

Diffusion of *p*-Aminoazobenzene in SBS Block Copolymer

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Synopsis

The temperature dependence of *p*-aminoazobenzene diffusion in a styrene-butadiene-styrene (SBS) triblock copolymer film, prepared from a toluene or ethyl acetate solution, was investigated in the temperature region from 40° to 110°C by using a sublimative desorption method. Parallel studies on the mechanical relaxations of this copolymer were carried out in the same temperature range to be compared with the diffusion data. The penetrant-diffusion characteristics were interpreted in terms of Fujita's free-volume theory with due consideration of the different SBS domain morphology. The value of B_d , defined as the diffusional volume ratio of a penetrant molecule to a segment, was then estimated as 0.45–0.55 above the T_g of the polystyrene phase or 0.7 below that temperature. Interestingly, sigmoidal desorption appeared in the range under the T_g of the polystyrene phase for film cast from ethyl acetate; the anomalous behavior was considered to reflect the slow relaxation process of the copolymer chain ascribable to the predominant exposure of the polystyrene phase on the film surface.

INTRODUCTION

A number of investigations have been carried out on the structure and properties of styrene-butadiene-styrene (SBS) triblock copolymer, for example, by studying morphology by electron microscopy¹ or small-angle x-ray scattering technique²⁻⁴ and the mechanical characteristics by different dynamic or static methods.⁵⁻¹³

According to these studies, various domain structures are formed in the copolymer film when the composition ratio of polystyrene to polybutadiene is varied. Moreover, one of the most interesting features on the two-phase structure is that, even if the formation ratio is unchanged, the matrix polymer in the copolymer film is substituted from polybutadiene phase into polystyrene phase, or vice versa, according to whether or not the casting solvent has much stronger compatibility with the matrix polymer.¹⁴

Although many papers referring to the SBS copolymer have been published, no diffusional approach concerned with the internal structure of this copolymer can be found except for the work by Odani et al.,¹⁵ who have reported the diffusivity and solubility of inert gases into the copolymer being explained by the two-phase model composed of respective homopolymers. Hence, further studies of another penetrant diffusion with reference to the SBS domain morphology will be required.

In the present study, the temperature dependence of the diffusion coefficient of *p*-aminoazobenzene (PAAB) in the copolymer film prepared from solution in a polar or nonpolar solvent is described using a sublimative desorption tech-

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nique in the range from 40° to 110°C, and the results are interpreted in terms of the segmental mobilities and the morphology of the styrene and butadiene phases.

EXPERIMENTAL

Sample Preparation

The SBS copolymer used in the present study was Kraton 1101 (manufactured by the Shell Chemical Company), the characterization of which has already been shown by Lewis and Price³ as follows: the copolymer has a weight-average molecular weight of 102,000 and a number-average molecular weight of 84,000; the chains are composed of 3 *cis*-, 34% *trans*-, and 6% vinyl polybutadiene, and a residue of 26% polystyrene; the weight-average molecular weight of the polystyrene block has been estimated as 13,300.

The copolymer was dissolved in toluene or ethylacetate (the water remaining in this solvent was removed) yielding a 5% solution and was cast into a film about 70 μ thick on a glass plate which was placed on mercury surface. After drying for 24 hr, the sample film, detached from the glass plate, was dried in vacuo at 50°C for two days, followed by annealing in 85°C water to relax internal stress. Then the sample was air dried. The films cast from toluene and ethyl acetate are abbreviated as T-film and E-film, respectively, hereafter.

Dyeing

The film was dyed at 70° \pm 0.5°C at a concentration of 50 mg PAAB/1000 cc H₂O. The PAAB used for dyeing was recrystallized repeatedly from water, mp 126°C. Dye uptake curves are shown in Figure 1. The equilibrium dye concentration of the T- and E-film, both obtained after about 5 hr of dyeing, were 7.5 and 12.0 mg dye/g polymer, respectively. The dye amount in the copolymer film was determined by a spectrophotometric method; the absorbance of a monochlorobenzene solution dissolving the colored film was measured at the maximum situated at wavelength 377 m μ .

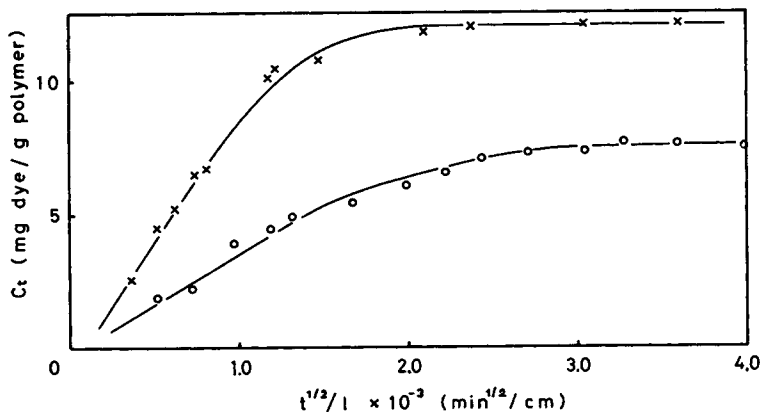


Fig. 1. Dye uptake curves for T-film and E-film: (X) SBS-E; (O) SBS-T.

