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Poly(methyl methacrylate) and Poly(butyl methacrylate) Swelling in Supercritical Carbon Dioxide

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ABSTRACT: Swelling of poly(methyl methacrylate) and poly(butyl methacrylate) samples in supercritical carbon dioxide and propagation of diffusion fronts in the samples were studied in situ at various temperatures and pressures using direct optical observation. The difference in the appearance of diffusion fronts in these polymers with different glass transition temperatures was observed. The diffusion coefficients of carbon dioxide molecules in the polymers were determined both from swelling kinetics and from motion of diffusion fronts. A good agreement between these two values was found. The dependences of the diffusion coefficients and equilibrium swelling degrees of the polymers on pressure and temperature of supercritical carbon dioxide during sample exposure were determined and discussed.

Introduction

The behavior of different classes of polymers in supercritical (sc) media, in particular, in supercritical carbon dioxide (scCO$_2$), has been widely studied in recent years.[1−3] The interest in this field is due to the fact that scCO$_2$ is a solvent or a plasticizer for a wide range of polymers and low molecular mass compounds. Moreover, scCO$_2$ has a number of advantages compared to the traditional solvents: it is inexpensive, environmentally friendly, nonflammable, and easy to remove from the polymer when the processing is over. The interest in this sc fluid is also due to the possibilities of modification of morphological and functional properties of polymers by swelling in scCO$_2$. The study of polymer swelling during sorption in scCO$_2$ conditions is of great importance for understanding of the interaction between CO$_2$ molecules and polymer matrix.

The technique of direct observation of sample dimensions is widely used in studies of polymer behavior during sorption/desorption processes.[4−9] For example, authors of refs 4−7 combined this approach with the in situ measurement of mass changes during exposure of polymer samples in CO$_2$. They performed a comparative analysis of the dependences of both mass sorption and volume swelling degrees on pressure (up to ∼6−10 MPa[4−6] and 30 MPa[7]) for different rubbery and glassy polymers, including PMMA.[5−7] Von Schnitzler and Eggers[8] analyzed the kinetics of sample swelling in scCO$_2$ measured by a similar approach to determine the diffusion coefficient of CO$_2$ in poly(ethylene terephthalate). Royer et al.[9] studied the kinetics of swelling of polymer melts in scCO$_2$ media by monitoring the position of the phase boundary and determined both swelling degrees and diffusion coefficients.

On the other hand, there is only a few articles concerning the technique of determination of diffusion coefficient by measuring the dynamics of propagation of diffusion fronts. Such propagation can be clearly seen in transparent polymers interacting with a solvent or a plasticizer. Authors of refs 10−14 observed the motion of diffusion fronts in different systems (but no one includes sorption in sc conditions) and noticed[11−14] the linear dependence of the front position on square root of time (Fickian diffusion). The determination of the diffusion coefficient[11−13] from the data was accomplished by taking into account the curve slope.

Another type of diffusion front propagation dynamics is often observed for sorption by glassy polymers. In such systems sharp fronts move at constant velocity, and this behavior is usually referred as case II diffusion. The intermediate behavior can also be observed; for example, McDonald et al.[15] studied a transition between Fickian and case II transport for ingress of a solvent (toluene) into a polymer (polystyrene). Different theories were put forward to explain this kind of dynamics.[16,17] However, the doubts about the origin of case II behavior still remain. Samus and Rossy[18] have criticized some models of “non-Fickian” diffusion and have indicated that when the kinetics of plasticization is properly taken into account, there is no reason to imply a violation of Fick’s law. Morrisey and Vesely[14] studied diffusion of methanol in PMMA, which was regarded since Thomas and Windle work[16] as a typical case II system. Using very precise optical measurements, they[14] have found Fickian kinetics of both front propagation and swelling process. The initial time lag was shown to be responsible for “case-II-like” kinetics. This work[14] gave rise to some doubts about the data of ref 16 for swelling of this system.

