CO_2 Sorption and Dilation of Poly(methyl methacrylate)

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ABSTRACT: Sorption of CO_2 in poly(methyl methacrylate) at 35−200 °C and concurrent dilation of the polymer at 35−85 °C over a pressure range up to 50 atm were studied. Dissolution and Flory−Huggins interaction parameters for the gas in the polymer, not only in the rubbery state but also in the glassy state, were estimated by analyzing the sorption data above the glass transition temperature (T_{g0}, 105 °C). Isothermal glass transition of the polymer/gas system was observed on isotherms of sorption and dilation below T_{g0}. Partial molar volumes of sorbed CO_2 determined from the sorption and dilation isotherms increased with increasing concentration to the glass transition concentration. These isotherms were also analyzed on the basis of extended dual-mode models of sorption and dilation. From obtained parameters of the dual-mode models, nonequilibrium properties such as mean size and number of microvoids for the pure polymer and the CO_2-sorbed polymer in the glassy state were evaluated. The mean size, dependent upon CO_2 exposure history of the polymer, was in the range of 20−100 A^3, and the number of microvoid ((1−18) × 10^{20} voids/cm^3) was dependent upon both temperature and the exposure history.

Introduction

Amorphous polymers can sorb gases and concomitantly dilate. The sorption and dilation of the polymers below and above the glass transition temperature are very different in their behavior.[1−4] These phenomena reflect the difference in microscopic structures of the respective thermodynamic states, namely, the nonequilibrium nature of the glassy state and the liquid-like nature of the rubbery state. Accordingly, an analysis of sorption and dilation isotherms for gas penetrants would give us valuable information on the microstructure of the polymers.

In this paper, sorption of CO_2 in poly(methyl methacrylate) and concurrent dilation of its film specimen are studied over a wide range of temperatures and pressures. Sorption isotherms above the glass transition temperature are analyzed according to the Flory-Huggins dissolution theory, and the thermodynamic interaction between the polymer and the gas is investigated. Sorption and dilation data below the glass transition temperature are analyzed on the basis of dual-mode models of sorption and dilation. Nonequilibrium structural properties, such as size and number of microvoids for the pure polymer and the gas-sorbed polymer in the glassy state, are evaluated from estimated values of the dual-mode parameters. The concentration dependence of the nonequilibrium properties is discussed from the viewpoint of plasticization due to sorbed CO_2.

Experimental Section

Poly(methyl methacrylate) (PMMA; medium molecular weight grade; density, 1.19 g/cm^3 at 25 °C), purchased from Aldrich Chemical Co., was used in the forms of film and powder. Films about 120 μm thick were prepared by casting a benzene solution of the polymer onto a glass plate. After slow evaporation, the remaining solvent was removed by placing the films, each loosely placed between sheets of filter paper, in a vacuum oven at about 110 °C for two months. The complete removal of the residual solvent was confirmed by measuring the glass transition temperature of the film specimens. The glass transition temperature, T_{g0}, of the solvent-free polymer was 105 °C according to the DSC measurement at a heating rate of 20 °C/min.

Carbon dioxide of 99.99% purity, supplied by Takachiho Chemical Industry, was used without further purification.

Sorption and desorption isotherms of CO_2 in the polymer were obtained by use of two types of microbalances: a Cahn 2000 placed in a pressure vessel for measurements at 35−85 °C and a Sartorius S3D-P for measurements at 100−200 °C. The former apparatus has been described elswhere.[1,3,4] The latter is an improved apparatus of the Sartorius System, which consists of an electronic microbalance placed in a pressure vessel with two chambers, a constant temperature air-bath, and auxiliary furnaces. The apparatus is designed to measure sorption of gases at pressures up to 70 atm from room temperature to 350 °C (Figure 1). In this study, the microbalance was kept at 25 °C, the air bath for the chambers was regulated at 100−200 °C, and the auxiliary furnaces kept the upper part of the chambers 20−40 °C higher than the temperature of the air bath to prevent a convection flow of ambient gas near the polymer specimen and the counterbalance in the chambers.

Dilation of the film specimen due to gas sorption was measured at 35−85 °C by observing with a cathetometer changes in the length of film strips (about 70 mm long and about 3 mm wide) which were suspended in a glass cell. The cell is placed in an air bath together with the vessel containing the Cahn microbalance.[3,4]

Results

Sorption isotherms of CO_2 in PMMA above and below the glass transition temperature were measured. The isotherms at 100−200 °C were linear in the pressure range investigated (0−20 atm), whereas those at 35−85 °C were concave toward the pressure axis at low pressures and became linear or convex above an inflection point with increasing pressure (Figures 2 and 3).