Diffusion Coefficient

In order to measure the dye diffusion coefficient in the dry polymer, a sublimative desorption apparatus was prepared after Okajima and coworkers, who have described the equipment in detail elsewhere.¹⁶ The diffusion coefficient D was calculated from the initial gradient I of a reduced desorption curve as follows:

$$D = \frac{\pi}{16} I^2 \quad (1)$$

where

$$I = \frac{d(M_t/M_\infty)}{d(t^{1/2}/L)} \quad 0 < M_t/M_\infty < 0.6 \quad (2)$$

The dye amount M_t desorbed in time t was obtained from the difference between the dye initially existing in the film, M_0 , and that remaining there after the desorption, M'_t . Therefore,

$$M_t = M_0 - M'_t$$

A desorption time of three or four days was necessary to obtain M_∞ the dye amount desorbed in infinite time, at every temperature. The dye concentration within a film is so small (less than 1.5 wt-%) that D is assumed constant in this concentration range. Film thickness L was measured on an electric micrometer after desorption was completed.

Mechanical Properties and Small-Angle X-Ray Scattering

Stress relaxation measurements were made on an ordinary apparatus, shown in the literature by Ferry,¹⁷ in the temperature range from 40° to 110°C. The sample length and strain applied, respectively, are 50 mm and 2%. Dynamic mechanical properties were measured on a Rheovibron viscoelastometer Model DDV-IIc (Toyo-Baldwin Co.). The temperature range was -150°-120°C, and applied frequency was 3.5 Hz.

Small-angle x-ray scattering (SAXS) studies were carried out by using a Roter Flex RU-3 (Rigaku Denki Co.) with a slit-collimated small-angle x-ray camera and a scintillation counter probe. Copper K_α radiation was generated under the power conditions of 40 kV and 100 mA; a nickel filter was mounted on an x-ray window to remove K_β radiation.

RESULTS AND DISCUSSION

Domain Morphology

The dynamic mechanical properties are shown in Figure 2. The loss peaks, clearly appearing at -85°C and about 70°-80°C in both the T- and E-film, can be assigned to the glass transition of polybutadiene (PB) and polystyrene (PS), respectively.¹⁴ One can observe that the storage modulus of the E-film decreases sharply around 80°C by nearly two orders of magnitude, as a result of the fact that the primary dispersion of the PS domain takes place in this temperature. On the other hand, this modulus of the T-film decreases in the vicinity of the

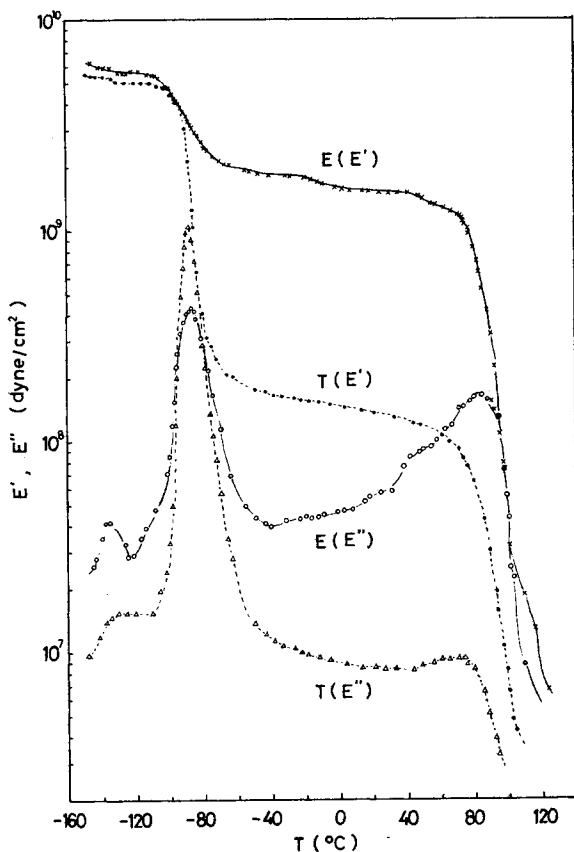


Fig. 2. Dynamic mechanical properties for T- and E-films.

transition for the PB domain (ca. 85°C). The continuous phase for the E-film is, therefore, largely composed of the PS domain, whereas the matrix polymer for the T-film is considered to be the PB domain from these results. That the storage modulus function of the E-film decreases in two steps, one around the PB transition to a smaller extent, and the other around the PS transition as described above, indicates that some part of the PB phase is also continuous in the E-film when the relaxation properties of this film are explained by a mechanical parallel model composed of the PS and PB domains.

