Sorption and Partial Molar Volume of Small Molecules in Glassy Polymers

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ABSTRACT: The sorption of atoms (He, Ar) or molecules (N_2, CO_2, H_2O, SO_2, CH_4, C_2H_6, C_3H_8) in polymers is described by assuming a continuous distribution of dissolution energies. The energy distribution arises from a volume distribution of the intermolecular space yielding different elastic distortion energies when occupied by solute molecules. On the basis of statistical fluctuations of the free volume and Eshelby's elasticity theory it will be shown that a Gaussian distribution of sorption energies is appropriate for small molecules in glassy polymers. The width of the Gaussian distribution can be calculated, and it agrees well with values obtained by fitting experimental sorption data. The entropy changes of the small molecules during sorption are about the same as for the gas/solid transition. The dependence of volume changes on gas pressure provides information on the size and distribution of intermolecular space.

1. Introduction

Solution and diffusion of atoms in metallic glasses,[1] ions in silicate glasses,[2] and molecules in glassy polymers show universal features. In all cases the diffusion coefficient increases with increasing solute concentration and the activity coefficient becomes larger at higher solute contents. This behavior is qualitatively explained by saturation of low-energy sites with dissolved particles. Then an increase in solute concentration requires the occupation of sites with higher energy with a concomitant increase of solute activity and a decrease of the average activation energy for diffusion. Often the simplest case of a distribution of site energies which are two energetically different sites is used, in order to obtain closed solutions from the fundamental relations of statistical thermodynamics allowing an easy, quantitative evaluation of experimental data.

In the framework of glassy polymers the concept of two sites or two energy levels of dissolutions, respectively, has been called the dual-sorption model.[3-5] It is assumed that besides regular sites, where dissolution according to Henry's law occurs, holes are present in the glassy polymer acting as saturable traps for the absorbed molecules (mostly absorbed from the gaseous state) according to a Langmuir isotherm. Then the total concentration c can be written as[5]

$$c = c_D + c_H = k_D p + \frac{C'_H b p}{1 + bp} \tag{1}$$

where c_D and c_H are the partial concentrations in regular sites and holes, p is the partial pressure of the gas, k_D is Henry's dissolution constant, and b and C'_H are the hole affinity and the hole saturation constants. C'_H is interpreted to be proportional to the free volume quenched in at the transition from the liquid to the glassy state, which is expected not to change with temperature below the glass transition temperature, T_g.[6] However, experimental values of C'_H decrease strongly with temperature.[5] Another drawback of the dual-sorption model is that its parameters are difficult to calculate from known properties of the polymers and the dissolved gasses, although for the condensable solute CO_2 the Langmuir capacity has been predicted from dilatometric data[5] and correlations appear to exist between k_D and parameters of the Lennard–Jones potential of the gas[6] and/or the free volume of the polymer.[7]

In the present study it will be shown first that a Gaussian distribution of site energies is more appropriate than the two-(energy-)level system of the dual-sorption model. On the basis of the free volume considerations of Bueche[8] and the elasticity calculations of Eshelby,[9] the width of the distribution function will be calculated. Secondly, the relation between concentration and pressure is presented as derived in detail elsewhere.[1,2] When the experimental pressure/concentration isotherms are fit to the equations derived, values of the average free energy of the Gaussian and its width are obtained which are compared with theoretical values. Finally, consequences with respect to the partial molar volume and the concentration dependence of the diffusion coefficient of small molecules in glassy polymers will be shortly discussed. The difference between free energy and free enthalpy is considered to be small for solids and thus the term free energy is used very often although the term free enthalpy is correct.

2. Site Energy Distribution

A gas molecule is considered to be inserted as a stiff sphere of volume V_g into a hole of volume V_h. The hole shall be part of the normal interstices between macromolecules and part of the free volume of the glassy polymer. According to Eshelby,[9] the volume change or the partial molar volume V_p, respectively, is given by

$$V_p = \gamma(V_g - V_h) \tag{2}$$

where the factor γ is related to Poisson's ratio ν by

$$\gamma = 3\frac{1 - \nu}{1 + \nu} \tag{3}$$

Equation 2 requires close contact between the "surfaces" of the hole and the molecule, which has to be the case for $V_g > V_h$, where the molecule has to be squeezed into the hole. However, for $V_g \leq V_h$ the molecule shall be dissolved into the hole without straining the glassy polymer and, therefore, the partial molar volume shall be nil.

For glassy polymers ν is about $^1/_3$ and, therefore, eq 3 yields $\gamma = 1.5$. The volume increase above $V_g - V_h$ is due to a shear deformation of the elastic matrix (polymer).

The elastic energy stored this way in the polymer is given by[9]

$$G_{el} = \frac{2}{3}\mu_s \frac{(V_g - V_h)^2}{V_h} \tag{4}$$

where μ_s is the shear modulus of the polymer. G_{el} has to be provided during dissolution of the gas. For the liquid or rubbery state of the polymer μ_s is several orders of magnitude smaller and, therefore, the elastic energies become negligible. G_{el} is considered to be a part of the total free enthalpy of dissolution, but it will be the part which gives rise to the distribution of this enthalpy.

If we furtheron assume that the holes in the polymer have different sizes, the free energy of dissolution should vary according to the elastic energy of insertion given by eq 4. In addition the partial molar volume of the penetrant molecule varies according to eq 2. In order to determine the corresponding distribution function, the hole volume distribution has to be determined first.

The volume of all holes shall be the free volume of the polymer, and local fluctuations of the latter shall correspond to fluctuations of the hole volume around an average value V_{h0}. Thus following Bueche's treatment,[8] the distribution function is obtained as

$$f(V_h) = f_0 \exp[-B(V_h - V_{h0})^2/2V_{h0}RT] \tag{5}$$

where f_0 is a prefactor, B is the bulk modulus, and R and T have the usual meaning. Equation 5 corresponds to the volume fluctuations of a small system being embedded in a large system as it is calculated in standard textbooks on statistical thermodynamics (i.e. ref 10, p 37). The distribution of hole volume will be frozen in at the glass transition temperature T_g, and it is shown in the Appendix A that the free energy G of dissolution of molecules into the holes of a glassy polymer is described by a Gaussian function, too:

$$n(G) = n_0 \exp[-(G - G_0)^2/\sigma^2] \tag{6}$$

where σ is the width of the distribution given as (cf. Appendix A)

$$\sigma = \frac{2(V_g^2 - V_{h0}^2)\mu_s}{3V_{h0}} \sqrt{\frac{2RT_g}{BV_{h0}}} \tag{7}$$

where B is the bulk modulus in the liquid state at $T \geq T_g$ whereas μ_s is the shear modulus at T. The average free energy G_0 corresponds to the free energy change of the following reaction of a molecule M

