ELSEVIER

Polymer 42 (2001) 10021–10026

polymer

www.elsevier.com/locate/polymer

Pressure-dependent permeation of noble gases (He, Ne, Ar, Kr, Xe) through thin membranes of oriented polypropylene (OPP) studied by mass spectrometry.

Holger Nörenberg[a,*], V.M. Burlakov[a], H.-J. Kosmella[b], G.D.W. Smith[a], G.A.D. Briggs[a], T. Miyamoto[c], Y. Tsukahara[c]

[a]*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*
[b]*GKSS Geehsthacht, Außenstelle Teltow, Kantstr. 55, D-14513 Teltow, Germany*
[c]*Technical Research Institute, Toppan Printing Company, 4-2-3 Takanodai-Minami, Sugito, Saitama 345-8508, Japan*

Received 23 May 2001; received in revised form 19 July 2001; accepted 31 July 2001

Abstract

A mass spectrometric method has been used to study transmission of noble gases (He, Ne, Ar, Kr, Xe) through thin polymer membranes of OPP and PET. The transmission of gas originating from a confined volume in a gas cell through the membrane is measured by a mass spectrometer. Due to depletion of gas inside the gas cell, transmission decreases as a function of time, which is taken as a measure for permeation. For the smaller noble gases helium and neon gas transmission is found to be an exponential function of time indicating a pressure independent permeability for PET and OPP. For the permeation of heavier noble gases xenon, krypton and — to a lesser extent — argon through OPP a pressure dependent permeability was found. A model takes into account the higher solubility for bigger gas atoms as they have a higher probability to condense in cavities of the free volume of the polymer.

There is good agreement between experimental and calculated data. Sensitivity of the mass spectrometric method is discussed for argon isotopes ^{40}Ar, ^{38}Ar and ^{36}Ar and shows an instrumental detection limit of less than 0.1%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gas permeation; Mass spectrometer; Polymer membrane

1. Introduction

Polymer membranes are used as barrier films to prevent gas permeation (applications include food packaging, organic light emitting diodes, proton conductors in fuel cell) or to separate individual components of gas mixtures. In order to optimize barrier and selectivity properties, a much better understanding of gas permeation through polymer membranes is necessary. For such studies, noble gases as permeants offer the advantage of a range of atomic sizes while being chemically inert and having reduced interaction with the polymer. Only a few measurements have been published about Kr and Xe permeation through polymers so far [1–6]. In many systems (polymer and permeant gas) permeability is a pressure dependent quantity [7]. This is the case for krypton permeation through polypropylene (PP) too, where studies in the pressure range up to 100 bar [4] have shown that permeability is pressure dependent.

We have used a mass spectrometric method [8] to study the transmission of inert gases through membranes of oriented polypropylene (OPP) and polyethylene terepthalate (PET). Using a fixed volume of gas which depletes during permeation, this method offers the advantage of measuring pressure dependent permeation data. Permeability for neon and argon estimated with a mass spectroscopic method was found to be in good agreement with control experiments [8]. In this article we will focus on the pressure dependence of permeability at low gas pressures for permeation of noble gases through OPP and PET.

2. Experiments

There are a number of experimental methods to measure permeation through polymer membranes [9]. The mass spectrometric method used in this study has been described in detail elsewhere [8]. Fig. 1 shows the principle of

---

[*] Corresponding author. Tel.: +44-1865-273-735; fax: +44-1865-273-783.

E-mail address: holger.norenberg@materials.oxford.ac.uk (H. Nörenberg).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00560-2

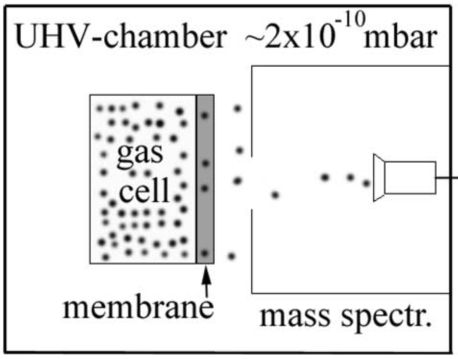

Fig. 1. Principle of measuring gas transmission through thin membranes with a mass spectrometer. A vessel (gas cell) is introduced into the UHV system facing a mass spectrometer, and the partial pressure is measured as function of time.

