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Transport of gases and vapors in methacrylic copolymers of varying side chain length

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Abstract

The gas transport properties of copolymers of dodecyl methacrylate with ethyl methacrylate and hydroxypropyl methacrylate have been studied. The diffusion, solubility and permeability of oxygen, nitrogen, carbon dioxide, methane, ethane and ethylene have been measured in the temperature range 0–50 °C, and activation energies and heats of solution have been obtained. A comparison with the data available in the literature on acrylates and other methacrylates of varying aliphatic side chain length has been performed. The diffusion coefficient of gases increases with the side chain length in a way similar to that found for homologous acrylates. A representation of log(D) as a function of the inverse of the fractional free volume shows that all acrylates and methacrylates of lineal alkyl side chain fall on the same straight line.

Keywords: Gas transport; Methacrylates; Diffusion

1. Introduction

Along the last decade, our knowledge on the actual values of diffusion through some polymer families, mostly those of industrial interest, as polyimides or polysulfones, has been largely increased [1] and efforts to obtain structure-property correlations by means of systematic studies in polymers have been performed [2]. The compromise between chain stiffness and free volume in these families, which leads to permeable and selective membranes, has been well established [2–5]. Aromatic groups introducing rigidity in the backbone, bulky substituents separating chains and the introduction of hexafluoroisopropylidene are among the well-known almost classical groups of tailor-made high-performance gas separation membranes.

However, a look at the latest literature and reviews [1,2,6] shows that the actual data on many other polymeric systems has changed little, and scarce systematic work has been performed on many polymeric families. Until very recently, for example among methacrylic and acrylic polymers scarce data were available [1,2,6], and most work related to poly(methyl methacrylate) [1,7] and poly(ethyl methacrylate) [8,9] even though methacrylic systems, especially poly(HEMA) [10,11], are extensively used for instance in biocompatible materials and contact lenses, an area in which transport properties are of extreme importance. Some systematic work has lately appeared showing the effect of the alkyl side chain length [12,13] of acrylates on their gas transport properties. The diffusion coefficients of carbon dioxide and methane increase progressively as the alkyl side chain becomes longer, and more so with the inclusion of the first methylene groups.

In this work we present the diffusion, solubility and permeability data of some permanent gases and vapors in two copolymer of dodecyl methacrylate (DMA) with hydroxypropyl methacrylate (HPMA) and ethyl methacrylate (EMA). The transport data of several permanent gases and vapors in these copolymers are presented in the temperature range 0–50 °C, and compared to previously reported data on acrylates and methacrylates [1,12,13]. This has been done with the aim of correlating the transport parameters with defined structural characteristics (glass transition temperature, fractional free volume) of the polymeric family.

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2. Experimental

2.1. Materials

Photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (Irg651) was generously given by Ciba SC and thermal initiator 2,2′-azo-bis-isobutironitrilo (AIBN) from Scharlau. Both were used as received.

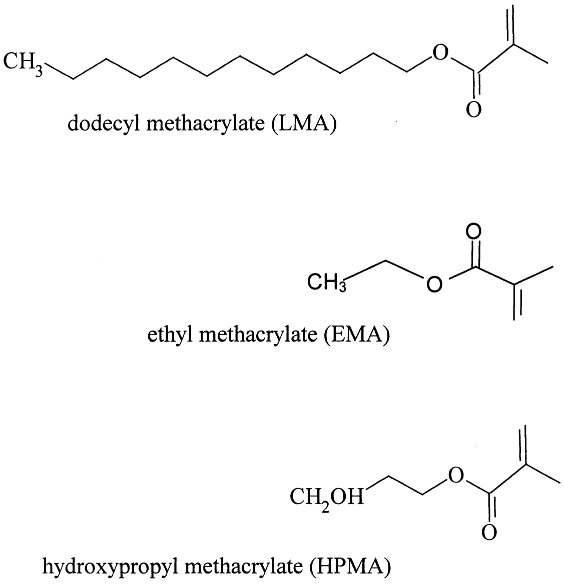
Monomers: hydroxypropyl methacrylate (HPMA), dodecyl methacrylate (DMA), ethyl methacrylate (EMA), diethylenglycol dimethacrylate (DEGDMA) from Aldrich were all previously purified by distillation (Scheme 1).