$$\text{M (gas)} \rightarrow \text{M (in average hole of polymer)} \tag{8}$$

It is convenient to define $n(G)\,dG$ in eq 6 as the fraction of holes with free energies in the interval $G,G+dG$. Summation over all sites gives

$$\int_{-\infty}^{\infty} n(G)\,dG = 1 \tag{9}$$

and the prefactor n_0 becomes

$$n_0 = 1/\sigma\sqrt{\pi} \tag{10}$$

Instead of talking about holes in the structure of the glassy polymer, the term sites could have been used as well for interstices between the macromolecules of the polymer. The concentration of dissolved gases in polymers is usually given as cm^3(gas)/cm^3(polymer) which is easily converted into number of molecules/cm^3(polymer). In order to transform that into a concentration which is defined as the fraction of sites being occupied (=number of molecules/number of sites), the number of sites per cm^3 polymer has to be known. Different ways of estimating the number of holes or sites in the polymers lead to similar figures for N_0, as shown in Appendix B. In the following a value of $N_0 = 6.7 \times 10^{21}/\text{cm}^3$ will be used.

3. Calculation of Composition Pressure Isotherms

If we assume that the energetically different holes or sites introduced before are filled with one molecule per site only, the thermal occupancy of sites is described by Fermi–Dirac statistics.[1,2,10,11] The concept was developed for hydrogen in metallic glasses and its results for solution and diffusion have been described in detail elsewhere.[1,2] Only the most important features will be repeated in this study.

The partial concentration c_G of molecules in sites lying within the free energy window $G,G+dG$ is the product of the number of sites $n(G)\,dG$ and the thermal occupancy

$$c_G = n(G)dG \frac{1}{1 + \exp[(G - \mu)/RT]} \tag{11}$$

where μ is the chemical potential of the dissolved gas or its Fermi level, respectively, which is related to the gas pressure p by the well-known relation

$$\mu = \mu_0 + RT \ln p \tag{12}$$

Summation over all partial concentrations or integration over all energies leads to the total concentration c

$$c = \int_{-\infty}^{\infty} \frac{n(G)\,dG}{1 + \exp[(G - \mu)/RT]} \tag{13}$$

Independent of the form of $n(G)$ (Gaussian, two-level, etc.), eq 13 is a general relation between concentration and chemical potential (pressure) and it includes the dual-sorption model (eq 1) as a special case.[1] One may also state that a Langmuir saturation for all the different sites has been assumed which becomes obvious by inserting eq 12 into eq 11:

$$c_G = \frac{pn(G) \exp[-(G - \mu_0)/RT]}{1 + p \exp[-(G - \mu_0)/RT]} \tag{14}$$

Thus the Gaussian sorption model when compared with the dual-sorption model corresponds to an extension of the two terms of eq 1 to an infinite number of terms (eq 13) without increasing the number of parameters. In the latter case we have three as well (N_0, σ, and G_0) but the value of at least two of the parameters (N_0, σ) can be estimated or calculated.

When a Gaussian distribution is assumed for the sites, eqs 6, 10, and 13 have to be combined, yielding

$$c = \frac{1}{\sigma\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{\exp\{-(G - G_0)^2/\sigma^2\}}{1 + \exp[(G - \mu)/RT]}\,dG \tag{15}$$

The last equation can be considered as an implicit equation between the chemical potential μ or the pressure p, respectively, and the concentration c. It might be evaluated by numerical integration in a computer or by using one of two limiting cases as discussed in ref 2.

If the polymer is in the rubbery or liquid state, its shear modulus will be several orders of magnitude smaller than in the glassy state and, according to eq 7, the width of the Gaussian distribution will be very small and the Gaussian function degenerates to a Dirac–δ function. Then eqs 12

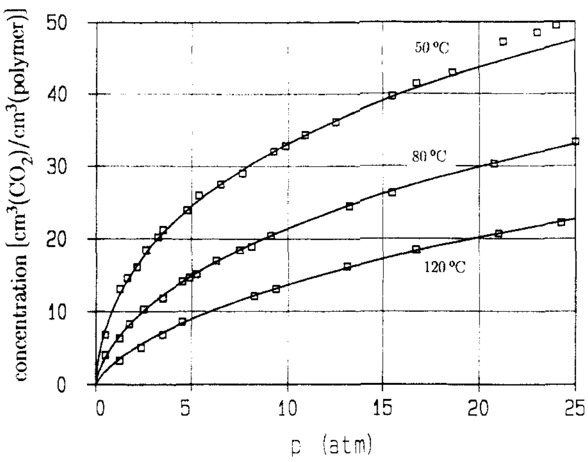

Figure 1. Pressure-concentration isotherms for CO_2 in polyimide. Data points are from ref 20. The lines are calculated using eqs 12 and 15 with $\mu_0 = 0$, $G_0(50\ °C) = 17.7$, $G_0(80\ °C) = 21.2$, and $G_0(120\ °C) = 24.65$ kJ/mol and $\sigma = 13$ kJ/mol.

and 15 yield for $c \ll 1$

$$c = p \exp[(\mu_0 - G_0)/RT] \qquad (16)$$

This proportionality between concentration and pressure is called Henry's law and it is fulfilled for dissolution of small molecules in rubbery polymers.[5,12,13]

For the glassy state of a polymer Henry's law is not valid which has been demonstrated for a large variety of polymers and solute molecules and which is explained in the present study by a Gaussian distribution of dissolution energies. In order to evaluate the width σ and the average value G_0 of the Gaussian distribution, experimental data from a large number of different systems as published in many papers[4,7,14-41] were used by enlarging figures or by plotting sorption isotherms with the aid of the published dual-sorption parameters. These data plots were compared with isotherms calculated from eq 15 by varying σ and G_0 until a good fit of the experimental data was achieved. G_0 is the change of free enthalpy during dissolution with respect to the gas at temperature T and at 1 atm pressure, i.e. $\mu_0 = 0$. Therefore, the quantities free enthalpy of dissolution and free enthalpy of a site will be the same. Usually, data with $c > 40$ cm³(gas)/cm³ polymer were disregarded, as then the glassy polymer is subject to swelling.[17,18,32,34,38] Some examples of experimental data and calculated composition-pressure isotherms are shown in Figures 1-3. As sorption isotherms were measured at different temperatures the average sorption free enthalpy varied linearly with temperature as shown in Figure 4 for two examples and as expressed by the relation

$$G_0 = H_0 - TS_0 \qquad (17)$$

where H_0 is the average enthalpy and S_0 the average entropy of dissolution. For the case of CO_2 in PET which was only 40% amorphous it was assumed that dissolution occurs in the amorphous phase only and, therefore, the number of sites N_0 was reduced from 6.7×10^{21} to 2.7×10^{21} cm^{-3}. Values of the various quantities are compiled in Tables I-V, where Table I contains all data for CO_2, Table II for CH_4, Table III for N_2, and Table IV for other gasses (He, Ar, SO_2, H_2O, C_2H_6, C_3H_8 and $CClF_3$). Table V compiles a few results on sorption of CO_2 for polymers above the glass transition temperature, where Henry's law is valid ($\sigma = 0$).