The glass transition temperature T_g of the PS domain for the T-film is about 10°C lower than that for the E-film. This feature of the T_g will be further discussed in terms of the morphological difference between the T-film and the E-film in a later section.

Figure 3 illustrates the photographic SAXS patterns and 2θ scanning intensities of both films. A peak of the scattering intensity distinctly appears in the T-film, while it is quite diffuse in the E-film. A uniform scattering intensity distribution for the T-film indicates no preferential orientation of the structural elements in the film. The long period is estimated to be ca. 360 Å ($2\theta = 15^\circ$). Comparing the results obtained by Price and Lewis³ with those of the present authors, this sharp SAXS pattern for the T-film is ascribed to a periodic structure where lamella-like PB and PS domains are formed in the T-film.

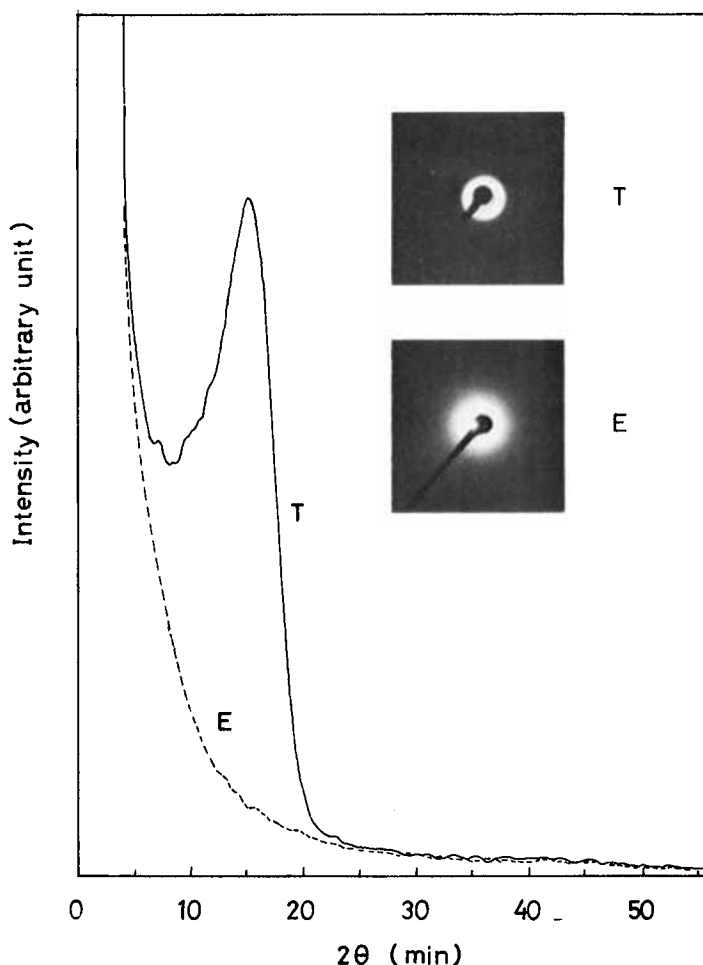


Fig. 3. SAXS data for T- and E-films. The photograph of the T-film shows a Debye-Scherrer pattern.

The diffuse SAXS intensity in the E-film, however, implies that the PS domain interpenetrated with the PB domain has a less periodic structure than that of the T-film. The domain structures for the T- and E-film deduced from these mechanical and SAXS data are schematically shown in Figure 4.

Temperature Dependence of Diffusion Coefficient

Reduced desorption curves of the PAAB for the T-film at various temperatures are shown in Figure 5. The plot of D versus the reciprocal absolute temperature yields a nearly straight line as shown in Figure 6. When examined in detail, however, the experimental points slightly deviate from the straight line in the temperature range above ca. 70°C. The trifling change of D around 70°C corresponds to the weak mechanical absorption (E'') for the T-film at the same temperature (see Fig. 2). Therefore, the deviation is considered to be due to the glass transition of the PS domain. The cause of this deviation is explained as described below.