The transport properties have been tested using seven gases supplied by Praxair. They have been nitrogen and oxygen purity 6.0, carbon dioxide purity 4.8, methane purity 5.0, ethane and ethylene purity 4.0.

2.2. Films preparation and curing conditions

Samples containing photoinitiator (1 wt%) and the mixture of monomers were prepared by stirring all components until homogeneous solutions were obtained. These samples were (previously) degassified in a vacuum line prior to a pre-polymerization process by exposure of UV–vis light for 5 min in order to reach an appropriate viscosity to facilitate its manipulation. The irradiation source consists of an ATLAS SUNTEST XSL equipment, provided with Xenon lamps with a power output of 550 W/m^2 that emits polychromatic light.

Once the formulations were pre-polymerized, they were applied as a uniform layer coating between two low-density polyethylene (LDPE) films and using different spacers which permit to obtain membranes of controlled thickness. The role of the LDPE films was also to prevent oxygen diffusion from the atmosphere into the sample during the irradiation at room temperature. In addition to these PE films, two glasses filters were used to avoid scratching. Samples were then irradiated again with the same light source for 15 min, time which allows the system to polymerize until limited conversion was obtained. After irradiation, films were selected with tack-free characteristics and without defects on the surfaces. The residual monomer was removed by immersion in hexane and vacuum drying until constant weight.



Scheme 1. Chemical structure of the monomers.

The fractional free volume (FFV) was obtained by applying FFV $= (V - 1.3V_w)/V$, where V is the polymer specific volume, and V_w is the specific Van der Waals volume.

2.3. Thermal analysis

The glass transition temperature of the membranes were determined by differential scanning calorimetry using a Shimadzu DS50 calorimeter. The measurements were carried out between 50 and 150 °C under nitrogen atmosphere at a heating rate of 5 °C/min and quenched with a cooling rate of 200 °C/min. 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 midpoint of the DSC curves measured from the extension of the pre- and post-transition baseline. The composition and glass transition temperature of the four copolymers appear in Table 1. The homopolymer T_g are—65 °C for DMA, 76 °C for HPMA and 65 °C for EMA; then, all copolymer T_gs are higher than the values calculated from Fox equation. This is due to crosslinking, and, as shown in Table 1 as the crosslinking degree increases so does the deviation from the calculated values.

2.4. 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 downstream, prior to any measurement, by means of a Edwards turbomolecular pump. At the low pressure side, a MKS Baratron type 627B

Table 1
Composition (molar fraction) and T_g of the four copolymers

Sample	DMA	HPMA	EMA	DEGDMA	T_g (°C)
CP1a	0.360	0.627	–	0.013	–
CP1b	0.356	0.625	–	0.025	27
CP2	0.655	0.326	–	0.021	−8
CP3	0.740	–	0.180	0.080	−15

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 20–80 °C by means of a water bath.

Prior to any measurement, vacuum is kept overnight in order to remove any rests of 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. Pressure data are recorded every 5 s.

Calculation of the transport coefficients has been performed from the straight line characteristic of the steady state of gas diffusion through the membranes and from the whole pressure curve, fitted with Eq. (1)

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^\infty \frac{(-1)}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) \qquad (1)$$

where Q_t is the amount of diffusant traversing the membrane, l is the membrane's thickness, C_1 is the concentration of diffusant at the upstream side of the membrane and D is the diffusion coefficient. In the present work this fitting has been done essentially to check that the rise in pressure at the downstream chamber corresponds to Fickian diffusion across the membrane. It has been estimated that errors in the diffusion coefficient are in average 10% and in solubility 20%.