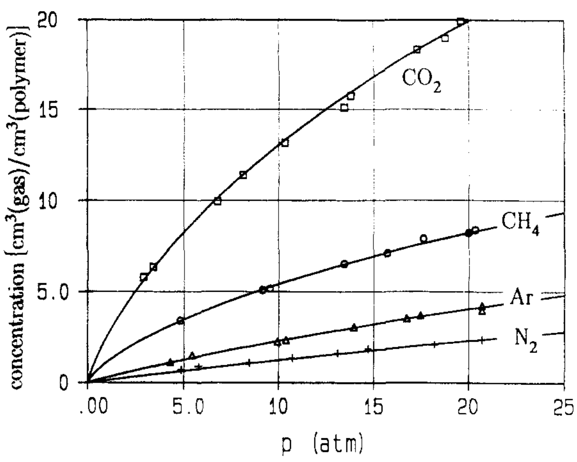

Figure 2. Pressure-concentration isotherms for various gases in polystyren. Data points are from ref 31 for $T = 308$ K. The lines are calculated using eqs 12 and 15 with $\mu_0 = 0$ and G_0 and σ values given in Tables I-IV.

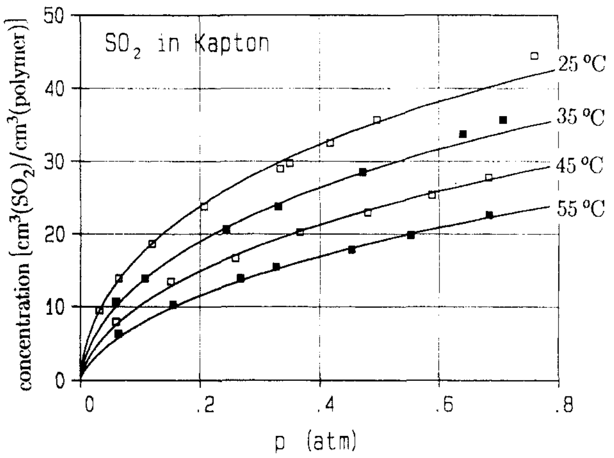

Figure 3. Pressure-concentration isotherms for SO_2 in Kapton. Data points are from ref 37. The lines are calculated using eqs 12 and 15 with $\mu_0 = 0$, $G_0(25\ °C) = 8.5$, $G_0(35\ °C) = 9.7$, $G_0(45\ °C) = 10.9$, and $G_0(55\ °C) = 12.1$ kJ/mol and $\sigma = 12$ kJ/mol.

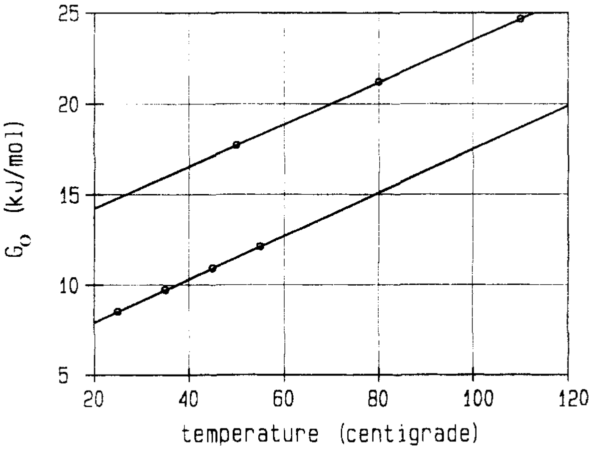

Figure 4. G_0 values obtained from fitting the Gaussian model to the experimental data shown in Figures 1 and 3 plotted versus temperature.

4. Width σ of the Sorption Energies

For the case of CO_2 in PEMA[30] the quantities in eq 7 have been measured or can be calculated and, therefore, can be compared with the experimental value of $\sigma = 8$ kJ/mol. The following numbers are provided in refs 30 and 35: $B(T \geq T_g) = 2.5 \times 10^9$ Pa, $T_g = 334$ K, $V_p = 3 \times 10^{-5}$ m³, and $B(T = 310\ \mathrm{K}) = 3 \times 10^9$ Pa. In the glassy state ($\nu = {}^1/_3$) the shear modulus can be calculated as $\mu_s = B/(2$

Table I
Gaussian Parameters for CO_2 in Various Polymers[a]

molecule	polymer	σ (kJ/mol)	G_0 (kJ/mol)	H_0 (kJ/mol)	S_0 (J K^{-1} mol^{-1})	ref
CO_2	PET[b]	9.5		−20.8	124	14
	PET	11		−16	127	15
	PET	9	19.6 (30)			41
CO_2	PC	7	16			16
	PC(cond)[c]	10	17.6			17
	PC	7	16			18
	PC(cond)[c]	11.5	18.2			18
	PC(cond)[d]	16	18.7			18
	PC(cond)[c]	10	17.6			19
	TMPC	9.5	15.2			17
	TCPC	10.5	16.4			17
	TBPC	11	16.8			17
CO_2	PI	13		−20	116	20
	PI	12	17.6 (25)			21
	PI	11.5	20.8 (80)			22
	PI	12.5		−17.6	117	23
	PI	10.5	16.5			24
	PI	11	18.2			24
	PI	13	21.1			24
	PI	11	20.3			24
	PI	11	22.5 (80)			22
	Kapton	11	23.5 (80)			22
	Kapton	15	25.4 (60)			25
	Kapton	7		−22	114	26
CO_2	Bis-PEI[e]	12	17.7			27
	Bis-PA	10	17.3			27
	Bis-PH	10	21			27
CO_2	cellulose	9	16	−24	130	28
CO_2	PVB	11		−50[f]	168[f]	29
CO_2	PEMA	8		−24.4	133	30
CO_2	PIO	10		−27.4	140	7
CO_2	PS	9	19.6 (25)			31
CO_2	PSUL	13		−16	115	32
CO_2	copolyest	9	18.45			19

[a] G_0 values are for 35 °C or the temperature given in brackets. [b] 40% amorph. [c] Conditioned by exposure to high gas pressure. [d] Measured during desorption. [e] On Bisphenol basis. [f] Values were omitted during averaging.

