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Polymer 40 (1999) 3605–3610

polymer

Polymer Communication

Poly(ether imide)s: correlation of positron annihilation lifetime studies with polymer structure and gas permeability

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Received 5 June 1998; received in revised form 26 June 1998; accepted 14 July 1998

Abstract

This paper describes the results of positron annihilation lifetime measurements on a series of poly(ether imide)s for which permeabilities and permselectivities for gas separation have been determined previously. Positron lifetimes and intensities vary systematically with changes in polymer structure and correlate with the permeabilities in separation of carbon dioxide and methane. Some apparent scatter in the data might, in part, be associated with differences in the interactions of *ortho*-positronium with molecular cavities as polymer structures are varied. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ether imide); Positron annihilation lifetime measurements; Gas permeability

1. Introduction

In previous papers, the synthesis, thermal properties and gas permeabilities of a series of novel poly(ether imide)s were described [1,2]. Permeabilities to carbon dioxide (P_{CO_2}) and methane (P_{CH_4}) and permselectivities for carbon dioxide/methane separations ($\alpha_{CO_2/CH_4} = P_{CO_2}/P_{CH_4}$) were found to vary systematically with changes in the chemical structure of the membrane polymer. A linear relationship (1) between permeabilities to the two gases, as well as a strong trend between high permeability and high glass transition temperature (T_g), was identified.

$$P_{CO_2} = (27.13 \pm 0.60)P_{CH_4} + (1.46 \pm 0.26) \qquad (1)$$

Results indicated that rigid polymers incapable of inefficient packing led to highly permeable membranes. The presence of bulky substituents, which hinder bond rotation, enhance gas permeability, while the nature of the substituent influences permselectivity; permeabilities correlated with Van der Waals volumes of the permeants. A correlation between diffusion coefficient and permeant size, expressed as Van der Waals volume of the permeant, has also been reported for poly(vinyl chloride) [3] and a number of reviews have highlighted correlations between the penetrant size and the diffusion coefficient [4–8].

Over the last 10 years, the positron annihilation lifetime spectroscopy (PALS) technique has been used to explore the size and number of molecular-scale voids in amorphous materials [9]. It has been found that void structures exhibit characteristics similar to those expected for the free volume in amorphous materials. A correlation has been reported between the void structure, as measured by PALS and the gas permeabilities of amorphous materials [9]. Thus, correlations have been reported between $\log D$ (D = diffusion coefficient of the permeant) and the reciprocal of τ_3 (the lifetime of *o*-positronium) for glassy polymers, [10] between $\log(D/T)$ and $(v_{h,Ps}I_3)^{-1}$ in rubbery polymers, [11] where $v_{h,Ps}$ is the volume of pores calculated from τ_3, and I_3 is the percentage intensity from the decay of *o*-positronium, between D and $\tau_3 I_3$ for norbornene polymers, [12] and a strong, non-linear correlation between $\log D$ and $(v_{h,Ps}I_3)^{-1}$ for a series of polyimides [13].

This paper reports the PALS characteristics for the poly(ether imide)s referred to above and identifies correlations between these parameters and gas permeability data and chemical structure.

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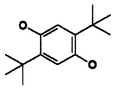
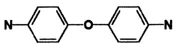
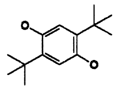
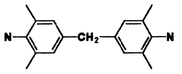
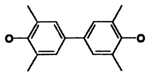
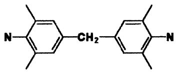
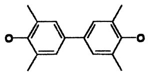
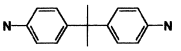
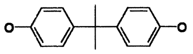
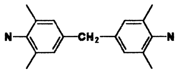
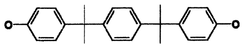
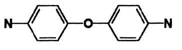
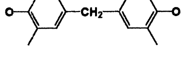
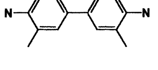
PII: S0032-3861(98)00539-4

