DIFFUSION OF ORGANIC SOLVENTS IN ISOBUTYLENE-BASED POLYMERS

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Abstract — Diffusion behavior of several organic solvents in polyisobutylene (PIB) and in poly(p-methylstyrene-co-isobutylene) (PMS-BR) with different monomer ratios has been studied. The experiments have been conducted over a temperature range of 50 to 100°C using a conventional gravimetric sorption technique. The PMS-BR copolymers contained 2, 7, and 15 weight percent p-methylstyrene, respectively. Although employing temperatures were far above the glass transition temperatures of polymers, the diffusion coefficients are correlated well with the Vrentas-Duda free-volume theory. For all the solvents, the PIB shows the highest diffusivity while the copolymer with the 15% p-methylstyrene gives the lowest value. This behavior can be explained by the amount of fractional free-volume present in a system.

INTRODUCTION

Molecular diffusion of low molecular weight components and impurities is important step in the polymerization process. The rate of the polymerization reaction can be controlled by molecular diffusion of monomers, initiators, long-chain radicals, or low molecular weight condensation products. After formation of the polymer, volatile residuals like monomers, solvents, and impurities must be removed to control product properties as well as to meet health, environmental, and safety regulations. These polymer devolatilization processes can involve molecular diffusion of the low molecular weight materials from polymer melts or solid particles.

The Vrentas-Duda diffusion theory [Vrentas and Duda, 1977a, b], which is based on free-volume concepts, has been used for correlating and predicting the diffusion behavior in polymer/solvent systems. In that theory, the free-volume between the molecules is continuously redistributed by thermal fluctuations. Diffusion of a molecule is considered to be related to the probability that a fluctuation will produce a hole of sufficient size to accommodate the migration of the molecule. Although the Vrentas-Duda free-volume theory has succeeded in correlating and predicting the diffusion coefficients of solvents in several polymers [Ju et al., 1981; Duda et al., 1982; Vrentas et al., 1985; Zielinski and Duda, 1992], it has been suggested that free-volume theories will fail at temperatures far above the glass transition temperature of the polymer, T_{g2} [Arnould, 1989]. Moreover, few studies have been conducted with complex systems such as copolymers, composites, and network-polymers [Frensdorff, 1964; Zielinski, 1992; Hong and Duda, 1996].

Recently, a new class of isobutylene-based random copolymers in a wide range of monomer ratios has been developed from the copolymerization of isobutylene and p-methylstyrene (PMS) [Exxon* Bromo XP-50 Brochure, 1991]. The copolymers have low permeability, high damping performance, and a glass transition temperature around −60°C, which is similar to that of polyisobutylene (PIB). In this study, diffusion behavior was investigated for several organic solvents in PIB and in random poly(p-methylstyrene-co-isobutylene) (PMS-BR). The purposes of the present work are; (1) to test the correlative capability of the Vrentas-Duda theory at temperatures far above T_{g2} and (2) to study the effect of the composition in the copolymers on diffusivity and free-volume parameters.

EXPERIMENTAL

The mutual diffusion coefficients were measured for several organic solvents; n-hexane, n-pentane, cyclohexane, toluene, and chloroform in PIB and in three PMS-BR copolymers containing 2, 7, and 15 weight percent of the PMS, respectively. The experiments were conducted over a temperature range of 50 to 100°C with a conventional vapor sorption apparatus in which the polymer samples are exposed to a step change in the vapor pressure of the solvents while being maintained at constant temperatures. The vapor sorption apparatus used in this study utilized a quartz spring and isothermal conditions were maintained by a condensing vapor [Duda et al., 1973]. By setting the pressure above a reboiler fluid, the temperature where the fluid boils is determined. The vapor of the boiling fluid surrounds the outer wall of the sorption chamber and thereby establishes experimental temperatures.

