

Free volume and intrinsic microporosity in polymers

Peter M. Budd,^{*a} Neil B. McKeown^b and Detlev Fritsch^c

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The concept of free volume is useful for explaining aspects of the chain mobility and permeability of polymers, even though its precise definition is subject to debate. Polymers that trap a large amount of interconnected free volume in the glassy state behave in many respects like microporous materials and potentially find application in membrane separations and heterogeneous catalysis. The development is outlined of a new type of polymer, for which the molecular structure contains sites of contortion (*e.g.* spiro-centres) within a rigid backbone (*e.g.* ladder polymer). These polymers of intrinsic microporosity (PIMs) include both insoluble network polymers and soluble non-network polymers that may be processed into membranes or other useful forms. Experimental methods are discussed for elucidating the free volume or micropore distribution, and the behaviour of PIMs is compared with that of the ultrapermeable polymer poly(1-trimethylsilyl-1-propyne).

*Peter.Budd@manchester.ac.uk



Peter M. Budd

Peter M. Budd is a Senior Lecturer at the University of Manchester, with interests in physical chemistry and polymer science. He received his PhD in polymer chemistry from Manchester in 1981, then spent eight years as a research chemist at BP's laboratories in Sunbury-on-Thames, before returning to Manchester as a lecturer. His current research focuses on novel materials and processes for molecular separations and transformations.



Neil B. McKeown

Neil B. McKeown received his PhD in organic chemistry from the University of East Anglia in 1987. After four years post-doctoral research in Toronto, he returned to the UK to take up a lectureship in polymer chemistry at the University of Manchester. In 2004 he was appointed as a Professorial Research Fellow at Cardiff University. His research interests involve the synthesis of functional organic materials including phthalocyanines and microporous polymers.

Introduction

“Nature—unqualified Being—has two forms that make it up: the atoms, and the void where atoms are placed and travel their varied paths.” Lucretius, *The Nature of Things*, Book I, lines 419–421, transl. F. O. Copley.¹

According to the philosophy of Epicurus (*ca.* 341–271 BC), as expressed by the Latin poet Lucretius (*ca.* 99–55 BC), all things are made up of matter—atoms in constant motion—and void, without which atoms could not move. The same distinction between “occupied volume” and “free volume” is employed today by polymer scientists to help explain aspects of polymer chain mobility and of the transport of small molecules through polymers. A glassy polymer may be considered to contain a certain amount of frozen free volume as isolated elements. If the proportion of free volume is increased to the extent that it is effectively interconnected, the polymer may take on the characteristics of a microporous material (*i.e.*, containing pores of dimensions <2 nm). Such



Detlev Fritsch

Detlev Fritsch, born in 1952, joined Merck KgaA, Germany in 1967 for an apprenticeship as a laboratory assistant. Later, he attended the Freie Universität Berlin, completing his PhD in organic chemistry in 1984. He joined GKSS-Forschungszentrum in Geesthacht, Germany in 1987, where he now heads a group for polymer synthesis and membrane development. His focus is on new polymers, membrane development and membrane processes.

polymers offer considerable scope for application in molecular separations and heterogeneous catalysis, and have properties that complement those of conventional microporous materials such as zeolites and activated carbons.

This article explores the territory that lies between dense polymer systems and porous solids. Key ideas are outlined concerning free volume in polymers and a new approach is discussed for generating polymers with molecular structures that give rise to intrinsic microporosity.

Free volume and the glass transition

The idea that molecular motion in liquids and solids requires molecule-sized holes was developed by Eyring² and others. These holes, which collectively make up the free volume, are constantly moving in the liquid state. Doolittle³ related the viscosity of a liquid to its relative free volume. In the context of polymers, a hole, or free volume element, may be considered to be similar in size to a segment of a polymer molecule and more than one may be required for mobility (*i.e.*, motion in polymers involves cooperative movement of portions of a polymer chain). Fox and Flory⁴ suggested that the glass transition, T_g , represents an iso-free volume state, occurring at a critical fractional free volume for large scale movement of polymer segments. The fractional free volume, f_v , in the glassy state may be calculated as 0.025 (*i.e.*, 2.5% free volume) on the basis of the Williams–Landel–Ferry (WLF) equation,⁵ which describes the temperature dependence of viscosity and relaxation times for amorphous polymers, and which may be derived on the basis of the Doolittle relationship. A substantially larger f_v at T_g may be inferred from Simha and Boyer's relationship, $(\alpha_R - \alpha_G)T_g = 0.113$, where α_R and α_G are the coefficients of thermal expansion in the rubbery and glassy states, respectively.⁶ Other attempts to quantify free volume give further different values, depending on the assumptions made about what constitutes free volume.

