. Cryst. Liquid Cryst.*, **14**, 191 (1971).
- (30) G. Kämpf, H. Krömer, and M. Hoffmann, *Kolloid-Z. Z. Polym.*, **247**, 820 (1971).
- (31) P. R. Lewis and C. Price, *Polymer*, **13**, 20 (1972).
- (32) T. Uchida, T. Soen, T. Inoue, and H. Kawai, *J. Polym. Sci., Part A-2*, **10**, 101 (1972).
- (33) A. Douy and B. Gallot, *Makromol. Chem.*, **156**, 81 (1972).
- (34) E. Pedemonte, A. Turturro, U. Bianchi, and P. Devetta, *Chem. Ind. (Milan)*, **54**, 689 (1972).
- (35) G. Kraus, K. W. Rollmann, and J. O. Gardner, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2061 (1972).
- (36) A. Douy and B. Gallot, *Makromol. Chem.*, **165**, 297 (1973).
- (37) E. Pedemonte, A. Turturro, U. Bianchi, and P. Devetta, *Polymer*, **14**, 145 (1973).
- (38) J. Dlugosz, M. J. Folkes, and A. Keller, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 929 (1973).
- (39) R. Mayer, *Polymer*, **15**, 137 (1974).
- (40) A. D. Slukin, V. A. Kuznetsova, and V. A. Lazben, *Polym. Sci. USSR*, **A**, **15**, 1707 (1974).
- (41) T. Soen, T. Inoue, K. Miyoshi, and H. Kawai, *J. Polym. Sci., Part A-2*, **10**, 1757 (1972).
- (42) D. J. Meir, *ibid.*, *Part C*, No. **26**, 81 (1969).
- (43) D. F. Leary and M. C. Williams, *ibid.*, *Polym. Phys. Ed.*, **11**, 345 (1973).
- (44) (a) E. J. Meehan, *ibid.*, **1**, 175 (1946); (b) G. M. Burnett, P. Meares, and C. Paton, *Trans. Faraday Soc.*, **58**, 723 (1962); (c) D. N. Cramond and J. R. Urwin, *Europ. Polym. J.*, **5**, 35 (1969).
- (45) R. S. Silas, J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).
- (46) T. L. Smith and R. A. Dickie, *J. Polym. Sci. Part C*, No. **26**, 163 (1969).
- (47) P. R. Lewis and C. Price, *Polymer*, **12**, 258 (1971).
- (48) H. Kushida, "Chohakuseppenho" ("Techniques for preparing ultrathin sections in electron microscopy") Kobundo, Tokyo, 1971, pp. 90-105.
- (49) (a) C. Rogers, J. A. Meyer, V. Stannett, and M. Szwarc, *Tappi*, **39**, 737 (1956); (b) W. Heilman, V. Tammela, J. A. Meyer, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **48**, 821 (1956).
- (50) M. Axelbank, *Rev. Sci. Instr.*, **21**, 511 (1950).
- (51) S. Dushman and A. H. Young, *Phys. Rev.*, **68**, 278 (1945).
- (52) P. S. Pillai, D. I. Livingston, and J. D. Strang, *Angew. Makromol. Chem.*, **27**, 219 (1972).
- (53) G. Kämpf, H. Krömer, and M. Hoffmann, *J. Macromol. Sci.-Phys.*, **B6**, 167 (1972).
- (54) W. R. Krigbaum, S. Yazgan, and W. R. Tolbert, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 511 (1973).
- (55) L.-P. Blanchard, J. Hesse, and S. L. Malhotra, *Can. J. Chem.*, **52**, 3170 (1974).
- (56) H. G. Kilian and K. Boueke, *J. Polym. Sci.*, **58**, 311 (1962).
- (57) H. J. Bixler and O. J. Sweeting in "The Science and Technology of Polymer Films," Vol. 2, O. J. Sweeting Ed., Wiley-Interscience, Inc., New York, 1971, Chap. 1.
- (58) C. E. Rogers, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **49**, 1933 (1957).
- (59) P. Meares, *J. Amer. Chem. Soc.*, **76**, 3415 (1954).

- (60) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941, p. 524.
- (61) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," 2nd Ed., McGraw-Hill Book Co., New York, 1968, p. 632.
- (62) P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
- (63) R. M. Barrer, *Trans. Faraday Soc.*, **39**, 237 (1943).