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Diffusion of gases and vapors through methacrylates with oxyethylene units in the pendent chain

P. Tiemblo[a,*], F. García[b], J.M. García[b], C. García[a], E. Riande[a], J. Guzmán[b]

[a]Instituto de Ciencia y Tecnología de Polímeros, (CSIC), Calle Juan de la Cierva 3, 28006 Madrid, Spain
[b]Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain

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Abstract

The diffusion of He, Ar, O_2, N_2, CO_2, CH_4, CH_3CH_3 and CH_2CH_2 has been determined in three polymethacrylates with one, two and three oxyethylene units as side chains. For these three rubbery polymers we have used the acronyms PEEMA, PDEMA and PTEMA, respectively. The results have been compared to those of poly(ethyl methacrylate) on one hand, and on the other with previous results on methacrylates of varying length alkyl side chains. It has been found that the oxyethylene units side chains methacrylates show diffusion coefficients which are slightly lower than those methacrylates bearing alkyl side chain, when comparing polymers with the same number of atoms in the side chain. These diffusion data are put in relation to relevant structural features such as the glass transition temperature and the fractional free volume of both families of rubbery methacrylates.

Keywords: Poly(methacrylates); Free volume; Gas difussion

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1. Introduction

The major interest in gas separation polymeric membranes is usually devoted to developing materials with improved selectivity for given gases and vapor mixtures [1–5] These membranes are generally characterized by their high glass transition temperatures and, therefore, their gas transport properties at normal temperatures reflect the behavior of a material in non-equilibrium state. This is the origin of the well-known effect that preparation has on the end properties of glassy membranes as their structure is not determined only by the composition, but also by their 'history'. This characteristic is the basis of much of the membrane technology [6], and membrane preparation, processing and conditioning play a critical role on the final transport properties, what sometimes leads to inappropriate conclusions. In addition, being glasses in a non-equilibrium state, their structure is time-dependent and so are many properties of these materials, among which are certainly transport properties [7,8]. This second characteristic is, however, very often unimportant from practical view points for membranes are used at temperatures well under their glass transitions and therefore the time evolution of the structure is very slow.

On the other hand, rubbery membranes at room temperature, normally with very low selectivity, are very important to basic studies on gas transport properties because their transport properties can be considered as inherent to a material of a given chemical structure. Consequently, we believe that a more intensive research on the transport properties of polymers at temperatures over their glass transition should be carried out in order to acquire a deeper insight on the influence of the chemical structure on these properties. Acrylates and methacrylates with side chains are a very interesting family of rubbery polymers [9–13] on which in the past we performed gas transport studies. We studied a family of methacrylate copolymers with alkyl side chains of different lengths [14] and compared their properties to those reported by Mogri and Paul which studied diffusivities and permeabilities in acrylates of varying length alkyl side chain [11].

We studied in particular the transport of O_2, N_2, CO_2, CH_4, CH_3CH_3, CH_2CH_2 in several copolymers of ethyl methacrylate, hydroxypropyl methacrylate and dodecyl methacrylate. It was found that, as in the case of acrylates

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[*] Corresponding author. Tel.: +349-1-5622900; fax: +349-1-5644853.
E-mail address: ptiemblo@ictp.csic.es (P. Tiemblo).

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[11], as the side chain length increases so do the diffusion coefficient of gases. In fact, a very good correlation exists between the diffusion coefficient for the gases mentioned above and the average length of the side chain. It seemed that the local heterogeneities caused by the existence of side chains of different lengths did not affect the final value of the diffusion coefficient, and that the copolymer membrane behaved in the same way as a homopolymer of side chain length equal to the average.

In this work we continue studying the gas transport of methacrylic polymers with very low glass transition temperatures. In this case the side chain is not a long alkyl chain but it incorporates ether linkages, which are known to be very flexible. We have studied the transport of He, Ar, O_2, N_2, CO_2, CH_4, CH_3CH_3, CH_2CH_2, in the temperature range 5–45 °C in polymer network membranes prepared by polymerisation and crosslinking reactions of three different methacrylates that incorporate one, two or three oxyethylene units: 2-ethoxyethyl methacrylate (EEMA), (2-(2-ethoxyethoxy) ethyl methacrylate) (DEMA) and 2-[2-(2-ethoxyethoxy)ethoxy]ethyl methacrylate (TEMA). The properties of these will be compared with those reported for membranes of poly(ethyl methacrylate) [15], which because of its structure can be considered as the first member of this series of ether side chain methacrylates.

Another goal of the present work is to analyse the diffusion coefficients of the membranes according to the free volume theories, trying to establish a correlation between the gas properties and the molecular structure of the polymer membrane.

