

Plasticization of gas separation membranes*

M. Wessling, S. Schoeman, Th. van der Boomgaard and C.A. Smolders

University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

For the investigation of the plasticizing effect of carbon dioxide on polymers used for gas separation membranes new experimental methods have been developed that measure the sorption kinetics as well as the dilation kinetics. Comparing dilation and sorption kinetics at low and elevated pressures gives information about different types of swelling behaviour depending on the pressure level. Volume relaxation in the form of a slow volume increase in time can be observed above a certain pressure, called plasticization pressure. An interpretation of these experimental facts as a process of slow loosening of densely packed entanglements is suggested. By using sorption kinetics experiments at various temperatures the plasticizing effect of CO₂ is apparent by a decreasing activation energy for diffusion with increasing penetrant concentration.

Keywords: plasticization; sorption; swelling kinetics; dilation; polyimides

Introduction

Gas separation using membranes has been demonstrated to be an economical alternative to cryogenic and adsorptive or absorptive gas separation processes. Although a number of gas separation modules are available on the market, which house a variety of different polymeric membranes (polyimide, Ube; polysulphone, Monsanto; cellulose acetate, Air Products), a lot of effort is still being put into the synthesis of new polymeric materials to gain higher permeabilities and selectivities. Understanding the factors affecting the permeability and selectivity of a polymer is an important goal for researchers in order to find heuristic rules for the synthesis of optimal tailor-made polymers. The synthesis of hexafluorodihydrate-based polyimides^{1,2}, polytriazoles and polyoxadiazoles^{3,4} led to families of polymers with outstanding gas separation characteristics.

Normally, characterization of the tailor-made polymers occurs at low to moderate pressures with gases of interest like N₂, O₂, CH₄, He and CO₂, although in practice membranes are exposed to high pressures. Infrequently high pressure performance experiments of the material are performed, but are often predicted from low pressure experiments. In the presence of CO₂ in particular, the extrapolation to high pressure applications is doubtful⁵.

Experimental deviations from theoretical predictions are attributed to the plasticizing effect of CO₂. This plasticizing effect is observed as a considerable loss in selectivity, as shown for mixed gas experiments of CO₂/CH₄ at different upstream pressures in *Figure 1* for two polyimides.

A second phenomenon attributed to the plasticizing effect of CO₂ is shown schematically in *Figure 2*. Upon increasing the upstream pressure, the permeability of a

glassy polymer normally decreases, which is extensively described and explained for a number of polymers by the dual sorption model⁶. However, the permeability of some polymers does not decrease further with further increasing upstream pressure, but increases considerably⁷. The values obtained for the permeabilities are now not equilibrium values as for low upstream pressures, but they increase in time. These time-dependent relaxation processes are claimed to have their origin in the non-equilibrium glassy state of the polymer. It is stated that the sorbed CO₂ swells and therefore loosens the polymer matrix.

Equilibrium dilation (swelling) experiments have been made in the past for a number of polymers⁸⁻¹⁰, which are not of real interest for actual gas separation applications because of their low permeabilities and selectivities, respectively. In this paper a few polymers from the 6FDA family will be investigated and furthermore it will focus on the dilation kinetics. Experiments comparing the kinetics of mass uptake (sorption) and the volume increase (dilation) due to sorption might give a deeper understanding of the plasticizing effect of CO₂.

Experimental

Sorption

For the determination of the solubility of gases, and additionally of the sorption kinetics, a pressure decay method was used. With the pressure decay method, which has been used by other researchers^{11,12}, it is not possible to determine the sorption kinetics due to a significant decrease of the absolute pressure in time. This changing pressure in time causes a complex time-dependent boundary condition of the differential equation describing the diffusion process of the penetrant molecules into the depth of a polymer film.