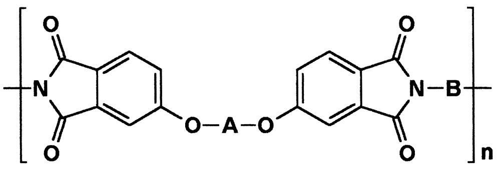
Table 1
Polymer structures, T_gs, gas permeability data and positron annihilation data for poly(ether imide)s

Code	O–**A**–O	N–**B**–N	T_g/°C	P_{CO_2} barrer	α_{CO_2/CH_4}	τ_3/ns	σ_{τ_3}/ ns	I_3/ %	σ_{I_3}
I1			263	19	22.0	2.238	0.032	17.8	0.3
I2			270	49	19.0	2.456	0.014	20.5	0.1
I3			> 420	40	27.3	2.395	0.018	17.60	0.3
I4			299	13.3	35.4	2.263	0.013	17.6	0.2
I5			249	6.5	37.3	2.081	0.046	14.2	0.4
I6			194	2.05	38.0	1.827	0.030	11.1	0.2
I7			> 420	22	30.1	2.478	0.017	15.3	0.2

2. Experimental

2.1. Materials

The method of synthesis and the characteristics of the poly(ether imide)s with structure (I) have been reported previously [1,2].



(I)

Units **A** and **B** in (I) were varied to influence the packing of the imide chains and modify the available free volume between the chains for small molecule diffusion. Aromatic units **A** and **B** in the polymers studied are identified in Table 1 along with previously determined gas permeability and permselectivity data [1,2].

Samples used for the positron annihilation studies were dense films prepared by slow solvent evaporation from polymer solutions (3 wt%) in dichloromethane in flat-bottomed Petri dishes (Anumbra), as for gas permeability measurements. The transparent, yellow films, thickness 30–60 μm, were annealed for 3 days at 120°C under vacuum. The samples investigated are coded as indicated in Table 1.

2.2. Positron annihilation lifetime measurements (PALS)

The PALS set-up used was a state-of-the-art, fast-fast system. The system incorporates a high counting efficiency and good resolution. The BaF_2 cylindrical (40 mm diameter × 15 mm thick) scintillators were used with Hamamatsu H2431 photo-multiplier tubes (PMTs) which have borosilicate windows. A conveniently fast scintillation component of 600 ps lies in the UV region at 220 nm. The front face and sides of the scinillators were wrapped with PTFE tape which, because of its high UV reflectance, improves both time and energy resolution [14]. One disadvantage of the high efficiency of BaF_2 detectors is a high probability of start-stop ‘‘pile-up’’ [15]. To avoid this, and the subsequent reduction in timing resolution, the detectors were arranged with 90° geometry, preventing both annihilation γ-rays being detected. The scintillators were coupled to the PMTs using a high viscosity (100 000 cps) silicone oil, which has been shown to have low UV absorption.

The rise time of the tubes, 0.7 ns, is suitably short for timing purposes. This configuration gave count rates of 150–300 cps and an instrument resolution of 220–240 ps FWHM for a 50 μCi source and 90° source-sample geometry. The time-to-amplitude converter used in the system was a Canberra 2145 instrument. A $^{22}_{11}NaCl$ source was used. The resolution of the equipment was determined by measurement of a benzophenone crystal. A source correction of 7.4% at 382 ps was therefore used in the analysis of all PALS spectra reported in this paper. The lifetime components were calculated using POSITRONFIT, [16,17] a least-squares analysis of the data which uses a sum of decaying exponentials to describe the lifetimes and intensity parameters. This program uses a mathematical model which expresses the polymer spectrum as a convoluted expression (symbol *) of the instrument resolution function and a finite number (n) of negative exponentials:

$$y(t) = R(t)^{*}\left(N_t \sum_{i=1}^{n} \alpha_i \lambda_i e^{-\lambda_i t} + B\right) \qquad (2)$$