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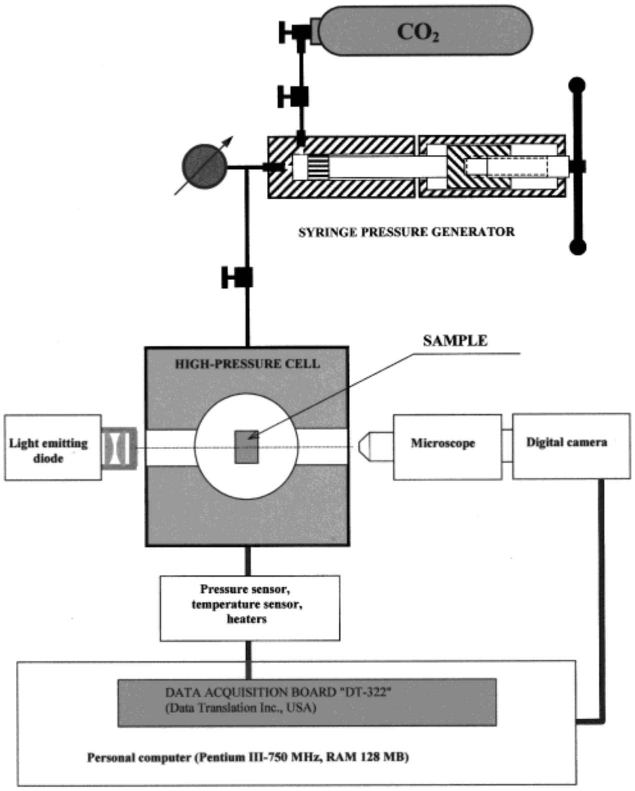

Figure 1. Experimental setup.

In this article we have applied for the first time the approach of diffusion coefficient determination by analyzing the diffusion front propagation in polymers, which are exposed to supercritical media. We have also compared the data of this approach with the results of volumetric measurements of the swelling kinetics for different pressures and temperatures.

The samples of poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) were chosen for the investigation to elucidate the effect of difference in molecular weights and glass transition temperatures.

Experimental Section

An original experimental setup shown in Figure 1 was developed to study the polymer behavior in $scCO_2$ (critical parameters: pressure $P = 7.38$ MPa, temperature $t = 31.1$ °C, density $\rho = 470$ kg/m^3).[19,20] A syringe press with 150 mL volume was used to provide the pressure up to 25 MPa. A system of valves allows the CO_2 access to the reaction cell. The pressure generator and the reaction cell are provided with mechanical manometers to allow control of the pressure and the inlet and outlet of gas. The reaction cell was also equipped with electronic pressure and temperature sensors.

The problem of the in situ study of the processes in $scCO_2$ required the development of special high-pressure cell. The high-pressure cell for physical and chemical studies has an inner volume of approximately 10 cm^3 and was made of stainless steel. The wall thickness is several times greater than the calculated limiting values for pressure range used (up to 25 MPa). This allowed the heaters, capillary inlets, and temperature sensor to be built in the cell bulk. The adaptive proportional-integral-differential temperature control allows a precision better than ±0.2 °C. Experiments were carried out in temperature range 38−65 °C.

Silica glass windows with thickness of 10 mm mounted with indium seals were used to implement the optical channel in the high-pressure cell. In situ observations of polymer samples were performed with an optical microscope equipped with Logitech QuickCam Pro digital camera. The information was recorded in the form of raster images (640 × 480 pixels) to the computer hard drive at fixed time intervals. A super-bright light-emitting diode was used for lighting.

Table 1. Properties of the Polymers Studied

polymer	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n	ρ (kg/m^3)	T_g (°C)
PMMA-h	4098[a]	2530.4[a]	1.6[a]	1170	125
PBMA-h	2236[a]	861.4[a]	2.6[a]	1070	22
PMMA-l	120[b]			1188	114
PBMA-l	320[b]	73.500[b]	4.4[b]	1070	15

[a] Data were measured in the laboratory by GPC. [b] Data were supplied by Aldrich.

The setup was controlled by a personal computer (IBM-compatible), provided with the DT-322 data acquisition board (Data Translation Inc.). Original software was developed to control the experiment in real time.

The experimental observation of $scCO_2$ sorption by the polymer samples was performed in the following manner. A rectangular polymer sample with dimensions of 1−5 mm (typical values ~2 × 2 × 4 mm^3) was placed into the high-pressure cell. Then the cell was sealed and heated to a given temperature. Subsequently the CO_2 pressure was increased to the value necessary to achieve the sc conditions. Optical observations were made with the CCD camera through the optical channel of the cell. Such an experimental technique allows simultaneous real-time observations of the volume swelling process in sc fluids and the sorbate diffusion front propagation in polymer samples.