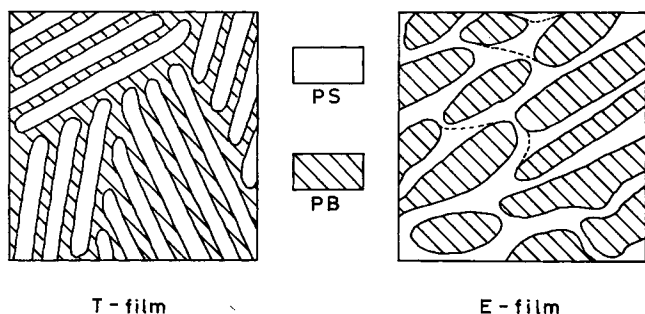


Fig. 4. Schematic domain structure of SBS films. Hatched and blank sections illustrate PB and PS domains, respectively. Dotted lines in the E-film display the partially continuous portion of the PB domain.

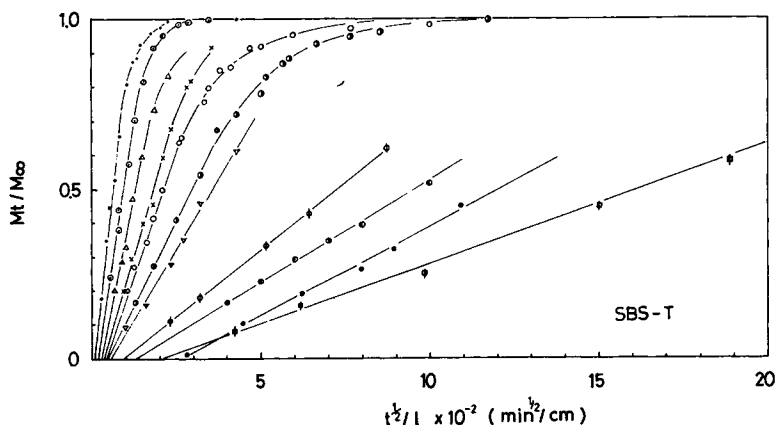


Fig. 5. Reduced desorption curves for T-film at various desorption temperatures: (●) 110°C; (○) 100°C; (△) 90°C; (X) 86°C; (◊) 82°C; (◐) 75°C; (▽) 70°C; (◑) 61°C; (◒) 55°C; (◓) 51°C; (◔) 40°C.

The dye molecule diffuses mainly through the continuous, rubbery PB phase of the T-film in the temperature range below the T_g of the PS domain. As the temperature is raised above the T_g , the chain segments of the PS domain take part in transporting the PAAB molecule with their segmental motion. The difference in the chain segments as medium of diffusion of the penetrant brings about the change of the apparent activation energy required to make a hole for diffusion. Based upon the data in Figure 6, the activation energy for the PAAB to diffuse in the PB domain is estimated as 24.7 kcal/mole in the range below 70°C. The slight curvature above that temperature does not enable one to obtain an activation energy.

The desorption data for the E-film are shown in Figures 7 and 8. Each reduced desorption curve above 78°C is a straight line up to $M_t/M_\infty = 0.6$; hence, the diffusion process is Fickian. However, as seen in Figure 8, the curves below 78°C are sigmoidal in shape. One cannot obtain any definite diffusion coefficient from the data below 78°C by simple use of eq. (1). Thus, an expedient method, without theoretical basis up to now, is attempted to obtain an apparent diffusion coefficient as follows: First, the sigmoidal curve up to $M_t/M_\infty = 0.6$ is divided into two straight lines, as shown in Figure 8. Second, two diffusion coefficients are calculated from the slopes of these lines using eq. (1) (D_L and D_H denote the

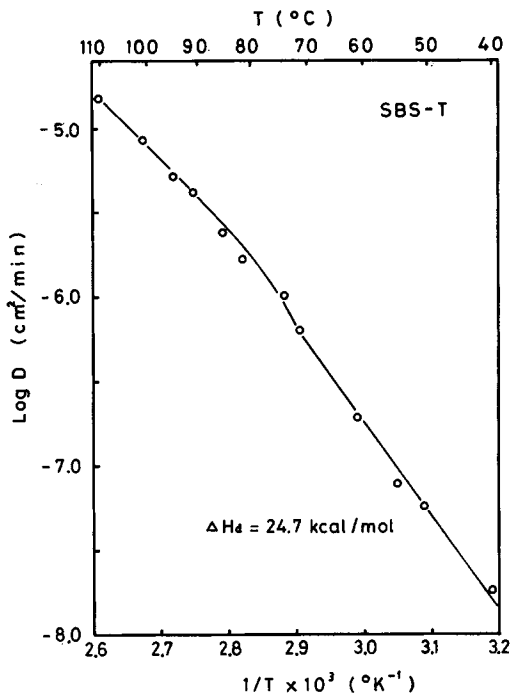


Fig. 6. Arrhenius plot of diffusion coefficient for T-film. A slight change in D is observed around 70°C .