2. Experimental

2.1. Materials

The commercial monomers 2-ethoxyethyl methacrylate (EEMA) and 2-(2-ethoxyethoxy)ethyl methacrylate (DEMA) (Aldrich, 99%) and the crosslinker 1,2-ethanedioldimethacrylate (Aldrich, 98%) were purified by distillation under high vacuum. 2,2′-Azobisisobutyronitrile (AIBN) (Fluka, 98%) was recrystallized twice from methanol, and dried under high vacuum at room temperature. All other materials were commercially available and used as received unless otherwise indicated.

2.2. Synthesis of 2-[2-(2-ethoxyethoxy)ethoxy]ethyl methacrylate (TEMA)

This monomer was prepared by direct esterification of triethyleneglycolethylether with methacryloyl chloride by using the following procedure: 4.40 g (0.042 mol) of methacryloyl chloride dissolved in 20 ml of ethyl ether was added dropwise to a solution of 10 g (0.041 mol) of 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, 4.7 g (0.047 mol) of triethylamine in 50 ml of ether at 0 °C under nitrogen atmosphere. When the addition of methacryloyl chloride was completed, the mixture was heated with stirring at 25 °C overnight. The resulting unclear solution was filtered to remove the ammonium salt, and washed thoroughly with water. The ether layer was dried with anhydrous sodium sulfate and the solvent was removed by vacuum rotary distillation. The pale yellow liquid was twice vacuum distilled to render a dense colorless liquid. Yield: 60%; bp: 85–90 °C (1×10^{-4} mm Hg).

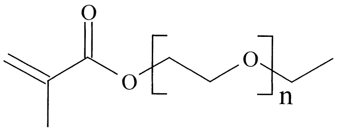
2.3. Preparation of the membranes

The membranes were prepared by radical polymerization of the monomers using 1 wt% of 1,2-ethanedioldimethacrylate as crosslinking agent and AIBN (1 wt%) as initiator. The nominal crosslinking ratio, i.e. the ratio between number of moles of the monomer to the crosslinking agent, was the same in all cases. The reactions were carried out in silanized glass moulds of 100 μm thickness in oxygen free atmosphere at 70 °C for 5 h. The networks thus prepared were extracted three times in dioxane for a period of time of 48 h. Finally, they were dried at room temperature for 1 week and the residual solvent eliminated under high vacuum. The general structure of the polymers appears in Scheme 1. According to the number of oxyethylene units in the side chain they have been named as PEEMA ($n = 1$), PDEMA ($n = 2$) and PTEMA ($n = 3$). The thickness of the membranes has ranged from 75 to 110 μm.

2.4. Thermal analysis

The glass transition temperature of the membranes were determined by differential scanning calorimetry using a Perkin–Elmer DSC-7 calorimeter. The measurements were carried out between −80 and 100 °C under nitrogen atmosphere at a heating rate of 10 °C min^{-1} and quenched with a cooling rate of 200 °C min^{-1}. Probes were little fragments of film samples put into a covered 20 μl aluminium pans. The T_g values reported were taken from the second runs and correspond to the onset of the DSC curves measured from the extension of the pre- and post transition baseline. In Table 1 the values of the three samples are reported.

Thermal analysis has also been used to check that no detectable crystallinity is present in these samples.



Scheme 1. General structure of the methacrylates with oxyethylene units as side chain. The polymer with $n = 1$ has been called PEEMA, $n = 2$ PDEMA and $n = 3$ PTEMA.

Table 1
Characterization of the samples

Sample	T_g (K)	ρ (g cm^{-3})
PEMA	334	1.124
PEEMA	257	1.060
PDEMA	229	1.068
PTEMA	218	1.075

2.5. Density determination

The density of membranes derived from EEMA and DEMA was accomplished with a 5 ml Weld pycnometer device at 25 °C. Proper membrane of 200 mg was introduced in the dried pycnometer, and the solvent added to the device. The density was obtained from the different weights of pure solvent and the solvent–membrane system. The solvent chosen did not swell membranes, and it was water for membranes of EEMA and DEMA and hexane for the membrane derived from TEMA.

This density values (Table 1) were used to estimate the fractional free volume (FFV) at 25 °C by applying $\mathrm{FFV} = (V - 1.3V_\mathrm{w})/V$ where V is the polymer specific volume, and V_w is the specific Van der Waals volume, which was estimated by using the HYPERCHEM computer program, version 5.01.