3. Results and discussion

The transport of oxygen, nitrogen, carbon dioxide, methane, ethane and ethylene has been measured at 1 bar in the four copolymers in the temperature range 0–50 °C.

3.1. Effect of crosslinking degree

To check the effect of slight modification of the crosslinking degree on the membrane's performance, copolymer 1 was crosslinked with two DEGDMA amounts, 1% (CP1a) and 2% (CP1b). Fig. 1 shows the diffusion coefficients of oxygen, methane, ethylene and ethane in the range 0–40 °C in Arrhenius coordinates. No strong effect of crosslinking could be seen, though copolymer CP1b, which is more crosslinked tends to have lower diffusion coefficients and slightly stronger slopes in the Arrhenius representation, as expected in a system with a higher crosslinking degree [14–16]. No significant changes were seen in the solubility coefficient either.

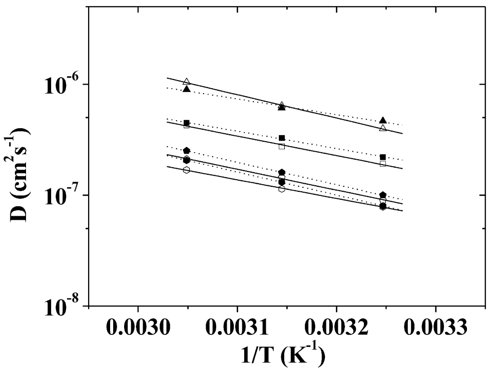


Fig. 1. Diffusion coefficient of some selected gases represented in Arrhenius coordinates for copolymers CP1a (solid symbols) and CP1b (open symbols). Oxygen (▲), methane (■), ethane (⬟) and ethylene (●).

It is important to know up to what point crosslinking affects transport coefficients in these membranes, as some of them must be crosslinked in order to obtain materials with adequate mechanical properties, specially as the content of dodecyl methacrylate increases. As shown in Table 1, copolymer CP3 is crosslinked with a 0.08 molar fraction of DEGDMA in order to enable its handling. Apparently in our copolymers slight differences in crosslinking degree do not strongly affect the transport data. Hereafter, the data of CP1b will be used to compare with the other two copolymers.

3.2. Transport coefficients at 35 °C and 1 atm

Tables 2 and 3 show the diffusion, solubility and permeability of the six measured gases in the three copolymers, in poly(ethyl methacrylate) and in poly(isoprene) and in poly(decylacrylate) PA-IO. The addition of flexible, low-T_g dodecyl methacrylate increases substantially the diffusivity in the polymer, and surprisingly also solubility. Copolymer CP1, which has a content of 50 wt% of DMA, shows diffusion coefficients which range from 0.8×10^{-7} $cm^2 s^{-1}$ for the slowest gas (ethane) to 4×10^{-7} $cm^2 s^{-1}$ for the quickest (oxygen); copolymer CP3, with a 90 wt% of DMA shows for ethane a $D = 3.4\times10^{-7}$ $cm^2\ s^{-1}$ and for oxygen $D = 17.5\times10^{-7}$ $cm^2\ s^{-1}$. As for solubility, the increase in the content of DMA from 50 wt% (CP1) to 90 wt% (CP3) causes a rise in solubility in all gases, but most specially in ethane (over four-fold), followed by methane (over three-fold), and a two-fold rise in oxygen, nitrogen and carbon dioxide. Permselectivity is, however, small and very similar in the three copolymers (Table 4), even if over one order magnitude increases are seen in the actual values of permeability between the slowest (CP1) and quickest