The polymers used in this study were provided by Exxon Chemical Company. All solvents used were of reagent-grade quality and used without further purification. Since the diffusion coefficients were expected to be low, relatively thin samples (approximately 0.5 mm) were used to reach the equilibrium in a reasonable time scale. Initially, several problems were encountered with sample preparation, and which included:

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(1) entrapment of air bubbles in the polymer samples and (2) distortion of flat polymer samples upon heating. The difficulties were overcome by pressing hot polymer samples, with a Carver laboratory press at 120°C, on to thin sheets of aluminum foil. To conduct experiments polymer disks, still attached to the foil, were cut and fitted to aluminum buckets which were then placed into the sorption column. This procedure eliminated all previous problems. In order to reduce the possibility of any internal stress which may have been introduced at the time of pressing, the solvent vapor was introduced into the polymer samples 2-3 times in a sorption/desorption cycle.

Each experiment consisted of measuring the weight gain of the polymer sample as a function of time. If the data are plotted as a fractional approach to equilibrium versus the square root of time, the diffusivity can be obtained from the initial slope of the plot. More details of the experimental technique are provided by Hong [1994].

THEORY

According to free volume theories, two requirements must be satisfied before molecules of jumping unit can migrate; (1) a hole of sufficient size must appear adjacent to the molecules, and (2) the molecules have enough energy to jump into this void. Thus, the rate of migration can be the product of two probabilities; (1) the probability that a fluctuation in local density will produce a hole of sufficient size, and (2) the probability that jumping unit will acquire sufficient energy to overcome attractive forces in order to jump into the voids.

Furthermore, by assuming that (1) the binary mutual diffusion coefficients can be related to the individual self-diffusion coefficients through an expression proposed by Bearman [1961], (2) the contribution of the polymer self-diffusion coefficient to the binary mutual diffusion coefficient is negligible, and (3) the Flory-Huggins model [Flory, 1953] accurately describes the thermodynamic behavior of polymer/solvent systems, Vrentas and Duda proposed the free-volume theory for diffusion [Vrentas and Duda, 1977a, b]. In this theory, the solvent self-diffusion coefficient, D_1, and the polymer/solvent binary mutual diffusion coefficient, D, are given by

$$D_1 = D_o \exp\left(\frac{-E}{RT}\right)$$

$$\times \exp\left[\frac{-(\omega_1 \hat{V}_1^* + \xi\omega_2\hat{V}_2^*)}{\omega_1\left(\dfrac{K_{11}}{\gamma_1}\right)(K_{21} - T_{g1} + T) + \omega_2\left(\dfrac{K_{12}}{\gamma_2}\right)(K_{22} - T_{g2} + T)}\right] \quad (1)$$

$$D = D_1(1-\phi_1)^2(1-2\chi\phi_1) \quad (2)$$

where $\hat{V}_i^*$ is the specific critical hole free-volume of component i required for a diffusive jump, ω_i is the weight fraction of component i, ϕ_i is the solvent volume fraction, χ is the polymer-solvent interaction parameter, and ξ is the ratio of molar volumes for the solvent and polymer jumping units. D_o is a constant pre-exponential factor, E is the energy per mole that a molecule must possess to overcome attractive forces which con-

strain it to its neighbors, and γ_i is an overlap factor for the component i which is introduced because the same free-volume is available to more than one jumping unit. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are free-volume parameters for the polymer. Finally, the subscripts 1 and 2 refer to the solvent and polymer, respectively.

For polymer/solvent systems, it has been suggested that the range of validity of the Bearman's relationship between self- and mutual diffusion coefficients is limited. Recently, a new model was proposed by Vrentas and Vrentas [1993], which extends the validity of the previous result to higher solvent weight fractions. Eq. (2) provides a useful approximation, however, for studying the binary mutual diffusion behavior in polymer solutions up to solvent weight fractions of 0.2 [Vrentas and Vrentas, 1993].