The properties of the polymer materials used in the experiments are presented in Table 1. The PMMA-h and PBMA-h polymers with high molecular weight were synthesized in the laboratory by bulk polymerization with AIBN as an initiator at 65 °C. The samples were prepared by cutting the polymer blocks. For PMMA-h samples we used an additional polishing procedure. The PMMA-l and PBMA-l polymers with low molecular weight were obtained from Aldrich. The samples were prepared by cutting of the film obtained by solvent casting. Polymers were dissolved to 30% solids in chloroform, cast into a film onto a cellophane substrate, and left at room temperature for 1 week before baking in a vacuum at 60 °C for 3 days. Measurements of glass transition temperatures were performed using a Perkin-Elmer DSC7 device.

A high-purity CO_2 (>99.997%, 0.0002% O_2, 0.001% H_2O) was used as received.

Results and Discussion

We have detected the formation of propagating diffusion fronts in PMMA and PBMA samples exposed in $scCO_2$. Experimentally obtained images of the fronts are presented in Figure 2. One can see that there is a difference in the appearances of the fronts for two types of samples studied (PMMA and PBMA). We believe that these fronts are seen due to the light refraction related to a significant gradient of sorbate concentration in the region of the fronts. For glassy PMMA samples the appearance of the fronts is most probably influenced by the plasticization due to absorbed CO_2. Indeed, the CO_2 sorption is accomplished by the decrease of glass transition temperatures.[21−23] Therefore, the diffusion front is most probably an interface between glassy and plasticized regions. Because of the difference in diffusion rates for plasticized and glassy polymer, there is a significant difference in sorbate concentration for these regions. This leads to the significant changes of concentration only in the interface region; i.e., a sharp diffusion front is formed. The diffusion front can be clearly seen as an optical boundary during CO_2 propagation from sample boundary to the central region of the sample. The sharp front formation can be regarded as an indication of the