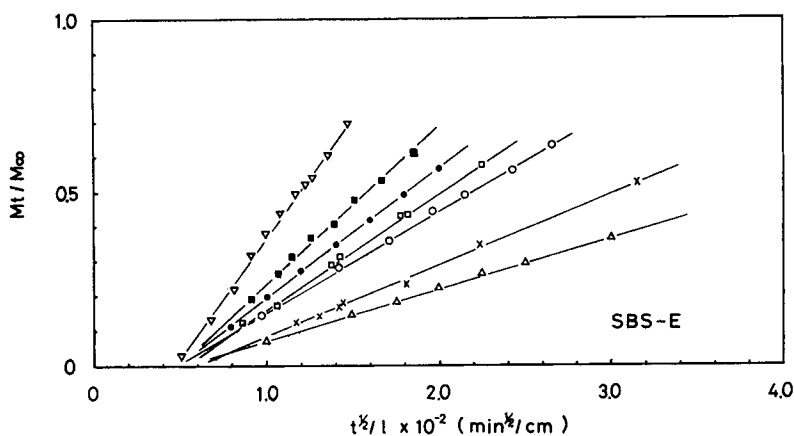


Fig. 7. Reduced desorption curves for E-film above 78°C : (∇) 110°C ; (\blacksquare) 100 ; (\bullet) 95 ; (\square) 90 ; (\circ) 88°C ; (\times) 86 ; (Δ) 18°C .

diffusion coefficients obtained from the lower portion and upper portion of the line, respectively. And finally, the apparent diffusion coefficient D_{AV} is calculated from $D_{AV} = (D_L D_H)^{1/2}$.

These diffusion coefficients are plotted as functions of the inverse absolute temperature in Figure 9. A break point clearly appears around 78°C ; it marks the distinction between Fickian and sigmoidal desorption. This drastic change in diffusivity around 78°C in the E-film corresponds to the marked mechanical absorption related to the glass transition of the PS domain, which is located at

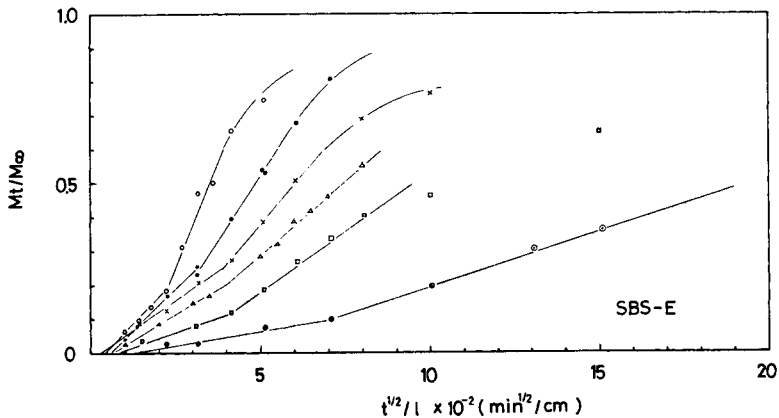


Fig. 8. Reduced desorption curves for E-film below 78°C: (O) 75°C; (●) 65; (X) 60; (Δ) 56°C; (□) 50°C; (○) 42°C.

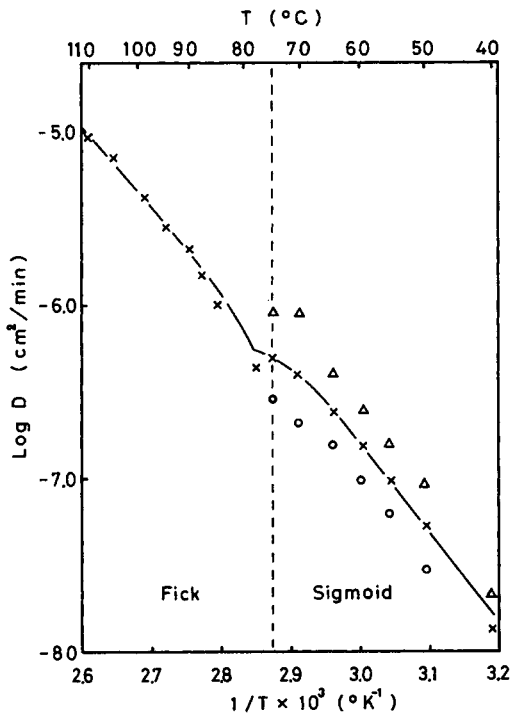


Fig. 9. Arrhenius plots of the three types of D for E-film (see text): (Δ) D_H ; (X) D_{AV} ; (O) D_L .

nearly the same temperature. Desorption of a considerable amount of the dye below the T_g shows that the principal medium transporting the PAAB molecule through the E-film is not the glassy PS but the rubbery PB which is assumed to form a partially continuous phase in the E-film from the mechanical data.