Table II
Gaussian Parameters for CH_4 in Various Polymers[a]

molecule	polymer	σ (kJ/mol)	G_0 (kJ/mol)	H_0 (kJ/mol)	S_0 (J K^{-1} mol^{-1})	ref
CH_4	PS	11.5	25.5 (25)			31
	PS	9	23.6	−7.2	100	33
CH_4	PC	10.5	23.7			17
	PC	11.5	26.1			34
	TMPC	11.5	22.6			34
	TMPC	9.5	20.1			17
	TMPC[b]	11	21.7			17
	TCPC	10.5	21.1			17
	TBPC	11.2	22			17
CH_4	PI	11	23.2			24
	PI	12.5	27			24
	PI	13.5	28.6			24
	Kapton	17.5	37.6 (60)			25
CH_4	Bis-PEI[c]	11.5	24.3			27
	Bis-PA	10.5	24			27
	Bis-PH	11.5	29.5			27
CH_4	PSUL	15	27.7			32
CH_4	copolyest	9	23.7			19

[a] G_0 values are for 35 °C or the temperature given in brackets. [b] Conditioned by exposure to high gas pressure. [c] On Bisphenol basis.

Table III
Gaussian Parameters for N_2 in Various Polymers

molecule	polymer	σ (kJ/mol)	G_0 (kJ/mol)	H_0 (kJ/mol)	S_0 (J K^{-1} mol^{-1})	ref
N_2	Bis-PEI[b]	10	26.7			27
	Bis-PA	8	25.2			27
	Bis-PH	8	28.9			27
N_2	PC	9	27			17
	TMPC	8	22.6			17
	TCPC	8.5	22.8			17
	TBPC	8.5	23			17
N_2	PS	7	23 (25)			31
N_2	PVB	8		−6.7	113	29
N_2	PSUL	11	27.5			32
N_2	copolyest	7	24.2			19

[a] G_0 values are for 35 °C or the temperature given in brackets. [b] On Bisphenol basis.

Table IV
Gaussian Parameters for Some Molecules in Various Polymers

molecule	polymer	σ (kJ/mol)	G_0 (kJ/mol)	H_0 (kJ/mol)	S_0 (J K^{-1} mol^{-1})	ref
He	PC	0	24.4			17
Ar	PS	8	23 (25)			31
Ar	PVB	8.5	26.4			29
Ar	PEMA	7		−2.2	78	35
Ar	copolyest	8	24			19
SO_2	Kapton	12	8.5 (25)			36
	Kapton	12		−27.3	120	37
SO_2	PC	9	7.9 (25)			38
SO_2	PA	9	10.5 (25)			38
H_2O[b]	polyelect	9	−2.6 (30)			39
C_2H_6	PSUL	19	26			32
C_2H_6	PET	13.5	29 (25)			15
C_3H_8	PS	14.5		−4.9	97.5	40
C_3H_8	PC	15		−10	110	40
$CHClF_3$	PS	13		−11.2	105	40

[a] G_0 values are for 35 °C or the temperature given in brackets. [b] Concentrations are given as moles of H_2O per moles of structural unit of the polymer. They were divided by an estimated factor of 10 to convert them into molecules of H_2O per site.

Table V
Sorption Parameters for Polymers in the Liquid State

molecule	polymer	σ (kJ/mol)	G_0 (kJ/mol)	H_0 (kJ/mol)	S_0 (J K^{-1} mol^{-1})	ref
CO_2	PVB	0		−16	97	29
CO_2	PET	0		−9.6	85	14
CO_2	PEMA	0		−13	85	30
CO_2	LDPE	0		−6.4	78	32

$+ 2\nu) = 1.13 \times 10^9$ Pa and with the volume of CO_2 $V_g = 4.6 \times 10^{-5}$ m^3 (see section 6) the average hole volume is obtained from eqs 2 and 3 as $V_{h0} = 2.6 \times 10^{-5}$ m^3. With these values eq 7 yields $\sigma = 12$ kJ/mol. In the light of the assumptions made during the derivation of eq 7 the agreement between experimental and theoretical values is considered to be good.

Because all of the quantities in eq 7 describing properties of the polymer matrix are rather similar, one would expect to have about the same value of σ for a given gas or molecule, respectively, in agreement with evaluated values of σ (Tables I–IV). Exceptions are polymers which were exposed to high gas pressures (so-called conditioning) before the measurement, leading to a larger width, and the group of polyimides also having larger σ values on the average. The latter may be understood by eq 7 because the glass transition temperature of polyimides is higher compared to other glassy polymers in Table V. Then a broader distribution of free volume was frozen in at higher temperatures giving rise to a broader distribution of site energies.

Inspection of Tables I–V shows that the width of the site energy distribution increases as the size of the molecule increases; averaging over the different polymers gives the following order:

$$\sigma(\mathrm{He}) = 0 < \sigma(\mathrm{Ar}) = 7.9 < \sigma(\mathrm{N_2}) = 8.5 < \sigma(\mathrm{CO_2}) = 10.6 < \sigma(\mathrm{CH_4}) = 11.6\ \mathrm{kJ/mol}$$

The few values available for H_2O and SO_2 range between 9 and 12 kJ/mol, as one would expect from their sizes to be about the same as CO_2 or CH_4, but the values for σ may not be representative in order to be included in the ranking. For the large molecules C_2H_6 and C_3H_8 the σ values are considerably larger, but more data are necessary to obtain reliable results. In general data on the sorption of different molecules in the same polymer are most helpful in studying the relationship between molecule volume and σ.

The correlation between σ and the volume of the molecule V_g is predicted by eq 7 assuming that the average hole size V_{h0} and the other quantities in eq 7 of the different polymers do not vary too much. The ranking of the σ values is valid with a few exceptions where $\sigma(CH_4)$ is slightly smaller than $\sigma(CO_2)$. By comparing the results of different studies on the same gas/polymer system, one has to take into account that the pretreatment of the polymer (annealing or conditioning) will affect the sorption data.[18,21]

The fact that He atoms do not have a distribution of site energies in PC ($\sigma = 0$) is obvious because their volume is smaller than the volume of the holes and elastic straining of the matrix does not occur. Thus molecules of different size can be used to obtain information on the volume distribution of the holes in a glassy polymer.