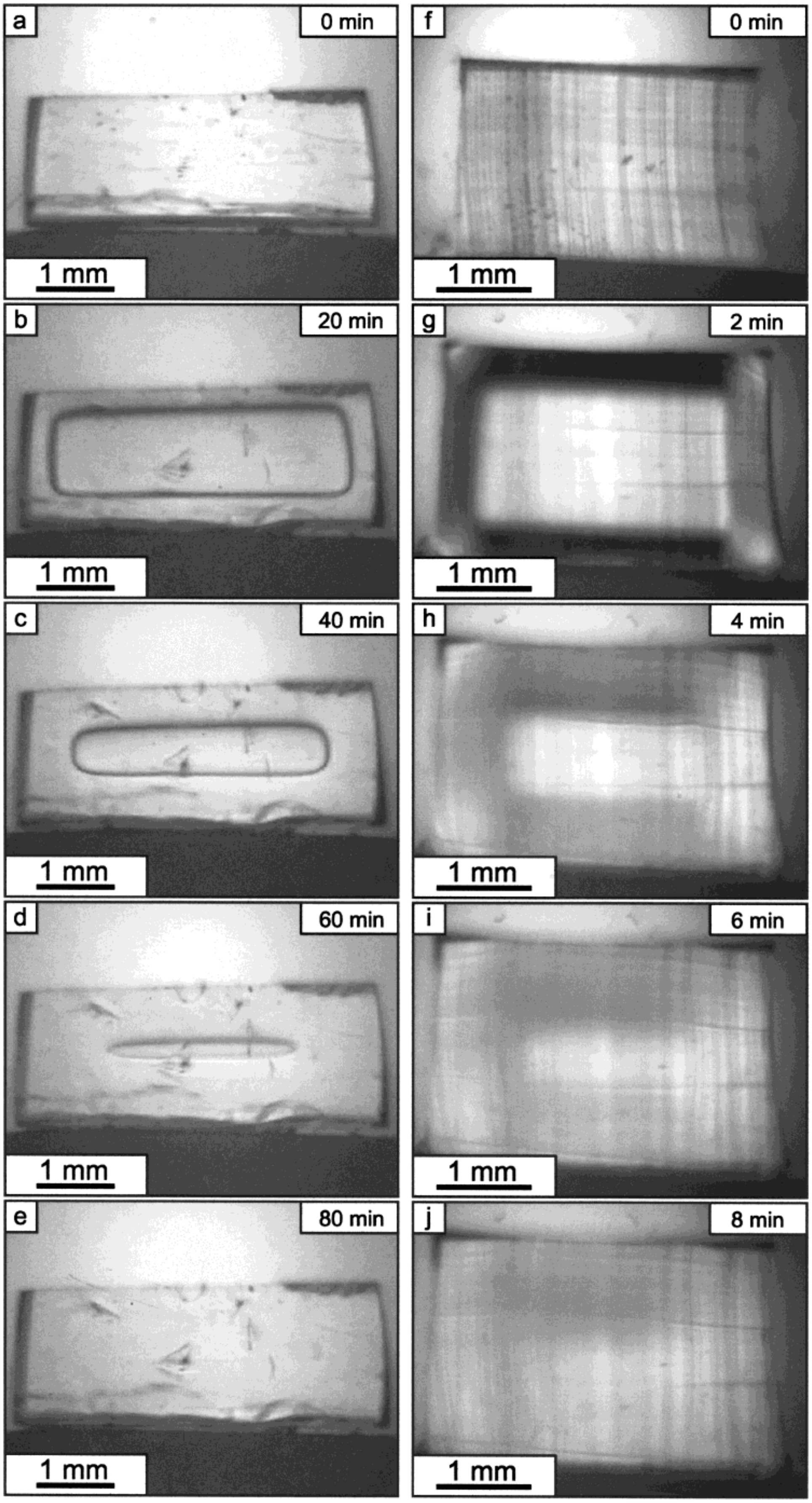

Figure 2. Stages of $scCO_2$ sorption by the PMMA (a−e) and PBMA (f−j) samples for different exposure times (indicated in right upper corners). Exposure at temperature 38 °C and pressure 9 MPa. Bars sizes are 1 mm.

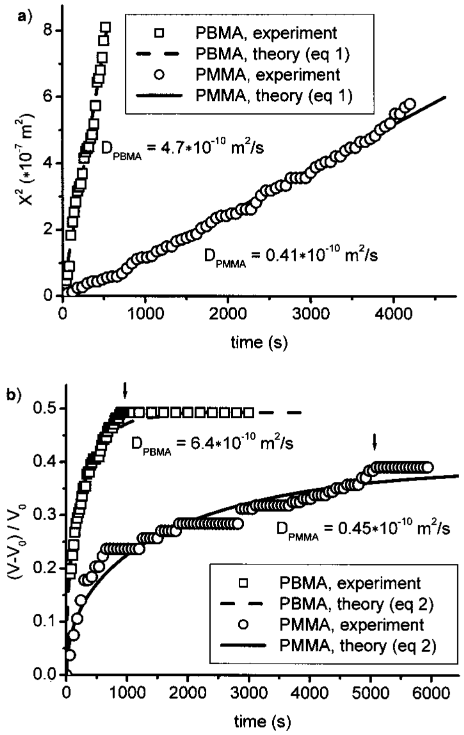

Figure 3. Typical results of the observation of the CO$_2$ diffusion front propagation in polymer samples (PMMA-h, PBMA-h) and their swelling. Exposure at temperature 38 °C and pressure 9 MPa. (a) Time dependence of the square of the diffusion front propagation distance (X^2). Diffusion coefficients were determined using eq 1. (b) Sample volume increase vs time. Diffusion coefficients were determined using eq 2.

abrupt dependence of diffusion coefficient in PMMA on sorbate concentration.

The PBMA samples are above glass transition temperatures under the experimental conditions, so the sharp interface is not formed during sorption in this case. Even if one takes into account that diffusion coefficient may depend on sorbate concentration, this dependence should be rather smooth. Consequently, the distribution of concentration gradient in the sample should also be smooth and the observed diffusion front should be broad. This is indeed the case for PBMA samples according to our observation (see Figure 2). Here, the diffusion front usually can be clearly seen only during the initial and intermediate periods of propagation. On the final stage it is hard to identify the front position exactly.

Typical results of propagation dynamics of the diffusion fronts in PMMA and PBMA samples are shown in Figure 3a. The distance of the diffusion front propagation was measured with respect to the sample center, because in this case the measurement is independent of the sample volume increase during swelling. It was found that for both PBMA and PMMA samples the square of the diffusion front propagation distance (X^2) vs time (t) could be approximated well by a linear function. This fact is an indication that the simple (Fickian) relation is valid:

$$X^2 = \alpha D t \tag{1}$$

where D is the apparent diffusion coefficient and α is the parameter to be estimated for experimental D determination.

Exact knowledge of the α parameter requires the theoretical consideration taking into account the dependence of diffusion coefficient on sorbate concentration. In the present article we use the estimation $\alpha \approx 3$, which was experimentally obtained by Vasenin et al.[11] for moderately swollen polymers. This estimation allows determination of diffusion coefficient from the analysis of our experimental data.

The obtained values of D were compared with the results of the swelling kinetics. In situ observation of the polymer swelling in scCO$_2$ allows measurements in two dimensions of the sample and thus to draw a conclusion on the dynamics of volume increase.