where $y(t)$ is an experimental raw datum, $R(t)$ is the instrument resolution function, N_t is the normalised total count, B is the background, λ_i is the inverse of the ith lifetime component (τ_i), and $\alpha_i\lambda_i$ (I_i) is its intensity. An experimental spectrum $y(t)$ is fitted to Eq. (2) by least-squares analysis to obtain lifetimes $\tau_I (= 1/\lambda_i)$ and corresponding intensities $\alpha_i\lambda_i$. Experimental values of τ_1 and τ_2 were approximately 0.15 ns (*p-Ps*) and 0.41 ns (free e^+), respectively, for all samples studied and, similarly, values of I_1 and I_2 were, approximately, 19 and 65%, respectively; these values were used in the data analysis to determine values of τ_3 and I_3 (*o-Ps*) for the long-lifetime component which reflect sizes and populations of voids capable of supporting molecular diffusion. Values thus calculated for *o-Ps* lifetime and intensity were, however, found to be virtually the same as those from a ‘‘free’’ analysis.

3. Results and discussion

The poly(ether imides) [1,2] were used in thin film format to provide comparison with the previous diffusion studies and because it is difficult to remove residual casting solvent from thick films. A special handling method was therefore adopted. Five sections of film were pressed together and bound with an adhesive label. This compound structure was placed either side of the source and a slice of copper foil was attached to either side; both to provide structural support and to ensure that any excess positrons annihilate within the media with a well-defined lifetime, rather than annihilating in air outside the sample. Data obtained are presented in Table 1; values of σ_{τ_3} and σ_{I_3} are standard deviations.

Statistical variations on both lifetimes and intensities are sufficiently small to be able to differentiate between the size of the voids and their number. Positron lifetimes, τ_3, are comparable to those observed for polystyrene at its glass transition temperature, however, the numbers of voids, reflected in the intensities I_3, are much smaller [18]. Of the poly(ether imide)s studied, sample I2, has the highest value of I_3, which indicates a large number of voids, and voids with almost the largest radius (second longest value of τ_3). In contrast, I6 has a smaller number of voids, lower I_3, and voids with the smallest radius, shortest τ_3. Permeabilities to carbon dioxide and methane were reported previously [1,2] (Table 1). The simple, strong linear dependence between P_{CO_2} and P_{CH_4}, identified previously, and detailed examination of data points in terms of molecular structure, suggested that variations in relative solubilities of the gases, due to different groups **A** and **B** in (I), were not responsible for variations in permselectivity; no structural moiety preferentially enhanced or reduced the permeability for either gas. Membranes were, therefore, assumed to act as simple molecular sieves and observed differences in permeability were attributed to variations in the concentration and suitablility of pores for gas diffusion. If this hypothesis is correct, a correlation between permeation and positron annihilation

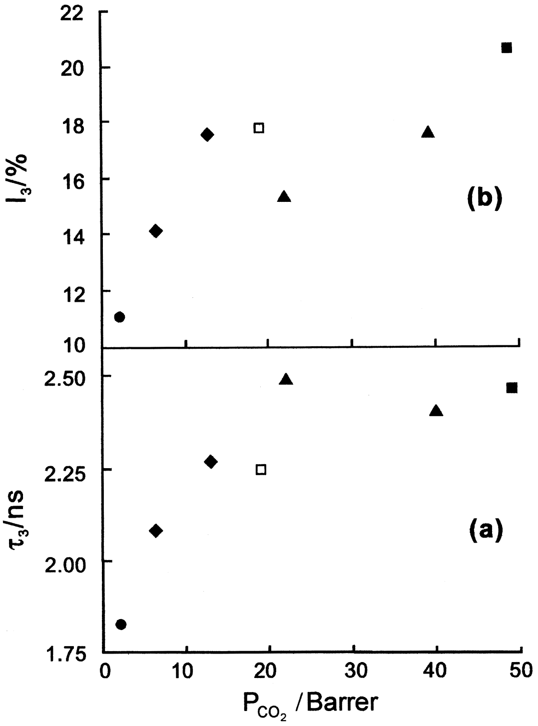


Fig. 1. Variations in (a) τ_3 and (b) I_3 with carbon dioxide permeability for a series of poly(ether imide)s. Symbols correlate with structural features of the polymers; ●, no *o*-methyl groups; ◆, *o*-methyl groups in one unit; ▲, *o*-methyl groups in two units; □, *t*-butyl group in one unit; ■, *t*-butyl group in one unit and *o*-methyl groups in one unit.

data would be anticipated; observed correlations are shown in Fig. 1a and b.