5. Free Enthalpy G_0 and Entropy S_0 of Sorption

The average free enthalpy change during sorption of small molecules G_0 according to eq 8 contains besides the elastic part given by eq 4 another part which arises from the nearest neighbor interaction of the molecule and the segments of the polymer. If the chemical bonds of the molecule remain unchanged during sorption, this nearest neighbor interaction will be mostly of the van der Waals type and, therefore, it may be described by Lennard-Jones potentials. As the Lennard-Jones potential of the gases describes melting and evaporation of gases quite well, a correlation exist between the parameters of this potential (namely the energy parameter ϵ) and the melting or boiling point. The Lennard-Jones parameter ϵ is a measure of the polarizability of the small molecules or their permanent dipole moment, which together with the corresponding quantities of the polymer segments determine the interaction energy. In addition the Lennard-Jones energy parameter ϵ is linearly dependent on the Lennard-Jones distance parameter r_0^6 which correlates with the size of the small molecules. The latter changes the elastic part of G_0. These arguments explain qualitatively why a correlation exists between solublity of small molecules (mainly determined by G_0) and the Lennard-Jones force constant or the boiling points, respectively. These correlations have been observed for glassy[15,17,19,22] and rubbery[13] polymers. An example is shown in Figure 5 between G_0 values at 308 K and boiling temperatures of some gases having about the same molecular volume, in order to account for a similar contribution from the elastic energy. The latter being about 10 kJ/mol for molecules of about the size of CO_2 as calculated from eq 4 and the parameters given at the beginning of section 4. The lowest values of G_0 correspond to those gases having a permanent dipole moment, as SO_2 and H_2O. The same arguments should hold for polymer segments; i.e. segments with permanent dipole moments should decrease G_0 and, therefore, increase the solubility.

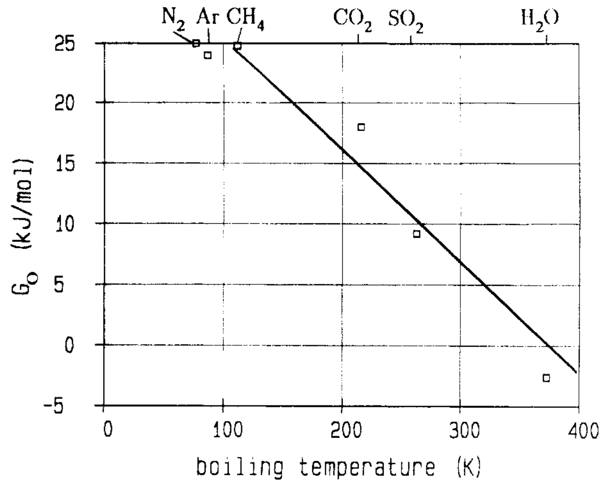

Figure 5. Average free enthalpy of dissolution G_0 of various gases in various polymers as given in Tables I–IV versus boiling point temperature.

Table VI
Boiling Point T_b, Standard Entropy S_{295}, Gas/Solid Transition Entropy $S_{g/s}$, and Entropy of Sorption in Glassy Polymers S_0 for Some Gases

	gas					
	Ar	CH_4	C_3H_8	CO_2	N_2	SO_2
T_b (K)	87	112	225	195[a]	77	263
S_{295} (J K^{-1} mol^{-1})	152	186	266	210	192	245
$-S_{g/s}$(J K^{-1} mol^{-1})	88	81	100	127	81	123
$-S_0$ (J K^{-1} mol^{-1})	113[b]	100[b]	104	124	78[b]	120

[a] Sublimation temperature. [b] One value only.

Most of the correlation discussed before is related to the enthalpy part of G_0 as the entropy S_0 is about the same for the various gases (cf. Tables I–IV). As shown in Table VI, the entropy change of the molecules from the gaseous state to solution in a polymer S_0 is about the same as during the transition from the gaseous state to the solid state $S_{g/s}$. The latter was calculated by adding the entropies of vaporization and fusion[42-44] (in the case of CO_2 the heat of sublimation was divided by the sublimation temperature). Table VI also contains the standard entropies S_{295} of the gases at 295 K and 1 atm. The magnitude of S_{295} is mostly determined by contributions from the translational degrees of freedom and smaller contributions from rotational degrees of freedom, the latter playing an important role for the larger molecules only. If we assume that the dissolved molecules do not rotate within the glassy polymers, all of the entropy content arising from translation and rotation in the gaseous state has to vanish during dissolution. However, the magnitude of the entropy of dissolution S_0 is smaller than S_{295}. It is assumed that the difference (70–160 J K^{-1} mol^{-1}) corresponds to an entropy gain due to vibrations (or rotations) of the small molecule in its site between the polymer segments.

In order to estimate the vibrational entropy of the dissolved molecules, the vibrational entropy of a Lennard-Jonesium (a solid of particles interacting via a Lennard-Jones potential) was calculated for the gases in Table VI by assuming the molecules to be Einstein oscillators vibrating with the Debye frequency.[45] Thus a vibrational

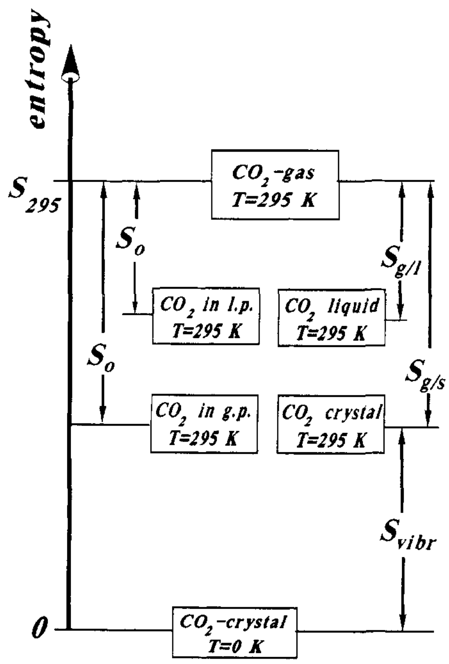

Figure 6. Schematic entropy diagram for CO_2 (representative for small molecules) containing the entropy levels of the gaseous, liquid, and solid states. The entropies of dissolution S_0 in a glassy polymer (gp) or a liquid polymer (lp) are shown for comparison. Note the similar magnitude of the entropy of a small molecule (cf. Table V) in its liquid state and in a liquid polymer or in its solid state and in a glassy polymer, respectively.

entropy of about 50 J K^{-1} mol^{-1} at 295 K was obtained for Ar, N_2, CO_2, and CH_4 which is the right order of magnitude but somewhat smaller than the difference of 70–90 J K^{-1} mol^{-1} between standard entropy and entropy of dissolution for these gases. From these entropy considerations it can be concluded that the dissolution of small gaseous molecules in glassy polymers resembles the transition from gaseous into the solid state. In a first-order approximation the difference between the S_0 values for the glassy and liquid state of the polymer should be the entropy change during solid/liquid transition, which is 50 J K^{-1} mol^{-1} for CO_2 in agreement with the 34 J K^{-1} mol^{-1} difference between the average values of S_0 for the glassy and liquid states (cf. Tables I and V). The various entropies of the gas molecules discussed in this section are shown schematically in Figure 6.

6. Volume Changes during Sorption and Diffusion

One of the most convincing arguments supporting the dual-sorption model[46] is the following: The holes in the structure of the glassy polymer are so large that incorporation of gaseous molecules does not change the overall volume of the polymer, whereas dissolution in normal sites gives rise to a volume change which is typical for dissolving the same molecule in various organic liquids and rubbery polymers. Then the volume change is proportional to the concentration c_D of molecules in normal sites (first term on the right-hand side of eq 1) which should be proportional to the partial pressure of the dissolved molecules in agreement with experimental findings.[30,35,46] However, recent measurements on CH_4 sorption in conditioned and unconditioned polycarbonates[34] and CO_2 sorption in conditioned polymers[18] reveal strong deviations from this proportionality between volume change ΔV and pressure p (cf. Figures 8 and 9).