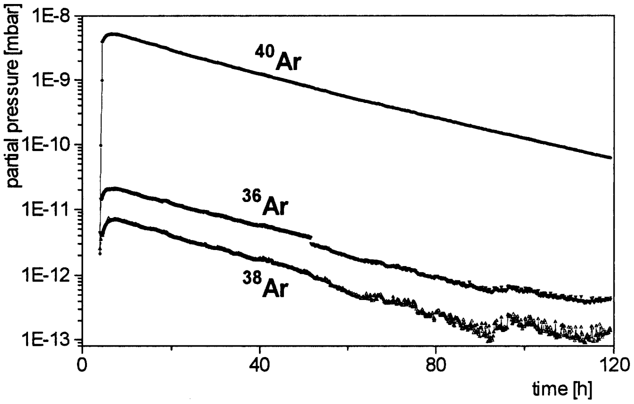

Fig. 2. Partial pressure as function of time for permeation of isotopes ^{40}Ar, ^{36}Ar and ^{38}Ar through OPP 20 μm thick.

measurement where a small container (gas cell) is filled with the gas of interest, covered with a polymer membrane, sealed and then introduced into a UHV system. After the gas cell has been positioned to face a mass spectrometer it records partial pressure as function of time, which is a decreasing function due to depletion of gas in the gas cell during permeation (Fig. 1). In a simple model the time constant and geometric parameters of the gas cell can be used to calculate permeability [8]. Prior to the experiment, the gas of interest was admitted to the vacuum chamber and the mass spectrometer was adjusted to maximize its reading and to reproduce the correct intensity ratios between different isotopes. For the experiments we used quadrupole mass spectrometer systems with channeltron detectors supplied by European Spectrometry Services (ESS).

The measured partial pressure vs time curves have been corrected against total pressure measured with an ionization gauge, taking into account sensitivity factors [10]. Due to limited accuracy in sample positioning partial pressure may vary between experiments. We will therefore focus on estimating time constants of partial pressure decay as a function of time as these quantities are independent of experimental geometry. Control experiments have been carried out on a GTR 30-XR device (Yanaco Inc.) which uses a chromatographic principle for gas detection [11], and with the pressure increase method using a Penning gauge (similar to [12]).

The sensitivity of the mass spectrometric method can be illustrated by studying gas transmission of isotopes. Fig. 2 shows the dependence of partial pressure on time for different isotopes of argon. The three naturally occurring isotopes ^{40}Ar, ^{36}Ar and ^{38}Ar have an abundance ratio of approximately 1600:6:1, which corresponds to 99.6, 0.34 and 0.06% [13]. In Fig. 2 even the less abundant isotopes can be clearly distinguished from the background. Experiments reproduce the abundance ratio to a good approximation (Fig. 2). Although the determination of a time constant from the less abundant isotopes ^{36}Ar and ^{38}Ar has a bigger error margin than ^{40}Ar (mainly due to noise and background), all three isotopes show a similar slope in logarithmic representation of partial pressure as function of time (Fig. 2). Hence, the mass spectrometric method is capable of measuring time constants of partial pressure decay of Ar-species which contribute much less than 0.1% to the total pressure.

PET and OPP (biaxially drawn) membranes were used for the permeation experiments because of the great practical importance of these materials [14]. At this stage of the investigation we have restricted the investigation to frequently used thicknesses of 20 μm for OPP and 12 μm for PET.