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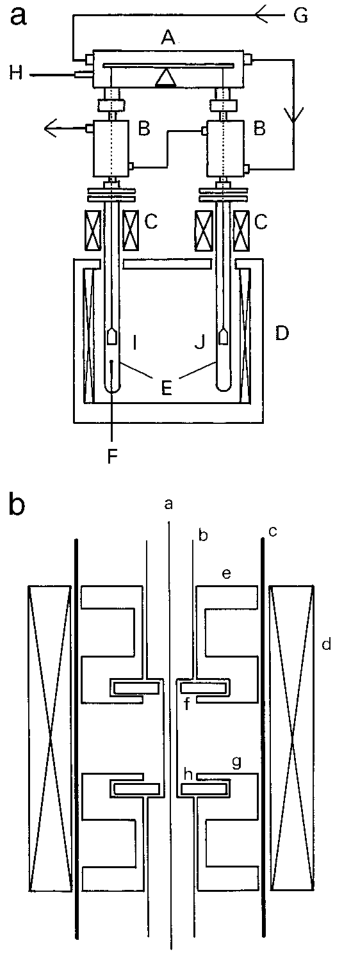

Figure 1. (a) Schematic diagram of sorption apparatus (Sartorius S3D-P): A, Sartorius microbalance; B, constant temperature water bath; C, auxiliary furnaces; D, constant temperature air-bath; E, pressure chambers; F, thermocouple; G, water inlet; H, gas inlet; I, polymer sample plus buoyancy corrective (gold wire); J, counterbalance (aluminum rod). (b) Cross section of auxiliary furnaces: a, wire hanger; b, hang down tube; c, pressure chamber; d, auxiliary furnace; e, upper baffle ferrule; f, upper baffle plate; g, lower baffle ferrule; h, lower baffle plate.

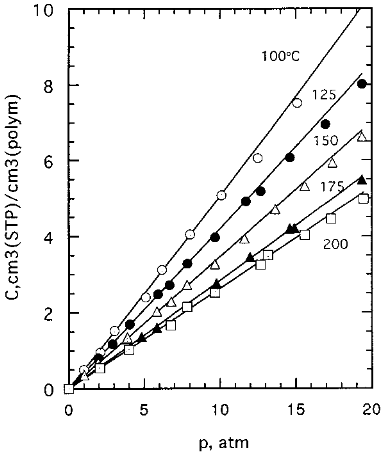

Figure 2. Sorption isotherms at 100–200 °C. Solid lines are isotherms calculated from a simplification of eq 3a, $C = k_D p/(1 - \bar{\sigma} k_D p)$.

The polymer specimens were used in the form of powder at 100–200 °C and in the form of film at 35–85 °C. A sorption isotherm above 200 °C could not be obtained, because decreases in the weight of the polymer specimen by thermal decomposition became too large to be neglected, and changes in the weight due to the sorption and the decomposition could not be separated.

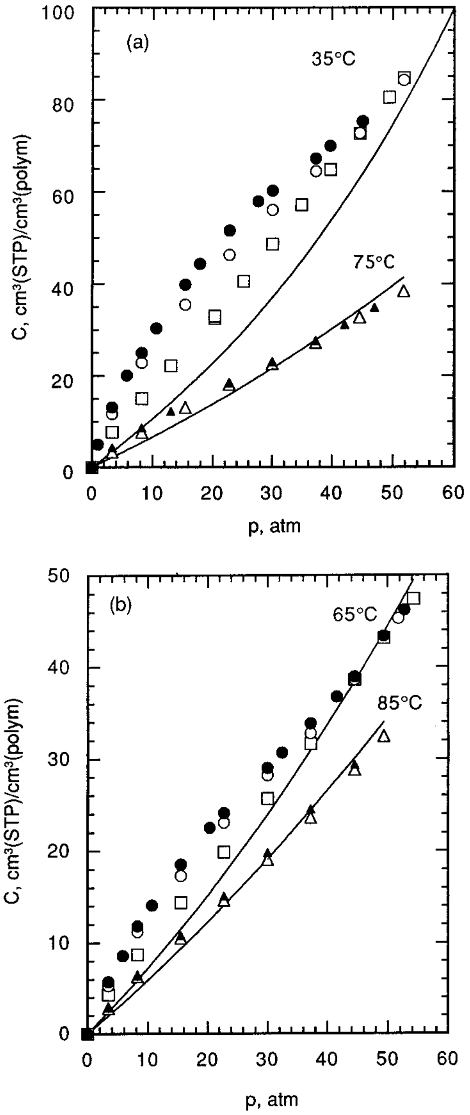

Figure 3. (a) Sorption isotherms at 35 and 75 °C and (b) Sorption isotherms at 65 and 85 °C: (□) first sorption run, (○) second sorption run, and (●) first and second desorption runs at 35° and 65 °C; (△) sorption run and (▲) desorption runs at 75 and 85 °C which were measured after the experiments at 35 °C; solid lines are dissolution isotherms calculated from a simplification of eq 3a, $C = k_D p/(1 - \bar{\sigma} k_D p)$.

