

Gas transport and sub- T_g relaxations in unmodified and nitrated polyarylethersulfones

K.M.P. Kamps, H.A. Teunis, M. Wessling and C.A. Smolders

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

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Abstract

Aromatic nitration has been used to modify the polymer main chain of polysulfone and polyethersulfone. Alteration in the gas separation characteristics of homogeneous membranes made out of these polymers could be observed upon nitration. Generally, separation factors for gas mixtures of CO₂/CH₄ increased while the permeability decreased. Remarkably, a decreasing diffusivity for both gases upon nitration could not be correlated with an increasing free-volume but was interpreted as an drastically decreased main-chain flexibility. The decrease of main-chain segmental mobility could be verified experimentally by a diminished amount of β -relaxations determined by torsional braid analysis.

Keywords gas and vapor permeation, solubility and partitioning

Introduction

Glassy polymers are frequently used as gas barrier materials and as gas separation membranes. Polyarylethersulfones, such as polysulfone (PSf) and polyethersulfone (PES) show acceptable gas separation characteristics [1–3]. In order to understand and to improve polymer properties affecting separation factors and permeabilities, polysulfone and polyethersulfone have been modified by means of aromatic ring nitration. This chemical modification might influence polymer properties like

- the specific free volume
- the polarity of the polymer matrix
- the torsional motion of intrachain segments.

These properties strongly affect diffusion and

sorption behaviour of the polymer. Aim of this study was therefore the improvement of the gas separation characteristics for the separation of CO₂ and CH₄ by chemical modification and the elucidation of the effects of chain modification on the key characteristics of a gas separation membrane, i.e. selectivity and permeability.

Background

Mass transport through a glassy gas separation membrane is mathematically well described by the dual-sorption model. The model has been suggested [4] on the basis of a nonlinear, concave sorption isotherm and a decreasing permeability with increasing feed pressure. The sorption mechanism consists of Langmuir and Henry's law contributions where gas molecules can sorb in the microcavities due to the glassy state of the polymer according to the

Correspondence to: M. Wessling, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Langmuir mode or by dissolution in the polymer matrix following the Henry mode. Mathematically the sorption isotherm is described by eqn. (1):

$$c = k_D p + \frac{c'_H b p}{1 + b p} \quad (1)$$

where K_D is Henry's law constant, c'_H a "hole saturation" constant and b a "hole affinity" constant

Assuming that two different populations of sorbed gas molecules have different mobilities (D_H for the Langmuir species and D_D for the Henry species) one obtains eqn. (2) for the permeability of the gas through the polymer matrix at zero downstream pressure [1]:

$$P = k_D D_D + \frac{c'_H b D_H}{(1 + b p)} \quad (2)$$

D_D is the diffusivity of penetrant molecules in the Henry mode and D_H in the Langmuir mode. Following the approach of Koros, Paul and Rocha [5] the effective diffusion coefficient of a penetrant molecule can be described depending on its concentration according to

$$D_{\text{eff}} = \left[\frac{1 + \frac{F K}{(1 + \alpha c_D)^2}}{1 + \frac{K}{(1 + \alpha c_D)^2}} \right] D_D \quad (3)$$

in which F is the ratio of D_H and D_D , α is the ratio of b and k_D and

$$K = \frac{c'_H b}{k_D} \quad (4)$$

Experimental

Materials and nitration procedure

Polysulfone P-1700 (PSf) was supplied by Union Carbide and polyethersulfone Victrex® by ICI. All materials used for the chemical

modification, salts, solvents and polymers were dried before use, ammonium nitrate was recrystallized from ethanol.

