polymer report

Molecular weight dependence of gas permeability and selectivity in copolyimides

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The gas permeation behaviour of a number of polyimide copolymers, including a series of copolyimides of identical structure with different molecular weights, have been investigated. Permeabilities and selectivities were found to vary over a broad molecular weight range at high molecular weights. Differences in permeability with molecular weight can be comparable to differences due to marked changes in chemical structure.

(Keywords: copolyimide; molecular weight; gas diffusion; permeability; selectivity)

INTRODUCTION

Considerable effort has been devoted in recent years to varying the chemical structures of high-performance polymers in order to optimize one property or another. We have investigated gas-permeability behaviour of polyimides and poly(etherimide)s. To this end we have, for example, incorporated bulky side groups into poly(etherimide)s[1] and also investigated isomeric poly(etherimide)s by interchanging diamine and bisphenol moieties[2]. In a separate exercise we have investigated a series of copolyimides based on hexafluorobisanhydride (6FDA) to modify permeabilities and selectivities in gas permeability.

It is generally understood that, for any individual polymer, the value of a material property is a function of molecular weight at low molecular weights, but attains a plateau value at some 'high' molecular weight which varies with polymer type. It is also usually presumed that the transition from dependence to independence of property on molecular weight corresponds to the transition from brittle to non-brittle behaviour for an inherently tough material. Most properties are presumed to be independent of molecular weight at higher molecular weights.

Koros *et al.*[3], in a recent review, noted that several factors can influence selectivities in gas separation membranes. They pointed out that, for example, differences in processing procedures for polymers with the same chemical structure influence selectivities. In this report we draw attention to the fact that at 'high' molecular weights permeability characteristics can continue to show molecular weight dependence and that molecular weight variations, even at high molecular weight, may lead to changes in properties equal to differences caused by modifying the chemical structure.

We describe the influence of molecular weight of three chemically identical copolymers on gas-permeability behaviour and compare these with changes in chemical constitution of copolymers of similar molecular weight. In this study all copolymers were based on commercially available materials. All the copolymers were prepared by identical procedures and any reagent used in different copolymers was from the same batch of material. Processing procedures for the several polymers were identical.

EXPERIMENTAL

Materials

6FDA (Riedel de Haan), bis(4-aminophenyl) ether (4,4′-ODA) (ultra-pure, BP) and tetramethylbenzidene (TMB) (99%+, Aldrich) were used as supplied. 3,4′-Diaminodiphenyl ether (3,4′-ODA) (Mitsui Petrochemical Industries) was recrystallized from tetrahydrofuran (THF), and *m*-phenylenediamine (m-PDA) (Lancaster Synthesis) was purified by sublimation. *N*,*N*-Dimethylacetamide (DMAC) was anhydrous ($<0.005\%$ water, Aldrich). Other materials were general laboratory reagents.

Isopropylidene bisaniline (IPBA) was synthesized according to the procedure of Liu *et al.*[4]. Aniline hydrochloride, acetone and water were reacted under nitrogen at 145°C in a glass pressure bottle for 8 days. After cooling, the mixture was neutralized and extracted. Excess aniline was removed by reduced-pressure distillation. Yields of up to 55% were achieved with molar ratios of aniline hydrochloride:acetone:water of 2.25:1:7.9. The product was recrystallized from water to provide a material of sufficient purity to produce high-molecular-weight polymer. The final product had a melting point of 132–133°C.

Preparation of copolymers

The several copolymers were prepared by a conventional two-stage process involving synthesis of the

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poly(amic acid) followed by chemical imidization in solution[5]. All copolymers were prepared from 6FDA with an equimolar mixture of two diamines. The diamines were dissolved in DMAC at room temperature and an equimolar amount of 6FDA (based on total diamines used) was added. The mixture was allowed to react to form the poly(amic acid) for various times between 2 and 12 h. An equivolume mixture of acetic anhydride and pyridine was added to imidize the poly(amid acid); the mixture was allowed to react for 12 h. Polymers were precipitated into methanol and were reprecipitated from THF or chloroform. The compositions of the final copolymers were confirmed by ^{1}H n.m.r. spectroscopy on solutions of the copolymers.

Characterization of polyimides

The molecular weights of the copolymers were determined by gel permeation chromatography using an instrument calibrated with polystyrene standards. The columns were PL-gel polystyrene beads and the mobile phase was THF.

Sample preparation

Samples were fabricated as dense films by solvent casting from dilute solution in dichloromethane or chloroform. The films were preheated for several days at 200°C under vacuum to remove residual solvent.

Gas permeation

The permeability of the copolymers (P_i) to an individual gas i was determined for the transport of carbon dioxide, oxygen, nitrogen and methane using pure gases (BOC or Air Products, used without further purification) at 35°C for various pressures in the range 100–650 kPa. Films (40–70 μm thick) cast from dichloromethane were used. Selectivities between gases i and j ($S_{i,j} = P_i/P_j$) were calculated from these permeabilities.

Glass-transition temperatures

Glass-transition temperatures (T_gs) of the polymers were determined by differential scanning calorimetry using a Perkin Elmer DSC2 with a heating rate of 20°C min^{-1}.