Generally, one of the reasons for a sigmoidal behavior in diffusion is the slow relaxation of the polymer chain in the glassy state¹⁸; the surface concentration of a sorbent does not reach an equilibrium value instantaneously on account of the long relaxation time of the glassy polymer. Since the glassy PS domain exposed predominantly at the E-film surface may depress the relaxation of the PB chain in the neighborhood, the surface concentration of the dye would not reach

a zero-penetrant concentration instantaneously in the range below the T_g when a vacuum is applied in the desorption experiment. This situation explains the sigmoidal desorption. The anomalous behavior in the desorption disappears in the range above the T_g , for the segmental mobilities of the PS domain enhanced above that temperature increase the relaxation of the whole SBS chain at the film surface sufficiently.

The line of the D_{AV} in Figure 9 has a slope that decreases almost linearly with increase in T^{-1} over the range below 70°C . The apparent activation energy for the PAAB diffusing in the E-film below the T_g of the PS domain is estimated as ~ 25 kcal/mole, which is quite close to the value for the T-film in the same temperature region.

The fairly good agreement in the activation energies of diffusion between the T- and E-film, however, does not necessarily imply that the method of estimating D_{AV} is justified. This agreement is merely consistent with the view that the PAAB molecule diffuses through the PB domain in both types of the SBS films below the T_g of the PS domain. Although a blocking or tortuosity factor,^{19,20} not investigated intensively in this study, is assumed to cause a considerable difference between these two films because of their conspicuous change in morphology, it is interesting to note that these activation energies almost agree with each other.

Stress Relaxation

Master curves of stress relaxation for both films are shown in Figure 10, where the reference temperature is 60°C . The superposition is fairly good for the T-film, whereas it is not tolerable for the E-film, especially in the longer-time region.

The shift factors used in constructing the master curves are plotted against the reciprocal absolute temperature in Figure 11. One break point is observed on each of these two lines: 70°C for the T-film and 80°C for the E-film. That

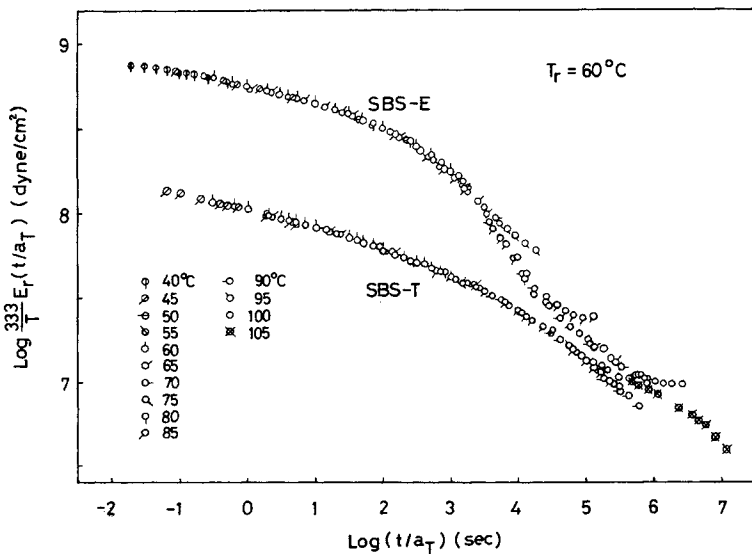


Fig. 10. Master curves of stress relaxation for T- and E-films. Reference temperature is 60°C :

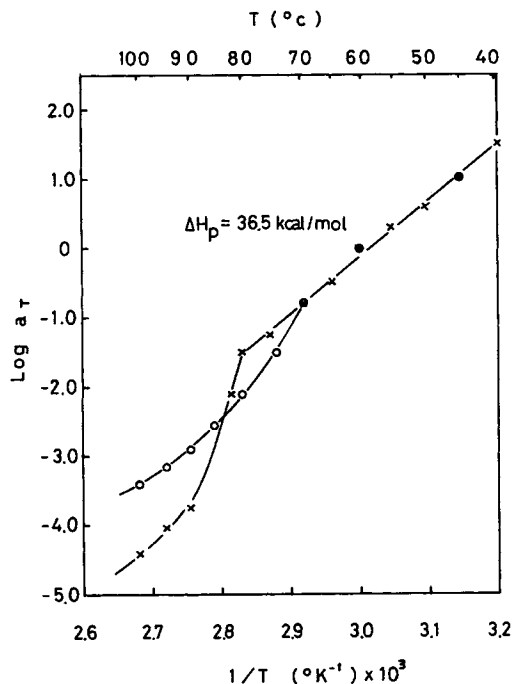


Fig. 11. Arrhenius plots of $\log a_T$ for T- and E-films: (O) SBS-T; (X) SBS-E.

these two break points are ascribable to the T_g of the PS domain is not at variance with the fact that the diffusion and dynamic mechanical data have the transitions at nearly the same temperatures. The T_g of the PS obtained from various independent methods in the present study are collected in Table I.

