Relevance of Elastic Energies during Sorption of CO_2 Molecules in Glassy Polymers Demonstrated for Two Very Similar Polyimides

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ABSTRACT: Data on CO_2-sorption in and corresponding volume changes of three polyimides are evaluated in the framework of a recent model where elastic distortion of glassy polymers during dissolution of small molecules is taken into account. Due to the chemical identity and structural similarity of the polymers, differences in the behavior of CO_2 can be attributed solely to differences in the distribution of the intermolecular space (holes). Thus the polyimide with the lowest volume change has the smallest elastic energy and, therefore, the largest solubility of CO_2. The evaluation yields values of the average free energy of sorption and the width and average volume of the distribution of holes.

1. Introduction

In a recent thesis by M. Wessling,[1] the sorption of CO_2 and the corresponding volume dilatation have been studied for various polyimides. It is the major purpose of the present study to show that his experimental results demonstrate the importance of elastic energies arising from the incorporation of CO_2 molecules in smaller holes of the intermolecular space. Two of the polyimides studied in ref 1 and described in Figure 1 differ by a phenyl ring only which is either in the para or the ortho position within the backbone of the polymer. A third one is a copolymer of the two containing 50% of each monomer. Therefore, dissolved CO_2 molecules interact with segments which are chemically identical and differences in their behavior can be attributed to differences in free volume only.

Although the three polymers differ only slightly with respect to density and glass transition temperature (cf. Table 1) CO_2-sorption and corresponding volume changes are remarkably different as shown in Figures 2 and 3. An explanation of this effect can be provided quantitatively in the framework of a model developed recently.[2] For the purpose of a direct comparison of the experimental results with predictions of the model, its main assumptions will be repeated in the following section briefly.

2. The Concept of Hole Volume Distribution

Sites between macromolecules are called holes in the following. It is assumed that they have spherical shape and their volume is varying according to a Gaussian distribution as proposed by Bueche[3]

$$n(V_h) = \frac{N_0}{\sigma_V\sqrt{\pi}}\exp\left[-\frac{(V_h - V_h^\circ)^2}{\sigma_V^2}\right] \quad \text{with}$$

$$\sigma_V = \sqrt{\frac{2kT_gV_h^\circ}{B}} \quad (1)$$

where N_0 is the number of holes which was estimated in ref 2 to be 6.5×10^{21} cm^{-3}, $V_h^\circ$is the average volume of holes, σ_V is the width of their volume distribution, k is Boltzmann's constant, T_g is the glass transition temperature, and B is the bulk modulus of the liquid polymer at T_g. Equation 1 was derived for the liquid state, and it is assumed in ref 2 that it remains unchanged for $T < T_g$. If a molecule with a volume larger than the hole is dissolved, the polymer is elastically distorted. The corresponding elastic energy is calculated in ref 2 using the continuum solution for a

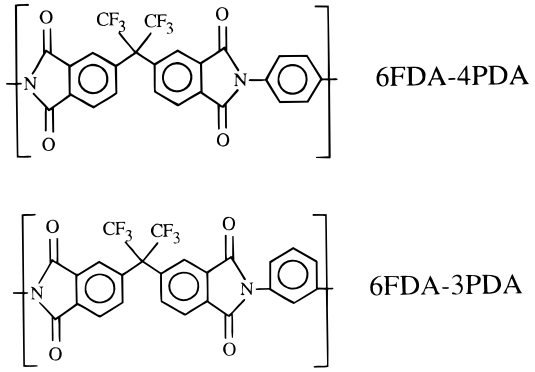

Figure 1. Structure of the polyimides 6FDA−4PDA and 6FDA−3PDA.

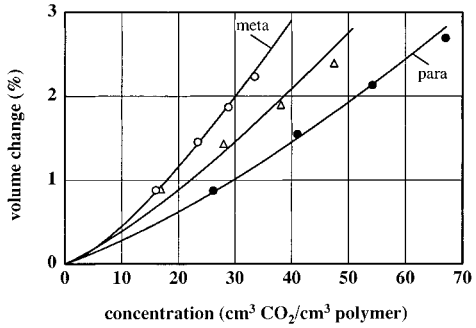

Figure 2. Measured volume change of 6FDA−4PDA (●, para position), 6FDA-3PDA (○, ortho position) and 6FDA-34PDA (△, copolymer) as a function of CO_2 concentration. The data points were taken from enlargements of figures presented in ref 1. The solid lines are calculated as described in refs 5 and 7 by using one fitting parameter for each curve (cf. Table 2).