Data in Fig. 1a and b show strong relationships between the permeability and positron data but there are further detailed correlations with the chemical structures of the several polymers examined. In Fig. 1a and b, data points are coded to indicate different types of substituent units on the polymer chain which, as noted previously, influence gas permeability and permselectivity. Thus, I6 (filled circle) has the lowest values of both I_3 and of τ_3. These data are consistent with its chemical structure and the earlier conclusion that a relatively flexible polymer (isopropylidine and ether hinges in **A** and **B**), with no substituent *ortho* to either the ether linkage to the phthalimide moiety or to the imide ring (see structures in Table 1) to hinder bond rotation, allows close packing of the polymer and a lack of voids to support gas permeation; this polymer also has the lowest T_g, commensurate with its flexible structure (Table 1). In contrast, sample I2, which has the highest value of I_3 and almost the longest τ_3 consistent with a high content of large voids, has high gas permeabilities. In this polymer both **A** and **B** units have *ortho*-substituents which hinder rotation about the linkages to both the ether and imide units, consistent with poor packing of bulky, bent polymer chains and the polymer has a high T_g.

Hindering methyl-substituents on either the **A** or **B** unit in the poly(ether imide) *ortho* to the linkages to either the ether or imide units, as in I4 and I5 (diamond symbols), enhance values of I_3, τ_3, gas permeability and T_g, relative to I2. This observation is consistent with the previous conclusion that such groups increase the stiffness of the polymer chains, hinder chain packing and increase the concentration of voids capable of supporting gas diffusion [1]. Further, hindering methyl-substituents on the **A** unit in the anhydride residue (I4) have a greater influence than substituents on the diamine residue **B** (I5) as they are more effective in reducing available chain conformations; *ortho*-substituents on the diamine unit only restrict rotation about a rigid rotor, the phenylene ring [1].

Introducing pairs of hindering residues into both dianhydride and diamine moieties (samples I3 and I7, triangles in Fig. 1a and b) increases gas permeabilities further and also increases values of τ_3. Introduction of such substituents also increased values of T_g; no T_g was observed below 420°C. These observations are again consistent with hindering substituents restricting chain mobility, increasing the sizes of voids and enhancing permeability and T_g. There is not the same influence on values of I_3, related to the numbers of voids, which are not raised in line with the permeability and sizes of voids. However, polymers I3 and I4, which both have tetramethylbiphenylene units in the anhydride moiety, have similar values of I_3 and there is a relative increase in permeability on introducing *ortho*-methyl groups into moiety **B**. Sample I7, while having methyl groups in both moieties, has a flexible hinge in the anhydride moiety and this reduces the concentration of voids (reduced I_3) despite the rigid diamine moiety.

Single, bulky *tert*-butyl groups *ortho* to the ether link in the dianhydride moiety increase gas permeability, but reduce permselectivity, and are associated with high values of both I_3 and τ_3 (samples I1 and I2). It was previously noted that single *tert*-butyl groups do not provide the same restriction to bond rotation as do two methyl groups, but provide greater enhancement of permeability [2]. It is difficult to relate changes in I_3 and τ_3 to specific changes in polymer structure, relative to samples with methyl-substituents, but it is noted that the additional presence of hindering methyl groups in the diamine unit (I2) provides higher values of both I_3 and τ_3 as well as of gas permeability. Two pairs of hindering methyl groups raise the permselectivity more than they raise permeability.