As shown in Figure 3, sorption/desorption hysteresis was observed only in the concave part of the isotherms, and sorption isotherms of subsequent runs do not coincide with that measured first for a newly prepared (as-cast) film specimen. Sorption and desorption isotherms were reproducible from the second run. The sorption and desorption measurements at 75 and 85 °C were made after the experiments at 35 °C. The hysteresis decreased with increasing temperature and was hardly observed at the high temperatures.

Solubility coefficients, $S = (C/p)_{p\cong 0}$, were obtained from initial slopes of sorption isotherms, where C and p are the concentration in cm^3(STP)/cm^3(polym) and the pressure in atm, respectively. The coefficients are shown in the form of a van't Hoff plot in Figure 4. As can be seen in the figure, the relation is a straight line with an inflection, which should correspond to the glass

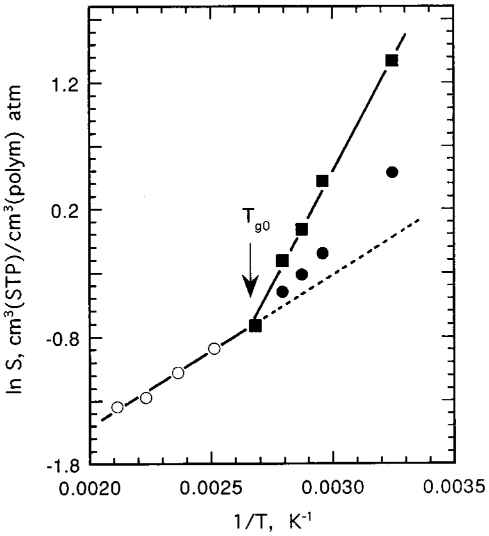

Figure 4. Van't Hoff plot of solubility coefficients: (■) $S = k_D + C'_{H0}b$ below the glass transition temperature T_{g0}; (○) $S = k_D$ above T_{g0}; (●) $S = dC/dp$ above the glass transition concentration C_g.

transition point. At temperatures above T_{g0}, S is equivalent to the so-called Henry's law coefficient, k_D. The temperature dependence of the coefficient can be described as

$$k_D = k_{D0} \exp(-\Delta H/RT) \qquad (1)$$

where the preexponential factor, k_{D0}, is 0.0202 cm^3(STP)/cm^3(polym)atm and the heat of dissolution, ΔH, is −2380 cal/mol.

Dilation of the polymer during the sorption was measured at temperatures below T_{g0} as length elongation of the film specimen, $l_s = (L - L_0)/L_0$, where L and L_0 are the lengths at p and $p = 0$ (or C and $C = 0$), respectively. Two specimens cut in the cross direction of the film were used in the measurement. No difference in length elongation was observed between the specimens within the accuracy of the experiments. However, variations in thickness of the specimens during the sorption could not be measured because the changes were too small. Hence, dilation isotherms were plotted as length elongation versus pressure. As shown in Figure 5, these dilation isotherms are very similar in shape to the corresponding sorption isotherms. Dilation as well as sorption exhibited hysteresis in the low-pressure part of the isotherms.

Assumed to be isotropic, volumetric dilation is given, corrected for the compression of polymer by pressure of gas, as $(1 + l_s)^3(1 + \beta_{T0}p)$, where β_{T0} is the isothermal compressibility of the pure polymer. Representative data of volumetric dilation were plotted versus concentration by use of the sorption isotherms, where values of β_{T0} (2.6×10^{-5} atm^{-1}) from the literature were employed in the calculation.[5] As shown in Figure 6, the isotherms are convex at low concentrations and become linear with increasing concentration. Hysteresis almost disappeared in the second sorption run and desorption runs.

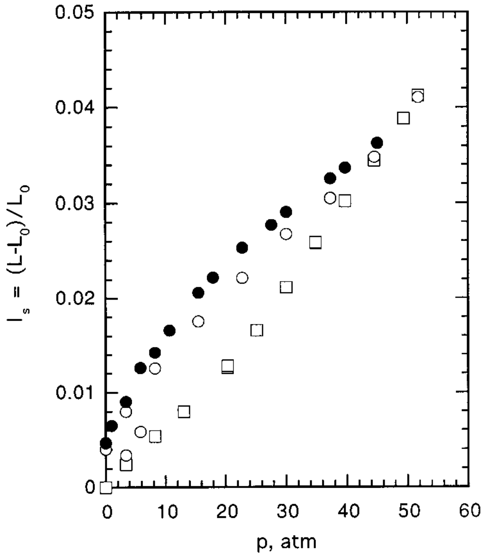

Figure 5. Dilation isotherm plotted as elongation vs pressure at 35 °C. Symbols are the same as in Figure 3a.