Table 2
Diffusivity and solubility parameters at 35 °C and 1 atm

Sample[a]	$D \times 10^7$ (cm^{2}s^{-1})						$S \times 10^4$ (cm^3 (STP)/cm^3 cm Hg)					
	N_2	O_2	CH_4	CO_2	CH_3CH_3	CH_2CH_2	N_2	O_2	CH_4	CO_2	CH_3CH_3	CH_2CH_2
p(ema) [1]	0.3	1.1	–	0.3	–	–	7.5	11.1	–	150	–	–
CP1	2.8	4.0	1.9	1.6	0.8	0.9	10	18	30	157	124	128
CP2	6.5	11.9	5.5	5.6	2.4	2.7	20.8	28.9	68.2	302	334	303
CP3	13.3	17.5	7.7	10.3	3.4	–	20.9	41.3	99.5	328	524	–
PA-10 [12]	–	–	19.8	17.7	–	–	–	–	24	147	–	–
Polyisoprene [1]	11.7	17.3	8.9	12.5	4.0	–	8.1	13.3	34.0	122	–	–

[a] The thickness of the films used in the experiments were about 190 μm.

(CP3) copolymer. At 35 °C then, the incorporation of dodecyl methacrylate in the backbone leads to both an increase in solubility and in diffusivity, and thus in permeability, with no changes in permselectivity.

3.3. Transport coefficients in the range 0–50 °C

The transport coefficients have been measured in the range 0–50 °C for all six gases. The results appear summarized in Figs. 2–4. Fig. 2 shows a comparison of the diffusion coefficients of the gases in copolymer 1 and 2 (Fig. 2a) and copolymers 2 and 3 (Fig. 2b). As indicated in Section 3.2, in the temperature range under study, the diffusion of all six gases decreases in the order: copolymer 3 > copolymer 2 > copolymer 1, i.e. diffusivity decreases as the content in dodecyl methacrylate diminishes. Very slight differences in the slope of the Arrhenius representation can be seen between the three copolymers. The activation energies of diffusion are collected in Table 5. The activation energies should increase on going to the right of the table, i.e. as the size of the gas increases and as a whole, this is the trend in Table 5, though some unexpected values appear, which have been marked with a star. Fig. 3 shows some selected Arrhenius representations of the solubility of some of the gases. As occurred at 35 °C, it is seen that the solubility coefficient increases in the whole temperature range for the six gases as the content in DMA increases. The values of the heat of solution appear in Table 6. It is not only the solubility coefficient but also the heat of solution that increases as the content of DMA increases. In Table 6 it can be seen how, on going downwards for all six gases there is a very important increase of ΔH_s. Two unexpected values appear, one is the high negative value of ΔH_s of nitrogen in EMA, which has been taken from the literature [1], and the other is the low value for methane in CP3. The permeation of the six gases as a function of temperature appears depicted in Fig. 4. The actual values of permeation are a result of diffusivity and solubility which have already been described, and both solubility and diffusivity increase with the DMA content, permeability, which is the product of

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

Sample	N_2	O_2	CH_4	CO_2	CH_3CH_3	CH_2CH_2
p(ema) [1]	0.17	0.89	–	3.79	–	–
CP1	2.8	7.2	5.7	25.1	9.7	11.5
CP2	13.6	34.3	37.4	168	81	81
CP3	27.8	72.3	76.9	338	179	–
PA-10 [12]	–	–	47.8	261	–	–
Polyisoprene [1]	9.45	23.4	30.2	156	–	–

$$1 \text{ barrer} = \frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2 \text{ s cm Hg}} \times 10^{-10}.$$