Table 1. Glass Transition Temperature T_g and Density of the Polyimides[1]

polyimide	glass transition temp (K)	density (g/cm^3)
6FDA-4PDA	637 k	1.481
6FDA-3/4PDA	597 k	1.477
6FDA-3PDA	586 k	1.467

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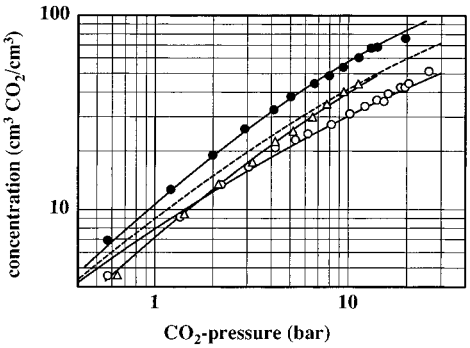

Figure 3. Double logarithmic plot of the measured CO_2-concentration in 6FDA−4PDA (●), 6FDA−3PDA (○) and 6FDA−34PDA (△) vs CO_2 pressure. The data points were taken from enlargements of figures presented in ref 1. The solid lines are calculated as described in refs 2 and 4 by using two fitting parameters $G° - \mu°$ and σ_G for each curve (cf. Table 2). Variation of the first parameter moves the curves parallel in the direction of the log p axis whereas the slope and curvature are solely determined by the choice of σ_G. The arithmetic average of the theoretical curves for 6FDA−4PDA and 6FDA−3PDA is shown as a dashed curve.

stiff sphere being inserted in a smaller hole of an elastic matrix. The results are only slightly different if the sphere has the same elastic constants as the matrix[4,5] yielding

$$G_{el} = \frac{2\mu_s}{3\gamma}\frac{(V_g - V_h)^2}{V_h} \quad \text{and} \quad V_p = V_g - V_h \qquad (2)$$

where V_g is the volume of the molecule dissolved, μ_s is the shear modulus of the polymer, $\gamma = 1.5$ for an elastically isotropic polymer with a Poisson number of $\nu = {}^1/_3$, and V_p is the differential partial molar volume, i.e., the volume change associated with the insertion of one molecule in a site of volume V_h. Equations 1 and 2 give a Gaussian distribution for the site energies as well if a linear expansion of eq 2 is used[2]

$$n(G) = \frac{N_0}{\sigma_G\sqrt{\pi}} \exp\left[-\frac{(G - G°)^2}{{\sigma_G}^2}\right] \qquad (3)$$

where G is the Gibbs free energy for dissolving a molecule in a hole which contains the elastic part given by eq 2 and a residual part G_r. The latter stems from a van der Waals interaction of the dissolved molecule with neighboring segments of the polymer and vibronic contributions to entropy. Both quantities are assumed to be the same for all holes. $G°$ and σ_G are the mean value and the width of the Gaussian distribution of G, being related to the parameters of the hole distribution by[2,4]

$$G° = G_r + G_{el}(V_h = V_h°) = G_r + \frac{2\mu_s}{3\gamma}\frac{(V_g - V_h°)^2}{V_h°} \quad \text{and}$$

$$\sigma_G = \frac{2\mu_s}{3\gamma}\frac{{V_g}^2 - {V_h°}^2}{{V_h°}^2} \qquad (4)$$

The thermal occupancy of sites is determined by Fermi−Dirac statistics which includes both minimizing energy and maximizing entropy. Which of the two plays the major role in minimizing the free energy depends in a sensitive way on temperature, concentration and width of the distribution σ_G.[6] Thus water molecules have a vanishing width and are distributed over all sites, whereas CO_2 molecules occupy the larger sites of the distribution preferentially.[5] By fitting sorption data, i.e., concentration-pressure isotherms, the parameters σ_G and $G° - \mu°$ are obtained, where $\mu°$ is the standard chemical potential of dissolved molecules in the gaseous phase. The average hole volume $V_h°$ can be evaluated from the measurements of volume changes during sorption.

This concept has been used in refs 2, 4, 5, and 7 to explain experimental findings for a large variety of small molecules and polymers. However, only in a few cases had volume changes been measured, allowing an independent calculation of σ_V via eq 1 and eq 4. Both values deviated systematically by about 30%. In the light of the various approximations used in the concept, this was considered to be good agreement and evidence for the validity of the model. In the present study the same procedure is applied to the data presented in Figures 2 and 3. It turns out that these data are much better examples for the usefulness of the new concept than the previous ones, because the three polyimides differ with respect to $V_h°$ considerably despite their chemical similarity. Therefore, the different behavior of CO_2 can be attributed to different hole sizes only.