*Paper presented at GAS Separation International, Austin, TX, USA, 22-24 April 1991

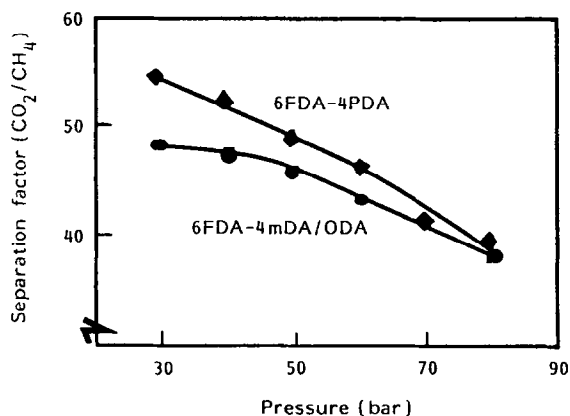


Figure 1 Separation factor for a 20/80 vol% gas mixture of CO_2/CH_4 at 30 bar upstream pressure and 25°C

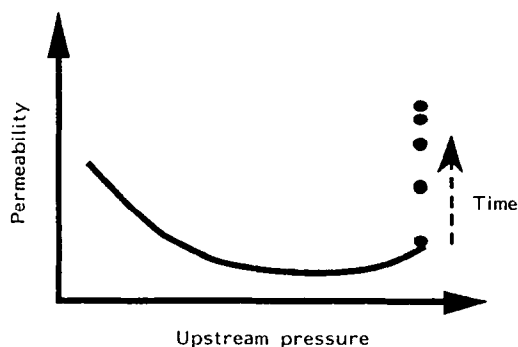


Figure 2 CO_2 permeability in a glassy polymer depending on the upstream pressure value and on time

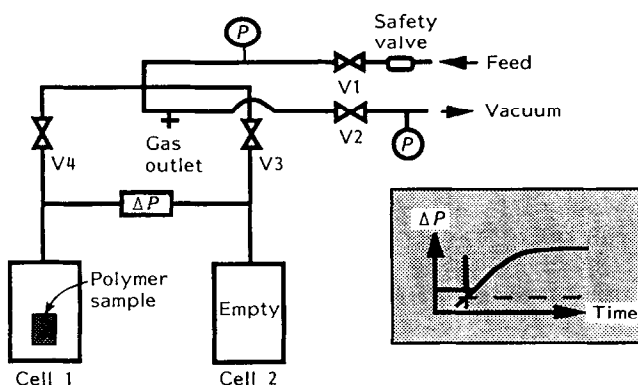


Figure 3 Experimental set-up for the determination of sorption isotherms and sorption kinetics

A set-up has been designed, as shown in *Figure 3*, that measures a minute pressure difference between a cell containing the polymer sample and an empty reference cell. Overall pressure changes in the sample cell are small (< 5%) compared to the total pressure in the cell and will not be considered as a time-dependent boundary condition in the mathematical analysis of the sorption kinetics.

Sorption isotherms were obtained by the following procedure: the cells were evacuated for at least 10 h and then suddenly pressurized to the pressure p_0 by opening valves 3 and 4. After a very short time valves 3 and 4 were closed again and a pressure decrease in the sample cell compared to the reference cell could be observed due to sorption of penetrant molecules into the polymer film until equilibrium was reached. Additional pressurization was used to obtain higher sorption values. During the time

when valves 3 and 4 were opened sorption had already occurred. This missing initial sorption was later calculated by extrapolating the recorder plot to the time $t = 0$ s. Extrapolation was achieved by fitting the data from the recorder plot after transforming the time axis into a square-root-of-time axis to a straight line. The physical background of this extrapolation will be explained below.

From the pressure change in time an effective diffusion coefficient can be calculated from the slope of the relative mass uptake against the square root of time^{13, 14}

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{l^2} \right)^{1/2} \quad (1)$$

where M_t is the mass uptake at time t , M_∞ the mass uptake at infinite time, D the diffusion coefficient and l the membrane thickness. The diffusion coefficient obtained is an effective diffusion coefficient within the concentration range corresponding to the pressure of the previous sorption run and the pressure of the actual one.