According to the results of Fox and Flory,²¹ the T_g of homogeneous polystyrene is estimated to be 87°C when the molecular weight of the PS is taken as 13,300, which corresponds to the molecular weight of the PS for the present SBS. The T_g of the PS domain for the T-film, as shown in Table I, is considerably lower than the value estimated from the Fox-Flory relation. The temperature for the E-film, however, is closer to the value than that for the T-film. One of the reasons for this discrepancy between the T_g of the homopolymer and that of the copolymer may be the plasticization effect on the PS domain with the PB molecule.

A more important explanation for the depression in T_g of the PS domain, in particular, is given in terms of the grain boundary relaxation mechanism²² for

TABLE I
Observed T_g Values of Polystyrene in SBS Copolymer^a

Film	Method of estimation	T_g , °C
T	Dynamic mechanical	70
	Stress relaxation	70
	Diffusion	70
E	Dynamic mechanical	80
	Stress relaxation	80
	Diffusion	78

^a The T- and E-films are cast from toluene and ethylacetate, respectively.

a graft or block copolymer where the glassy and rubbery domains are closely and alternately contacted with each other. As the domain structure for the E-film is observed to be not periodic compared with that for the T-film, the grain boundary relaxation may be much more prominent in the T-film. Hence, the depression of the T_g for the T-film is expected to be larger than that for the E-film. The diffusional behavior of the PAAB in the SBS film is presumably influenced intimately by this relaxation through the segmental motion of the SBS chain, since the T_g values of the PS domain determined from the diffusion data are in good agreement with the mechanical results.

An apparent activation energy for the segmental motion of polybutadiene was estimated from the slope of the linear portion in Figure 11. The energies of both films are almost identical to each other because the experimental points are on the same line over the range from 40° to 70°C. The value of this energy obtained is 36.5 kcal/mole, which is in good agreement with previous workers' result.¹¹

Relation Between Diffusivity and Segmental Mobility

Fujita²³ has derived a relation between a diffusion coefficient and a temperature shift factor of viscosity, a_T :

$$\log (D_0/RT) = C - B_d \log a_T \quad (3)$$

where D_0 is the diffusion coefficient extrapolated to zero penetrant concentration, C and B_d are constants, T is the absolute temperature, and R is the gas constant. The value of B_d is defined as the diffusional volume ratio of a penetrant to a polymer segment; in the range above T_g , the value has been observed to vary from 0.7 to 0.8 in the solvent diffusion studies of amorphous polymers.

In Figure 12, $\log(D/RT)$ is plotted versus $\log a_T$ obtained from the stress relaxation data. Linear portions appear in these plots except in the vicinity of \log

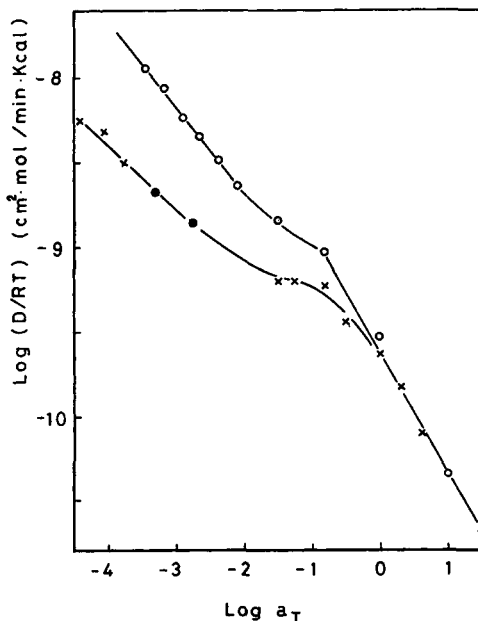


Fig. 12. Fujita's plots for T- and E-films: (O) SBS-T; (X) SBS-E.

$a_T \approx -1$. These nonlinear sections may be ascribed to the glass transition of the PS domain. One obtains the B_d value from the slopes of the linear portions, and these values are shown in Table II.