While definite correlations are identified in Fig. 1, the parameters τ_3 and I_3 are not varied independently. It is often considered that there should be a correlation between ln D and the free volume fraction in the polymer. The free volume is often considered to be related to the product $\tau_3 I_3$; τ_3 is related to the size of voids and I_3 contains information on the number of pores in the polymer. In the absence of any evidence indicating preferential solubility of any gas with any particular structural moiety, we have assumed that diffusion coefficients and permeabilities are linearly related within this family of polyimides. We therefore sought and have identified a strong correlation between

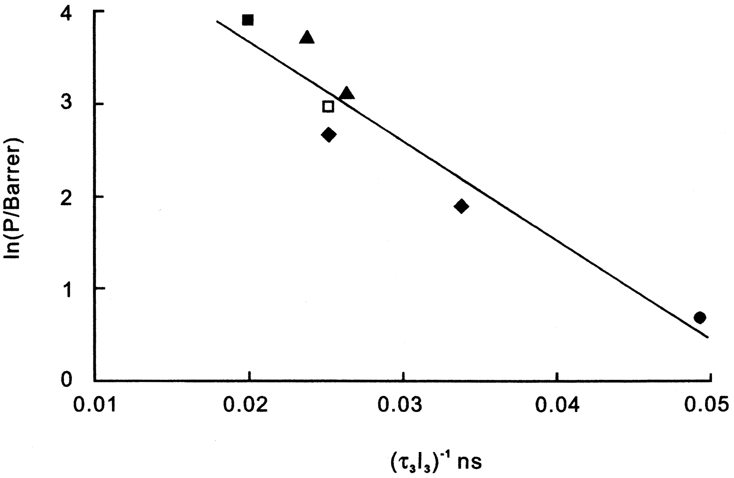


Fig. 2. Variation in permeability to carbon dioxide for a series of poly(ether imide)s. Symbols correlate with structural features of the polymers as described for Fig. 1.

ln P and $(\tau_3 I_3)^{-1}$ (Fig. 2) (line obtained by linear regression, is $\ln P = -106.6(\tau_3 I_3)^{-1} + 5.77$) consistent with a definite relationship between ln D and free volume fraction. The apparent scatter in the data in Figs. 1 and 2 might be a result of a lack of ability of the simple analysis used to account for subtle changes in the shapes and cross sections of the voids as polymer structures are varied.

These several results establish general correlations between the structural features of the polymers, their gas permeabilities and, individually, numbers and sizes of the voids in the polymers; factors which specifically control permselectivity are not yet identified. Quantitative correlation of permeability and permselectivity to the numbers and size distribution of voids and, possibly, to structural factors requires an examination of additional polymers with different combinations of hindering units and hinges in the aromatic units **A** and **B** of structure (I).

The observations reported here further reinforce the view of Koros [7] that ‘‘suppression of interchain packing by addition of bulky groups—which also cause simultaneous inhibition of interchain motion around flexible hinge points—tend to increase permeability without unacceptable loss in selectivity’’. Thus the structural features which were previously identified as raising gas permeability are now seen to correlate in general with increased numbers and size of voids in the polymer matrix.

4. Conclusions

It is concluded that the positron annihilation lifetimes and intensities determined for a series of poly(ether imide)s correlate well with chemical structures and previously determined gas permeabilities. Thus, high permeabilities are associated with high intensities and long lifetimes for positron annihilation. A polymer without hindering alkyl substituents had the lowest lifetimes and intensities, gas permeabilities and glass-transition temperature. Higher values of all parameters were found when methyl groups *ortho* to the linkages to the phthalimide residues were introduced. Introduction of *tert*-butyl groups also enhanced lifetimes, intensities and gas permeabilities and a combination of *tert*-butyl in one moiety (**A** in (I)) and *ortho*-methyl in the other (**B**) further enhanced these parameters. It was also concluded that there are strong correlations between the free-volume fraction in the polymers (related to $\tau_3 I_3$), their chemical structures and gas permeabilities Thus, it is seen that positron annihilation measurements correlate well with permeability data and might even have predictive behaviour and, as more information becomes available, is expected to enhance the understanding of the relationship between molecular packing and physical properties of the polymers.

Acknowledgements

JHD wishes to thank the EPSRC for provision of a Research Fellowship for the period of this study and also for a grant towards to upgrade of the positron annihilation lifetime equipment.

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