Although there are fourteen independent parameters in Eq. (2), grouping some of them means that only ten parameters ultimately need to be evaluated: K_{11}/γ_1, $K_{21}-T_{g1}$, K_{12}/γ_2, $K_{22}-T_{g2}$, $\hat{V}_1^*$, $\hat{V}_2^*$, χ, D_o, E, and ξ. The specific critical hole free-volumes, $\hat{V}_1^*$ and $\hat{V}_2^*$ can be estimated as the specific volumes of the solvent and the polymer, respectively, at absolute zero temperature from established group contribution methods [Harward, 1970]. K_{11}/γ_1 and $K_{21}-T_{g1}$ can be determined from viscosity data [Hong, 1995] or NMR relaxation data [Zielinski et al., 1992; Hong et al., 1996] of the solvent. K_{12}/γ_2 and $K_{22}-T_{g2}$ can be estimated directly from zero shear rate viscosity or indirectly from tabulated values of Williams-Landel-Ferry (WLF) constants [Williams et al., 1955; Ferry, 1980; Hong, 1995]. χ can be determined by correlating the solubility data with the Flory-Huggins Equation. Finally, the three remaining parameters: D_o, E, and ξ can be evaluated, using the diffusion data, from a non-linear regression.

RESULTS AND DISCUSSION

The Vrentas-Duda free-volume model was used to correlate the diffusion data as a function of temperature and concentration. Six out of the ten parameters in the Vrentas-Duda model were estimated a priori by the methods discussed previously. One should note that $\hat{V}_2^*$ values of PMS-BR copolymers were estimated from the values of monomers in the copolymers as follows

$$\hat{V}_2^* = \omega_{2a} \hat{V}_{2a}^* + \omega_{2b} \hat{V}_{2b}^* \quad (3)$$

where ω_{2i} and $\hat{V}_{2i}^*$ (i=a or b) are the weight fraction and specific critical hole free-volume of monomer A and B in the random copolymer, respectively.

In order to estimate polymer free-volume parameters, WLF constants for two of the polymer samples were determined using dynamic mechanical rheometry in conjunction with the principal of time-temperature superposition [Ferry, 1980]. A Rheometrics Mechanical Spectrometer (RMS-800) was used for all tests, which were conducted using parallel plate fixtures. Disk-shaped samples (~8 mm diameter) were cut from compression-molded sheets of the PIB and the PMS-BR (15%). Small amplitude oscillatory flow experiments were carried out over a frequency ω range from 10^{-1} to 10^2 sec^{-1} at temperatures ranging from -50 to 25°C. Storage $G'(\omega)$ and loss $G''(\omega)$ moduli and loss
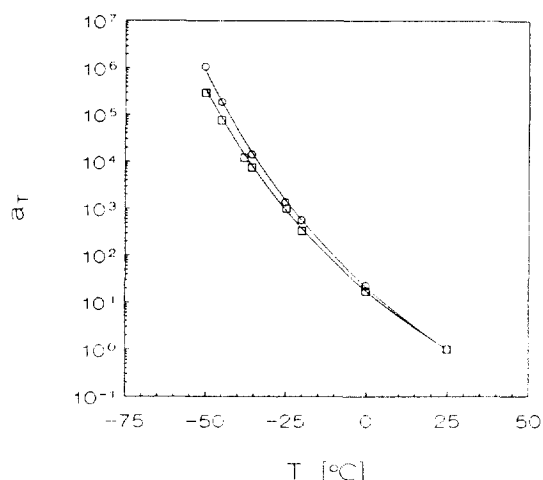
Fig. 1. Shift factors from time-temperature superposition of small amplitude oscillatory flow data to a reference temperature $T_0=25°C$: PIB ($\square$); PMS-BR (15%) ($\bigcirc$). Solid lines are fits of WLF equation, Eq. (4).