Nitration of the aromatic polyarylethersulfone was carried out according to a procedure as published earlier [6] with the following modifications: 0.05 mole of the polymer in 500 ml dry sulfolane was stirred mechanically and 0.055 mole of ammonium nitrate was added. To this mixture 0.165 mole of trifluoroacetic anhydride was added dropwise. The "in situ" formation of the trifluoroacetyl nitrate was exothermic and the temperature was controlled by a water bath. The reaction was allowed to proceed with stirring. Reaction times were in the order of 2-2.5 hr at 20°C for polysulfone and 4-6 hr for polyethersulfone. The reaction mixture was neutralized with equimolar amounts of triethylamine at 10°C and subsequently precipitated in 10 volumes of isopropanol under vigorous stirring. The well-divided product was filtered and washed with hot water to remove contaminating reaction products.

Proton NMR measurements were carried out with samples taken from amorphous films after complete solvent removal. These experiments in combination with infrared spectroscopy (and, in cases of low degree of nitration, together with elemental analysis) allowed a quantitative estimation of the number of substituted aromatic protons and the position of the nitro-substituent. Chemical shift of aromatic protons indicated that protons were substituted *ortho* to the aryl-ether bond as shown in Figs. 1(a) and (b). Chemical shifts of aromatic protons are shown only. Different degrees of nitration were obtained depending on reaction times. High performance liquid chromatography and low-angle light scattering were used to determine the influence of nitration on the mean molecular weight. For both PSf and PES a maximum reduction in molecular weight of around 20% was observed in the range of degree of nitration investigated. Based on the re-