The value of B_d is also estimated from the activation energy data,²³ as in the relation

$$B_d = \frac{\Delta H_d}{\Delta H_s} \quad (4)$$

where ΔH_d and ΔH_s denote the activation energies of penetrant diffusion and segmental motion, respectively. As already estimated in the preceding sections, $\Delta H_d = 24.7$ kcal/mole and $\Delta H_s = 36.5$ kcal/mole in the temperature region below 70°C. The value of B_d is, then, estimated as 0.68 from eq. (4).

Bell²⁴ applied eq. (3) to a crystalline polymer by substituting a_T for $E''\omega(\omega = 2\pi f$, where f is an applied frequency of strain) and obtained eq. (5):

$$\log(D_0/RT) = C' - B_d \log E'' \quad (5)$$

where C' is another constant. In Figure 13, $\log(D/RT)$ is plotted versus $\log E''$, the data of which are obtained from Figure 2. Linear portions are also observed in these plots above the T_g of the PS domain; thus, one can obtain the B_d values of the T- and E-film as 0.44 and 0.56, respectively, from eq. (5). It is noteworthy that Bell's relation holds only in the range above the T_g .

These values of the B_d , obtained from various methods and summarized in Table II, are divided into two groups, one above the T_g of the PS and the other below that temperature. In spite of the difference in the method of estimation, they agree very well within each group. The value of B_d below the T_g of PS approximates 0.70, which is larger than those of 0.45–0.55 above T_g . Since the diffusional volume of the PAAB molecule does not change over the experimental temperature range of the present study (i.e., no thermal decomposition of the dye is assumed), the difference in the B_d is caused by the change in the diffusional volume of the segment when the copolymer undergoes the PS glass transition. That the B_d above the T_g is smaller than the value below the T_g is probably ascribable to the fact that the chain segment of the PB phase plays a principal role in the segmental motion for diffusivity below the T_g of the PS domain. As the chain segment of the PS domain above the T_g takes part in this motion, the diffusional volume of the whole SBS chain segment above the T_g becomes larger than that of the PB domain because of the bulky pendent group in the PS chain. The B_d is proportional to the reciprocal value of the segment volume, and hence the B_d above the T_g becomes smaller than that below the T_g .

These B_d values above the T_g , in the range of 0.45–0.55, are close to the value

TABLE II
Experimental Values of B_d Estimated by Various Methods

Film	Temperature range	Fujita's relation		Bell's relation
		From shift factor	From activation energy	
T	$T > T_g = 70^\circ\text{C}$	0.55	—	0.56
	$T > T_g$	0.7	0.68	—
E	$T > T_g = 80^\circ\text{C}$	0.45	—	0.44
	$T > T_g$	0.7	0.68	—

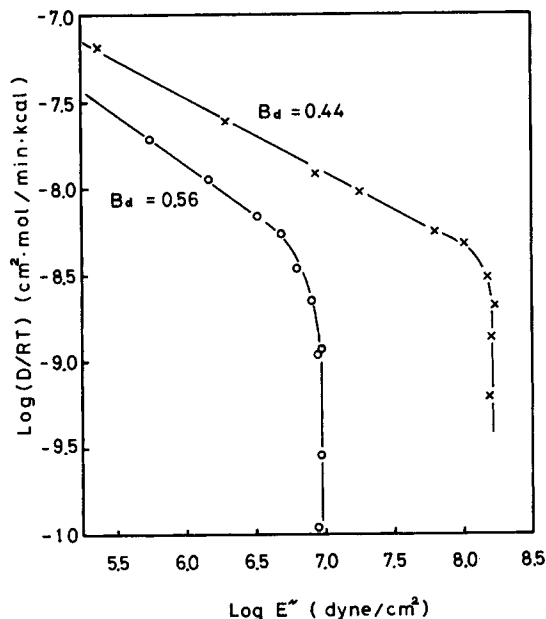


Fig. 13. Bell's plots for T- and E-films. E'' data are taken from Figure 2: (X) SBS-E; (O) SBS-T.

for the PAAB diffusion in amorphous homopolystyrene ($B_d = 0.53$), as recently reported by the present authors in this journal.²⁵ A slight difference observed between the B_d value of the T-film and that of the E-film above the T_g is presumably the consequence of some residual structures partly remaining in each of the films and resulting in somewhat different segmental motions of the SBS chain affecting the diffusivity.

Finally, although the appearance and causes of sigmoidal sorption in glassy polymers have been studied by many investigators,²⁶ very little is known about the sigmoidal behavior in desorption.²⁷ As seen in the above observation, penetrant desorption in the SBS copolymer also exhibits this anomalous behavior, which cannot be explained by a penetrant-plasticizing effect because of the small diffusant concentration involved. An investigation of this phenomenon is now in progress in this laboratory.

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