As follows from the diffusion theory,[24,25] the sorption behavior of a polymer sample in the form of a parallelepiped with dimensions l_x, l_y, l_z, in a medium with constant sorbate concentration is described by the solution of the diffusion problem with uniform boundary conditions and zero initial conditions:

$$\frac{M(t)}{M_\infty} = 1 - \frac{512}{\pi^6}\sum_{i=0}^{\infty}\frac{\exp\left(-\frac{\pi^2(2i+1)^2Dt}{l_x^{\,2}}\right)}{(2i+1)^2} \times \sum_{j=0}^{\infty}\frac{\exp\left(-\frac{\pi^2(2j+1)^2Dt}{l_y^{\,2}}\right)}{(2j+1)^2}\sum_{k=0}^{\infty}\frac{\exp\left(-\frac{\pi^2(2k+1)^2Dt}{l_z^{\,2}}\right)}{(2k+1)^2} \tag{2}$$

Here $M(t)$ is the sorbate mass, t is the time, M_∞ is the equilibrium sorbate mass, and D is the diffusion coefficient.

We suppose that in our case the relative increase of the sample volume is proportional to the mass of absorbed scCO$_2$ (the same assumption as in the ref 9):

$$\frac{V(t) - V_0}{V_\infty - V_0} = \frac{M(t)}{M_\infty} \tag{3}$$

Here V_0 is the polymer sample volume before swelling, and V_∞ is the volume of a saturated sample.

We plotted the sorption curves, i.e., relative increase of the sample volume vs time, and tried to fit those curves with the theoretical result, eq 2. The best-fit problem was solved by the least-squares procedure. This allowed the determination of the diffusion coefficient of scCO$_2$ in the polymer.

The typical swelling curves for PMMA and PBMA are shown in Figure 3b. The best-fit curves for the theoretical dependence (eq 2) and the corresponding values of the apparent diffusion coefficient D are also shown in Figure 3b. We consider these values as apparent ones, because eq 2 is valid only for the case when the value of D is independent of the sorbate concentration. On the other hand, according to the images of diffusion fronts (Figure 2), we believe that diffusion coefficients may depend on concentration both in PMMA and in PBMA samples. The obtained data show a good agreement with values of the diffusion coefficient calculated using eq 1 from the diffusion front propagation dependences. The results for different scCO$_2$ pressures and a fixed temperature (38 °C) are shown in Table 2. Table 3 shows the results for samples of polymers with different molecular weight (M_w). Table 4 presents the results for

Table 2. Measurement Results for the Apparent Diffusion Coefficient of CO_2 Molecules in Polymers and the Equilibrium Volume Swelling Degrees at Fixed Temperature (38 °C) and Different $scCO_2$ Pressures

polymer	press. (MPa)	$D_1{}^a$ ($\times10^{-10}$ m^2/s)	$D_2{}^a$ ($\times10^{-10}$ m^2/s)	swelling deg (vol %)
PBMA-h	9	4.8 ± 0.2	5.8 ± 0.8	41 ± 5
	12.5	6.2 ± 0.5	4.4 ± 0.4	46 ± 7
	15	4.6 ± 1.0	4.4 ± 0.4	47 ± 10
	20	5.6 ± 0.4	5.9 ± 0.5	49 ± 8
	25	6.9 ± 0.3	8.4 ± 1.3	53 ± 5
PMMA-h	9	0.33 ± 0.03	0.51 ± 0.08	22 ± 5
	12.5	0.43 ± 0.04	0.69 ± 0.09	24 ± 8
	15	0.65 ± 0.11	0.7 ± 0.2	35 ± 5
	20	0.60 ± 0.02	0.80 ± 0.04	29 ± 5
	25	0.64 ± 0.02	anomalous[b]	30 ± 2

[a] The values of D_1 and D_2 are obtained by measuring the propagation distance of the diffusion front vs time and by observation of the sample swelling kinetics, respectively. [b] The anomalous diffusion, when it is impossible to find the D_2 value using eq 2; see Figure 4b.