3. Results and discussion

A practical advantage of using noble gases for permeation experiments is the low background at their respective mass/charge values. This is an advantage because a low background leads to a better signal to noise ratio, and eliminates the need for background pressure correction and therefore permits a more accurate evaluation of the partial pressure as function of time. In the experiments, we actually study the transmission of gas through membranes of one particular thickness. When discussing the matter in more general terms we will use permeation instead of transmission.

3.1. Transmission of helium and neon through OPP and PET

Fig. 3 shows the dependence of mass spectrometrically estimated total pressure on time for permeation of different noble gases through OPP. For helium and neon the relationship between pressure measured by the mass spectrometer and time is exponential (Fig. 3) and a pressure-independent permeability K can be calculated according to: $K = \tau l$ with τ as pressure decay constant and l the length of the gas cell taken as a cylinder with cross section the same as the area of the membrane [8]. For permeation through OPP this concept

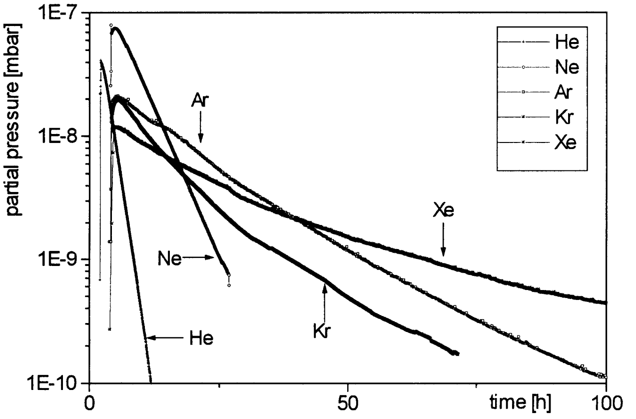

Fig. 3. Partial pressure as function of time for He, Ne, Ar, Kr and Xe permeation through OPP 20 μm thick.

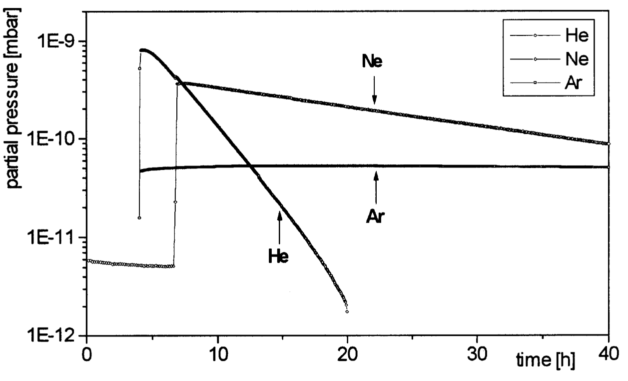

Fig. 4. Partial pressure as function of time for He, Ne and Ar permeation through PET 12 μm thick.

can be extended to include argon, although there is minor deviation from a single exponential behavior, which will be discussed in Section 3.2. Fig. 4 shows partial pressure vs time curves for transmission of He, Ne and Ar through PET. Helium and neon clearly show the exponential relationship.

Argon transmission through PET changes very slowly and therefore a quantitative study of gas transmission, which requires the measurement of change of this quantity is practically impossible. For the same reason transmission of Kr and Xe through PET is not amenable to study by this method. Table 1 compares the transmission coefficients obtained in our experiments with values from the literature. Given the different nature of the methods, the agreement is reasonable. Comparison of polymer samples is in general difficult because it is impossible to get identical samples due to structural fluctuations.

It is important to emphasize that the permeability is obtained from the decay of partial pressure which is a relative quantity and hence does not depend on the initial pressure inside the gas cell. Neither does permeability depend on the presence of other, non-interacting gases as we have shown for the permeation of air through OPP [8]. This concept is similar to radioactive decay where the decay constant (and half life) does not depend on the amount of the radioactive substance and the presence of other elements.