Table 1. Parameters used in correlations of diffusion coefficients for PMS-BR/solvent systems

Parameter	PMS-BR (2%)/ n-Hexane	PMS-BR (15%)/ n-Hexane	PMS-BR (15%)/ Cyclohexane	PMS-BR (15%)/ n-Pentane
$\hat{V}_1^*$ [cm³/g]	1.133	1.133	1.008	1.158
$\hat{V}_2^*$ [cm³/g]	1.002	0.981	0.981	0.981
K_{11}/γ_1 [cm³/g-K]	1.96×10^{-3}	1.96×10^{-3}	3.02×10^{-3}	2.41×10^{-3}
K_{12}/γ_2 [cm³/g-K]	3.13×10^{-4}	2.95×10^{-4}	2.95×10^{-4}	2.95×10^{-4}
$K_{21}-T_{g1}$ [K]	-41.08	-41.08	157.81	-38.39
$K_{22}-T_{g2}$ [K]	-118.10	-120.56	-120.56	-120.56
χ	0.69	0.71	0.72	0.62
ξ	0.65	0.64	0.49	0.46
D_o [cm²/s]	4.13×10^{-1}	3.65×10^1	5.98×10^{-1}	2.49×10^1
E [cal/mole]	4870	7920	7020	9230

Table 2. Parameters used in correlations of diffusion coefficients for PIB/solvent systems

Parameter	PIB/ Cyclohexane	PIB/ Toluene	PIB/ Chloroform	PIB/ n-Pentane
$\hat{V}_1^*$ [cm³/g]	1.008	0.917	0.510	1.158
$\hat{V}_2^*$ [cm³/g]	1.005	1.005	1.005	1.005
K_{11}/γ_1 [cm³/g-K]	3.02×10^{-3}	2.20×10^{-3}	7.12×10^{-4}	2.41×10^{-3}
K_{12}/γ_2 [cm³/g-K]	3.16×10^{-4}	3.16×10^{-4}	3.16×10^{-4}	3.16×10^{-4}
$K_{21}-T_{g1}$ [K]	157.81	102.72	29.43	38.89
$K_{22}-T_{g2}$ [K]	117.93	117.93	117.93	117.93
χ	0.55	1.17	1.09	0.77
ξ	0.43	0.53	0.35	0.43
D_o [cm²/s]	3.32×10^{-2}	1.42×10^{-3}	9.02×10^{-3}	7.32×10^1
E [cal/mole]	5240	1070	3780	9950
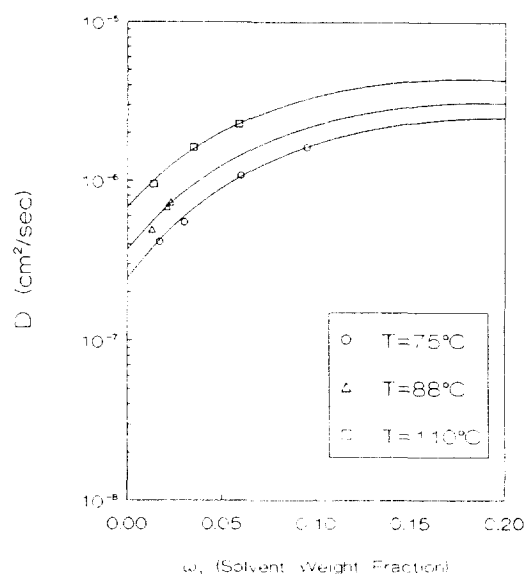
Fig. 2. Experimental data and theoretical correlations for PIB/ toluene mutual diffusion.

tangent tanδ (ω) curves versus ω at different temperatures were shifted to a reference temperature of 25°C according to the principal of time-temperature superposition. Overlap of shifted data from different temperatures was good over the approximately eight decades in ω covered by the master curves. The resulting shift factors for the two polymers are shown in Fig. 1. Also shown in this figure are the fits to the WLF equation [Williams et al., 1955].

