

## *cis*-폴리부타디엔에서의 *n*-헥산의 용해 및 확산

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### Sorption and Diffusion of *n*-Hexane in *cis*-Polybutadiene

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**요약** : *cis*-폴리부타디엔에서의 *n*-헥산의 흡수실험결과는 확산속도가  $9.65 \times 10^{-7}$  (cm<sup>2</sup>/sec)인 Fickian 이었다. 미분흡수실험 결과로부터 용해도 곡선을 얻었으며, 이는 Flory-Huggins ( $\chi=0.58$ ) 이론식과 일치하였다. 아울러 *n*-헥산의 확산속도는 농도의 함수로 나타났으며, 이를 Fujita의 자유부피이론으로 설명하고 필요한 상수를 구했다.

**Abstract** : Sorption experiments of *n*-hexane in *cis*-polybutadiene demonstrate that sorption behavior is Fickian with a diffusivity of  $9.65 \times 10^{-7}$  (cm<sup>2</sup>/sec). Differential sorption experiments yield the sorption isotherm at 25°C, which may be adequately described by Flory-Huggins theory with  $\chi=0.58$ . The *n*-hexane diffusivities are concentration-dependent and analyzed in terms of Fujita's free volume theory.

### INTRODUCTION

Diffusion of small molecules in rubbery polymers obeys Fick's law, and is thus described as Fickian. Models have been developed to predict the diffusion coefficient.<sup>1</sup> However they remain primitive, insofar as they do not account for chemical interactions between penetrant and polymer, and structure of polymer. Nonetheless, Fujita's free volume theory<sup>2</sup> is widely used, in part because it is easy to apply. The Flory-Huggins model is normally employed to predict solvent solubility in rubbery polymers.<sup>3</sup> In this study, concentration-dependent diffusion coefficient and

organic vapor solubility were explained in terms of the free volume theory and Flory-Huggins theory.

The penetrant mobility in a given medium,  $m_d$ , is assumed to be related to fractional free volume  $f$ , defined as the ratio of free volume to total volume, where free volume is equal to the total volume of a given system minus the occupied volume<sup>2</sup>.

$$m_d = A_d \exp(-B_d/f) \quad (1)$$

where the proportionality factor  $A_d$  is considered to be dependent primarily upon the size and shape of the diluent molecule and hence may be inde-

pendent of temperature and diluent concentration.  $B_d$  corresponds to the minimum hole required for a given diluent molecule to permit such a displacement. The quantity,  $f$ , should be a function of both temperature,  $T$ , and volume fraction of diluent,  $\phi_1$ , and is hereafter denoted by  $f(\phi_1, T)$ .

According to Fujita,<sup>2</sup> in a given polymer/diluent system,  $f(\phi_1, T)$  is assumed to increase with  $\phi_1$ .

$$f(\phi_1, T) = f(0, T) + \beta(T) \phi_1 \quad (2)$$

where  $\beta(T) = \chi(T) - f(0, T)$ , and  $\chi(T)$  is the fractional free volume of pure penetrant at temperature  $T$ . The free volume of a pure substance,  $f(0, T)$ , assumed to increase linearly with temperature<sup>2</sup>:

$$f(0, T) = f(0, T_g) + \alpha(T - T_g) \quad (3)$$

where  $T_g$  is the glass transition temperature of the pure substance and  $\alpha$  is the thermal expansion coefficient of its free volume, estimated to be as the difference between the observable thermal expansion coefficients above and below  $T_g$ .

The intrinsic diffusion coefficient  $D_a$  may be expressed theoretically as the product of two terms: the chain mobility term  $RTm_d$ , and the measure of thermodynamic nonideality,  $d\ln(a_1)/d\ln(\phi_1)$ , where  $a_1$  and  $\phi_1$  are the activity and volume fraction of the penetrant, respectively.<sup>4,5</sup> Since the mutual diffusion coefficient  $D^V$  equals to  $D_a(1-\phi_1)$ ,<sup>6</sup> it follows that

$$D^V = RTm_d \frac{d\ln(a_1)}{d\ln(\phi_1)} (1 - \phi_1) \quad (4)$$

There are several avenues for calculating the diffusion coefficient: half time method, long time method, and initial slope method.<sup>7</sup> Among them the initial slope method appears to give the most accurate result. Analytical solutions of Fick's second law with a constant diffusion coefficient were easily obtained from the reference 7. For a plane sheet, the analytical solution reduces to the following as time approaches zero,