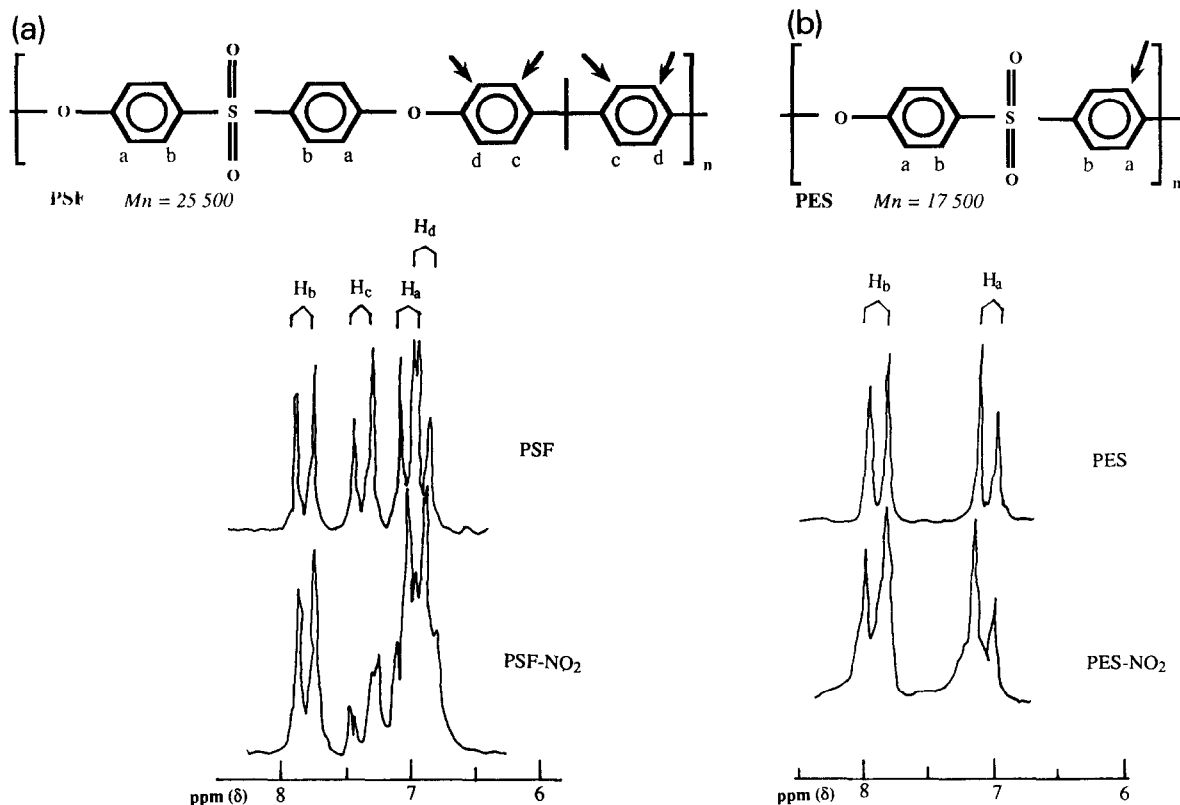


Fig 1 (a) NMR spectrum for aromatic nitration of polysulfone (PSf) (b) NMR spectrum for the aromatic nitration of polyethersulfone (PES)

sults published by Toi and Paul [7] the effect of the molecular weight change on the transport characteristics of the polymers can be assumed negligible.

Film preparation

Amorphous polymer films were prepared in a uniform manner in order to exclude the effect of different casting conditions on the transport properties of the films. Solutions (10–15 wt.%) in *N,N*-dimethylacetamide (DMAc) were filtered over a teflon filter (Millipore, 1.0 μm pore size) and casted at ambient temperature on a glass plate. The solvent was evaporated in a glove box under a constant, small stream of dry nitrogen. After evaporation of the solvent, the

films of 10–20 μm thickness were removed from the glass plates by rinsing with distilled water and dried in a vacuum oven at 150°C for 48 hr. Since the presence of residual solvent or sorbed water in the film strongly affects film characteristics [8]; infrared spectroscopy as well as thermogravimetric analysis (TGA) was used to characterize the state of the films.

Infrared spectroscopy was used to control the removal of DMAc and moisture. Polymer films investigated did not show any peaks in the range of 2900–3300 cm^{-1} which are typical for DMAc. It could be concluded that the residual solvent was reduced at least to a level of less than 2 wt.%. Water was determined to be less than 0.1 wt.%. The films were used without any pressure conditioning.

Calorimetric, mechanical and density measurements

Dynamic shear moduli were measured as a function of temperature with a Nyrenne torsion apparatus ATM 3 at a heating rate of $1^{\circ}\text{C}/\text{min}$. The frequency of oscillation was adjusted to be in the range of 0.5–1.5 Hz. Measurements were in the temperature range from -120°C up to 250°C . Thermomechanical data were obtained from film strips of 1 mm thickness and a width of 9 mm. Polymer strips were melt-pressed from dry thin membranes and it is assumed that the relaxation behaviour is governed by the characteristics of the thin membranes.

Densities of the polymers were measured by flotation of small samples in a density gradient column employing 2-ethyl-isohehexanol and tetrachloromethane. Later experiments have shown us that results obtained with these liquids (which might swell the polymer) agree well with densities determined by an experimental set-up based on the Archimedes principle incorporating a sensitive digital balance and water as liquid. Differential scanning calorimetric measurements were performed on a Perkin Elmer DSC-calorimeter at a heating rate of $20^{\circ}\text{C}/\text{min}$.

Sorption and permeability measurements

Gas sorption measurements were performed by means of a pressure decay method at $T=25^{\circ}\text{C}$. Two calibrated symmetrical sample volumes of about 15 ml were separated by a differential pressure transducer [9]. The polymer sample was placed in one of the cells while the other one was kept empty, working as a reference cell. Due to gas sorption into the polymer sample the pressure decreased in the first cell and the pressure difference between the sample cell and the reference cell is a sensitive measure for the concentration of the penetrant gas in

the polymer. Permeation experiments for pure gases were carried out at room temperature as described in Ref. [9]. Experimental selectivities were obtained with gas mixtures containing 20% CO_2 and 80% CH_4 .