Table 3. Measurement Results for the Apparent Diffusion Coefficient of CO_2 Molecules and the Equilibrium Swelling Degrees at Fixed Temperature (38 °C) for Polymers with Different M_w

polymer	press. (MPa)	M_w ($\times10^3$)	$D_1{}^a$ ($\times10^{-10}$ m^2/s)	$D_2{}^a$ ($\times10^{-10}$ m^2/s)	swelling deg (vol %)
PBMA-h	90	2236	4.8 ± 0.2	5.8 ± 0.8	41 ± 5
PBMA-l	90	320	5.6 ± 0.8	6.7 ± 0.8	23 ± 4
PBMA-h	250	2236	6.9 ± 0.3	8.4 ± 1.3	53 ± 5
PBMA-l	250	320	6.6 ± 0.5	anomalous[b]	36 ± 6
PMMA-h	90	4098	0.33 ± 0.03	0.51 ± 0.08	24 ± 5
PMMA-l	90	120	4.9 ± 1.7	anomalous[b]	29 ± 4
PMMA-h	250	4098	0.64 ± 0.02	anomalous[b]	30 ± 2
PMMA-l	250	120	6.8 ± 0.5	anomalous[b]	32 ± 6

[a] The values of D_1 and D_2 are defined as in Table 2. [b] The mark is defined in Table 2.

Table 4. Measurement Results for the Apparent Diffusion Coefficient of CO_2 Molecules in Polymers and the Equilibrium Swelling Degrees at Fixed Pressure (12.5 MPa) and Different $ScCO_2$ Temperatures

polymer	temp (°C)	$D_1{}^a$ ($\times10^{-10}$ m^2/s)	$D_2{}^a$ ($\times10^{-10}$ m^2/s)	swelling deg (vol %)
PBMA-h	38	6.2 ± 0.5	4.4 ± 0.4	46 ± 9
	50	6.3 ± 0.4	7.1 ± 0.6	21 ± 6
	55	9.8 ± 1.4	6.4 ± 1.0	34 ± 5
	65	9.4 ± 1.7	7.7 ± 1.9	31 ± 6
PMMA-h	38	0.43 ± 0.04	0.69 ± 0.09	26 ± 8
	50	0.44 ± 0.07	0.69 ± 0.10	32 ± 6
	65	0.5 ± 0.08	0.99 ± 0.12	10 ± 4

[a] The values of D_1 and D_2 are defined as in Table 2.

the different temperatures and a fixed $scCO_2$ pressure (12.5 MPa). In the tables the values of D_1 and D_2 are the diffusion coefficients obtained by measuring of the diffusion front propagation vs time (eq 1) and by monitoring of the sample swelling kinetics (eq 2), respectively.

We have found that in some cases the volume swelling kinetics cannot be described as Fickian (eq 2): the swelling curve is anomalous, because the volume increase has approximately a constant rate; see Figure 4. (This could be due to the eq 3 faults for such swelling systems.) Consequently, it is impossible to find the value of D_2 using our fitting procedure. ("Anomalous" marks were put in the tables instead of values.) This kind of kinetics of volume increase resembles case II diffusion, but surprisingly, the front propagation dynamics at the same time remains to be Fickian. Therefore, we are still able to find the value of D_1 using eq 1 because of the remaining linear relation between the square of the front propagation distance and the time (see Figure 4a).

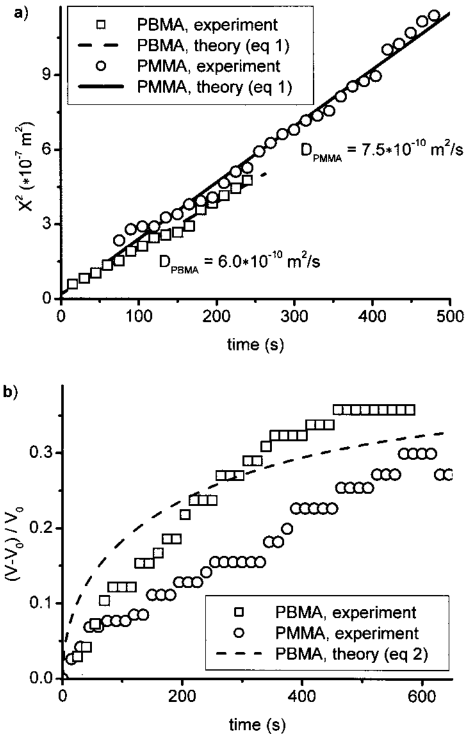

Figure 4. Observation of anomalous diffusion for swelling of low molecular weight PMMA-l and PBMA-l samples exposured at temperature 38 °C and pressure 25 MPa. (a) Time dependence of the square of the diffusion front propagation distance (X^2). Diffusion coefficients were determined using eq 1. In PBMA-l the diffusion front was difficult to observe at the final stage of propagation. (b) Sample volume increase vs time. Fickian diffusion curve (eq 2) is presented for comparison.