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left( \frac{\bar{D} t}{4L^2} \right)^{1/2} \quad (5)$$

where  $M_t$  denotes the amount of penetrant sorbed up to time  $t$  and  $M_\infty$  the corresponding quantity after infinite time.  $\bar{D}$  is the average diffusion coefficient and  $L$  is the half thickness of the plane sheet. Thus, from the initial slope in a sorption experiment,  $I = d(M_t/M_\infty)/d(t/L^2)^{1/2}$ , the diffusion coefficient follows as

$$\bar{D} = \frac{\pi}{4} I^2 \quad (6)$$

When the amount of swelling is negligible,  $\bar{D}$  is equal to  $D^V$ . Thus the mutual diffusion coefficient  $D^V$  may be obtained.

## EXPERIMENTAL

**Materials:** Amorphous *cis*-poly(1,4-butadiene) (PBD) was supplied by Polyscience Inc. (Catalog number 0750). The molecular weight range was 200,000 to 300,000. PBD was dissolved in *n*-octane and filtered with a fritted disc filter (maximum pore size 0.9 to 1.4  $\mu\text{m}$ ) for purification. *n*-Hexane (99mole % pure, supplied by Fisher Scientific Inc.) was chosen as a penetrant. It was used without further purification for sorption experiments.

**Film Preparation:** A 10 wt % PBD solution in *n*-octane was cast on a glass-caster, 3cm  $\times$  10cm  $\times$  0.5 cm deep. After evaporation of the solvent the film was stripped off and stored in a vacuum oven for at least 2 days before a sorption experiment. Thickness of the film was controlled by the amount of 10% PBD solution used.

**Sorption Experiment:** The amount of *n*-hexane sorbed at a given *n*-hexane vapor pressure was measured gravimetrically by using a quartz spring balance supplied by Ruska Instrument Inc. (U. S. A.). The sensitivity of the spring was 1.0 mg/mm. The pressure of *n*-hexane vapor was measured using a pressure sensor, Baratron 170, 315 BHS, supplied by MKS Instruments (U. S. A.). Displacement of the spring balance in response to solvent sorbing/desorbing was optically monitored using a cathetometer provided by Gaertner Scientific (U. S. A.). Differential sorption experiments were conducted to obtain solubilities and concentration-

dependent diffusivities. When a polymer sample pre-equilibrated with an activity  $a_0$  is exposed to a new activity  $a_1$ , penetrant diffuses into the polymer sample until a new equilibrium isotherm is established.<sup>8</sup> Differential sorption is termed where  $a_0 > 0$  and  $a_1$  is made incrementally greater than  $a_0$ .<sup>8</sup>

## RESULTS AND DISCUSSION

Diffusion of organic vapor in rubbery polymers obeys Fick's law. This implies that the diffusion coefficient  $D$  is at most a function of penetrant concentration. Fig. 1 shows  $n$ -hexane sorption data in PBD at  $p_1/p_1^0 = 0.4$ , where  $M_t/M_\infty$  is the fractional weight uptake in mg/mg at time  $t$ .  $M_\infty$ , the equilibrium solubility, is 7.9 mg of  $n$ -hexane per 100 mg of PBD at 25°C. The data fit closely to the solution of Fick's second law with a constant diffusivity of  $9.65 \times 10^{-7}$  (cm<sup>2</sup>/sec). This is consistent with the value for the same system reported by Odani et. al.<sup>9</sup> Fig. 2 indicates effectively thickness-independent sorption in samples with half-thickness,  $L$ , in the range 0.26 to 0.34 mm, which is a characteristic feature of Fickian sorption.