3. Permeation measurements

A lab made permeator has been used that consists of a gas cell in the middle of which the polymer membrane is placed. This membrane separates the upstream and downstream chambers. For the simplified equations relating the gas flow through the membrane to the transport coefficients to be valid, the downstream pressure has to be kept very low, negligible as compared to the upstream. This is accomplished by thorough evacuation of the dowstream, prior to any measurement, by means of a Edwards turbomolecular pump. At the low pressure side, a MKS Baratron type 627B absolute pressure transducer measures the pressure increase, while at the upstream a Gometrics pressure detector is used to control the gas pressure at which the experiment is performed. The Baratron 627B can be used in the pressure range 1–10^{-4} Torr. The Baratron is connected via a MKS power supply/readout unit to the PC, which records the pressure increase at given time intervals. The whole set-up is temperature controlled in the range 5–80 °C by means of a water bath.

Prior to any measurement, vacuum is kept overnight in order to remove any residual solvent from the membrane and to attain a downstream pressure as low as possible. Before any permeation experiment is performed, a measurement of the pressure increase due to imperfect vacuum isolation of the downstream chamber is recorded. This blank experiment is then subtracted from the permeation experiment performed immediately afterwards in order to calculate the gas transport coefficients from the corrected pressure curves. In that way the pressure increase is related solely to the gas diffusing across the membrane.

The permeability and diffusivity coefficients have been calculated from the curves measuring the pressure increase at the downstream. Eq. (1), derived from the integration of Fick's laws relates the amount of diffusant traversing the membrane to the thickness of the membrane l, to the concentration of diffusant at the upstream side of the membrane C_1 and to the diffusion coefficient D. In fact, only four terms of this summatory are enough for correct fitting of our pressure vs. time curves.

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) \qquad (1)$$

The diffusion coefficient is directly obtained from the fitting and the solubility parameter is directly proportional to C_1. The permeability P is obtained as $SD = P$.

3.1. Estimation of the penetrant molecular diameter

The size of the gas molecules has been estimated from viscosity data, as these data are readily available and provide a simple and straightforward way of obtaining an estimation of the molecular size for many gases and vapors. Making use of the available viscosity [16] data and of the equation relating viscosity to molecular weight and molecular diameter [17] from the kinetic theory of gases, an estimation of the molecular diameter can be done:

$$\eta = \frac{m}{3\sqrt{2}(\pi d^2)}\sqrt{\frac{8kT}{\pi m}} \qquad (2)$$

where η stands for viscosity, m stands for molecular weight and d stands for molecular diameter. As reported in a previous work [14], the agreement between kinetic diameter and the molecular diameter calculated from viscosity data is very good.

4. Results

The transport properties of these three oxyethylene side chain methacrylates have been measured in the temperature range 0–50 °C. Eight permanent gases and vapours have been studied: He, Ar, O_2, N_2, CO_2, CH_4, CH_3CH_3 and CH_2CH_2. In the following sections the results on the temperature dependence of the transport of these gases in the three polymers and a comparison between the diffusion data for these methacrylates and other related polymers are detailed.

4.1. Diffusivity, solubility and permeability in PEEMA, PDEMA and PTEMA in the range 0–50 °C

Tables 2 and 3 show the values of the diffusion and permeability data, respectively, obtained in this work at 35 °C and 1 bar; in Fig. 1 the temperature variation of diffusivity in some selected gases for the three methacrylates is shown. For all gases the diffusion coefficient increases in the order PEEMA < PDEMA < PTEMA. This is an expected result, as the length of the side chain increases the flexibility of the polymer, lowering its T_g (Table 1) and thus increasing the values of the diffusion coefficients of all gases. For comparison, data from the literature on poly(ethyl methacrylate) [15] has been included. As a matter of fact we have considered PEMA as the first member of a series of polymethacrylates with side chain of structure $(OCH_2CH_2)_nOCH_2CH_3$. For PEMA $n = 0$, PEEMA $n = 1$, PDEMA $n = 2$ and PTEMA $n = 3$. While PEMA is a glassy polymer at room temperature, the other three are rubbery. This is reflected in the diffusion coefficients, as shown in Fig. 2, where the variation of diffusion as the number of atoms in the side chain increases is depicted. Not all gases increase their diffusion coefficients in the same way: oxygen and carbon dioxide increase strongly as the T_g of the membrane decreases; argon and nitrogen increase uniformly as the number of atoms in the side chain increases, and finally the diffusion coefficient of the bulkier gases, methane, ethane and ethylene, increase strongly as T_g decreases. The way in which the physical and chemical structural changes affects each gas depends on its size and shape and on the way in which the existence of oxygen atoms in the side chain affects the interactions of the gas with the polymer matrix. It is expectable that very bulky gases which most probably have extremely low diffusion coefficients in glassy PEMA, will suffer strong increases in their diffusion coefficients as the polymer matrix becomes flexible. On the other hand, the uniform and gentle increase for Ar and N_2, which are of medium size and are not expected to interact very differently with oxygen than with carbon seems reasonable. The origin of the strong increase in diffusion for O_2 and CO_2 probably lies in the length increase of the side chain. In this connection, other authors [18] have found that interacting gases such as CO_2 may have their mobility hindered in highly polar matrixes because of the existence of specific interactions between the gas and the polymer. If this were the case, then as the concentration of carbonyl atoms in the matrix decreases (on going from PEMA to PTEMA), the diffusivity of CO_2 should be enhanced compared for example to N_2. In fact, in Fig. 1 it can be seen that while in PTEMA the diffusivity of nitrogen is in all the temperature range lower than that of CO_2, the diffusion coefficients for both gases are very similar in PDEMA, and finally CO_2 diffuses more slowly than N_2 in PEEMA. Solubility selectivity at 25 °C of those two gases in the three polymers is $\alpha_{PEEMA}(CO_2/N_2) = 49$, $\alpha_{PDEMA}(CO_2/N_2) = 44$ and $\alpha_{PTEMA}(CO_2/N_2) = 27$, a trend which supports the larger interaction of CO_2 in the methacrylates with larger concentration of carbonyl groups.