Densities

Densities of the copolymer films were determined by a density gradient column based on aqueous potassium iodide solutions.

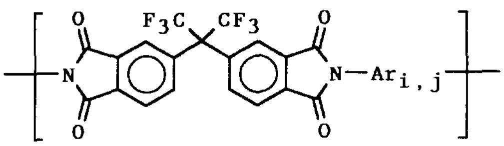
Tensile properties

Dumb-bells were die punched from chloroform-cast films ($\sim$100 μm thick) with the aid of a Wallace Press with type 2 cutter. Samples were subject to tensile testing on an Instron machine using a gauge length of 46 mm and a crosshead speed of 5 mm min^{-1}.

RESULTS

Nature of materials used

The copolyimides used were all based on 6FDA with equimolar mixtures of two diamines and have the general structure I. The diamines used in the syntheses are defined in *Table 1* together with the designations of the copolymers. It is assumed that in all cases the distribution of diamine residues is random.



I

Three samples of copolymer 6FDA/4,4'-ODA/IPDA of different molecular weights and one sample of each of 6FDA/TMB/3,4'-ODA and 6FDA/IPDA/m-PDA were studied. These copolymers and their molecular weights, T_gs, densities and mechanical properties are given in *Table 2*. The two higher-molecular-weight samples of 6FDA/4,4'-ODA/IPDA had virtually identical T_gs and tensile properties. Thus, it is seen that the three 6FDA/4,4'-ODA/IPDA copolymers had significantly different molecular weights, with M_w and M_{peak} varying by a factor of 2.5; values of M_{peak} correspond to the peak of the gel permeation chromatograms. All polymers had sufficiently high molecular weights that their films had excellent mechanical properties, were repeatedly creasable and yielded under tensile load. In our experience, good mechanical properties in polyimides require M_{peak} values in excess of 50–60 kg mol^{-1}; to yield under tension requires $M_{peak} > 85$ kg mol^{-1}. Recent work on several polyimides[2] indicates that values of M_n determined in this way are less reliable than values of M_w; absolute determinations of M_n by membrane osmometry and assuming a polydispersity close to two indicate that values of M_w quoted are somewhat greater than the true values.

Gas permeabilities

Carbon dioxide permeabilities and carbon dioxide/methane selectivities for the three 6FDA/4,4'-ODA/IPDA copolymers are presented in *Figure 1*. Although the polymers have the same density, within experimental error, and sufficiently high molecular weight to have excellent mechanical properties, there was a definite increase, outside experimental error, in both carbon dioxide permeability and carbon dioxide/methane selectivity with increasing molecular weight. A small systematic increase in methane permeability (0.63–0.71) was also measured, but this might be within experimental error. The data indicate that while in other respects, 6FDA/4,4'-ODA/IPDA copolymers were very similar, their abilities to separate carbon dioxide and methane improved with increasing molecular weight.

Since the 6FDA/4,4'-ODA/IPDA copolymers all had near-identical densities it is not clear how to attribute the differences in gas permeability with molecular weight since, for a given polymer, permeabilities might only be expected to vary with changes in molecular packing. It might be argued that 6FDA/4,4'-ODA/IPDA-1 has a

Table 1 Aromatic residues, $\mathrm{Ar}_{i,j}$, in structure I from diamines

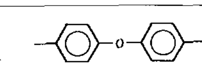
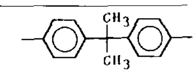
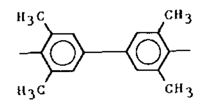
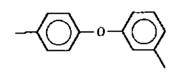
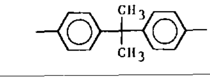
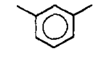
Polymer code	Ar_i	Ar_j
6FDA/4,4'-ODA/IPDA		
6FDA/TMB/3,4'-ODA		
6FDA/IPDA/m-PDA		

Table 2 Characteristics of copolyimides

Polymer code	Molar mass (kg mol^{-1}) M_n	M_w	M_{peak}	Film density (g cm^{-3})	T_g (°C)	Tensile modulus (GPa)	Tensile strength (MPa)
6FDA/4,4′-ODA/IPDA-1	44	137	120	1.395±0.006	305.7	2.61	84.87
6FDA/4,4′-ODA/IPDA-2	59	256	215	1.393±0.006	315.5	2.93	91.33
6FDA/4,4′-ODA/IPDA-3	84	339	298	1.396±0.019	316.2	2.83	90.75
6FDA/TMB/3,4′-ODA	48	166	157	1.362±0.001	310.8		
6FDA/IPDA/m-PDA	45	148	142	1.402±0.001	294.2		