Results and discussion

Effect of degree of nitration

Permselectivities of CO_2 over CH_4 and permeabilities of CO_2 are shown in Figs. 2(a) and (b) as a function of the degree of aromatic nitration. An increasing degree of nitration for PSf and PES results in a considerable increase in permselectivity. For PSf a degree of nitration of 1.8 per repeat unit results in a selectivity increase from 33.5 to 46. For PES the largest

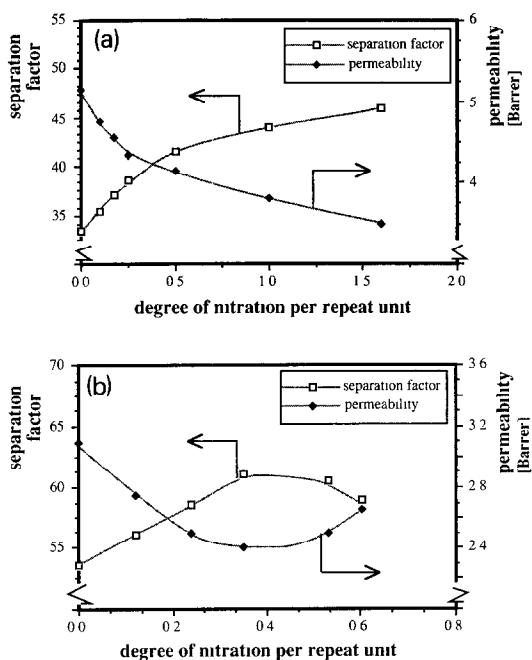


Fig 2 (a) Influence of degree of aromatic nitration of PSf on permselectivity and CO_2 -permeability for carbondioxide/methane gas mixtures (b) Influence of degree of aromatic nitration of PES on permselectivity and CO_2 -permeability for carbondioxide/methane gas mixtures

increase in selectivity was obtained for an degree of nitration at around 0.5. However, an increasing selectivity is accompanied by a decreasing permeability. An optimal degree of nitration has a much higher affect on PSf (27% increase) than on PES (11%).

Sorption and transport of pure gases

Experiments determining the diffusivity and solubility of the penetrant gas in a polymer can elucidate how the introduction of a polar substituents on the main polymer chain influences these two parameters. Sorption and permeation experiments were carried out with samples of PSf(NO₂)_{1.8}, PES(NO₂)_{0.5} and the unmodified polymers. Sorption and permeability values for PSf agree reasonable well with the range of data reported by McHattie et al [10]. Here, the term range is emphasized since McHattie et al. clearly point out that experimental data for the sorption and permeation behaviour of one specific polymer strongly depends on the circumstances of sample preparation. Nitration of the polymers resulted both for polysulfone and polyethersulfone in a decrease of the sorption of carbon dioxide as shown in Figs. 3(a) and (b). The sorption selectivity was hardly affected upon chemical modification.

For both polymers however, permeation experiments show a considerable decrease in the permeability after nitration for CH₄ (Figs. 4a and 5a) as well as for CO₂ (Figs. 4b and 5b). The decrease in permeability for methane is more pronounced than for carbon dioxide resulting in an increasing permselectivity. All the results shown in the above mentioned figures were obtained from PSf(NO₂)_{1.8} and PES(NO₂)_{0.5}. Solid lines in the plots are fitted curves according to the dual-sorption model. Fitting parameters are listed in Tables 1(a) and (b).