Independent of the relation between ΔV and p, it is a general experimental result that the partial molar volume $V_p = \Delta V/c$ of gases in glassy polymers increases with increasing concentration c. In the framework of the model presented in this study the partial molar volume depends on the size of a site V_h. Large values of V_h correspond to

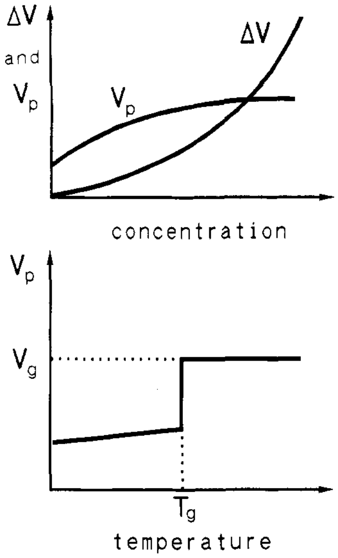

Figure 7. Schematic presentation of the measured and predicted volume change ΔV or partial molar volume V_p of small molecules in glassy polymers as a function of concentration and temperature (V_g = volume of the small molecule).

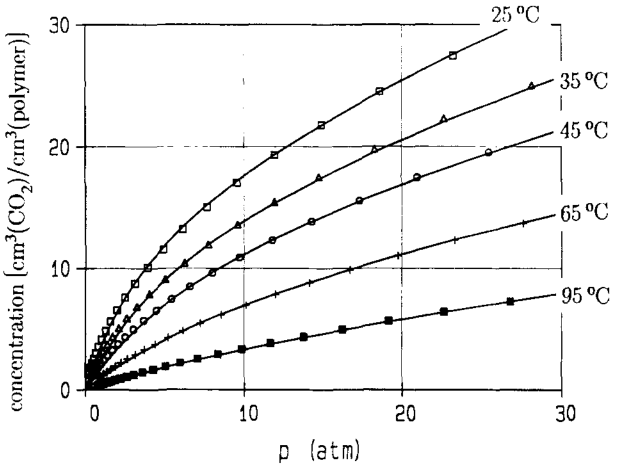

Figure 8. Pressure–concentration data as calculated from the Gaussian model (symbols) by using eqs 12 and 15, σ = 10 kJ/mol and G_0 = (−21 + 0.13T) kJ/mol. The solid lines are fitted to the data points by using eq 1 of the dual-sorption model with the parameters given in Table VII.

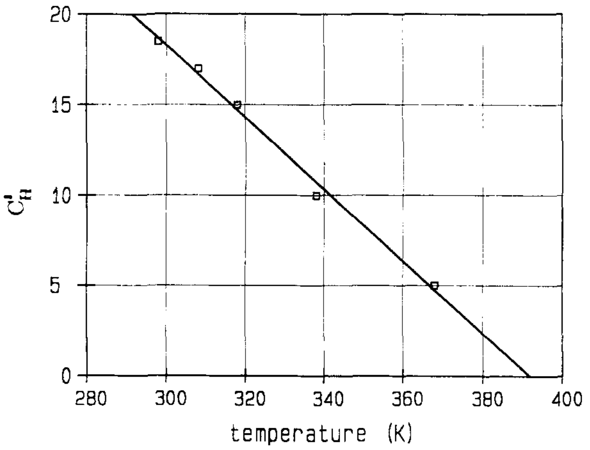

Figure 9. Hole saturation constant of the dual-sorption model C'_H as obtained from fitting the data of the Guassian model in Figure 8 and as compiled in Table VII plotted versus temperature.

low partial molar volumes (cf. eq 2) and low elastic energies (cf. eq 4), and therefore, they are occupied first, giving rise to low partial molar volumes at low concentrations. If the concentration is raised, sites of smaller volume V_h have to be occupied, leading to larger partial molar volumes.

For a liquid or rubbery polymer Poisson's ratio is $\nu = 0.5$ and eq 3 yields $\gamma = 1$. Then the partial molar volume should be $V_p = V_g - V_h$ (cf. eq 2), if the molecule of volume V_g is dissolved in a hole of volume V_h. However, above the glass transition temperature the macromolecules will have enough mobility to compensate the annihilation of a hole by the creation of another hole, in order to keep the free volume constant. Thus the partial molar volume will be identical with the volume of the small molecule $V_p = V_g$ (this is equivalent with the well-known method of determining the volume of a solid body by immersing it in a liquid). Therefore, measured values of V_p of CO_2 in different organic liquids and in silicone rubber are about the same, i.e. $V_p = 46 \pm 3$ cm^3/mol.[46] This value is larger than the molar volume of CO_2 in its solid state (ca. 27 cm^3/mol). Nevertheless, $V_g = 46$ cm^3/mol was used, because it reflects the interaction of the solute molecules with organic molecules. A similar interaction is expected to occur in the glassy polymer. In the glassy state the macromolecules are not mobile enough to create free volume after a hole has been occupied and the partial molar volume will be given by eq 2, yielding much lower values for V_p (about 20 cm^3/mol[18,30,35,46]). This dependence of V_p on temperature and concentration is shown schematically in Figure 7.

A quantitative evaluation of the volume change ΔV for a glassy polymer is achieved by averaging over the partial molar volume of the dissolved molecules in the various sites according to the following equation:

$$\Delta V = \int_{-\infty}^{\infty} V_p(G) c_G \, dG \qquad (18)$$

Note that V depends on G via eqs 2 and 4. For $V_h(G) \geq V_g$ no volume change is expected to occur and, therefore, the corresponding energy is used as a lower bound of the integral in eq 18. A detailed description of the evaluation procedure and comparison with experimental data are given elsewhere.[47]

The distribution of site energies for a given solute gives rise to a dependence of the diffusion coefficient on solute concentration as measured for hydrogen in metallic glasses[2,11] and alkali-metal ions in oxide glasses.[2,11] During an increase of solute concentration, sites of low energy are filled first and then sites of higher energy have to be occupied. Thus the average activation energy of diffusion decreases, leading to an increase of the solute diffusivity. The quantitative evaluation of these dependencies is based on averaging over the jump frequencies of the solute particles in the various sites.[2,11] This concept is applicable to experimental values of solute diffusion in glassy polymers, too, as shown in ref 48. It is worthwhile to note that the concentration dependence of D is determined by the width of the site energy distribution σ alone.[2] The width, however, is not an adjustable parameter as it stems from the sorption data of the same system.