Dilation

For the determination of the swelling of a polymer induced by the sorbed gas, a new experimental technique has been developed: a pressure cell with two glass windows was constructed containing a hanging polymer strip, as shown in *Figure 4*. A light source outside the cell illuminated the cell so that it was possible to detect a gold strip mark on the polymer sample by a line scan camera. Every diode on the camera was capable of detecting 64 intensity values. The resolution of the camera was $5.2 \mu\text{m}$. Picture data from the camera were input to a computer for further data acquisition. By this means it was possible, while simultaneously regulating the pressure in the sample cell, to make a scan every seven seconds. The experimental procedure for obtaining a dilation isotherm is the same as for the sorption set-up, the only difference being that the pressure in the cell could not be increased in a step form as for the sorption experiment, but by a speed of 3.6 bar min^{-1} .

Permeation

The experimental set-up for measuring the permeability depending on the upstream pressure and temperature is described in detail elsewhere¹⁴. Gases used were at least of 99.9% purity.

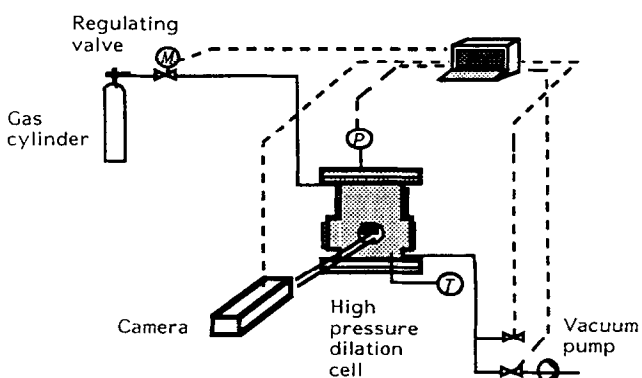


Figure 4 High pressure dilation set-up

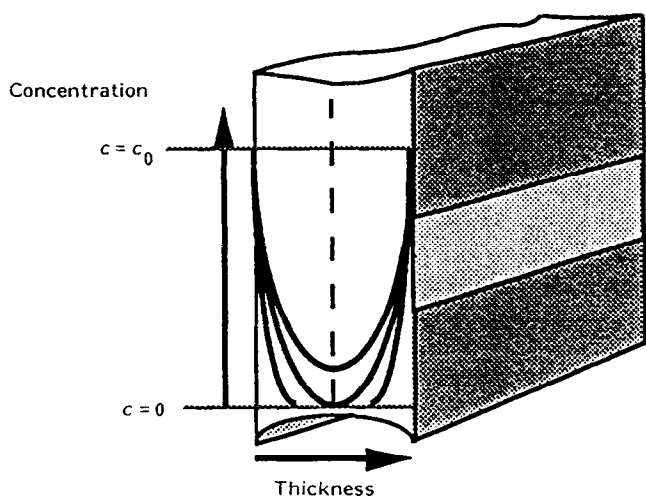


Figure 7 Geometric comparison of the diffusion and dilation process

can be observed at $t = 0$ when the first molecules are sorbed in the surface layer of the film or dilation might start at the time when the first molecules have reached the middle of the strip.

The sorption data for 6FDA-DAF can be analysed as usual¹³ by plotting the mass uptake versus the square root of time normalized for the membrane thickness. The dilation kinetics are replotted in the same way and both the mass uptake and the dilation kinetics are compared with the calculated time-dependent concentration in the middle of the polymer strip in *Figure 8*. Mass uptake and dilation kinetics are linear with the square root of time, confirming Fickian diffusion of CO_2 in the polymer. The comparison with the calculated concentration in the middle of the polymer film, which is given by

$$\frac{c - c_0}{c_1 - c_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right\} \quad (2)$$

is made to indicate that the delay between mass uptake and swelling is caused by the fact that the strip starts to dilate when the first penetrant molecules reach the middle of the strip. Once the diffusion fronts meet each other in the middle of the polymer strip, dilation in length direction progresses simultaneously with the mass uptake, but not in parallel with the concentration in the middle of the strip. Concluding this extensive comparison of