The values in Tables 2−4 have been obtained by averaging over three to four independent experiment realizations with different samples under the same exposure conditions. The obtained results show that the swelling kinetics and the equilibrium swelling degree for the considered samples depend on temperature and pressure in the cell. For PMMA the diffusion coefficient increases 1.5−2 times when the pressure increases from 9 to 25 MPa (see Tables 2 and 3). The analysis of the temperature dependence shows an increase of the diffusion coefficient ~1.5 times for both PMMA and PBMA upon temperature increase from 38 to 65 °C (see Table 4). At the same time the results for PBMA do not allow an unambiguous conclusion about the tendency of increase of the diffusion coefficient with the pressure increase.

We have found also that diffusion coefficient depends strongly on the molecular weight of polymer for PMMA samples (see Table 3). The obtained diffusion coefficient for PMMA-l with $M_w = 120 \times 10^3$ is about 10 times greater than one for PMMA-h with $M_w = 4098 \times 10^3$. At the same time for PBMA samples the diffusion coefficient is almost independent of M_w (Table 3).

Anomalous kinetics was observed for the volume swelling of low molecular weight polymers (both PMMA-l and PBMA-l, see Figure 4) and for the volume swelling of high molecular weight polymer PMMA-h under 25 MPa pressure (when the density of $scCO_2$ is highest). The origin of existence of anomalous kinetics for swelling together with normal (Fickian) kinetics for front propagation is not clear. The anomalous kinetics could be related to the relaxation of polymer matrix, which is not described by simple assumption of the eq 3. On the other hand, the degree of volume swelling is not so high; the values of 20−30% of the total volume increase correspond to 6−9% increase of each sample dimension. Therefore, we could suppose that the influence of swelling kinetics on front propagation kinetics is rather small. But the problem requires further studies to understand the mechanisms of transition between Fickian and anomalous diffusion in the polymers. The supercritical CO$_2$ could be a very appropriate media for such experiments, because of the unique possibility to tune up its physical and chemical properties by changing the temperature and pressure in a reaction cell.

Tables 2−4 show also the results for the equilibrium volume swelling degrees. It can be seen that for both PMMA and PBMA the dependences of the equilibrium mass swelling degree on scCO$_2$ pressure have the same character (see Tables 2 and 3). For the pressure increase from 9 to 25 MPa at temperature 38 °C the equilibrium volume swelling degree of PMMA and PBMA samples increases ~1.5 and ~1.3 times, respectively. This dependence is quite predictable according to literature data. Indeed, authors of refs 5 and 6 have shown the same type of dependence for PMMA swelling in scCO$_2$ for the pressure region up to ~11 MPa. Chang et al.[7] presented a sorption isotherm with similar tendency up to 30 MPa. Our values of measured volume swelling degree of PMMA correlate well with the data of ref 5 taking into account the experimental errors.

At the same time for a given pressure (12.5 MPa) with the temperature increase from 38 to 65 °C the equilibrium volume swelling degree of PMMA samples reaches the maximum value (at 50 °C) and begins to decrease with further temperature increase (see Table 4). Similar behavior of swelling degree was noticed by Wissinger and Paulaitis[5] for PMMA samples swelling in scCO$_2$ at pressure ~10 MPa.

The data obtained for samples of polymers with different molecular weights show that for PMMA the swelling degree does not depend significantly on the M_w, but for PBMA the samples of polymers with higher M_w are characterized by a higher value of swelling degree.

Figure 3b shows a slight, but noticeable, difference between the experimental and the theoretical swelling curves. This difference is observed as the presence of a region in the experimental curve where the rate of the sample size increase is greater compared to the theoretical curve (the region is marked with an arrow.) This region is observed at the time corresponding to the completion of propagation of the diffusion fronts in the sample. This effect is more pronounced for PMMA samples, whose shape corresponds to a long parallelepiped, i.e., when one dimension of the sample differs significantly from the others. We believe that this effect is due to the following phenomenon. During swelling the inner glassy region of the sample prevents volume expansion like a hard skeleton. Such constraint is released when the diffusion front reaches the center of the sample and the whole sample becomes plasticized. This explanation was introduced by Samus and Rossi,[18] and they noticed that observed features of the sorption curve, which have been ordinarily described as "non-Fickian", indeed could be explained in the frames of Fick law.

Error Analysis. Mean values in the tables have been obtained by averaging over three to four independent experiment realizations with different samples under the same exposure conditions. Standard errors of the mean values are approximately 10−15% for diffusion coefficients and ~20% for swelling degrees. The error values are mostly due to the peculiarities in sorption kinetics for different samples exposed at the same conditions. These errors can be due to the sample preparation technique (cutting and polishing for PMMA), for example, due to the differences in sample surface quality and so on. It should be noted that we have found no dependence of determined parameters on sample size.