3.2. Transmission of argon, krypton and xenon through OPP

Fig. 3 shows the partial pressure vs time curve for transmission of krypton and xenon through OPP (the partial pressure for the relevant gas is the sum over the partial pressures of the individual isotopes, see Table 2). The curves shown in Fig. 3 for krypton and xenon (and to a lesser extent argon) do not obey the single exponential relationship found for the lighter noble gases helium and neon [8] which is in agreement with published data of krypton permeability through PP [4]. It means that for the heavier noble gases permeability is not a constant but rather a pressure dependent function. Permeation is generally considered to be determined by diffusion and sorption. As the bigger mass of heavy noble gases is unlikely to result in faster diffusion we will focus on solubility. Gas may be dissolved in the polymer matrix, for heavier noble gases we will consider the possibility of pore condensation. When gases enter small pores of nm-size, interaction between gas atoms and pore walls become important. This is known as pore condensation and may lead to a lower critical temperature with the critical point shift inversely proportional to the pore width [15,16]. It has been suggested that a deep molecular potential well is formed where molecules tend to be adsorbed [17]. The adsorption effects are much more pronounced for heavier gases such as krypton and xenon. When xenon is admitted to porous carbon (pore size ∽1 nm)

Table 1

Comparison between transmission rates measured by mass spectrometry (at 35°C) and control experiments (chromatographic method) and literature values, units: cm$^3_{STP}$/m^2/day/atm

		Mass spectrometer at 35°C	Control experiment at 35°C	Lit. [6]
OPP 20 μm	He	38,300	22,300	38,000[a]
OPP 20 μm	Ne	13,300	6700	–
OPP 20 μm	Ar	4100	2600	–
PET 12 μm	He	22,000	7800	7630[b]
PET 12 μm	Ne	2500	900	–
PET 12 μm	Ar	–	100	–

[a] (PP at 33°C).

Table 2
Selection of physical properties of noble gases

	He	Ne	Ar	Kr	Xe
Isotopes[a] (a.u.) (>0.1%)	4	20,21,22	36,40	78,80,82–84,86	128–132,134,136
Kinetic diameter[b] (nm) [19]	0.26	0.275	0.34	0.36	0.396
Critical temperature (K) [20]	5.2	44.4	150.8	209.4	289.7
Critical pressure (bar) [20]	2.3	27.6	48.7	55.0	58.4

[a] Isotopes with more than 0.1% natural abundance.

[b] Intermolecular distance of closest approach for two molecules colliding with zero kinetic energy.

an increased proportion of Xe-dimers and Xe-trimers was observed even at sub-atmospheric pressures [17]. For carbon micropores, pressures of up to 1000 bar have been reported for Xe [18]. Table 2 summarizes physical properties of noble gases. Krypton and xenon are more condensable than the lighter noble gases because of their rather high critical temperature.

Polymers such as OPP do not have pores similar to carbon as used in Ref. [18]. However, in the 'free volume' concept [21] a similar argument can be applied. Our samples consist of crystalline and amorphous regions. Crystalline regions are believed to be impermeable and not contributing to solubility. In the amorphous regions there is inefficient packing of chains, the excess volume is called 'free volume' and can be considered as pores or cavities. The free volume allows conformational changes. This means the size of a single cavity of the free volume is in the range of up to a few interatomic distances. Table 2 shows that the kinetic diameters of noble gas atoms are of the order of magnitude of the cavities. There are very few atoms required in a cavity to reach the critical pressure. This should be considered qualitatively only as this macroscopic concept cannot be easily transferred to consider few atoms in a cavity. The picture of cavities in polymers is also used in theoretical calculations to model gas diffusion [22,23]. In some respect, the concept presented here takes advantage of ideas from the dual-mode model developed for permeation through glassy polymers [7,24,25]. We note that the experiments were carried out close to the glass transition temperature of OPP which implies relatively slow changes of conformation and hence a longer lifetime of cavities formed.