Table 2
Diffusion ($cm^2\,s^{-1} \times 10^7$) at 35 °C and 1 bar

	O_2	Ar	N_2	CO_2	CH_4	$CH_2{=}CH_2$	CH_3CH_3
PEMA	1.60	0.40	0.40	0.53	–	–	–
PEEMA	2.00	–	1.10	0.82	0.42	0.20	0.10
PDEMA	3.80	3.00	2.70	2.50	1.60	1.00	0.75
PTEMA	14.00	6.00	5.70	10.80	4.40	3.50	3.70
PEO [23][a]	14.40	–	12.00	9.10	6.90	–	–

[a] At 25 °C.

Table 3
Permeability (barrer) at 35 °C and 1 bar

	O_2	Ar	N_2	CO_2	CH_4	$CH_2{=}CH_2$	CH_3CH_3
PEEMA	1.45	–	0.385	8.56	1.23	2.8	1.79
PDEMA	11.4	8.7	3.6	133	11.4	38.5	21.7
PTEMA	3.9	5.2	2	74.4	4.8	16.7	6.5

Solubility coefficients have also been obtained for all the transport experiments, and in Fig. 3 they appear represented as a function of the critical temperature of the gases in PEEMA, PDEMA and PTEMA. This figure shows a roughly linear relationship between the critical temperature of each gas and the logarithm of solubility, and though the scatter of the data is somewhat important, no large deviations from linearity are found, indicating the absence of strong specific interactions.

4.2. Comparison with other methacrylates

In Fig. 4 the diffusion coefficients of CO_2 and CH_4 are represented as a function of the number of atoms of the alkyl side chain and the oxyethylene side chain in methacrylates

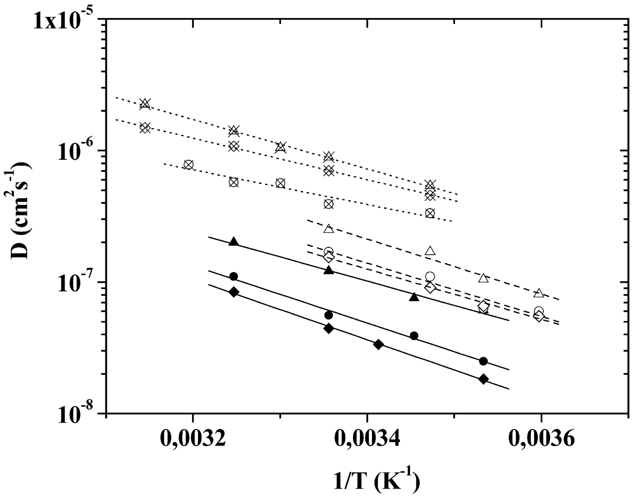


Fig. 1. Diffusion coefficients of oxygen (triangle), carbon dioxide (diamond) and nitrogen (circle) in PEEMA (solid), PDEMA (open) and PTEMA (cross-centered), as represented in Arrhenius coordinates.