3. Qualitative Interpretation

The total volume change of the polymer at a given CO_2 concentration is presented in Figure 2. The slope of the curves in Figure 2 corresponds to V_p. From an inspection of the data it can be concluded that the hole size decreases in the order 6FDA−4PDA, 6FDA−3/4PDA, and 6FDA−3PDA. The slight upward curvature of the data indicates that among the distribution larger sites are occupied first.

As the same segments are present in all three polyimides the free energy part G_r is expected to be the same but the elastic energy increases with decreasing hole size. Thus the free energy of dissolution increases with a concomitant increase of V_p, and the amount of CO_2 absorbed decreases in the same order as before. Therefore, in agreement with experimental data presented in Figure 3 CO_2 solubility is the lowest in 6FDA-3PDA and the highest in 6FDA−4PDA.

At a concentration of about 16 cm^3/cm^3 both 6FDA−3PDA and 6FDA−3/4PDA have the same volume expansion and, therefore, should have the same solubility. This prediction is in agreement with experimental findings (cf. Figure 3). For larger concentrations both volume change of and solubility in 6FDA−3/4PDA is between the values of 6FDA−3PDA and 6FDA−4PDA.

4. Quantitative Interpretation

During the discussion before we did not make use of the analytical expressions of the model. To do so we have to know the shear modulus μ_s at measuring temperature and the bulk modulus B in the liquid state at $T = T_g$. Both quantities are not known for the polymers of this study, and we have chosen the "typical" values $\mu_s = 0.9$ GPa and $B = 3$ GPa. A different choice within reasonable limits will not change the data presented in the following significantly.

When the experimental results were fit to the model, the parameters compiled in Table 2 have been used. It was pointed out in ref 4 that concentration−pressure isotherms are not very sensitive to the sorption model

Table 2. Fitting Parameters for the Theoretical Curves Shown in Figures 2 and 3 and Calculated Width of the Hole Size Distribution σ_V

polyimide	V_h° (cm^3/mol)	$G^\circ - \mu^\circ$ (kJ/mol)	σ_G (kJ/mol)	σ_V from σ_G (cm^3/mol)	σ_V from T_g (cm^3/mol)
6FDA−4PDA	28.8	10	5	8.1	10.1
6FDA−3/4PDA	25.3	12	6	6.5	9.1
6FDA−3PDA	19.7	15.7	10	5.6	8.0

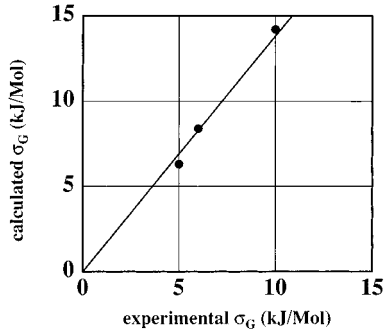

Figure 4. σ_G calculated from eq 4 (from Table 1, $V_g = 46$ cm^3/mol, σ_V from eq 1, $\gamma = 1.5$, $\mu_s = 0.9$ GPa, and $B = 3$ GPa) vs experimental values. Theoretical values are systematically larger by about 30%.

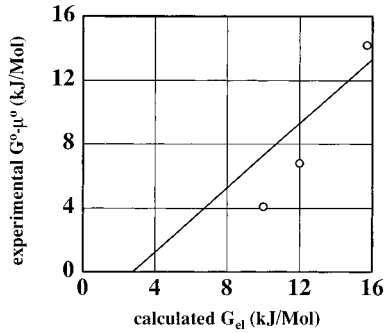

Figure 5. Test of the relation between G° and G_{el} given by eq 4 (instead of G° the accessible parameter $G^\circ - \mu^\circ$ is shown, with μ° being independent of G_{el}). The straight line has a slope of unity.

used for fitting and a dual-sorption isotherm can be applied yielding a similar good agreement with experiment. However, the fitting parameters of the model used in this study depend on well-defined quantities of the polymer or the dissolved species. The corresponding relationships (e.g. eqs 2 and 4) can be tested as done in the following for the polyimides of this study.

In agreement with eq 4 both $G^\circ - \mu^\circ$ and σ_G increase with decreasing average hole volume V_h°. In accord with previous evaluations[2,4] the calculated width of the free energy distribution via eqs 1 and 4 is about 30% larger than the experimental one as shown in Figure 4. The same systematic error leads to different results for the width of the volume distribution σ_V depending on whether it is calculated from eq 1 or from eq 4 (cf. Table 2). According to eq 4 G° should depend linearly on the elastic energy for holes with $V_h = V_h^\circ$. As shown in Figure 5 $G^\circ - \mu^\circ$ increases as the average elastic energy increases, which is equivalent to the average hole volume decreasing. The straight line through the data points should have a slope of unity and should intersect the abscissa at G_r. It is interesting to note that the G_r values (at ambient temperature) determined for other polymers and CO_2[2,4] are always a few kilojoules per mole. This can be understood since the van der Waals interaction between the atoms of CO_2 and atoms of segments of the polymers will not differ much.