Using the data together with eqn. (3) an ef-

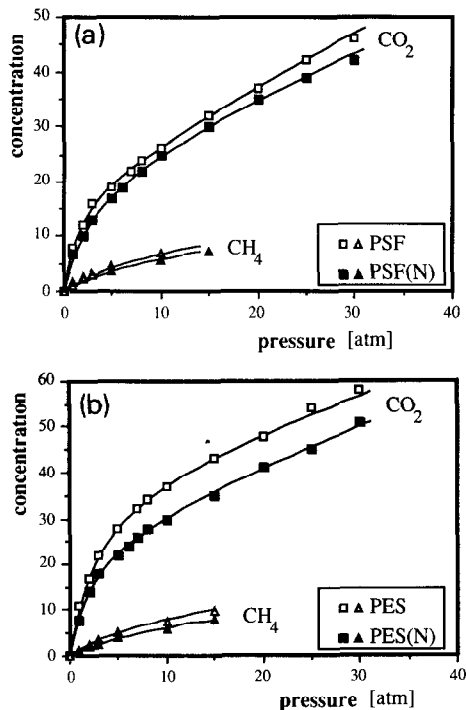


Fig. 3 (a) Sorption isotherm for carbon dioxide and methane in unmodified and nitrated PSf (b) Sorption isotherm for carbon dioxide and methane in unmodified and nitrated PES (Units cm³(STP)/cm³ polym.)

fective diffusion coefficient can be calculated which is also listed in Tables 1(a) and (b) for upstream pressures of 10 bar. For both polymers and both gases the diffusivity is diminished upon nitration. Furthermore, all these above listed data and plots show that the solubility of both gases CO₂ and CH₄ is affected. The sorption behaviour of PES which has a higher intrachain polarity is more strongly influenced than that of PSf. Remarkably, the diffusivity of CO₂ and CH₄ in PES is only slightly affected. Thus, the decrease in permeability upon nitration can be mainly attributed to a decrease in solubility. For PSf, aromatic ring nitration has a strong impact on the diffusivity for both gases. A decrease of around 35% for CO₂ and 50% for CH₄ can be observed.

Diffusion coefficients of penetrant molecules in polymeric membranes are frequently

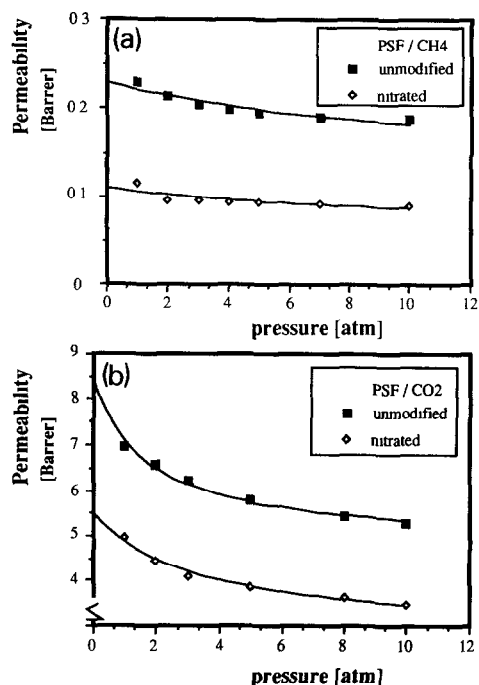


Fig 4 (a) CH₄-permeability in unmodified and nitrated PSf (b) CO₂-permeability in unmodified and nitrated PSf

correlated with the free volume of the polymer. Roughly spoken, the diffusivity of a penetrant molecule in a polymer matrix increases with increasing free volume [11]. Herein, the free volume is the difference in the specific volume of the pure polymer and the specific occupied volume of the polymer V_0 . The latter can be calculated by group contribution methods assuming its quantity as the specific volume of the equilibrium liquid polymer V_w at 0°K [12].

$$V_f = V - V_0 \quad (5)$$

Comparing the diffusivities of CO₂ and CH₄ taken from Table 2 it can be seen that this relation holds for the comparison of PSf and PES. Nitration of the polymer backbone results in an increasing free volume for both PSf and PES. However, from the experimental data shown above it can be stated that the diffusivity of both gases CO₂ and CH₄ decreases upon nitration.