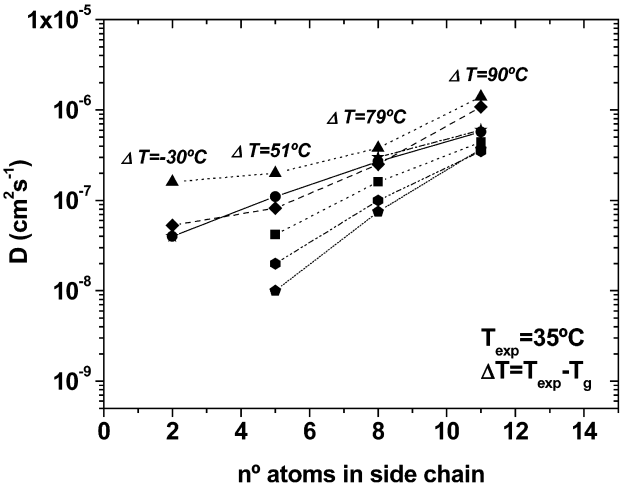


Fig. 2. Diffusion coefficients at 35 °C as a function of the number of atoms of the side chain. Oxygen (▲), methane (■), carbon dioxide (◆), nitrogen (●), ethane (⬟) and ethylene (⬢).

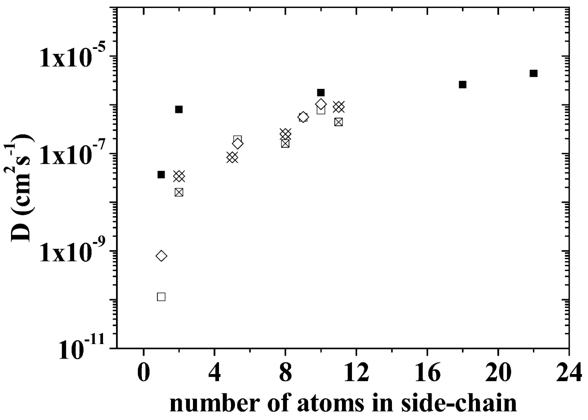


Fig. 4. Diffusion coefficients at 35 °C for methane (square) and carbon dioxide (diamond) as a function of the number of atoms of the side chain for ether side chain methacrylates (cross-centered), compared to other acrylates (solid) and methacrylates (open).

and in acrylates. The first member of the series is poly(methyl methacrylate), which is glassy and has very low diffusion coefficients. The second member is PEMA, which still is a glassy polymer at room temperature. As shown in the graph, there is an almost exponential increase in diffusion coefficients when more atoms are added in the side chain, irrespective of whether they are ether or carbon–carbon linkages. Methacrylates with oxyethylene side chains tend to have lower diffusion coefficients and there is a higher discrimination between methane and carbon dioxide. As compared to acrylates, the increase in diffusion coefficient is more progressive, for acrylates reach an almost constant value over three atoms in the side chain, i.e. over propyl acrylate. Fig. 5 shows the variation of T_g as a function of the number of atoms in the side chain for the acrylates and methacrylates which appear in Fig. 4. Acrylates have lower T_g for the same side chain length, though the difference tends to level off as the side chain becomes longer. Ether or alkyl side chain methacrylates have very similar T_g for the same side chain length.

In fact, though comparison with fractional free volume is very frequent, for rubbery polymers a very good correlation also holds between T_g and diffusion coefficient, as shown in Fig. 6. In this figure, diffusion data on carbon dioxide are compared to the T_g for a set of rubbery polymers. There seem to exist two correlations, one which holds for siloxanes and at higher T_g for acrylates and methacrylates with alkyl side chain, and another for the rest of polymers. For a given T_g, siloxanes and (meth)acrylates show diffusion coefficients which are about an order of magnitude higher than the other rubbery polymers. Diffusivity and T_g have in common that they both depend on the flexibility of the chain, i.e. as the flexibility increases, diffusivity increases and glass transition temperature diminishes. Both properties depend also on the fractional free volume in the polymer, so that when this free volume increases, diffusivity does so, while T_g decreases. A possible interpretation of the data in Fig. 6 is that the polymers in which diffusivity is higher for a given T_g have higher

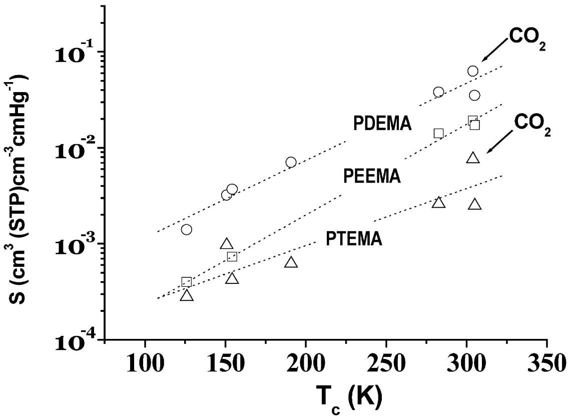


Fig. 3. Solubility coefficients at 35 °C of the measured gases as a function of critical temperature in PEEMA (□), PDEMA (○) and PTEMA (△).