$$\log a_T = -\frac{C_1^0(T-T_0)}{C_2^0+T-T_0} \qquad (4)$$

where T_0 is the reference temperature and C_1^0 and C_2^0 are the WLF constants. For PIB, we find $C_1^0=7.63$ and $C_2^0=178.2$ K, which are within 11% of reported values [Ferry, 1980], and for the PMS-BR (15%), we find $C_1^0=7.67$ and $C_2^0=180.2$ K. WLF constants for the PMS-BR (2%) and the PMS-BR (7%) were interpolated using values for the PIB and the PMS-BR (15%). These values were converted to C_1^{WLF} and C_2^{WLF} (WLF constants when a reference temperature is T_g), and C_1^{WLF} and C_2^{WLF} values were then used in the determination of polymer free-volume parameters appearing in the free-volume theory discussed in

the previous section [Hong, 1995].

χ values were obtained by correlating the solubility data with the Flory-Huggins equation. The dependence of χ values on temperature was ignored because, for the purposes of this study, single χ values were sufficient to describe thermodynamic behavior of polymer/solvent systems. The three remaining parameters: D_o, E, and ξ were evaluated, using the mutual diffusion coefficients, from the non-linear regression of Eq. (2). The parameters used to correlate the diffusion data are provided in Tables 1 and 2.

An examination of the diffusion data indicates that for all the solvents investigated, the diffusion coefficient depends on both concentration and temperature. The concentration dependence of the PIB/toluene system on diffusivity is stronger than that of the PIB/chloroform system (see Figs. 2 and 3). Because the probability of a toluene molecule, which is larger than chloroform, locating sufficient free-volume to take a diffusive step is lower than that of a chloroform molecule, small changes in the available free-volume caused by increases in solvent concentration can have a substantial impact on the diffusion coefficient. Although the experiments were conducted at temperatures more than 100°C above T_g, the correlation yields ex-
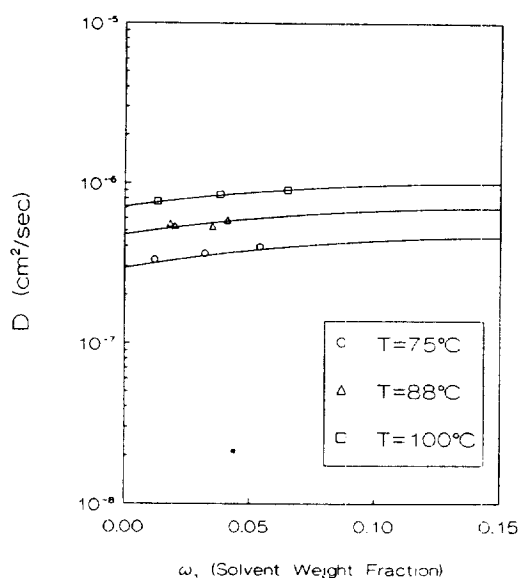
Fig. 3. Experimental data and theoretical correlations for PIB/ chloroform mutual diffusion.

Fig. 5. Comparison between mutual-diffusion coefficients of cyclohexane in isobutylene-based polymers.