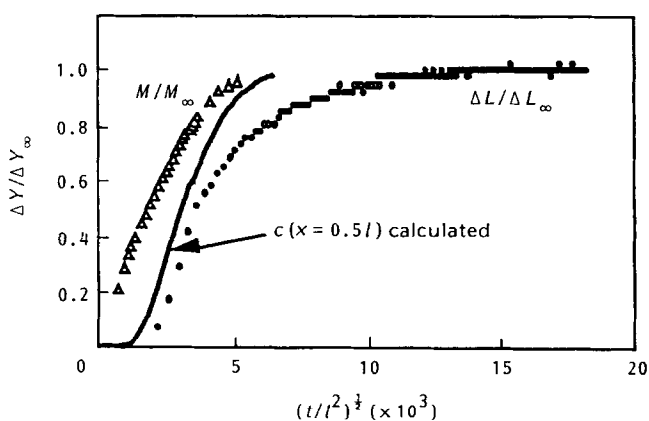


Figure 8 Diffusion-limited dilation kinetics in length direction for 6FDA-DAF and CO_2

dilation and sorption kinetics it can be stated, as already done for the equilibrium sorption and dilation experiments, that every sorbed penetrant molecule dilates the polymer instantaneously at low pressures as soon as the diffusion fronts meet in the middle of the polymer film thickness.

Plasticization

In the following subsections different plasticization phenomena will be described. It is not possible to define one specific phenomenon as *the* plasticization phenomenon. A number of physical properties are altered significantly by the presence of sorbed CO_2 molecules and these will be described below.

High pressure dilation kinetics. Plasticization of 6FDA-DAF by CO_2 was observed in a recent publication¹⁶ by permeation experiments at around 12 bar upstream pressure. As expected for glassy polymers, the permeability decreases with increasing upstream pressure. However, from the plasticization pressure upwards the permeability increases again. Unfortunately no time-dependent permeabilities were measured. Indeed, it is often seen⁷ that for a plasticized glassy polymer the permeability is not constant, but increases in time. For a number of 6FDA-based polyimides this has been measured in our laboratory, as shown in *Figure 9*.

The high amount of CO_2 swells the polymer to such an extent that chain segments may become more flexible due to the presence of CO_2 and may adapt to this new situation by rearranging towards a new configurational state. With the experimental possibility of investigating the kinetics of swelling, it is now possible to get more information about this mechanism. It could be shown that for a pressure step from 0 to 3 bar every molecule sorbed into the matrix causes an instantaneous swelling and within a certain limited time, sorption and swelling reach an equilibrium value. This has been proved to be true up to pressures smaller than the plasticization pressure. For higher pressures this is no longer true.

The lapse of time to reach the sorption equilibrium for a sorption experiment with an increase in applied pressure from 15 to 18 bar is as long as for a pressure step from 0 to 3 bar. However, in a dilation experiment where the pressure is changed from 15 to 18 bar dilation does not progress any more simultaneously with the mass uptake. In *Figure 10* it can clearly be seen that there is a

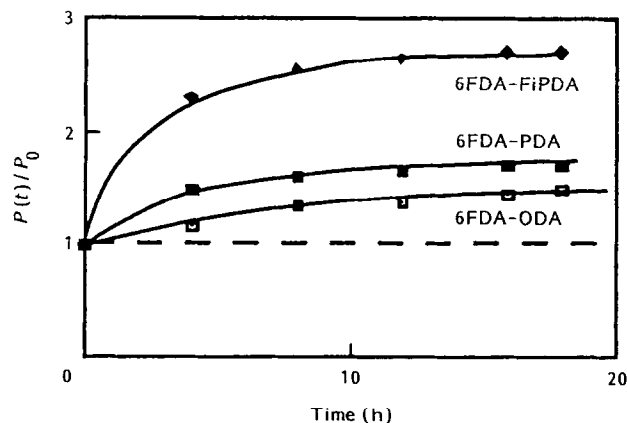


Figure 9 Time dependence of the permeability $P(t)/P_0$ for CO_2 in different polyimides at 30 bar upstream pressure and 25°C