### Sorption Isotherm

Dissolution of organic liquids in rubbery polymers is adequately described by either Flory-Hug-

gins theory or Prigogine's corresponding state theory.<sup>10</sup> The former is used in this treatment, because it is simpler and more widely used. According to the Flory-Huggins theory,<sup>3</sup>

$$\ln(a_1) = \ln(\phi_1) + (1 - \phi_1) + \chi(1 - \phi_1)^2 \quad (7)$$

where  $\chi$  is the Flory-Huggins interaction parameter. Blanks and Prausnitz<sup>11</sup> suggest a simple method to obtain  $\chi$ , a free energy parameter that includes both entropy  $\chi_S$  and enthalpy  $\chi_H$  contributions:

$$\chi = \chi_S + \chi_H \quad (8)$$

$\chi_S$  depends on the size and shape of solvent molecules and also those of polymer groups. These authors suggest a  $\chi_S$  value of 0.34 for nonpolar-nonpolar systems. According to Hildebrand-Scatchard regular solution theory<sup>12</sup>:

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (9)$$

where  $\delta_1$  and  $\delta_2$ , the solubility parameters of the solvent and polymer, are 7.3 and 8.3 (cal/cm<sup>3</sup>)<sup>1/2</sup> for  $n$ -hexane and PBD,<sup>13</sup> respectively; the molar volume,  $V_1$ , of  $n$ -hexane is 131.6 (cm<sup>3</sup>/mole). These values together yield  $\chi = 0.58$  for the  $n$ -hexane/PBD system at 25°C.

The equilibrium penetrant activity  $a_1$  is equal to  $p_1/p_1^0$  in an ideal system where  $p_1^0$  is the equilibrium vapor pressure at a given temperature. The

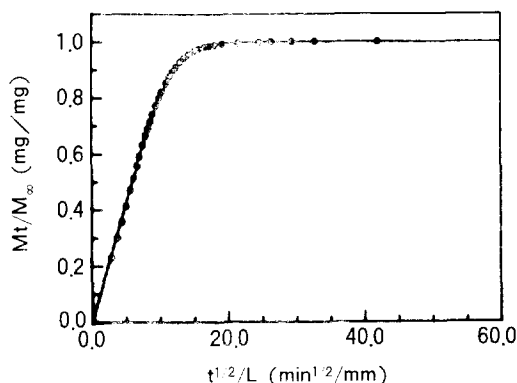


Fig. 1. Fit of Fickian sorption solution with a constant diffusivity of  $9.65 \times 10^{-7}$  (cm<sup>2</sup>/sec) to data for  $n$ -hexane in *cis*-polybutadiene at  $p_1/p_1^0 = 0.4$  and 25°C.  $L = 0.26$  mm

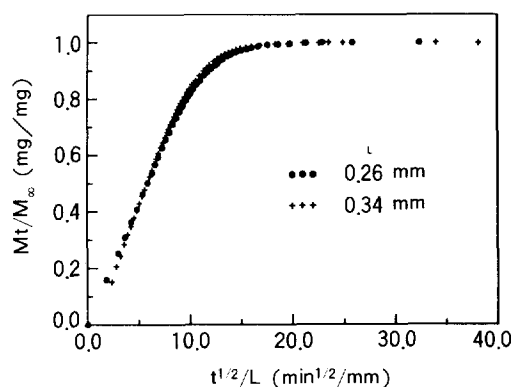


Fig. 2. Thickness dependence of  $n$ -hexane sorption behavior in *cis*-polybutadiene at  $p_1/p_1^0 = 0.4$  and 25°C:  $L = 0.26$  and 0.34 mm

solubility  $S$  is defined as the mg of sorbed penetrant per 100 mg of dry polymer :

$$S = \frac{\phi_1 d_1}{\phi_2 d_2} \times 100 \quad (10)$$

where  $d_1$  and  $d_2$ , the densities of solvent and polymer, are 0.655 and 0.901 (g/cm<sup>3</sup>) for *n*-hexane and PBD at 25°C, respectively. Thus,  $\phi_1$  in *n*-hexane/PBD system at a given activity may be calculated from equation (10).