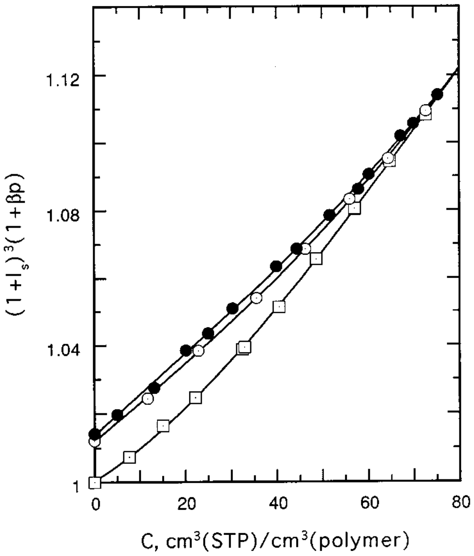

Figure 6. Volumetric dilation vs concentration at 35 °C. Symbols are the same as in Figure 3a.

Table 1. Saturated Vapor Pressures, Dissolution Parameters, Partial Molar Volumes, and Flory−Huggins Interaction Parameters[a]

T	p_0[b]	k_D[c]	$\bar{V}_R$[d]	χ[e]	$\bar{\sigma}$[f]
25	63.3	(1.12)	44.0	0.97	
35	(78.5)	(0.98)	44.9	0.87	0.0070
65	(139.2)	(0.69)	47.7	0.59	0.0065
75	(167.8)	(0.63)	48.6	0.47	0.0062
85	(193.3)	(0.57)	49.5	0.41	0.0061
100	(241.7)	0.495	50.9	0.31	0.0059
125	(337.7)	0.413	53.2	0.11	0.0052
150	(453.5)	0.341	55.5	−0.04	0.0047
175	(589.4)	0.285	57.9	−0.15	0.0044
200	(745.0)	0.256	60.2	−0.35	0.0035

[a] Units: T, °C; p_0, atm; k_D, cm^3(STP)/cm^3(polym) atm; $\bar{V}_R$, cm^3/mol; χ, dimensionless; $\bar{\sigma}$, cm^3(polym)/cm^3(STP). [b] Values in parentheses are hypothetical. [c] Values in parentheses are extrapolated from eq 1. [d] Calculated from eq 7. [e] Calculated from eq 6. [f] Calculated from eq 5.

Discussion

Dissolution in the Rubbery State. As mentioned above, sorption isotherms of CO$_2$ in PMMA at 100−200 °C are linear and described by the Henry's law, and the temperature dependence of Henry's law coefficient is expressed by eq 1. Values of k_D obtained by extrapolating to below T_{g0} of the equation (presented in Table 1), however, are much smaller than solubility coefficients dC/dp above inflections of sorption isotherms at 35−85

°C, as shown in Figure 4. Even below T_{g0}, the CO_2-sorbed polymer will be rubbery in the concentration range above the inflection point, which may correspond to the isothermal glass transition, as discussed in the following section. To include these facts above and below T_{g0}, the dissolution of CO_2 into PMMA in the rubbery state must be explained by the Flory-Huggins theory of dissolution.

The ordinary dissolution of a penetrant gas in a rubbery polymer is usually described by the Flory-Huggins equation[6]

$$\ln\frac{p}{p_0} = \ln v_1 + (1 - v_1) + \chi(1 - v_1)^2 \qquad (2)$$

where p_0 is the vapor pressure of the liquefied gas at the temperature of the experiment and v_1 is the volume fraction of the dissolved gas. The volume fraction is given by $v_1 = C\bar{V}_R/(V_S + C\bar{V}_R)$, where $\bar{V}_R$ is the partial molar volume of penetrant, in cm^3/mol, and V_S is the volume of a mole of ideal gas at 0 °C and 1 atm (22 410 cm^3/mol). At low concentrations, eq 2 was simplified by Suwandi and Stern as[6]

$$C_D = [k_D \exp(\sigma C)]p \qquad (3)$$

where $\sigma = 2(\chi + 1)\bar{V}_R/V_S$. As pointed out previously, however, this is a poor approximation in order to determine χ from experimental values of σ, because higher order terms of concentration are ignored in its simplification.[8] An approximation with the higher order terms, therefore, has to be used for correlating more accurately σ with χ. In the case of $(C\bar{V}_R/V_S)^2 < 1$, the Flory-Huggins equation is described, according to Suwandi and Stern's simplification, as[6]

$$\ln(C/p) = \ln k_D + \sum_{n=1}^{\infty}(-1)^{n-1}\,(n + 1)(\chi + 1/n)(C\bar{V}_R/V_S)^n \qquad (4)$$