7. Dual Sorption versus Gaussian Model

One of the major drawbacks of the dual-sorption model is that fitting of experimental data yields hole saturation constants C'_H which decrease with temperature. The parameters C'_H is a measure of the overall hole volume, and therefore, this annihilation of hole volume has to occur reversibly although the polymer is in the glassy state. In favor of a reversible structural change it has been often observed that the hole saturation constant decreases linearly with temperature, becoming zero at the glass transition temperature.[5,30] However, for SO_2 sorption in a polyimide with a glass transition temperature around 400 °C C'_H changed far below T_g and became zero at 90 °C. It will be shown in the following that this behavior is a consequence of a Gaussian distribution of site energies. In order to prove this, pressure–concentration values were calculated for a Gaussian distribution with typical average values for CO_2 $\sigma = 10$ kJ/mol and $G_0 = (-21 + 0.13T)$ kJ/mol at different temperatures. The corresponding data points are shown in Figure 8 and compared with lines as obtained from the dual-sorption model, i.e. eq 1. The parameters used to obtain the excellent agreement as shown in Figure 8 are compiled in Table VII. In Figure 9 the hole saturation constant obtained this way is plotted versus temperature, and it can be seen that in agreement with the experimental observations mentioned before, C'_H decreases about linearly with temperature intercepting the T axis around 390 K.

Table VII
Dual Sorption Parameters Used To Calculate the Lines Shown in Figure 9

T (K)	C'_H (cm^3/cm^3)	k_D ((cm^3/cm^3)/atm)	b (atm^{-1})
298	18.5	0.53	0.2
308	17	0.4	0.14
318	15	0.33	0.11
338	10	0.25	0.08
368	5	0.165	0.05

Both dual-sorption and Gaussian models are able to fit pressure–composition isotherms equally well; however, whereas the Gaussian model requires four fitting parameters (N_0, H_0, S_0, and σ) the dual-sorption needs at least six (k_D, b, C'_H, and at least three more to describe their temperature dependence). Moreover, the number of sites N_0 used in the Gaussian model was estimated and kept constant during all calculations, reducing the number of fitting parameters to three. The width σ of the Gaussian distribution can be calculated from measurable quantities, and it agrees with values obtained from pressure–composition data. The entropy values S_0 for dissolution are reasonable when compared with other entropy changes of the gas. Therefore, the parameters S_0 must not be changed arbitrarily. In addition the predicted dependencies of G_0, S_0, and σ on various properties of the gas or the polymer are in agreement with experimental findings.

If one accepts a rigid distribution of intermolecular space between the macromolecules of a glassy polymer and the assumption that incorporation of small molecules then gives rise to a distribution of energies of dissolution, the Gaussian model is a natural consequence of these considerations. To describe the relationship between size of the intermolecular space and site energy of a small molecule, Eshelby's continuum theory of elasticity may not be appropriate. It could be replaced by atomistic calculations like the one by Richards[49] developed for hydrogen in amorphous metals, obtaining a similar relation between site energy and site volume.

In very recent papers by Gusev and Suter[50] and Weiss et al.[51] a continuous-site model has been proposed for solutes in glassy polymers independently. Different from the present study, no physicochemical reasoning was provided for a specific type of distribution of site energies and its various parameters, yet it was shown that sorption results can be fitted by a variety of distribution functions equally well when compared with the dual-sorption model.

Appendix A: Distribution of Free Energies of Dissolution

The free energy of dissolution G of molecules from the gas phase (it might be any other state as well) is equivalent with the free energy change of the following reaction

$$\mathrm{M\ (gas)} \rightarrow \mathrm{M\ (in\ polymer)} \tag{A1}$$

During dissolution the elastic energy given by eq 4 has to be provided, which will be a part of G besides other contributions (namely due to van der Waals interaction) and will depend on the hole volume V_h. Expansion of G in a Taylor series around the average hole volume V_{h0} yields

$$G = G_0 + \left.\frac{\partial G_{el}}{\partial V_h}\right|_{V_h = V_{h0}} (V_h - V_{h0}) \tag{A2}$$

where G_0 is the free energy of the reaction given by eq A1 if only holes of volume V_{h0} are occupied. Insertion of eq 4 in eq A2 gives

$$G - G_0 = \frac{2}{3}\mu_s \frac{V_{h0}^2 - V_g^2}{V_{h0}^2}(V_h - V_{h0}) \tag{A3}$$

which is used to transform the distribution of eq 5 into a distribution of free energies of dissolution $n(G)$:

$$n(G) = n_0 \exp\left[-\frac{9BV_{h0}^3(G - G_0)^2}{8RT_g(V_{h0}^2 - V_g^2)^2\mu_s^2}\right] \tag{A4}$$

where n_0 is a prefactor which is related to the total number of holes. Equation A4 may be written in the usual form of a Gaussian function:

$$n(G) = n_0 \exp[-(G - G_0)^2/\sigma^2] \tag{A5}$$

where σ is the width of the distribution given as

$$\sigma = \frac{2(V_g^2 - V_{h0}^2)\mu_s}{3V_{h0}}\sqrt{\frac{2RT_g}{BV_{h0}}} \tag{A6}$$

According to the derivation presented here B is the bulk modulus in the liquid state at $T = T_g$ where the free volume is frozen in, whereas μ_s is the shear modulus at T where the molecules are incorporated. μ_s drops by several orders of magnitude on going from the glassy to the liquid state, and therefore, the Gaussian distribution becomes very narrow compared to the thermal energy RT.

Appendix B: Number of Sites (Holes) in a Glassy Polymer

There are several approaches to estimate for 1 cm^3 of polymer the number of sites, where a small molecule will be in a local equilibrium position. In the following, three estimations are listed.

1. The packing density of the gases (Ar, CO_2, CH_4, SO_2, N_2) in the liquid or solid state is about 2×10^{22}/cm^3. This would be the upper limit for the number of sites in a glassy (nonswelling) polymer. If we assume that only the free volume of the polymer is occupied by the molecules and that this free volume is present with a fraction of 0.15 of the total volume, the site density reduces to $N_0 = 3 \times 10^{21}$/cm^3. The latter number is an underestimation, as molecules are dissolved in holes of the polymer structure which are smaller than the volume of the molecules, giving rise to the overall volume change described by eq 2.

2. Using eq 2 and measured values of 30 cm^3/mol for the partial molar volumes of CO_2 in glassy polymers[30] and 46 cm^3/mol for the molecular volume,[18] a hole volume of 26 cm^3/mol is calculated for the holes (sites) in the glassy polymer. If it is again assumed that 1 cm^3 of the glassy polymer contains a free volume of 0.15 cm^3, the number of these holes becomes $N_0 = 3.5 \times 10^{21}$/cm^3.