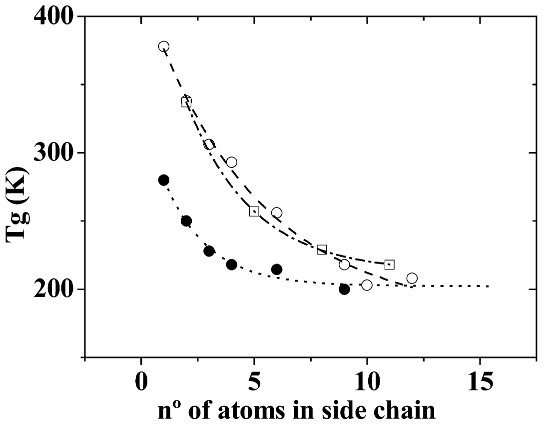


Fig. 5. Glass transition temperature of methacrylates and acrylates as a function of the side chain length. Ether side chain methacrylates (□), alkyl side chain methacrylates (○) and alkyl side chain acrylates (●).

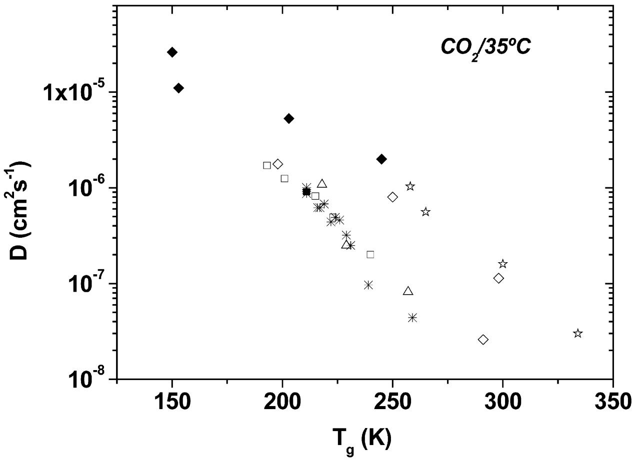


Fig. 6. Diffusion coefficient of CO$_2$ as a function of the T_g. Alkyl side chain methacrylates (☆), ether side chain methacrylates (△). Data on alkyl acrylates [11,24] (◇), ciclohexylacrylate [25] (◇), rubbers [26] (□). PEO/methacrylates [27] (✳), PEO (■) and silicone rubbers [28] (◆) have been taken from the literature.

fractional free volume, if we assume that the dependence on fractional free volume is stronger for diffusivity than for T_g. Then, free volume is more available in siloxanes and in the alkyl side chain (meth)acrylic polymers than in the rest.

4.3. Estimation of the fractional free volume at the glass transition from the temperature dependence of the diffusion coefficients

We have estimated the fractional free volume at the glass transition making use of data on the variation of the diffusion coefficients with temperature. This is done by direct application of the Doolittle equation and the Stokes–Einstein equation [19]. The former is an empirical relationship between the friction coefficient χ and the fractional free volume ϕ of the polymer:

$$\chi = A \exp\frac{B}{\phi} \tag{3}$$

where A and B are independent of temperature. A relation between the friction coefficient and the diffusion coefficient D is given by the Stokes–Einstein equation:

$$\chi = \frac{RT}{D} \tag{4}$$

The combination of Eqs. (3) and (4) allows to obtain the variation of the diffusion coefficient as a function of the fractional free volume:

$$\frac{D}{RT} = A^{-1} \exp\frac{-B}{\phi} \tag{5}$$

Parameter B is related to the volume of the penetrant and the free volume in the system. By assuming that ϕ is a linear function of temperature, $\phi = \alpha_f(T - T_\infty)$, where $\alpha_f = (1/V)(\partial V/\partial T)_p$, the Vogel–Fulcher equation for a diffusion process is obtained:

$$\frac{D}{RT} = D_0 \exp\left(\frac{m}{T - T_\infty}\right) \tag{6}$$

where T_∞ is the Kauzmann temperature, which is about 50 °C under the glass transition, and m is the slope of the Vogel–Fulcher equation. In PEMA, PEEMA and PDEMA, where the diffusion of argon, oxygen, nitrogen, carbon dioxide, methane, ethane and ethylene has been measured at five temperatures above T_g, Eq. (6) has been applied. A comparison of Eqs. (5) and (6) shows that at the glass transition temperature $m/(T_g - T_\infty) = B/\phi_g$ where ϕ_g is the fractional free volume at T_g. The ratio B/ϕ_g has been represented as a function of the gas size for oxyethylenic side chain methacrylates presented in this work (PEEMA, PDEMA and PTEMA) and for the alkylic side chain methacrylates CP2 and CP3, which are, respectively, copolymers of dodecyl methacrylate (DMA) and hydroxypropyl methacrylate (HPMA) (CP2) and docedyl methacrylate and ethyl methacrylate (CP3). The composition of these copolymers appears in Table 4. Figs. 7 and 8 show B/ϕ_g for these methacrylates. In Table 5, the values of ϕ_g/B have been collected. Data for PTEMA have not been included as dispersion for bulky gases was somewhat large. As shown in Table 5 and Figs. 7 and 8, the B/ϕ_g values calculated from diffusion data for our methacrylates are well above the value about 0.025 obtained for ϕ_g from mechanical or dielectrical properties [20] on similar alkyl side chain methacrylates. Moreover, the B/ϕ_g values calculated from diffusion data are dependent on the gas size, so that the larger the gas, the higher the ratio B/ϕ_g. The dependence of ϕ_g on the gas size is strong up to methane, and then tends to level off. If ϕ_g is assumed to be 0.025, then the variation of B with the gas size can be commented. According to the free-volume theories, $B = \gamma v^*/v_m$, where γ accounts for the overlap in free volume and varies from 0.5 to 1, v^* is the minimum critical volume needed to accommodate a diffusing molecule and v_m is the average free volume. As both v_m and γ must be the same for a given material at a given temperature, the variations in B shown in Table 5 account, according to the free volume theories, for the difference in the minimum critical volume necessary to accommodate each gas; it is very reasonable, then, that this should increase as the gas size does so.

Fig. 8 shows that the ratio B/ϕ_g increases in the order PEMA < PEEMA < PDEMA; comparison with the previous data depicted in Fig. 7 shows that copolymer CP2 lies in between PEMA and PEEMA, while PDEMA is far over.

Table 4
Molar composition of copolymers CP2 and CP3

Sample	DMA	HPMA	EMA	DEGDMA	T_g (°C)
CP2	0.655	0.326	–	0.021	−8
CP3	0.740	–	0.180	0.080	−15

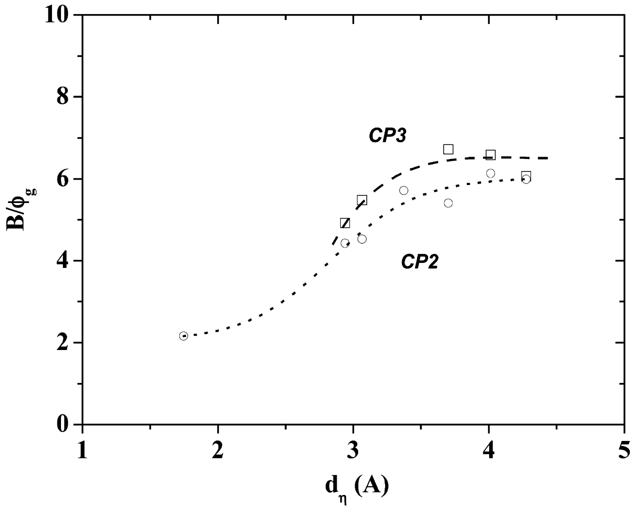


Fig. 7. B/ϕ_g as a function of the viscous gas diameter for CP2 and CP3.

CP3 is intermediate between CP2 and PEEMA. There seems to be an inverse correlation between T_g and ϕ_g/B; i.e. the higher the glass transition, the lower the value of ratio B/ϕ_g.

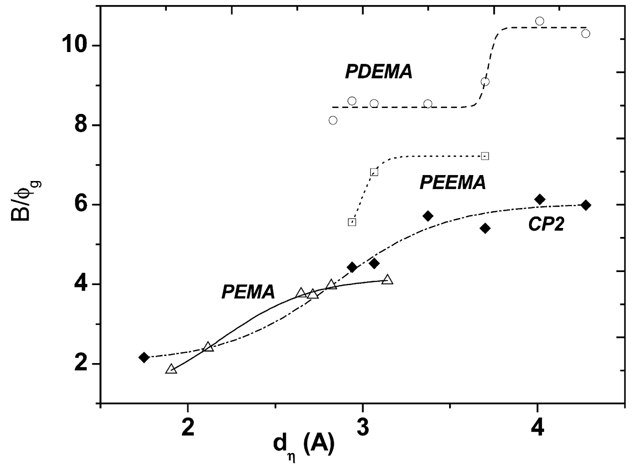


Fig. 8. B/ϕ_g as a function of the viscous gas diameter for the ether side chain methacrylates.