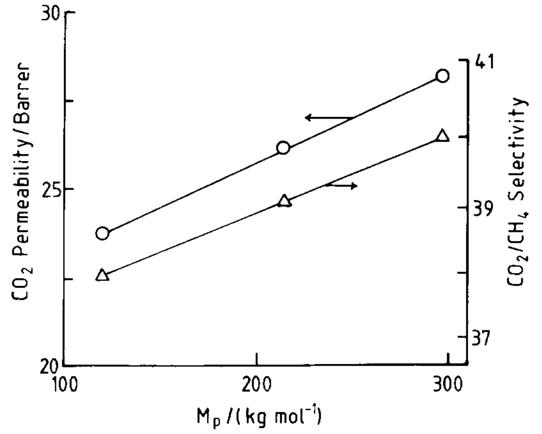


Figure 1 Variations of carbon dioxide permeability and carbon dioxide/methane selectivity with molecular weight for a series of chemically identical copolyimides (Barrer = 10^{-10} cm^3 (STP) cm (cm^2 s cm Hg)$^{-1}$)

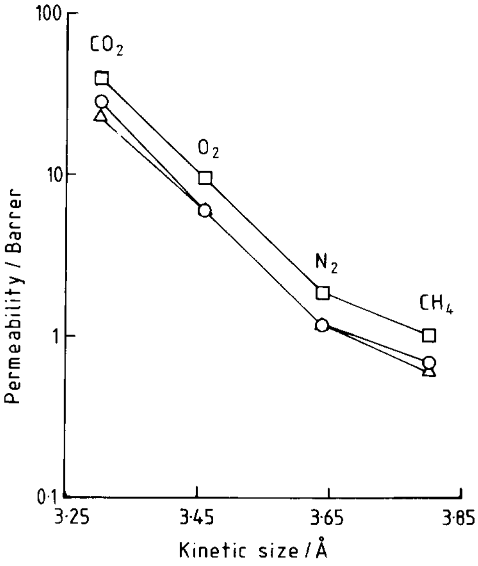


Figure 2 Permeabilities of copolyimides to various gases as a function of kinetic diameters: ○, 6FDA/4,4′-ODA/IPDA; □, 6FDA/TMB/3,4′-ODA; △, 6FDA/IPDA/m-PDA

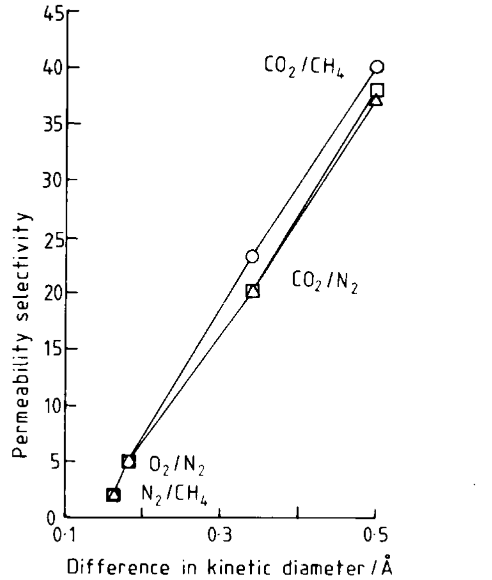


Figure 3 Variation in permeability selectivity for a series of pairs of gases with difference in kinetic diameters of the gases for a series of copolyimides: ○, 6FDA/4,4′-ODA/IPDA; □, 6FDA/TMB/3,4′-ODA; △, 6FDA/IPDA/m-PDA

molecular weight in the range where properties and free volume change with molecular weight; T_gs and tensile properties for 6FDA/4,4′-ODA/IPDA-1 are slightly lower than those of other samples. This view is counterbalanced by the variation in permeability for the higher-molecular-weight samples, where T_gs and mechanical properties are molecular-weight independent. The possibility of additional chain ends contributing towards enhancing molecular mobility in lower-molecular-weight samples was discounted because at 35°C all the polymers are well below their T_gs (*Table 2*). In any case, larger free volumes and molecular mobilities (i.e. lower molecular weights) would normally be expected to enhance permeabilities and reduce selectivities. We cannot attribute our observations to any specific molecular phenomenon but there may be a subtle influence of molecular weight on chain packing and numbers of chain entanglements when films are cast from solution.

To put the magnitudes of these changes into context, *Figure 2* compares the permeabilities of three chemically different copolymers of comparable molecular weights for a series of gases. Permeability data for the gases are plotted as functions of their kinetic sieving diameters. Similarly, *Figure 3* compares the permeability selectivities for several systems.

Comparison of the three sets of permeability data indicates that the differences in permeability and selectivity due to changes in molecular weight of 6FDA/4,4′-ODA/IPDA samples are comparable to changes obtained by marked modifications in chemical structures of the copolymers; for example, by incorporating *meta*-linked phenyl groups or pendent alkyl groups. Thus, even when polymers of 'high molecular weight' are investigated, gas permeabilities and selectivities may vary with molecular weight to such an extent that such variations may mask or confuse differences attributable to changes in chemical structure.

CONCLUSIONS

It was found that gas permeabilities of polymers of 'high' molecular weight can vary with molecular weight. Variations observed were comparable to those achieved by modifying the chemical structures of the polymers. Therefore, when deriving detailed structure–property relations, molecular weight effects should be considered in analysing permeability data. Ideally, to avoid ambiguity, polymers of comparable molecular weight should be investigated, although there may be problems in achieving this in practice.

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