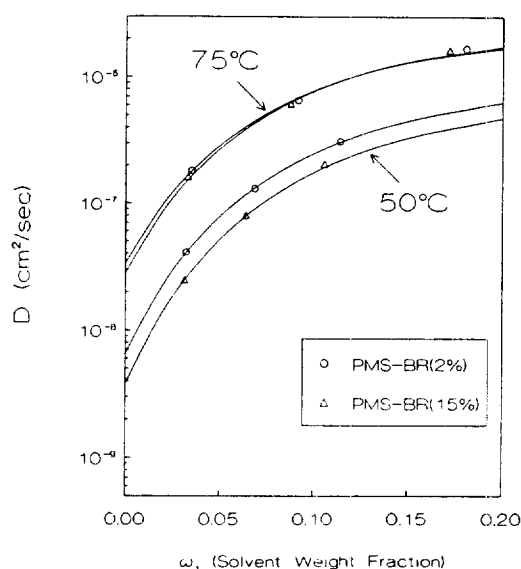**Fig. 4. Comparison between mutual-diffusion coefficients of n-hexane in isobutylene-based polymers.**
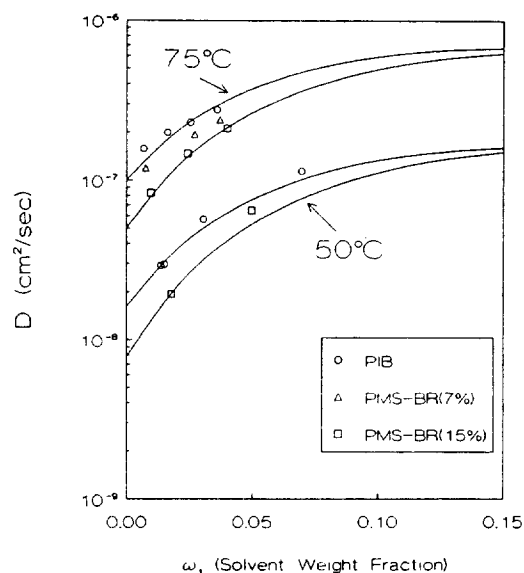
Fig. 6. Comparison between mutual-diffusion coefficients of n-pentane in isobutylene-based polymers.

cellent fits to experimental data for all the systems. The results indicate that the Vrentas-Duda free-volume diffusion model is still valid at temperatures more than 100°C above T_{g2}.

In order to see the effect on diffusivity of the composition in the copolymers, the diffusion coefficient data of PIB and PMS-BR copolymers with n-hexane, cyclohexane, and n-pentane are compared with each other in Figs. 4-6. In these figures, lines represent the theoretical correlations, using the free-volume theory as a function of temperature and concentration, for each polymer/solvent system. For the PMS-BR (7%)/n-pentane system in Fig. 6, the data are not correlated since the diffusion coefficients were measured only at 75°C. For all the solvents, the PIB shows the highest diffusivity, while the PMS-BR (15%) gives the lowest value. According to free-volume models, the rate of transport processes depends on the amount of fractional
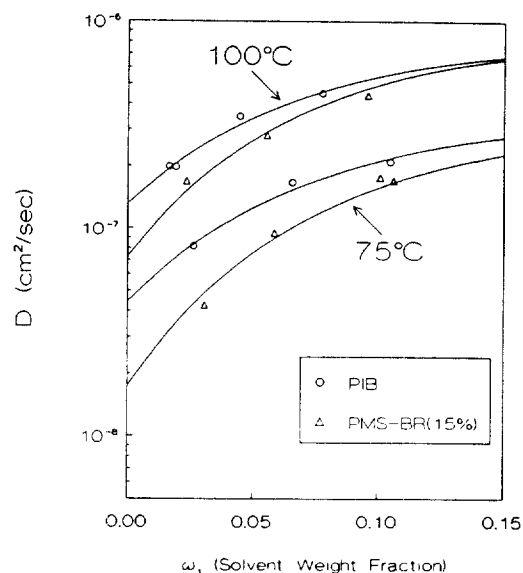
free-volume present in a system. It may be assumed that volume fraction of free-volume, f, increases linearly with temperature in accordance with the relation [Ferry, 1980].

$$f = f_g + \alpha_f (T - T_{g2})$$ (5)

where f_g is the fractional free-volume at T_{g2} and α_f is the constant. These parameters can be approximated from the WLF constants, C_1^{WLF} and C_2^{WLF}, as follows

$$f_g \approx \frac{1}{2.303 C_1^{WLF}}$$ (6)

$$\alpha_f \approx \frac{1}{2.303 C_1^{WLF}} C_2^{WLF}$$ (7)

The values of C_1^{WLF}, C_2^{WLF}, f_g, α_f, and T_{g2} for the PIB and

Table 3. Constants used to estimate f

	PIB	PMS-BR (2%)*	PMS-BR (7%)*	PMS-BR (15%)
C_1^{WLF}	15.02	14.81	14.76	14.50
C_2^{WLF} [K]	92.07	93.90	95.61	99.44
f_g	0.029	0.029	0.029	0.030
α_f [K^{-1}]	3.14×10^{-4}	3.12×10^{-4}	3.08×10^{-4}	3.01×10^{-4}
T_{g2} [K]	210	212	215	220
f at 50°C	0.064	0.064	0.062	0.061

*WLF constants for these polymers were interpolated.