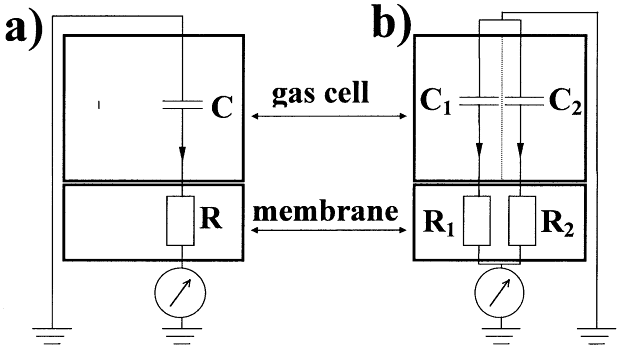

Fig. 5. Analogy between gas permeation and RC-circuit; (a) normal pathway, no condensation; (b) normal pathway through C_1 and R_1 and additional track through C_2 and R_2 which includes pore condensation.

Under sufficiently high gas pressure we expect condensation of Kr and Xe in cavities of OPP. This can be considered as opening an 'additional track' for gas permeation because of the higher amount of gas dissolved in the polymer. The condensation probability depends on the number of molecules entering a cavity per time and hence on the pressure inside the gas cell.

We have stated before that the slope of the partial pressure vs. time curves for gases that do not condense in cavities (He, Ne) does not explicitly depend on the initial pressure inside the gas cell [8] (the pressure in the gas cell, however, determines the position of the partial pressure vs. time curve with respect to the pressure axis). Components of mixtures permeate independently [8]. This allows us to consider the amount of gas using the 'additional track' separately from 'normal pathway' (without cavity condensation). Fig. 5(b) shows a 'gedankenexperiment' where the gas in the gas cell is divided by the dotted line into a part using the 'additional track' through R_2 and a part which permeates in a 'normal pathway' through the polymer R_1. Fig. 5(b) shows the corresponding RC-circuit where the two capacitors C_1 and C_2 correspond to the two gas volumes inside the gas cell and the two resistors R_1 and R_2 correspond to the 'normal pathway' and 'additional track' permeation pathways. After some time, when the initial response of the circuit is negligible, the total current or total gas permeation takes the form:

$$p(t) = A_1 \exp(-\tau_1 t) + A_2 \exp(-\tau_2 t) \qquad (1)$$

where p is the partial pressure, t the time and A_1, A_2, τ_1 and τ_2 are parameters. Fig. 6 shows a good agreement between experimental data and the double exponential fit for krypton and xenon permeation through OPP according to Eq. (1). Fit parameters are summarized in Table 3. Minor deviations of argon from a single exponential behavior (Fig. 3) can be explained by a second exponential function according to Eq. (1) too. It appears that values τ_2 given in Table 3 correspond to permeation through the 'additional track'.

This shows that a rather simple model can quantitatively account for pressure-dependent permeability. Fig. 5(a) represents the situation where there is no cavity condensation due to a low critical temperature as in the case of He and Ne. The ratio A_1/A_2 (Table 3) can be taken as measure

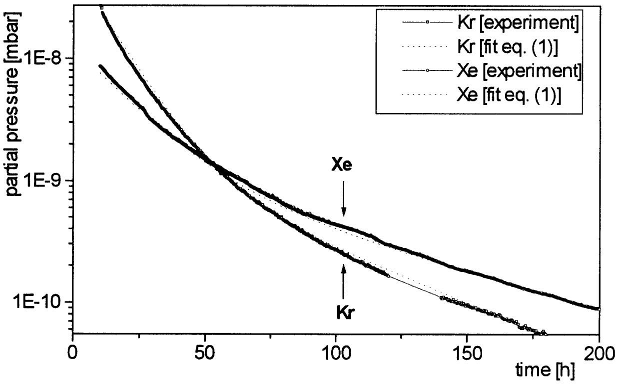

Fig. 6. Partial pressure as function of time for permeation of Kr and Xe through OPP 20 μm thick and curves fitted according to Eq. (1).

for the deviation of the curve shape from a single exponential behavior. For gases that are unlikely to condense we obtain a single exponential function with $A_1/A_2 = 0$ which is in agreement with our observations (see Figs. 3 and 4). The deviation of argon from single exponential behavior in the partial pressure vs time curve with an A_1/A_2 ratio of 0.07 is small but significant.