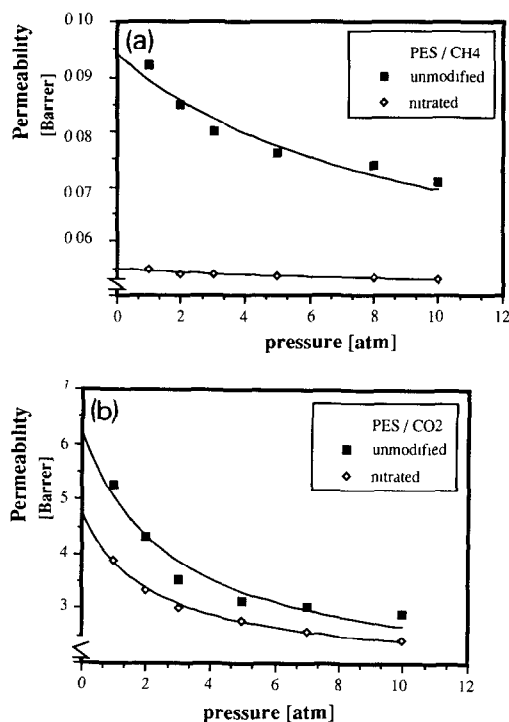


Fig 5 (a) CH₄-permeability in unmodified and nitrated PES (b) CO₂-permeability in unmodified and nitrated PES

Experimental results obtained are in contradiction with the free volume approach which quantitatively predicts an increasing diffusivity with increasing free volume.

Experiments carried out by Yampol'ski [13] might give a starting point to shed some light on this contradiction. It was found that for rubbery polymers the diffusivity of gases decreases with increasing glass transition temperature of the polymer but it increases for glassy polymers. Since a stiffening of the backbone of a polymer chain results in an increasing glass transition temperature, the decrease in diffusivity for rubbery polymers with an increasing T_g can be attributed to the inhibition of short chain segment motions which allow diffusional jumps. For glassy polymers, however, the behaviour changes into the opposite. An increasing glass transition temperature results in an

TABLE 1(a)

Dual-sorption parameters for sorption and permeation experiments of carbon dioxide in unmodified and nitrated PSf and PES

	k_D $\left(\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \cdot \text{atm}}\right)$	c'_H $\left(\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3}\right)$	b $\frac{1}{\text{atm}}$	D_D $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$	D_H $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$	K	D_{eff} $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$	
PSf	0.96	19.37	0.59	5.04	0.31	11.92	0.06	4.63
PSf(N)	0.78	22.19	0.3	3.49	0.41	8.56	0.12	3.08
PES	0.73	38.03	0.35	2.27	0.34	18.24	0.15	2.13
PES(N)	0.86	25.99	0.46	2.16	0.4	13.83	0.18	2.04

(b) Dual-sorption parameters for sorption and permeation experiments of methane in unmodified and nitrated PSf and PES

	k_D $\left(\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \cdot \text{atm}}\right)$	c'_H $\left(\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3}\right)$	b $\left(\frac{1}{\text{atm}}\right)$	D_D $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$	D_H $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$	K	F	D_{eff} $\left(\frac{\text{cm}^2}{\text{sec}}\right) \times 10^{-8}$
PSf	0.19	9.8	0.1	0.70	0.10	5.0	0.15	0.53
PSf(N)	0.16	9.0	0.09	0.38	0.06	4.78	0.17	0.28
PES	0.18	11.9	0.11	0.27	0.04	7.09	0.13	0.20
PES(N)	0.18	9.0	0.10	0.28	0.01	4.8	0.01	0.2

TABLE 2

Physical properties of unmodified and nitrated PSf and PES

Polymer	Density (g/ccm)	SFV ^a (ccm/g)	T_g (°C)	T_α (°C)	T_β (°C)	Rel amount of β -relaxation
PSf	1.230	0.123	191	188	25	10
PSf(N)	1.223	0.175	195	193	35	7.8
PES	1.368	0.097	228	220	37	14.5
PES(N)	1.380	0.118	234	231	52	9.3

^aSpecific free volume (eqn 5)

increasing diffusivity. Certainly, the interpretations made for the rubbery polymers are still valid but another fact mostly overwhelms the molecular motion argument: the inhibited chain packing due to the glassy state of the polymer. An increasing chain stiffness (which accompanies an increasing T_g) results in an increasing inhibition of tight chain packing, i.e. an increased free-volume. The nitration of PES and PSf verifies this phenomenon. Both polymers

show upon main-chain modification an increased glass transition temperature T_g (or T_α for the mechanical dynamical experiments) expressing the decrease in chain flexibility. As can be seen in Table 2 this results in a looser packing or larger free-volume. But still, a diffusional jump can only occur by bending the polymer chains [14] and this certainly depends on the flexibility of the chains for rubbery as well as for glassy polymers.