Considering first- to third-order terms, let us introduce an average $\bar{\sigma}$, in the concentration range from 0 to C, given by

$$\bar{\sigma} = \frac{1}{C}\int_0^C\left[2(\chi + 1)\frac{\bar{V}_R}{V_S} - 3\left(\chi + \frac{1}{2}\right)\left(\frac{\bar{V}_R}{V_S}\right)^2 C + 4\left(\chi + \frac{1}{3}\right)\left(\frac{\bar{V}_R}{V_S}\right)^3 C^2\right] \mathrm{d}C \qquad (5)$$

and use the following equation instead of eq 3, especially for estimating $\bar{\sigma}$ from χ:

$$C = [k_D \exp(\bar{\sigma} C)]p \qquad (3a)$$

Dissolution parameters k_D and $\bar{\sigma}$ of the rubbery PMMA/CO_2 system above and below T_{g0} were obtained from eqs 1 and 5. Results are summarized in Table 1. Values of χ and $\bar{V}_R$ used in calculations of $\bar{\sigma}$ will be given in the following section. Using eq 3a with these parameters, sorption isotherms for the ordinary dissolution of CO_2 in PMMA were obtained, which are shown as solid lines in Figures 2 and 3.

Thermodynamic Interaction. Thermodynamic interaction between polymer and penetrant is usually characterized by the Flory-Huggins interaction parameter, χ. In rubbery polymer/gas mixtures infinitely dilute with respect to the gas, the Henry's law coefficient is related to the interaction parameter as[7,8]

$$k_D = (V_S/\bar{V}_R p_0)\exp(-\chi - 1) \qquad (6)$$

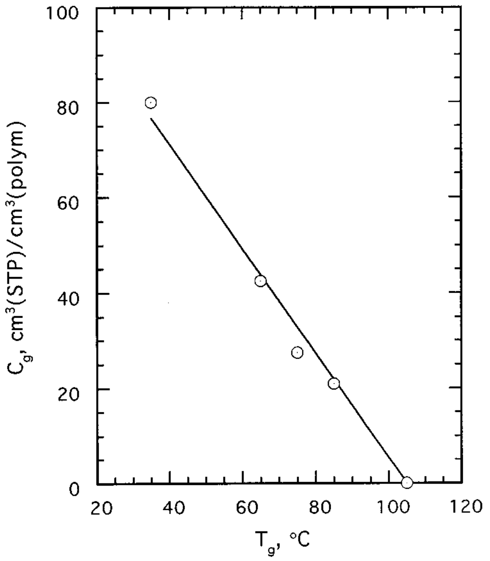

Figure 7. Relationship between concentration and temperature at the glass transition.

In order to evaluate χ from this relation, it is necessary to know values of p_0 and $\bar{V}_R$ in the relevant temperature region. Hypothetical values of the vapor pressures at temperatures higher than the critical temperature were determined by extrapolating of the linear relation, $\ln p_0 = 10.81 - 1986/T$, found below the critical point.[9] The partial molar volumes were estimated by use of the relation

$$\bar{V}_R = 44.0[1 + (2.1 \times 10^{-3})(T - 298)] \qquad (7)$$

which has been found to be valid for rubbery polymer/CO_2 systems.[10,11] The results are given in Table 1. It is clear that the interaction parameter decreases with increasing temperature, as can be expected.[12]

To ascertain the validity of the values obtained in this way, the χ value of 0.97 estimated for CO_2 in PMMA at 25 °C was compared with those for other polymers at the same temperature:[12] 0.97 for 1,2-polybutadiene; 1.2 for poly(ethylene-*co*-vinyl acetate); 1.9 for polyethylene; 1.3 for polypropylene; and 0.5−0.7 for poly(dimethylsiloxane). The comparison allows us to conclude that this method of evaluating χ at temperatures below T_{g0} is recommendable.

Isothermal Glass Transition. Sorption and dilation isotherms for gases in glassy polymers often exhibit an inflection when the gases are highly sorbed into and plasticize the polymers. The inflection is considered to correspond to the isothermal glass transition of the polymer/gas mixtures.[1,3,13] In Figures 3 and 5, such a transition of PMMA induced by CO_2 is exhibited by the inflection on both sorption and dilation isotherms.