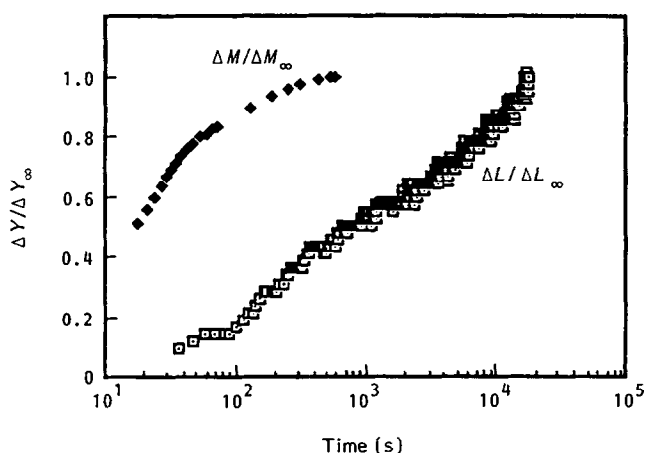


Figure 10 Dilation and sorption kinetics of CO₂ in 6FDA-DAF for a pressure step from 15 to 18 bar

remarkable difference between sorption and dilation. While the sorption equilibrium is reached within 700 s swelling still progresses. Although no extra gas is sorbed into the matrix volumetric sample changes still occur. The dilation experiment was stopped after 20 000 s due to memory problems with the computer. The sample was held at 18 bar for a longer time and after *ca.* 30 000 s no significant changes could be observed anymore.

Summarizing the experiments comparing swelling and sorption, it can be concluded that swelling occurs at high and low pressure levels in different ways. Swelling at low pressure levels will certainly influence the mass transport, i.e. higher degrees of swelling will enlarge the diffusivity of penetrant molecules. Since swelling below the plasticization pressure is instantaneous, it is concluded that the penetrant molecules loosen the matrix by separation of relatively short polymer chain segments. Long chain rearrangements made possible by loosening more densely packed entanglements occur only above the plasticization pressure.

A first series of experiments evaluating the question of whether the loosening of denser packed entanglements is a thermally activated process is shown in Figure 11. For each of the temperatures the pressure was increased from 15 to 18 bar. Raising the temperature has an enhancing effect on the dilation kinetics and seems to verify the conclusion that disentanglement is faster at higher tem-

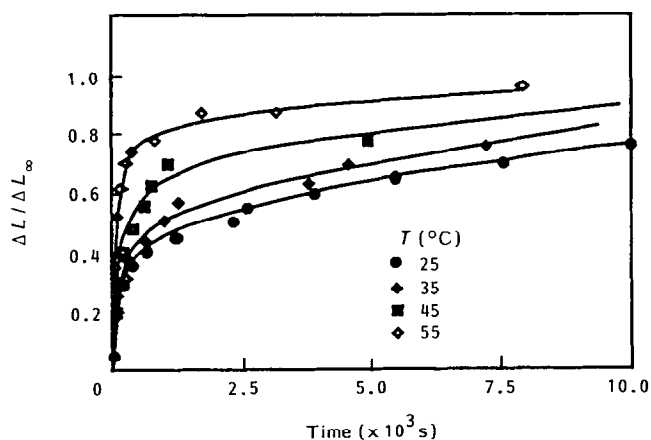


Figure 11 Dilation kinetics for a pressure step from 15 to 18 bar CO₂ in 6FDA-DAF at different temperatures

peratures, thus thermally activated. However, the result might be affected by the fact that the degree of swelling itself depends on the temperature due to temperature dependence of the penetrant concentration. Future experiments will investigate the aspects of a thermally activated process at 'isodilated' states of the polymer.

Depression of the glass transition temperature. Every sorbed carbon dioxide molecule swells the polymer, as has been shown above. The structure of the polymer matrix itself is changed in a way that polymer chains are separated by penetrant molecules, the matrix is loosened and polymer chains become more flexible. Polymer chain flexibility is often correlated with the glass transition temperature of a polymer. Simha and Boyer have shown that a higher glass transition temperature correlates with an increasing chain stiffness¹⁷. Permeation experiments can also be used to study the influence of a certain CO₂ concentration in a membrane on its structure. At the glass transition temperature the permeation rates often increase drastically due to the glass-rubber transition. The hypothesis is that an increasing upstream pressure causes a larger overall concentration in the membrane and a more flexible matrix, thus a decrease in the glass transition temperature. The T_g can be easily determined in a plot of the logarithm of the permeability versus the inverse temperature in kelvin, as shown schematically in Figure 12. Normally these experiments are made at one fixed upstream pressure.