The consideration of cavity condensation as reason for pressure-dependent permeability is supported by previous experimental results. A pronounced pressure dependency of permeability for various gases through PP was shown for gases with a high critical temperature, such as Kr, N_2O and CO_2 whereas gases with a low critical temperature (H_2, He, Ne, N_2, O_2, Ar) did not show such a behavior [4].

Experimental observation points to the fact that the choice of polymer material has influence on the pressure dependence of permeability too. Between PP and LDPE, a much less pronounced such dependency was found for LDPE [4] which has an approximately 100°C lower glass transition temperature T_g. T_g itself does not determine the size of the cavities but may indirectly influence the life-time of cavities as in polymers with lower T_g backbone motion is more restricted and a higher life-time can be expected. The exact mechanism of cavity formation is not well understood and other processes such as localized secondary relaxations may play a role.

The tendency of gases with a higher critical temperature to have a higher permeability at increased pressures was observed in silicone rubber [26] and polydimethylsiloxane (PDMS) [27]. On the other hand side, a decreasing permeability through polysulfone was found for CO_2, which has a critical temperature comparable to Xe. Koros and Paul reported linear sorption isotherms for CO_2 in PET [24] above the glass transition temperature. These examples show, that for permeant gases other than noble gases permeability is influenced by chemical interaction between polymer and permeant too.

The time constant τ_1 given in Table 3 decreases from He to Xe with the exception of Kr where the value is higher than for argon and xenon. This behavior might be caused by the complex interplay between enhanced sorption for heavier noble gases [1] (they are more condensable, see Table 2), and slower diffusion [3]. These opposite contributions to permeability may be responsible for the high value for τ_1 in krypton. Whether this is indeed the case, requires further study to reduce error margins of the experiments. A similar effect, however, has been observed in studies of noble gas permeation through polyethylene where neon showed the lowest permeability among the noble gases [3]. Applying the simple relationship between time constant and transmission rate $K = \tau l$ [8] a time constant τ of 1.9 day^{-1} for krypton at about 1 bar feeding pressure at 35°C corresponds to a gas transmission rate of 4800 $\text{cm}^3_{\text{STP}}/\text{m}^2/\text{day/bar}$ which is in reasonable agreement with a value of 2090 $\text{cm}^3_{\text{STP}}/\text{m}^2/\text{day/bar}$ that we have estimated in a control experiment by the pressure increase method under similar conditions. This calculation relies on the assumption of equal pressures inside the gas cell and in the mass spectrometer. In the case of a condensable gas a significant amount of gas is dissolved in the membrane and the given gas transmission should be considered as a rough estimate only.

Table 3
Fitting parameters for partial pressure vs. time curves for Kr and Xe permeation through OPP 20 μm thick according to Eq. (1)

OPP 20 μm	τ_1 (day^{-1})	τ_2 (day^{-1})	A_1/A_2
Helium	15.3	–	0
Neon	5.3	–	0
Argon	1.6	0.24	0.007
Krypton	1.9	0.5	0.04
Xenon	1.4	0.35	0.08

Further study will be necessary to disentangle the complex relationship between the nature of the permeating gas, the structure and properties of the polymer, and other experimental conditions to come to a quantitative understanding of processes that determine permeation of a wide range of gases through polymers. The simple model introduced above neglects the case that gas atoms may jump between pathways. One possible way to get an improved model for permeation of heavy noble gases is to assume a pressure dependent activation energy [28].