Measured solubilities, and those predicted from equations (7) and (10) with  $\chi=0.58$ , are compared in Fig. 3. The close agreement confirms that

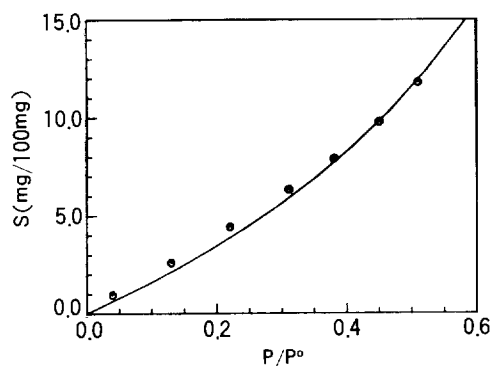


Fig. 3. Sorption isotherm of *n*-hexane in *cis*-polybutadiene at 25°C : (○) experimental data ; (—) the Flory-Huggins theory (equation (7)) with  $\chi=0.58$ .

Table 1. Diffusivity and Solubility of *n*-Hexane in *cis*-Polybutadiene

$a_1$	$D^V \times 10^6$ (cm <sup>2</sup> /sec)	$S$ (mg/100mg)	$\phi_1$
0.04	0.79	0.95	0.01
0.13	0.88	2.60	0.04
0.22	0.91	4.40	0.07
0.31	0.88	6.32	0.08
0.38	0.96	7.91	0.10
0.45	0.92	9.78	0.12
0.51	0.86	11.97	0.14

$a_1$ , *n*-hexane activity ;  $D^V$ , mutual diffusion coefficient,  $S$  and  $\phi_1$ , cumulative solubility and volume fraction of *n*-hexane.

Flory-Huggins theory accurately predicts solubility for *n*-hexane/PBD system.

#### Diffusion Coefficient

Differential sorption measurements showed that *n*-hexane diffusivity is concentration-dependent (Table 1). At activities above 0.6 the dimension of the sample changed markedly and sorption was therefore discontinued. As described previously,  $D^V$  is equal to  $\bar{D}$  when  $\phi_1$  is very small. Actually  $\phi_1$  is at most 0.03 for each differential sorption step in this experimental range, and thus we set  $D^V$  to be  $\bar{D}$ , which may be calculated from the initial slope method by using equation (6).

Fig. 4 is a graph of  $\log(D^V)$  vs.  $\phi_1$ .  $D^V$  goes through a maximum near  $\phi_1=0.12$ . This agrees well with the results of Odani et. al.<sup>9</sup> In many systems of rubbery polymer/organic solvents, diffusivity changes with the concentration of the solvents over a range of orders of magnitude.<sup>1</sup> However, it changes inconsequentially upon the concentration of solvents in PBD with high *cis* content. With increasing amount of *cis* content of PBD, the concentration dependence of such organic solvents as dichloromethane and benzene is ineffectual.<sup>11</sup> In the case of benzene/PBD (98% *cis* content) the diffusivity remains nearly constant up to 10% (by volume) of benzene.

Incorporation of the equations (1) and (7) into

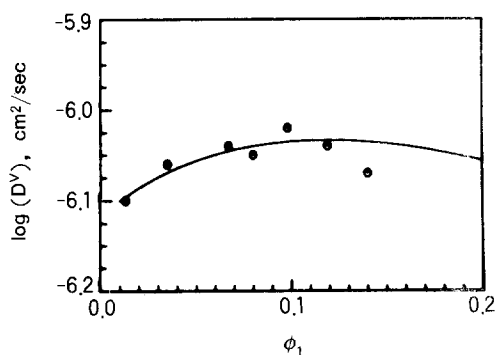


Fig. 4. A graph of mutual diffusion coefficient,  $D^V$ , vs.  $\phi_1$  for *n*-hexane/*cis*-polybutadiene system at 25 °C : (○) experimental data ; (—) theoretical prediction with  $f(0, T)=0.088$ ,  $\beta(T)=0.44$ ,  $B_d=0.11$ ,  $A_d=1.08 \times 10^{-16}$ (mole sec/g) and  $\chi=0.58$  in equation (11).

equation (4) yields :

$$\frac{D^v}{A_d RT} = \exp[-B_d/f(\phi_1, T)] \times [1 - \phi_1 - 2\chi\phi_1(1 - \phi_1)](1 - \phi_1) \quad (11)$$

There are four principal parameters in equation (11) :  $f(0, T)$ ,  $\chi(T)$ ,  $B_d$ , and  $A_d$ . The first two,  $f(0, T)$  and  $\chi(T)$ , may be estimated from physical properties of the corresponding materials.  $B_d$  and  $A_d$  are determined by fit to experimental data.