In this study a series of experiments has been made at different upstream pressures. A shift of the glass transition towards lower temperatures was expected for experiments with carbon dioxide. Furthermore, experiments made with an inert gas like helium should show no glass transition depression.

Unfortunately, 6FDA-based polyimides have very high glass transition temperatures around 300°C, which is almost infeasible for experimentation. Therefore, it was decided to take PVC as a model system, for which T_g is 82°C as determined by DSC analysis.

Permeation experiments were made in such a way that the temperature was kept constant and subsequently the pressure was increased stepwise. After the measurement of all upstream pressures the temperature was increased to the new set point. The temperature range evaluated was from 40°C to 110°C, well above the glass transition temperature.

Experimental results of three subsequent cycles with CO₂ for the first two runs and helium for the third are

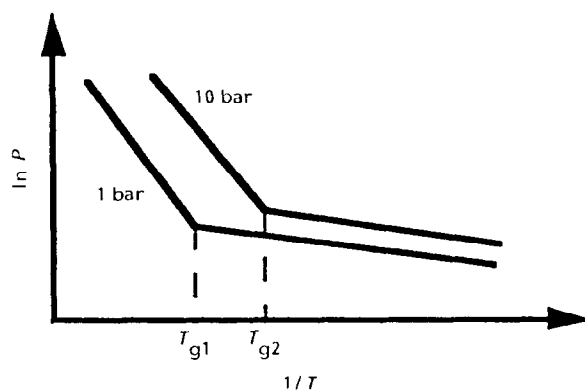


Figure 12 Glass transition temperatures determined by permeation experiments

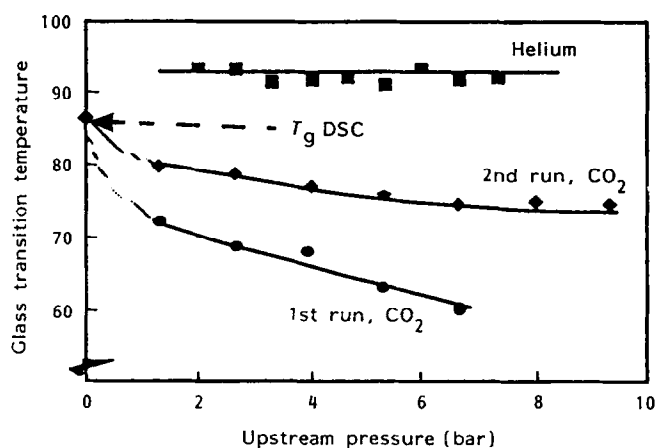


Figure 13 T_g depression in PVC by absorbed CO_2

shown in Figure 13. In the first run the increasing upstream pressure results in a distinct decrease in the glass transition temperature. In the second, the glass transition temperature is still affected, but not as strongly as in the first. Probably the slow cooling from 110°C above T_g down to 40°C after the first CO_2 cycle has annealed the polymer. Helium in the third cycle does not show any significant change of the glass transition temperature. Helium as an inert gas does not interact with the polymer, which therefore does not swell and alter the polymer matrix. It is not surprising that the values for T_g determined by DSC deviate from the values obtained by permeation experiments with helium. Since the glass transition does not occur at a certain temperature, but in a certain temperature range, different glass transition temperatures are determined depending on the experimental method¹⁸.

Activation energy for diffusion. Disentanglement of polymer chains at elevated pressure, observed by dilation experiments, and T_g depression by absorbed CO_2 molecules, determined by permeation experiments, visualize the plasticization effect of CO_2 on glassy polymers. A third phenomenon can be found experimentally through the investigation of the sorption kinetics at different pressures and temperatures. Here the influence of pressure and temperature on the diffusivity of a penetrant molecule in a polymeric matrix is studied. The polymer used is 6FDA-44ODA. Diffusion coefficients were obtained by applying Equation (1) to the experimental data for a sorption run at a certain pressure. Since this pressure corresponds to an equilibrium concentration, by varying the pressure an experimental relation between the diffusion coefficient and the concentration is obtained. Since carbon dioxide swells the polymer matrix considerably, the diffusivity strongly depends on the concentration of the penetrant molecules. An often-used mathematical relation is of an exponential form. Apparent diffusion coefficients depending on the concentration at three different temperatures are shown in Figure 14. The exponential relation fits the experimental data well.