PMS-BR copolymers are provided in Table 3. The estimated values of f at 50°C are also shown for comparison. Although the f value differences among the polymers are small, the trend is similar to the trend of the diffusivities. In other words, the PIB has the highest f value as well as the highest diffusion coefficients among the polymers. The differences in f values are consistent with glass transition temperatures of the polymers. The diffusivities of the polymers are distinguishable at lower ranges of solvent concentration and/or temperature, but merge as concentration and/or temperature increase. This is because all the systems have sufficient free-volume for molecules to migrate at higher temperatures and/or solvent concentrations.

CONCLUSIONS

The results presented confirm that the Vrentas-Duda free-volume model is an excellent tool for correlating mutual diffusion coefficient data over wide ranges of temperature and concentration. This theory can be applied to the random copolymer/solvent systems with minor modification. The results also indicate that as monomer ratio of p-methylstyrene in the copolymers increases, the diffusion coefficient decreases. The difference of diffusivity values between polymer/solvent systems can be explained by the concept of fractional free-volume of the polymer.

ACKNOWLEDGEMENT

NOMENCLATURE

a_T : temperature shift factor
C_1^0 : WLF parameter
C_2^0 : WLF parameter [K]
C_1^{WLF} : WLF parameter when a reference temperature is a glass transition temperature
C_2^{WLF} : WLF parameter when a reference temperature is a glass transition temperature [K]
D : polymer/solvent binary mutual diffusion coefficient [cm^2/s]
D_o : constant pre-exponential factor in Eq. (1) [cm^2/s]
D_1 : solvent self-diffusion coefficient [cm^2/s]
E : energy required to overcome attractive forces from neighboring molecules [cal/mole]
f : fractional free-volume

f_g : fractional free-volume at the glass transition temperature
G' : storage modulus [Pa]
G'' : loss modulus [Pa]
K_{11} : solvent free-volume parameter [cm^3/g-K]
K_{21} : solvent free-volume parameter [K]
K_{12} : polymer free-volume parameter [cm^3/g-K]
K_{22} : polymer free-volume parameter [K]
R : gas constant
T : temperature [K]
T_0 : reference temperature [K]
T_{g1} : solvent glass transition temperature [K]
T_{g2} : polymer glass transition temperature [K]
$\tan\delta$: loss tangent
$\hat{V}_1^*$: specific critical hole free-volume of solvent required for jump [cm^3/g]
$\hat{V}_2^*$: specific critical hole free-volume of polymer required for jump [cm^3/g]
$\hat{V}_{2a}^*$: specific critical hole free-volume of monomer A in random copolymer [cm^3/g]
$\hat{V}_{2b}^*$: specific critical hole free-volume of monomer B in random copolymer [cm^3/g]

Greek Letters

α_f : volume expansion coefficient in Eq. (5) [K^{-1}]
γ_1 : solvent overlap factor which accounts for shared free-volume
γ_2 : polymer overlap factor which accounts for shared free-volume
ξ : ratio of critical molar volume of solvent jumping unit to that of polymer jumping unit
ϕ_1 : solvent volume fraction
χ : Flory-Huggins polymer/solvent interaction parameter
ω : frequency [sec^{-1}]
ω_1 : solvent weight fraction
ω_2 : polymer weight fraction
ω_{2a} : weight fraction of monomer A in random copolymer
ω_{2b} : weight fraction of monomer B in random copolymer

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