4. Conclusions

We have investigated the pressure-dependent transmission of noble gases through membranes of OPP and PET with a mass spectrometer. Helium and neon show an exponential decay of partial pressure as a function of time for OPP and PET which indicates pressure-independent permeability. In extension to this model we suggest that permeation of heavier noble gases (krypton, xenon and — to a lesser extent — argon) through OPP is strongly influenced by interaction with cavities in the free volume of the polymer. In these cases permeability becomes pressure-dependent. A quantitative explanation in analogy with a simple electrical RC-circuit reproduces the experimental data in good approximation with a sum of two exponential functions. Gas transmission coefficients determined by mass spectrometer show reasonable agreement with those obtained by other methods. Mass spectrometry is very sensitive to small amounts of less abundant isotopes of noble gases.

Acknowledgements

This research was carried out in the Oxford Toppan Centre which is supported by the Toppan Printing Company Ltd, and is located in the Department of Materials at Oxford University.

References

[1] Lundstrom JE, Bearman RJ. J Polym Sci Polm Phys Ed 1974;12:97.
[2] Allen SM, Stannett V, Hopfenberg HB. Polymer 1981;22:912.
[3] Miyake H, Matsuyama M, Ashida K, Watanabe K. J Vac Sci Technol 1983;A1:447.
[4] Naito Y, Mizoguchi K, Terada K, Kamiya Y. J Polym Sci 1991;B29:457.
[5] Shelby JE. Handbook of gas diffusion in solids and melts. Materials Park: ASM International, 1996. p. 135.
[6] Pauly S. Permeability and Diffusion Data. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook, 4th ed. New York: Wiley, 1999. p. VI/435.
[7] Erb AJ, Paul DR. J Membr Sci 1981;8:11.
[8] Nörenberg H, Miyamoto T, Tsukahara Y, Smith GDW, Briggs GAD. Rev Sci Instrum 1999;70:2414.
[9] Nörenberg H, Deng C, Kosmella H-J, Henry BM, Miyamoto T, Tsukahara Y, Smith GDW, Briggs GAD. Soc Vac Coater, 43rd Ann Tech Conf Proc 2000;43:347.
[10] Holanda R. J Vac Sci Technol 1973;10:1133.
[11] Oishi M, Ishimuro Y. 18th Jpn Symp Thermophys Prop, Nara, Jpn 1997:121.
[12] Tanioka A, Fukushima N, Hasegawa K, Miyasaka K, Takahashi N. J Appl Polym Sci 1994;54:219.
[13] CRC handbook of chemistry and physics. 76th ed. Boca Raton: CRC Press, 1995.
[14] Karger-Kocsis J. Polypropylene: structure and morphology. London: Chapman & Hall, 1995.
[15] Thommes M, Findenegg GH. Langmuir 1994;10:4270.
[16] Machin WD. Langmuir 1994;10:1235.
[17] Aoshima A, Suzuki T, Kaneko K. Chem Phys Lett 1999;310:1.
[18] Kaneko K. Colloids Surf 1996;A109:319.
[19] Breck DW. Zeolite molecular sieves. New York: Wiley, 1974. p. 636.
[20] Reid RC, Prausnitz JM, Poling BE. The properties of gases and liquids. New York: McGraw Hill, 1987.
[21] Rogers CE. In: Comyn J, editor. Polymer permeability. London: Elsevier, 1985. p. 14.
[22] Müller-Plathe F. J Chem Phys 1992;96:3200.
[23] Gusev AA, Müller-Plathe F, van Gunsteren WF, Suter UW. Adv Polym Sci 1994;116:207.
[24] Koros WJ, Paul DR. J Polym Sci Polym Phys Ed 1978;16:1947.
[25] Sada E, Kumazawa H, Xu P, Nishigaki M. J Membr Sci 1988;37:165.
[26] Jordan SM, Koros WJ. J Polym Sci B Polym Phys 1990;28:795.
[27] Merkel TC, Bondar VI, Nagai K, Freeman BD, Pinnau I. J Polym Sci 2000;B38:415.
[28] Burlakov VM. In preparation.