The relation between concentration and temperature at the inflection of sorption isotherms is presumably linear, as shown in Figure 7. The straight line gives the proportionality constant β ($= -\mathrm{d}T_g/\mathrm{d}C_g$) as 0.92. This value of β is almost the same as those found for other glassy polymer/ CO_2 systems: 0.87 and 0.94 for poly(ethyl methacrylate);[3,14] 1.1 for poly(vinyl benzoate);[1,15] 0.8 for poly(vinyl butyral);[15] and 1.1 for poly(vinylidene

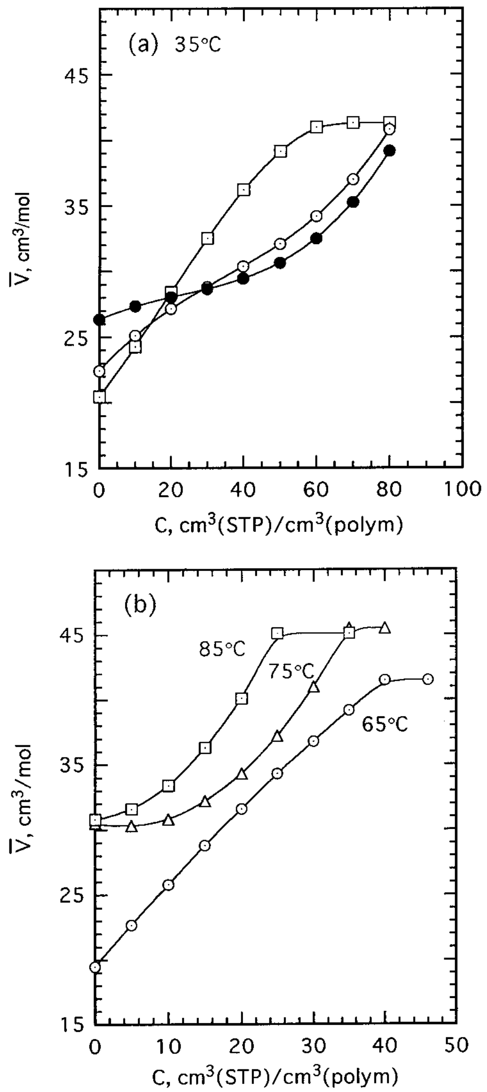

Figure 8. (a) Concentration dependence of partial molar volume at 35 °C: (□) first sorption run, (○) second sorption run, and (●) desorption runs. (b) Concentration dependence of averaged partial molar volume for sorption and desorption runs at (○) 65 °C, (△) 75 °C, and (□) 85 °C.

fluoride)/PMMA blend.[13] This suggests that the plasticizing abilities of CO_2 are nearly the same for such glassy polymers.

Partial Molar Volumes. In order to elucidate not only mechanisms of sorption and dilation but also microstructures of glassy polymers, it is important to know the partial molar volumes of penetrants in the polymers. From the slopes of the volumetric dilation isotherms (Figure 6), the partial molar volume, $\bar{V}$, of CO_2 in PMMA was obtained as a function of concentration and temperature.

As shown in Figure 8, the partial molar volume increases with increasing concentration and temperature, and the molar volumes of 40−45 cm^3/mol obtained at high concentrations are almost the same as $\bar{V}_R$, that is, the partial molar volumes of dissolved CO_2 in rubbery polymers.[3,10,11] This indicates that, as concentration increases, the polymer is plasticized and isothermally changes from the glassy state to the rubbery state. Concentration dependence of partial molar volume apparently changes after an exposure to high-pressure CO_2, that is, the partial molar volume of the as-cast specimen at relatively high concentrations is much larger than that of the CO_2-conditioned one (Figure 8a). This difference can be understood by considering that there are fewer preexisting microvoids or free spaces to accommodate gas molecules in the as-cast PMMA film than in the CO_2-conditioned film.

Dual-Mode Analysis of Sorption and Dilation Data. Sorption and dilation isotherms below T_{g0} were analyzed on the basis of dual-mode models of sorption and dilation in order to give a systematic description.

The dual-mode sorption model, which had been proposed by Barrer et al. in 1958 for interpreting the sorption behavior of gases in glassy polymers,[16] was improved by incorporating of the plasticization of polymer by sorbed gas molecules.[13,17] According to an extended model proposed by Kamiya et al., the concentration of sorbed gas in glassy polymer is described as[3,17]

$$C = C_D + C_H \quad (8)$$

$$C_D = [k_D \exp(\bar{\sigma}C^*)]p \quad (8a)$$

$$C_H = C'_{H0}bp(1 - C^*/C_g)/(1 + bp) \quad (8b)$$

Here, C_D and C_H are concentrations of a dissolved species D and a Langmuir species H at gas pressure p, C'_{H0} and b are Langmuir adsorption parameters, C_g is the glass transition concentration, and C^* is the effective concentration, defined as $C^* = C_D + fC_H$, where f is a ratio of the plasticizing ability of H species to that of D species ($0 \leq f < 1$). In the rubbery state above C_g, the concentration is described by eq 8a with $C^* = C$, since C'_{H0} and hence C_H are zero according to the prerequisites of the dual-mode sorption model.