There are a number of contributions to a polymer's specific volume, V ($= 1/\rho$, where ρ is polymer density), as indicated in Fig. 1a. Firstly, there is the molecular volume, a useful estimate of which is the specific van der Waals volume, V_w , which can be calculated by group contribution methods.^{7,8} When molecules are packed in a condensed phase, there is a limit to the packing density which can be achieved, so each molecule actually requires more space than its molecular volume. Typically, V_w is multiplied by 1.3, based on the packing density of a molecular crystal at 0 K. Some workers regard this as the occupied volume, in which case the fractional free volume is given by eqn. (1).

$$f_v = (V - 1.3V_w)/V \quad (1)$$

For a variety of glassy polymers, this approach gives values of f_v in the range 0.11–0.23.⁹ The free volume may then be subdivided into two types: interstitial free volume, which is spread amongst all the molecules, and hole free volume, which is localised but readily redistributed.¹⁰ It is the hole free volume that is of relevance to the WLF equation.

Whilst some workers define the occupied volume as the volume of the liquid at equilibrium at 0 K,¹⁰ in which case it

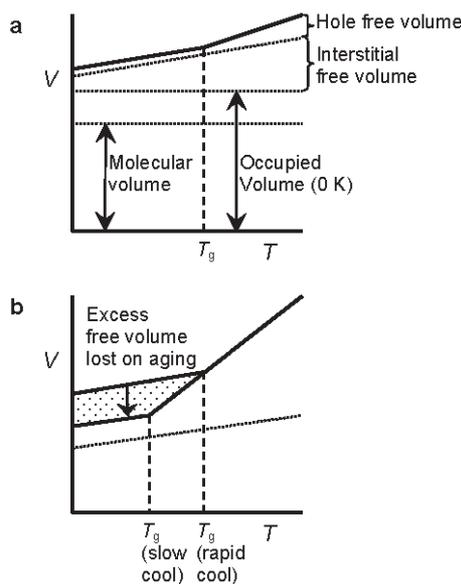


Fig. 1 (a) One interpretation of the contributions to the specific volume of a polymer and their dependence on temperature. (b) Illustration of kinetic effects and the process of physical aging.

is independent of temperature, others include the effect of thermal vibrations in the occupied volume. A picture presented in many polymer textbooks is that the occupied volume increases approximately linearly with temperature throughout the glassy and rubbery regimes, whilst the free volume is approximately constant in the glassy state but increases rapidly with temperature in the rubbery state.^{11,12} Despite the lack of consensus as to the definition of free volume, it has proved a remarkably useful semi-quantitative concept.

Experimentally, T_g is marked by a change in the slope of a plot of V versus T , which is the kind of behaviour expected for a second-order thermodynamic transition. However, T_g is very strongly influenced by kinetic effects and over the years there has been much debate as to whether T_g is a purely kinetic phenomenon, or whether it overlies a genuine thermodynamic transition. If a rubber is cooled rapidly, the observed T_g is higher than if it is cooled slowly (typically, a tenfold change in cooling rate leads to about a 3 K change in T_g). If the sample is then held at constant temperature a little below T_g , it is found that V decreases over time, a process referred to as isothermal volume recovery or physical aging (Fig. 1b). This can be understood in terms of excess free volume trapped on rapid cooling and slowly lost on physical aging. The aging process is accompanied by changes in the mechanical and permeation properties of the polymer.