The energy required for a diffusional jump can be obtained from the Arrhenius equation

$$D = D_0 \exp\left\{-\frac{E_D}{RT}\right\} \quad (3)$$

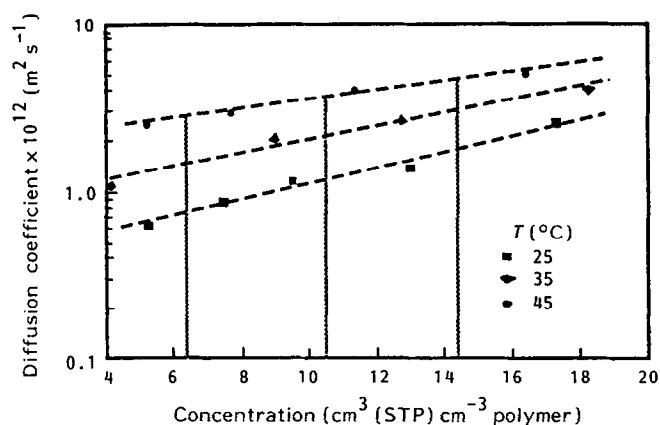


Figure 14 Concentration-dependent diffusion coefficients of CO_2 at different temperatures in 6FDA-44ODA

D is the diffusion coefficient at the temperature T , subscript 0 stands for infinite temperature, R is the universal gas constant and E_D is the activation energy for diffusion. This energy depends on a number of factors like chemical structure of the polymer, physical properties of the penetrant molecule, but also on the physical properties of the polymer matrix. Since it has been seen that CO_2 affects the polymer matrix, a further calculation of the activation energy for diffusion, depending on the concentration of the penetrant molecules, using the Arrhenius equation and the interpolated diffusion coefficients should show the plasticizing effect of carbon dioxide. Results of these calculations are shown in Figure 15. With increasing concentration the activation energy for diffusion decreases significantly by about 30% over the concentration range investigated. This concentration range corresponds to a pressure range from 0.5 to 3 bar.

The activation energy for diffusion is the energy required to separate polymer chains for a diffusional jump. The penetrant molecule can jump from its actual position into the newly opened space. Thus a decreasing activation energy with increasing concentration shows that the carbon dioxide absorbed has already loosened the matrix at low pressures and less energy is required for the bending of chains in order to create new void volume.

No experiments have been made at lower concentration and it is therefore not possible to state whether the maximum at the concentration $c = 6 \text{ (cm}^3\text{(STP) cm}^{-3}\text{)}$

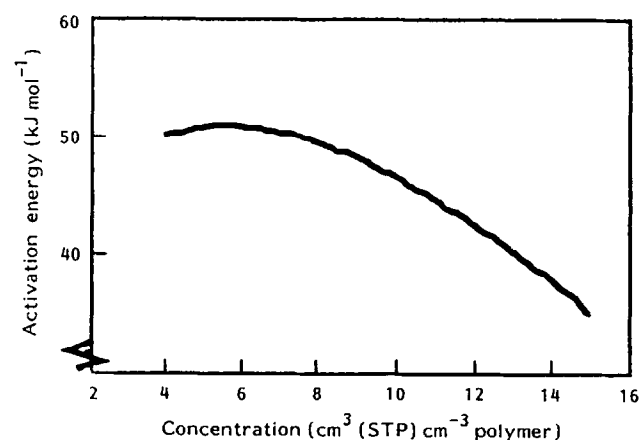


Figure 15 Concentration-dependent activation energy for the diffusion of CO_2 through 6FDA-44ODA

polymer) is significant. We are inclined to say that the activation energy for lower concentrations does not depend on the concentration. Further experiments will be made at higher pressures.