A significant dispersion of the measured values for the PBMA and PMMA-l can have the following explanation. The diffusion coefficient for scCO$_2$ in PBMA and PMMA-l is approximately 1 order of magnitude greater than the diffusion coefficient in PMMA-h, so the diffusion process goes ~10 times faster. The perturbations of the sc fluid and the density fluctuations during ingress of scCO$_2$ and the initial exposure stage can influence the sorption processes. To describe this situation, we can define the characteristic diffusion time τ (taking into account eq 2):

$$\tau = \frac{l_{\mathrm{eff}}^{2}}{\pi^2 D}$$

where l_{eff} is determined by

$$\frac{1}{l_{\mathrm{eff}}^{2}} = \frac{1}{l_x^{2}} + \frac{1}{l_y^{2}} + \frac{1}{l_z^{2}}$$

If the relaxation time for the initial fluctuations is greater than or comparable to the characteristic diffusion time τ (as is apparently the case for PBMA), such fluctuations can greatly influence the measured values. It is interesting to compare the magnitude of errors in Tables 2−4 with literature data. Muth et al.[26] determined the diffusion coefficient of CO$_2$ in swelling poly(vinyl chloride) using the gravimetric technique and obtained a standard deviation in the range of 1−15%. Therefore, our accuracy of the diffusion coefficient measurement corresponds to a comparable range.

Royer et al.[9] presented the graphs of the dependences of measured equilibrium swelling degrees for poly(dimethysiloxane) on CO$_2$ density, pressure, and temperature. Taking into account the indicated error bars, we can conclude that the authors have achieved an ~5−6% error level. But because they have studied the swelling behavior of melts, the swelling have been observed only in one direction. Our error value of ~20% for the swelling degree of a three-dimensional sample corresponds to about 6% values of errors for each dimension. Therefore, we have achieved the same level of accuracy.

Morrissey and Vesely[14] performed measurements of front propagation and volume expansion of swelling polymers. They determined the correlation coefficient in linear fitting procedure for dependence of front penetration distance on the square root of time. The coefficient was defined as an indication of accuracy for one experimental realization. Authors constructed a specially designed cell for precise monitoring of the front position and demonstrated that they increased the accuracy (the value of the correlation coefficient) from 0.9977 (“cut and measure method”) up to 0.9992. The accuracy was achieved due to the special cell design and the application of video camera together with the distance measurement software. But this approach to the determination of error provides information only about the error due to the set up used, since the analysis is performed for one experimental realization. For comparison, we obtained the typical range ~0.98−0.995 for the values of correlation coefficient calculated using the procedure of ref 14. However, the errors in Tables 2−4 obtained by statistical analysis of the data are higher due to the differences in sorption kinetics for different samples; therefore, optical observation errors are not dominant, and the achieved accuracy is sufficient.

Another important observation should be pointed out. We have found that samples of low molecular weight polymers (PMMA-l, PBMA-l) retain their shape only during initial and intermediate periods of sorption. At the final stage of sorption (after the front propagation is over), the sample shape changes have been observed. We believe that these changes are due to considerably sample plasticization with CO_2. As a result, the sample shape is changing from the initial parallelepiped to somewhat like a droplet without sharp corners or edges. This phenomenon can influence the results of measurements of both equilibrium swelling degree and diffusion coefficient D_2 (using eq 2) for such samples. But the procedure of D_1 determination (using eq 1) is still valid in all cases because any noticeable shape changes begin only after the front transition process is over.

Conclusion

We have performed the study of sorption by polymer samples in supercritical CO_2 conditions using technique of direct optical observation. Two different approaches to the determination of diffusion parameters were applied: the first one was the well-known volumetric method, and the second one was the method of analysis of diffusion front propagation. The results of two methods were found to be in good agreement. We believe that the method of front propagation analysis is convenient and reliable. However, this method has at least one general limitation: it can be successfully applied only to the study of optically transparent samples. Also, the development of a proper theory is necessary to obtain more precise estimation of the α parameter in the eq 1. Anomalous kinetics has been found in some cases for swelling process together with the usual Fickian dynamics for front propagation. We believe that supercritical CO_2 is a very appropriate media to study the transition between Fickian and anomalous behavior of swelling polymer due to the unique possibility to tune up the physical and chemical properties of solvent (plasticizier) by changing temperature and pressure in the reaction cell.

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