Volumes of the dilated polymer below and above the glass transition concentration are given, according to an extended dual-mode model by Kamiya et al., as[3,4]

$$V_G = V_g[1 - \tau_G\beta\alpha_{G0}(C_g - C^*)] \quad (9)$$

$$V_R = V_g[1 - \tau_R\beta\alpha_{R0}(C_g - C)] \quad (10)$$

where V_g is the volume at the glass transition, and α_{i0} and τ_i are the thermal expansion coefficient of the pure polymer and the coefficient correlating the sorptive dilation with the concentration, respectively, where subscript i represents the glassy state G or the rubbery state R. In the region of temperature above T_{g0}, the volume of polymer/gas mixture can be described by eq 10 with $C_g = 0$, because the polymer is always in the rubbery state and no isothermal glass transition occurs.

Dual-mode sorption parameters k_D, $\bar{\sigma}$, C'_{H0}, b, and f were estimated by analyzing the data of sorption and dilation according to eqs 4−9 in the following way: Estimations of k_D and $\bar{\sigma}$ were mentioned above. The parameter f is determined, using the values of k_D and $\bar{\sigma}$, by fitting the dilation data to the following equation of length elongation derived from eqs 8 and 9.[3,14]

$$\begin{aligned} 3l_s &= [\tau_G\beta\alpha_{G0}/(1 - \tau_G\beta\alpha_{G0}C_g)]C^* \\ &= [\tau_G\beta\alpha_{G0}/(1 - \tau_G\beta\alpha_{G0}C_g)][(1 - f)k_Dp + \\ &\qquad fC]/[1 - (1 - f)\bar{\sigma}k_Dp] \end{aligned} \quad (11)$$

where the compression of polymer by the hydrostatic pressure of gas is neglected, that is, $(1 + l_s)^3(1 + \beta_T p) \cong 1 + 3l_s$. The remaining parameters C'_{H0} and b were estimated by fitting the sorption data to eq 8 with the

Table 2. Dual-Mode Sorption Parameters and Mean Size of Microvoids[a]

T	C'_{H0}	b	f	v_0[c]	notes
35	12	0.2	0.5	38	first sorption
	47	0.1	0.7	23	second sorption
	67	0.07	0.7	23	desorption
65	5	0.2	0.5	38	first sorption
	17	0.07	0.5	38	second sorption
	25	0.05	0.5	38	desorption
75[b]	16	0.03	0.5	38	sorption and desorption
85[b]	8	0.04	0.5	38	sorption and desorption

[a] Units: C'_{H0}, cm^3(STP)/cm^3(polym); b, 1/atm; f, dimensionless; v_0, A^3. [b] Sorption and desorption at these temperatures were measured after the experiments at 35 °C. [c] Calculated from eq 13.

Table 3. Number and Mean Size of Microvoids for Pure Glassy PMMA[a]

T	$N_0 \times 10^{-20}$	v_0[b]	notes
35	3.2	70	as-cast film
	13−18	13−18	CO_2-conditioned film
65	1.3	96	as-cast film
	5−7	19−28	CO_2-conditioned film
75	4.3	22	CO_2-conditioned film
85	2.1	30	CO_2-conditioned film

[a] Units: N_0, voids/cm^3(polym). [b] Calculated from the relation $v_0 = V_H/N_0$, using eq 14.

above-obtained values of k_D , $\bar{\sigma}$, and f. Results on the dual-mode parameters are summarized in Tables 1 and 2. As mentioned above, concentrations of dissolved gas at temperatures below T_{g0} were calculated using the values of k_D and $\bar{\sigma}$ in Table 1 and are shown as solid lines in Figure 3. The calculated amounts of sorption above or near C_g are somewhat different from those obtained experimentally. Although the reason for this disagreement is not clear, the effect on the estimation of the dual-mode parameters will be not very significant, because the dual-mode analysis was carried out only at low concentrations ($C \ll C_g$).

Nonequilibrium Structural Properties. Nonequilibrium properties such as number and size of microvoids for the pure PMMA and the PMMA with sorbed CO_2 in the glassy state can be obtained from the dual-mode parameters C'_{H0} and f. According to the dual-mode sorption model, the hole saturation constant, C'_{H0}, or $C'_H = C'_{H0}\ (1 - C^*/C_g)$, is related to microvoids, which are assumed to exist in the structural volume of glassy polymers.[18] Assuming that each microvoid accommodates only a gas molecule, the number of microvoids is equal to the hole saturation constant multiplied by N_A/V_S, where N_A is the Avogadro number. Therefore, the microvoid number, N, of the glassy polymer with sorbed gas is given by

$$N = N_0(1 - C^*/C_g) \qquad (12)$$

where N_0 ($=N_A C'_{H0}/V_S$) is the microvoid number of the pure PMMA. Values of N_0 at different conditions of temperature and CO_2 conditioning are presented in Table 3. The number of microvoids obtained using eq 12 are shown in Figure 9. As can be seen in the figure, the number decreases to zero as the concentration increases to the glass transition concentration. This is the behavior of microvoid disappearance due to the plasticization of PMMA by CO_2 in the glassy state.