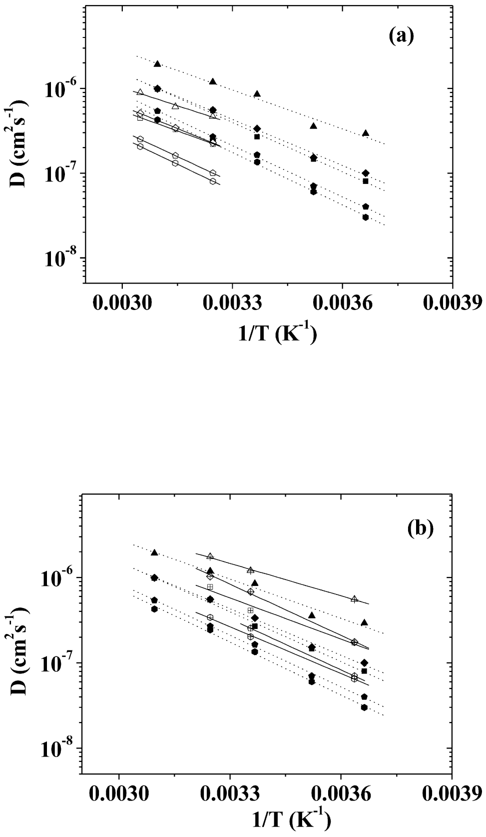


Fig. 2. Diffusion coefficients in the range 0–50 °C of oxygen (▲), methane (■), carbon dioxide (◆), ethane (⬟) and ethylene (⬢) in (a) copolymer CP1 (open symbols) and CP2 (solid symbols) and (b) copolymer CP3 (open cross centered symbols) and CP2 (solid symbols).

Table 4
Permselectivity, diffusivity and solubility selectivity at 35 °C and 1 atm

Sample	$\alpha_p(O_2/N_2)$	$\alpha_p(CO_2/CH_4)$	$\alpha_s(O_2/N_2)$	$\alpha_s(CO_2/CH_4)$	$\alpha_d(O_2/N_2)$	$\alpha_d(CO_2/CH_4)$
p(ema) [1]	5.2	–	1.5	–	3.7	–
CP1	2.6	4.4	1.8	5.2	1.4	0.84
CP2	2.5	4.5	1.4	4.4	1.8	1.0
CP3	2.6	4.4	2.0	3.3	1.3	1.33
PA-10 [12]	–	5.5	–	6.1	–	0.89
Polyisoprene [1]	2.5	5.2	1.6	3.6	1.5	1.4

both, increases strongly with DMA content. It is remarkable that, though the measurements have been done across T_g, no effect is seen in the Arrhenius representation. This is not unusual, and has for long been reported for other gas/polymer systems [17].

3.4. Comparison with other acrylates and methacrylates

Recently the first systematic work on gas transport behavior in alkyl side chain acrylates has appeared in the literature [12,13]. It was shown that as the number of carbons in the alkyl chain increases, so do the diffusion coefficients of methane and carbon dioxide, in a roughly exponential way. However, the diffusion coefficient of the first member of the series, poly(methyl acrylate) is too low to be included in the trend. In Fig. 5 a comparison between the data by Mogri and Paul [12] on acrylates of increasing side chain length, and our data on methacrylates is performed. The data for alkyl side chains of 18 and 22 (octadecyl acrylate and behenyl acrylate) given by the authors are extrapolated from the molten state to 35 °C. Both sets of data look very similar, and again in the case of methacrylates, the first member of the series, poly(methyl methacrylate) shows much lower diffusion coefficients. It has to be taken into account that while the acrylates are homopolymers, some of the methacrylates in Fig. 5 are copolymers and the number of atoms in the alkyl side chain is in these cases calculated as a molar average. However, as shown in Fig. 5, the same trend is followed by the homopolymers ($n = 1$ and $n = 2$) and by copolymers ($n_{av} = 5.3$, $n_{av} = 9$ and $n_{av} = 10$). Apparently the hydroxyl group present in copolymers CP1 and CP2 does not have an important effect on the diffusivity nor on solubility.