3. The number of sites shall be equal to the number of segments of the macromolecules. This concept is the basis of the successful Flory–Huggins theory of polymer solutions.[52,53] With an average molecular weight of 100 per segment and a density of 1 g/cm^3 for the glassy polymer the number of sites becomes $N_0 = 6 \times 10^{21}$/cm^3.

Although the three estimations presented are rather different, they yield a site density for small molecules which differs by a factor of 2 only. For the comparison of the calculated concentrations, diffusivities, and partial molar volumes with experimental data, the value of $N_0 = 6.7 \times 10^{21}$/cm^3 has been used for the density of sites. It is at the upper limit of the values estimated before, but it yields the simple conversion factor of 250 for transforming the concentration given as molecules per sites into cm^3 of gas per cm^3 of polymer.

A different choice of the site density or the conversion factor changes the calculated concentrations, diffusivities, and partial molar volumes or the evaluated width σ and the average free energy of sorption G_0 only slightly. Thus a decrease of N_0 by a factor of 4 lowers σ by 40% and G_0 by 60%; however, the temperature dependence of G_0, i.e. the average entropy of sorption S_0, does not exhibit significant changes.

References and Notes

(1) Kirchheim, R. *Acta Metall.* **1982**, *30*, 1069.
(2) Kirchheim, R.; Stolz, U. *J. Non-Cryst. Solids* **1985**, *70*, 323.
(3) Barrer, R. M.; Barrie, J. A.; Slater, J. *J. Polym. Sci.* **1957**, *23*, 315.
(4) Michaels, A. S.; Vieth, W. R.; Barrie, W. R. *J. Appl. Phys.* **1963**, *34*, 13.
(5) Paul, D. R. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 294.
(6) Pace, R. J.; Daytner, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1103.
(7) Maeda, Y.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 957, 981 and 1005.
(8) Bueche, F. *J. Chem. Phys.* **1953**, *21*, 1850.
(9) Eshelby, J. D. In *Solid State Physics*; Seitz, F., Turnbull, D., Eds.; Academic: New York, 1956.
(10) Hill, T. L. *Introduction to Statistical Thermodynamics*; Addison-Wesley: London, 1962; p 431.
(11) Kirchheim, R. *Prog. Mater. Sci.* **1988**, *32*, 261.
(12) Stannett, V. In *Diffusion in Polymers*; Crank, J., Park, C. S., Eds.; Academic Press: London, 1968; p 41.
(13) Van Ammerongen, G. J. *Rubber Chem. Technol.* **1964**, *37*, 1065.
(14) Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1947.
(15) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J. Appl. Phys.* **1963**, *34*, 1 and 13.
(16) Jordan, S. M.; Fleming G. K.; Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 2305.
(17) Muruganandam, N.; Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polm. Phys. Ed.* **1987**, *25*, 1999.
(18) Fleming, G. K.; Koros, W. J. *Macromolecules* **1990**, *23*, 1353.
(19) Masi, P.; Paul, D. R.; Barlow, J. W. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 15.
(20) Okamoto, K.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2621.
(21) Hachisuka, H.; Tsujita, Y.; Takizawa, A.; Kinoshita, T. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 11.
(22) Okamoto, K.; Tanaka, K.; Yokoshi, O.; Kita, H. *J. Polym. Sci., Polm. Phys. Ed.* **1989**, *27*, 643.
(23) Okamoto, K.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y. *J. Polym. Sci., Polm. Phys. Ed.* **1989**, *27*, 1221.
(24) Hirose, T.; Mi, Y.; Stern, S. A.; St. Clair, A. K. *J. Polym. Sci., Polm. Phys. Ed.* **1991**, *29*, 341.
(25) Chern, R. T.; Koros, W. J.; Yui, B.; Hopfenberg, H. B.; Stannett, V. T. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1061.
(26) Uragami, T.; Hopfenberg, H. B.; Koros, W. J.; Yang, D. K.; Stannett, V. T.; Chern, R. T. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 779.
(27) Barbari, T. A.; Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polm. Phys. Ed.* **1988**, *26*, 729.

(28) Stern, S. A.; de Meringo, A. H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 735.
(29) Kamiya, Y.; Mizoguchi, K.; Naito, Y.; Hirose, T. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 535.
(30) Kamiya, Y.; Mizoguchi, K.; Hirose, T.; Naito, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 879.
(31) Vieth, W. R.; Tam, P. I.; Michaels, A. S. *J. Colloid Interface Sci.* **1966**, *22*, 360.
(32) Kamiya, Y.; Hirose, T.; Mizoguchi, K.; Naito, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1525.
(33) Vieth, W. R.; Frangoulis, C. S.; Rionda, J. A., Jr. *J. Colloid Interface Sci.* **1966**, *22*, 454.
(34) Pope, D. S.; Fleming, G. K.; Koros, W. J. *Macromolecules* **1990**, *23*, 2988.
(35) Kamiya, Y.; Mizoguchi, K.; Naito, Y.; Bourbon, D. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 225.
(36) Koros, W. J.; Patton, C. J.; Felder, R. M.; Fincher, S. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1485.
(37) Felder, R. M.; Patton, C. J.; Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1895.
(38) Davis, E. G.; Rooney, M. L. *Kolloid-Z. Z. Polym.* **1971**, *49*, 1043.
(39) Hirai, Y.; Nakajima, T. *J. Macromol. Sci., Phys.* **1991**, *B30*, 141.
(40) Barrie, J. A.; Williams, M. J. L.; Munday, K. *Polym. Eng. Sci.* **1980**, *20*, 21.
(41) Toi, K. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *14*, 1829.
(42) D'Ans-Lax. *Taschenbuch für Chemiker und Physiker* (*Textbook for Chemists and Physicists*), 3rd ed.; Springer-Verlag: Berlin, 1967.
(43) *Gas-Encyclopedia*; Elsevier: Amsterdam, 1967.
(44) *CRC Handbook of Chemistry and Physics*; CRC Press, Inc.: West Palm Beach, FL, 1979.
(45) Kittel, C. *Introduction to Solid State Physics*, 4th ed.; John Wiley & Sons: New York, 1971; pp 95–110 and 201–218.
(46) Fleming, G. K.; Koros, W. J. *Macromolecules* **1986**, *19*, 2285.
(47) Kirchheim, R. To be published.
(48) Kirchheim, R. To be published in *Proceedings of DIMAT-92, International Conference on Diffusion in Materials*, Sept 1992, Kyoto, Japan.
(49) Richards, P. M. *Phys. Rev.* **1983**, *B27*, 2095.
(50) Gusev, A. A.; Suter, U. W. *Phys. Rev.* **1991**, *A43*, 6488.
(51) Weiss, G. H.; Bendler, J. T.; Shlesinger, M. F. *Macromolecules* **1992**, *25*, 990.
(52) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(53) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.