The mean size of microvoids, v_0, can be evaluated from the plasticizing ability ratio, f. The ratio is equivalent to the ratio of a volume increment caused by a Langmuir species H to that by an ordinary dissolved species D, because the plasticization of polymer is considered to be proportional to its volume change induced by sorbed molecules. Assuming that the space occupied by a mole of sorbed gas in polymers in the glassy state is equal to the partial molar volume $\bar{V}_R$ in the rubbery state, the ratio is given as[3,14]

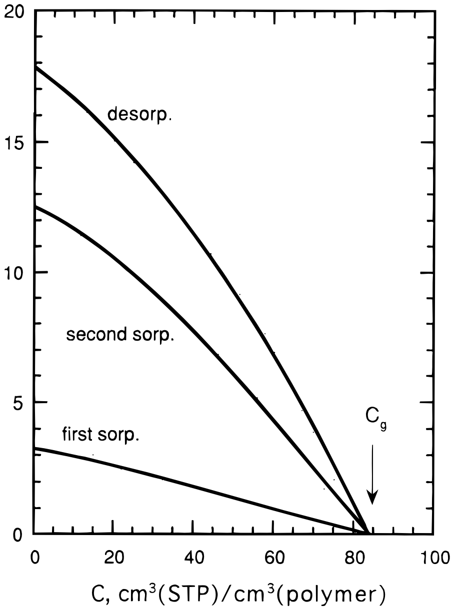

Figure 9. Concentration dependence of microvoid number calculated from eq. 12 at 35 °C.

$$f = (\bar{V}_R - N_A v_0)/\bar{V}_R \qquad (13)$$

Using this relation with the obtained values of f, v_0 values of the glassy PMMA with sorbed CO_2 were obtained as averaged values in the concentration range from zero to C_g (Table 2).

The mean size of microvoids for a penetrant-free glassy polymer can also be evaluated by dividing its unrelaxed volume by N_0.[4] This is the only method to obtain the mean size in the case of $f = 0$, that is, a microvoid larger than the molecular volume of dissolved gas. The unrelaxed volume in a unit volume of the glassy polymer is given by

$$V_H = (\alpha_{R0} - \alpha_{G0})(T_{g0} - T) \qquad (14)$$

where $\alpha_{R0} = 5.7 \times 10^{-4}$ °C^{-1} and $\alpha_{G0} = 2.5 \times 10^{-4}$ °C^{-1}.[5] The mean size of microvoids of the pure polymer is obtained by dividing V_H by N_0, as shown in Table 3.

Compared with the mean sizes of microvoids calculated from the plasticizing ability ratios, the v_0 values obtained from the unrelaxed volume and the number of microvoids are of the same order of magnitude. The microvoid sizes of the pure polymer, unconditioned and conditioned by high-pressure CO_2 (v_0 in Table 3), are respectively twice and half the sizes of the CO_2-sorbed polymer (v_0 in Table 2). These sizes, however, are said to be in fairly good agreement, considering uncertainties in values of the parameters used in the calculations.

Conclusions

Sorption of CO_2 in poly(methyl methacrylate) at 35−200 °C and concurrent dilation of the polymer at 35−85 °C over a pressure range up to 50 atm are measured. Sorption isotherms at 100−200 °C are linear in the investigated pressure range, 0−20 atm. Isotherms of sorption and dilation at 35−85 °C are similar in shape, that is, concave at low pressures and linear or convex at high pressures. In concave parts of both isotherms, hysteresis appears according to increasing and decreasing of pressure.

On the basis of sorption data above 100 °C, dissolution parameters and the Flory-Huggins interaction parameter for the polymer/gas system are estimated over the temperature range 25−200 °C. From sorption and dilation isotherms below the glass transition temperature, the relation between temperature and concentration at the glass transition and the partial molar volumes of sorbed gas in the glassy state are determined.

Sorption and dilation data at 35−85 °C are also analyzed according to extended dual-mode models of sorption and dilation. From evaluated values of the dual-mode parameters, nonequilibrium properties such as size and number of microvoids for the pure polymer and the polymer with sorbed gas in the glassy state are estimated. The mean size of microvoids dependent upon CO_2 exposure history of the polymer is in the range of 20−100 A^3. The microvoid number of the pure polymer ((1−18) × 10^{20} voids/cm^3 at 35−85 °C) is dependent on both temperature and the CO_2 exposure history and the number of the gas-sorbed polymer decreases to zero as concentration increases to the glass transition concentration. The polymer exposed to high-pressure CO_2 at the glassy state has a smaller mean size and a larger number of microvoids than the as-cast polymer film.

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