The glass transition temperature  $T_g$  and thermal expansion coefficient of free volume  $\alpha$  for PBD at 25°C are 167 °K,<sup>12</sup> and  $4.8 \times 10^{-4} (^{\circ}\text{K}^{-1})$ ,<sup>15</sup> respectively. These values yield  $f(0, T)$  0.088 from equation (3), when  $f(0, T_g)$  is set at 0.025 on the basis of iso-free volume theory.<sup>15,16</sup>  $T_g$  of *n*-hexane may be estimated to be 60 °K from the following semiempirical relationship between  $T_g$  and molecular weight,  $M_w$  for the homologous series of polymethylenes.<sup>17</sup>

$$T_g(^{\circ}\text{K}) = 1130/(6.2 + 1060/M_w) \quad (12)$$

A thermal expansion coefficient  $\alpha_T$ , for *n*-hexane, of  $2.13 \times 10^{-3} (^{\circ}\text{K}^{-1})$ , may be estimated from the following relationship

$$\alpha_T = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \left( \frac{\partial \ln(1/d)}{\partial T} \right)_p \quad (13)$$

using the data for density,  $d$ , variation with temperature obtained from reference 18.  $\alpha_T$  is assumed to be approximately identical to  $\alpha$ . Using the above values for  $T_g$  and  $\alpha$ , and  $\chi(T_g)=0.025$ ,

equation (3) yields  $\chi(T)=0.53$  for *n*-hexane and  $\chi(T)$  is then 0.44. The results are summarized in Table 2.

Concentration-dependency of diffusion coefficients is manifested only through  $B_d$ , with fixed values of  $f(0, T)$  and  $\chi(T)$ .  $B_d$  may be estimated to be 0.11, on the basis of data on  $D^v$  vs.  $\phi_1$ , together with equation (11) which indicates that the curvature of a plot of  $\log(D^v)$  vs.  $\phi_1$  is a function only of  $B_d$ . Using the values of three parameters obtained above,  $A_d$  may be then estimated to be  $1.08 \times 10^{-16}$  (mole sec/g) from the best fit to experimental values.

The solid line in Fig. 4 was obtained from equation (11) with  $f(0, T)=0.088$ ,  $B_d=0.11$ ,  $\chi(T)=0.44$ ,  $A_d=1.08 \times 10^{-16}$  (mole sec/g), and  $\chi=0.58$ . These results confirm that Fujita's free volume theory and Flory-Huggins theory together accurately fit the diffusion coefficient for *n*-hexane in rubbery PBD.

## CONCLUSIONS

Sorption data for *n*-hexane/PBD were found to be obeyed by Fick's second law. Flory-Huggins equation with  $\chi=0.58$  fits to *n*-hexane solubility data. The concentration dependence of the diffusion coefficients of *n*-hexane in PBD is consistent with the Fujita's free volume and Flory-Huggins solution theories, of which parameters were obtained semi-empirically.

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**Table 2.** Physical Properties of *n*-Hexane and *cis*-Polybutadiene

Materials	$T_g(^{\circ}\text{K})$	$\alpha(^{\circ}\text{K}^{-1})$	$f(0, T)$	$\chi(T)$
<i>n</i> -hexane	60	$2.13 \times 10^{-3}$	—	0.53
<i>cis</i> -polybutadiene	167	$4.8 \times 10^{-4}$	0.088	—

$T_g$ , glass transition temperature ;  $\alpha$ , thermal expansion coefficient of free volume ;  $f(0, T)$ , fractional free volume of *cis*-polybutadiene at 25°C ;  $\chi(T)$ , fractional free volume of *n*-hexane at 25°C.

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