Table 5

ϕ_g/B for CP2, CP3, PEMA, PEEMA and PDEMA

Gas	ϕ_g/B				
	PEMA	CP2	CP3	PEEMA	PDEMA
He	0.595	0.460		–	–
Ar	0.302	–		–	0.123
O_2	0.305	0.230	0.203	0.180	0.116
N_2	0.281	0.220	0.182	0.147	0.117
CO_2	0.270	0.180	0.149	0.138	0.110
CH_4		0.175	–	–	0.117
CH_3CH_3		0.167	0.165	–	0.097
$CH_2{=}CH_2$	–	0.162	0.152	–	0.094

In this connection, it is interesting to bear in mind the work by Matsuoka [21,22] on free volume and cooperative relaxation. In these works a temperature T^* is defined, which is the same for all polymers, and at which conformers are able to relax individually; at that temperature dynamics are those of independent units, with exponential regime governing relaxations. As the temperature is lowered, a crossover to cooperative dynamics takes place and conformers are no longer able to relax individually but must relax together with their neighbors in domains which increase in size, z, on decreasing temperature. At $T = T^*$ $z = 1$, while as temperature decreases, z increases and it tends to infinity near the Kauzmann temperature. As the temperature approaches the Kauzmannn temperature at about 50 K under the glass transition, the 'Doolittle free volume' extrapolates to zero, while this does not happen with the real free volume, which would vanish at 0 K. The Doolittle free volume is described by [22]:

$$\ln \tau = \ln \tau_g + \frac{1}{\alpha_f(T - T_0)} - \frac{1}{\alpha_f(T_g - T_0)} \tag{7}$$

where τ is the relaxation time, T_0 is the Kauzmann temperature and α_f is the thermal expansion of the free volume fraction, $f = (V - V_0)/V$, and V_0 is the occupied volume at T_0. The following relationship is proposed:

$$\frac{\Delta\alpha}{\alpha_f} = \frac{T^* - T_0}{T^*} \tag{8}$$

where $\Delta\alpha$ is the difference in thermal expansion coefficient between the glass and the liquid, and α_f is the thermal expansion coefficient of the fractional free volume [22]. As the glass transition temperature decreases both $\Delta\alpha$ and α_f tend to be more similar, while the opposite is true as the glass transition increases. As the ratio $(T^* - T_0)/T^*$ is always smaller than unity then $\Delta\alpha$ is always smaller than α_f. An implication of Eq. (8) is, as explained by the author, that the amount of free volume trapped at T_g is greater for a glass vitrified at a higher temperature.

In fact, this is what is seen if comparing the T_g of each of the systems shown in Figs. 7 and 8 (Table 6) with the actual values of the ratio B/ϕ_g, for a given gas, what is shown in Fig. 9 for oxygen and carbon dioxide. Fig. 9 shows a roughly linear correlation between T_g and ϕ_g/B for oxygen, nitrogen and carbon dioxide, and though the ϕ_g/B values are different for each of the gases, as the glass transition temperature of the sample is lowered ϕ_g/B tends to be become independent of the gas. Unfortunately we do not

Table 6

Glass transition temperatures and fractional free volume at 25 °C as obtained from density measurements (FFV) for the polymers compared in Figs. 7 and 8 and PTEMA

Sample	T_g (K)	FFV
PEMA	338	0.155
CP2	300	0.187
CP3	258	0.190
PEEMA	257	0.201
PDEMA	229	0.195
PTEMA	218	0.191

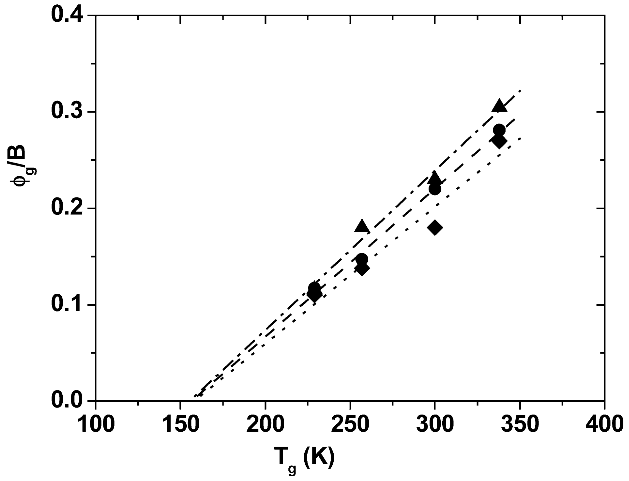


Fig. 9. ϕ_g/B as a function of T_g for carbon dioxide (◆), nitrogen (●) and oxygen (▲).

have data enough to perform the same comparison for other gases of different sizes so that further interpretation becomes speculative.

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