The parameters V_h°, $G^\circ - \mu^\circ$, and σ_G in Table 2 were obtained by minimizing the sum of squared deviations between experimental data and data from the model. Nevertheless, there are uncertainties stemming from systematic and statistical errors of the experimental procedure. However, the first ones should not change relative differences of sorption and expansion of the various polymers. The statistical errors are expected to be not too large, because regular and smooth changes of pressure, concentration, and volume expansion were measured. It is always difficult to determine whether the minimum searched for during the fitting procedure is shallow or not, i.e., whether any other choice of the parameters leads to similar good agreement between experimental and theoretical data. However, fitting sorption data in a double logarithmic plot as in Figure 3 offers the advantage[4] that the slope of the theoretical curves solely depends on σ_G whereas the parameter $G^\circ - \mu^\circ$ causes a constant shift in the direction of the pressure axis. Concomitant increases of both parameters leads to similar solubility data but different slopes. Changes of slopes can be detected with the naked eye if the values of the parameters are changed by more than ±10%.

The larger average volume of 6FDA−4PDA when compared with 6FDA−3PDA should give a smaller density which is in contradiction with experimental findings (cf. Table 1). The density of 6FDA−4PDA is 1% larger but V_h° is about 30% larger. It appears to be unrealistic to conclude that the number of sites is smaller by 30% in the case of 6FDA−4PDA. However, in accordance with volume changes measured for H_2O in Bisphenol A−polycarbonate[5] we propose the following: CO_2 molecules occupy only a small fraction of all holes which are in the large volume tail of the volume distribution and which can be approximated by a Gaussian (with $N_o = 6.5 \times 10^{21}$ cm^3 a concentration of 50 cm^3 of CO_2/cm^3 of polymer corresponds to 20% of the sites filled). However, extrapolating from the features of a small fraction of large sites to the general distribution may lead to considerable errors. H_2O molecules have the advantage that their individual molecular volumes are about the same as that of one of the holes, and therefore, they occupy most of the sites with the same probability. Measuring their properties leads to a more reliable value of V_h°.

Unaffected by these considerations, 6FDA−4PDA offers more of the larger holes than 6FDA−3PDA. This is understandable because of the larger glass transition temperature of the first one, which may stem from a stiffer backbone of the macromolecules. Random entanglement of stiffer segments may leave larger holes in the structure.

Values obtained for σ_V from eq 4 are proportional to the square root of the product $T_g V_h^\circ$ as shown in Figure 6 with a slope being 30% different from the theoretical one of $2^{1/2}k/B$ (cf. eq 1). This again is the same systematic deviation observed before.

The different values of σ_G, σ_V, and G_{el} may arise from a variation of the elastic constants B and μ_s as well. But

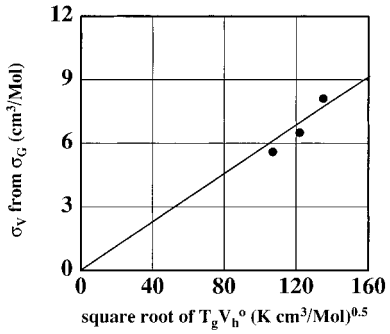

Figure 6. Test of the relation between σ_V and T_g and as proposed by eq 1.

according to eqs 1 and 4, they have to be changed by a factor of 4 or 2 in order to account for a change by a factor of 2 in σ_G. Such large variations of elastic constants are not expected to occur for the very similar polymers of this study.

5. The Copolymer 6FDA-3/4PDA

A first-order approximation for the copolymer would be a superposition of the two distribution functions of hole volume of 6FDA−4PDA and 6FDA−3PDA. In the framework of the concept used in this study this should lead to a CO_2 concentration which is equal to the arithmetic average of the two basic polymers. However, the dashed line in Figure 2 corresponding to the average does not agree with measured data. The behavior of the copolymer at low concentrations resembles that of 6FDA−3PDA; i.e., the large sites of 6FDA−4PDA are not formed in the copolymer.

6. Conclusion

Taking elastic distortions during the sorption process of CO_2 into account leads to a self-consistent description of CO_2 solubility and volume expansion for two polyimides which differ only slightly with respect to the structure of the repeat unit. Thus CO_2 molecules or small molecules in general can be considered as probes for the intermolecular space in a polymer. Knowing the sorption and volume change of two polymers and the corresponding copolymer may provide information on which of the larger holes present in the pure polymers is formed in the copolymer as well.

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