If the diffusion data are represented as a function of the inverse of the fractional free volume (FFV) (Fig. 6), then all acrylates and methacrylates fall on the same straight line, except for PMMA, which again shows very low diffusion coefficients as compared to the other polymers. This is very probably because at 35 °C PMMA is the only glassy polymer in both series. In Fig. 6 another glassy methacrylate, *tert*-butyl methacrylate, is included; the diffusion coefficients of this polymer are also very low if compared

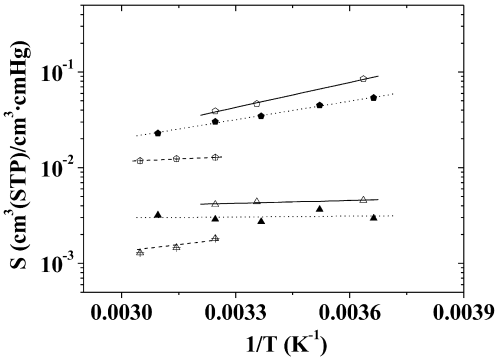


Fig. 3. Solubility parameter of oxygen (▲) and ethylene (⬢) in CP1 (cross centered symbols), CP2 (solid) and CP3 (open).

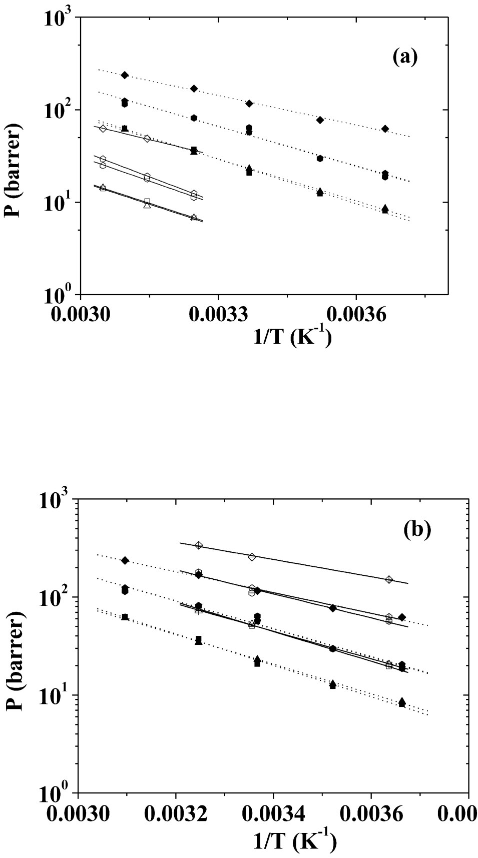


Fig. 4. Permeability in the range 0–50 °C of oxygen (▲), methane (■), carbon dioxide (◆), ethane (⬟) and ethylene (⬢) in (a) copolymer CP1 (open symbols) and CP2 (solid symbols) and (b).

Table 5
Activation energies for diffusion in kJ mol^{-1}

Sample	O_2	N_2	CO_2	CH_4	CH_2CH_2	CH_3CH_3
p(ema) [1]	31.8	42.7	33.1	–	–	–
CP1	27.1	–	33.6	30.0*	39.9	41.9
CP2	26.5	29.2	33.8	35.8	38.0	37.0
CP3	28.8	31.9	38.3	30.6*	39.4	35*

Table 6
Heat of solution of the six gases in copolymers CP1, CP2 and CP3, and in p(ema)

Sample	O_2	N_2	CO_2	CH_4	CH_3CH_3	CH_2CH_2
p(ema) [1]	4.6	− 2.1*	− 4.2	–	–	–
CP1	4	–	− 10.7	1.1	− 8.7	− 4
CP2	1.5	3.9	− 14.1	− 6	− 10.6	− 11.7
CP3	− 5	0.6	− 21.4	− 1.6*	− 11.6	− 17.6

with other acrylates and methacrylates with the same FFV. Being glassy, the stiffness of the chain is much larger than for rubbery acrylates and methacrylates, which brings about lower diffusivity and higher possibility to discriminate molecules because of their size. In fact, these two glassy methacrylates are able to separate CH_4 and CO_2 by their size, while in the rubbery acrylates and methacrylates this is not possible as the diffusion coefficient of both gases is the same.