Conclusions

Comparison of sorption and dilation kinetics for CO₂ in 6FDA-DAF at low and at high pressures have shown two different mechanisms of swelling. Below a certain pressure every sorbed molecule contributes instantaneously in the dilation of the polymer matrix. Above this plasticization pressure volume relaxation occurs. Time lapses to reach swelling equilibrium are two orders of magnitude larger than for sorption, suggesting that the mechanism of loosening of densely packed entanglements occurs. Furthermore, plasticization can also be found at low concentrations of carbon dioxide, indicated by the depression of the glass transition temperature and a concentration-dependent activation energy for diffusion.

References

- 1 Kim, T.-H., Koros, W.J., Husk, G.R. and O'Brien, K.C. Relationship between gas separation properties and chemical structures in a series of aromatic polyimides *J Membrane Sci* (1988) 27 45
- 2 Smit, E. Modelling of diffusion of gases through membranes of novel polyimides *PhD Dissertation* University of Twente, The Netherlands (June 1991)
- 3 Gebben B., Mulder, M.H.V. and Smolders, C.A. Gas separation properties of a thermally and chemically polytriazole membrane *J Membrane Sci* (1989) 46 29
- 4 Hensema, E. Polyoxadiazole and polytriazole gas separation membranes: Synthesis and properties *PhD Dissertation* University of Twente, The Netherlands (September 1991)
- 5 Barbari, T.A., Koros, W.J. and Paul, D.R. Gas transport in polymers based on bisphenol-A *J Polym Sci, Polym Phys Edn* (1988) 26 709-727
- 6 Barrer, R.M., Barrie, J.A. and Slater, J. Sorption and diffusion in ethyl cellulose. Part III. Comparison between ethyl cellulose and rubber *J Polym Sci* (1958) 27 177
- 7 Puleo, A.C., Muruganandam, N. and Paul, D.R. Gas sorption and transport in substituted polystyrenes *J Polym Sci, Polym Phys Edn* (1989) 27 2385-2406
- 8 Hirose, T., Mizoguchi, K. and Kamiya, Y. Dilation of polyethylene by sorption of carbon dioxide *J Polym Sci, Polym Phys Edn* (1986) 24 2107
- 9 Fleming, G.K. and Koros, W.J. Dilation of polymers by sorption of carbon dioxide at elevated pressures, 1. Silicone rubber and unconditioned polycarbonate *Macromolecules* (1986) 19 2285
- 10 Sefcik, M. Dilation and plasticization of polystyrene by carbon dioxide *J Polym Sci, Polym Phys Edn* (1986) 24 957
- 11 Koros, W.J. and Paul, D.R. Design considerations for measurement of gas sorption in polymers by pressure decay *J Polym Sci, Polym Phys Edn* (1976) 14 1903
- 12 Chiou, J.S. and Paul, D.R. Sorption and transport of CO₂ in PVF₂/PMMA blends *J Polym Sci, Polym Phys Edn* (1986) 32 2897
- 13 Crank, J. *The Mathematics of Diffusion* 2nd Edn, Clarendon Press, Oxford (1975)
- 14 Blume, I., Smit, E., Wessling, M. and Smolders, C.A. Diffusion through rubbery and glassy polymer membranes *Makromol Chem. Macromol Symp* (1991) 45 237-257
- 15 Berens, A.R. and Huvar, G.S. Interaction of polymers with near-critical carbon dioxide *ACS Symp Ser 406, Supercritical Fluid Science and Technology* (Ed. K.P. Johnston and J.M.L. Penninger)
- 16 Walker, D.R.B. and Koros, W.J. Transport characterization of a polypyrrolone for gas separations *J Membrane Sci* (1991) 55 99
- 17 Simha, R. and Boyer, R.F. General relation involving the glass transition temperature and coefficients of expansion of polymers *J Chem Phys* (1962) 37 1003
- 18 Hirose, T., Mizoguchi, K. and Kamiya, Y. Gas transport in poly(vinyl benzoate) *J Appl Polym Sci* (1985) 30 401