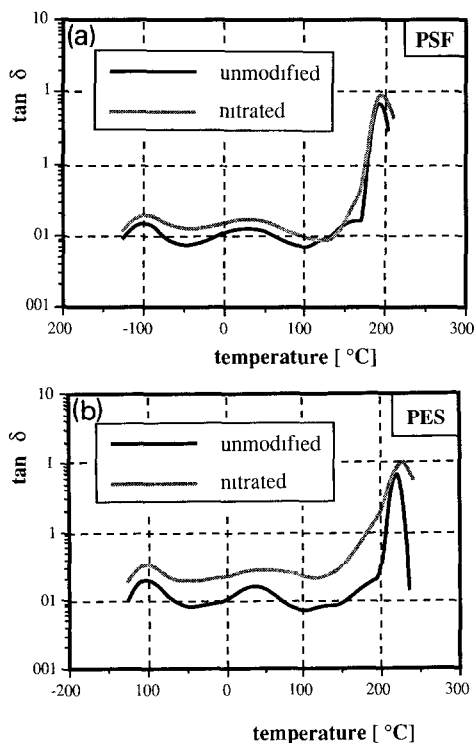


Fig 6 (a) Dynamical torsion experiments carried out with unmodified and nitrated PSf (b) Dynamical torsion experiments carried out with unmodified and nitrated PES

Hensema [15] carried out a systematic variation of the *meta* and *para* content of dianiline substituents in the back bone of polytriazoles. He observed an increasing diffusivity with an increasing density, i.e. packing density and decreasing free volume, respectively. From these results it could be concluded that besides the free volume effect, variations in short range chain flexibilities like rotational degrees of freedom might strongly influence the ease of a diffusional jump. Furthermore, Seymore and Light [16] could correlate the diffusivity of O_2 in different PETs to the short range chain flexibility expressed by the amount of secondary β -relaxations.

β -Relaxations in polyarylethersulfones have been interpreted as an onset of an increased intrachain segmental mobility, e.g. phenyl ring

mobility [17]. We carried out dynamic torsion experiments investigating the effect of nitration on the intrachain segmental mobility. The effect of nitration on the dynamic loss modulus, $\tan \delta$, for PSf and PES is shown in Figs. 6(a) and (b). Relaxation temperatures and the amount of β -relaxations which have been obtained as the area under the relaxation curve are shown in Table 2.

For PES as well as for PSf the amount of β -relaxations decreases upon nitration. Interpreting a decrease in the amount of β -relaxations as a decrease in intrachain segmental flexibility one would expect the diffusivity of a gas to decrease, too. Hence, the experimentally determined decreasing diffusivities of CH_4 and CO_2 listed in Tables 1(a) and (b) are in accordance with this interpretation.

Conclusions

Nitration of polyarylethersulfones decreases the permeability, solubility and diffusivity of CO_2 and CH_4 . The selectivity towards CO_2/CH_4 mixtures can be improved for PSf by 28% and for PES by 18%.

An increasing free-volume upon nitration accompanied by a decreasing diffusivity for CO_2 and CH_4 emphasizes that not only a single factor like the free-volume or a free-volume distribution affects mass transport through polymeric membranes. Main-chain nitration also decreases the segmental mobility. A fine interplay between free-volume and main-chain segmental mobility determines the transport rate of penetrant molecules in the polymeric membranes.

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