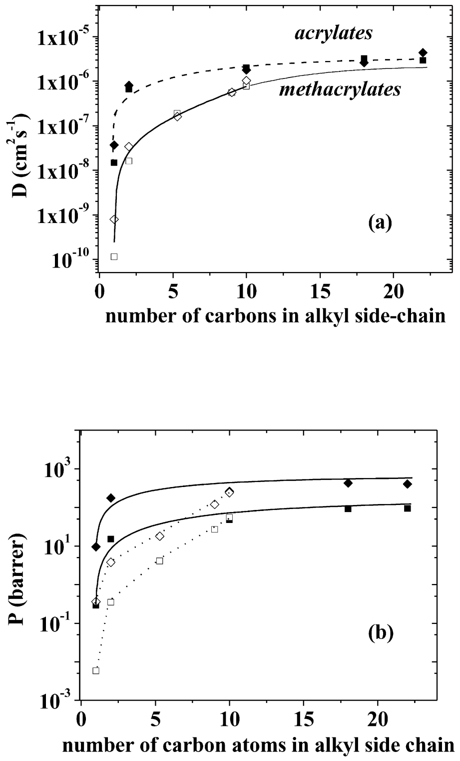


Fig. 5. Methane (■) and carbon dioxide ((◆) diffusion (a) and permeability (b) coefficients in acrylates [12] (solid symbols) and methacrylates (open symbols) as a function of the number of carbon atoms in the alkyl side-chain. The data for behenyl acrylate and octadecyl acrylate, taken from the literature [12] are extrapolated to 35 °C from the molten state.

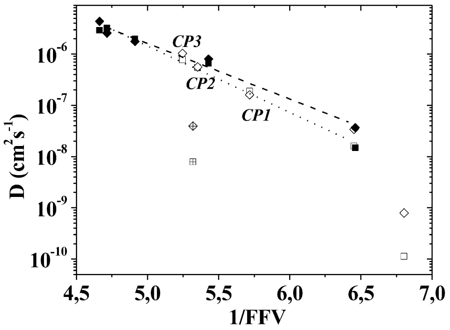


Fig. 6. Methane (■) and carbon dioxide ((◆) diffusion coefficients in acrylates [12] (solid symbols) and methacrylates (open symbols) as a function of the inverse FFV. The cross centered symbols correspond to tertbutyl methacrylate. Data of POA, PEA and PMA have been taken from Ref. [12].

The effect of adding methylenes in the side chain of acrylates and methacrylates is then mainly that of increasing FFV. Up to about 12 carbon atoms in the alkyl side chain, in methacrylates and acrylates there is a progressive increase of FFV, and consequently a decrease of T_g and increase of the diffusivity (Fig. 7), and a unique straight line fits data of both polymer families when representing $\log(D)$ as a function of FFV^{-1}, which according to Fujita's expression

$$D = D_0 \exp\left(-\frac{B_D}{FFV}\right) \tag{2}$$

implies that B is the same for each gas in both lineal side chain acrylates and methacrylates, given that they are rubbery. The flexibility of the chain in these polymers must be very large as no discrimination between two gases of different sizes as methane and carbon dioxide is possible; only in poly(ethyl methacrylate) and poly(methyl acrylate) a slight effect of the gas size can be seen. The fact that copolymers and homopolymers fall on the same line seems to indicate that copolymerization is random and that the effect of copolymerization on FFV may be considered additive.

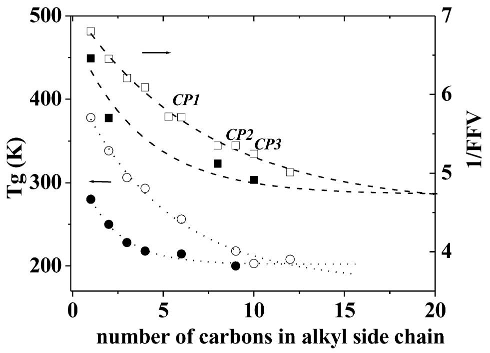


Fig. 7. FFV^{-1} and T_g as a function of the alkyl side chain length.

Acknowledgements

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