Transport of small molecules through polymers

The transport properties of small molecules in polymers are of significance because of the effect a molecular penetrant can have on the mechanical and other properties of a polymer, and are of particular relevance to barrier polymers (where the aim is to inhibit transport), controlled release polymers (where transport of an active agent out of the polymer should happen in a predetermined fashion) and membrane polymers (where

preferential transport of one component of a mixture is desired). Membrane processes that utilise polymers include gas separation (e.g., nitrogen generation from air), vapour permeation (e.g., recovery of volatile organic compounds from gas streams), pervaporation (e.g., dehydration of ethanol) and reverse osmosis (e.g., desalination of water).¹³ Of special interest here is gas separation, which has provoked a great deal of research into the relationships between polymer structure and transport properties.

The permeation of small molecules through an amorphous rubbery membrane, driven by a partial pressure difference across the membrane, is often understood in terms of a solution–diffusion model. Gas molecules on the high-pressure side of the membrane dissolve in the polymer, diffuse down a concentration gradient, and desorb on the low pressure side of the membrane. The permeability coefficient, P , is the product of a solubility coefficient, S , and a mutual diffusion coefficient or diffusivity, D (eqn. (2)).

$$P = SD \quad (2)$$

The permeability of small molecules through an amorphous glassy membrane is usually much lower than for a rubbery material, although there are exceptions as will be discussed later. For glassy polymers, P often decreases with increasing pressure, but may subsequently increase because of plasticization. The decrease in P may be understood in terms of a dual-mode sorption model.^{14–18} Excess free volume in the glassy state is assumed to exist as isolated microvoids, within which sorption of small molecules occurs. Small molecules may also dissolve in and diffuse slowly through dense regions of polymer. There is thus a local equilibrium between dissolved molecules (for which Henry's law is assumed to apply) and sorbed molecules (for which a Langmuir model is employed). The pressure-dependence of P is a consequence of the shape of the adsorption isotherm, which is concave to the pressure axis.

The diffusion process involves both small molecule and polymer motion. The mobility of polymer segments is slow compared to translational motion of small molecules, so the limiting step in diffusion is generally considered to be the movement of a polymer segment to provide a space into which a small molecule can move. Diffusion coefficients may be related to the fractional free volume (eqn. (3)).¹⁹

$$D = A \exp(-B/f_v) \quad (3)$$

Various forms of eqn. (3), differing in the definitions of A and B , have been used to describe the mobility of small molecules in rubbery^{20–22} and glassy^{23,24} polymers. Since small molecules can themselves contribute free volume to the system, diffusion coefficients may depend strongly on concentration.

Thran *et al.*⁹ have investigated the correlation between D and f_v for several gases in a range of glassy polymers. They conclude that, whilst D for weakly interacting molecules is determined largely by f_v , other factors also have an influence. There is a dependence on the polymer structure, which is related to the stiffness of the polymer chains and to the cohesive energy. There is also a dependence on the nature of

the penetrant, and it is suggested that very small species, in particular H_2 and He , are able to diffuse through the fixed interstitial free volume rather than being dependent on fluctuations in the hole free volume.

For membrane processes, the ability to discriminate between components of a mixture is important, and for a mixture of two species, A and B, the selectivity, $\alpha_{A/B}$, may be expressed as a ratio of permeabilities (eqn. (4)).

$$\alpha_{A/B} = P_A/P_B = (S_A/S_B)(D_A/D_B) \quad (4)$$

In terms of the solution–diffusion model, selectivity may arise either through the solution term (solubility selectivity) or through the diffusion term (mobility selectivity). For rubbery polymers, with their high free volumes, values of D are relatively high and the mobility selectivity is low. Rubbery polymers are most commonly employed for their ability to separate large organic vapour molecules from smaller gas molecules, because of their high solubility selectivity. On the other hand, conventional, low free volume, glassy polymers exhibit low values of D and show a high mobility selectivity, smaller gas molecules diffusing more rapidly than larger ones.

For gas separations, most attention has been paid to glassy polymers, because high selectivities can be achieved. However, glassy polymers usually exhibit much lower permeabilities than are desirable for practical application. It has been found that modifications to the polymer structure that improve permeability generally lead to a decrease in selectivity and *vice versa*. In other words, there is a trade-off between selectivity and permeability. Robeson²⁵ demonstrated an upper bound in double logarithmic plots of selectivity against permeability for a wide range of polymers. Robeson's 1991 upper bound for O_2/N_2 is shown in Fig. 2, together with more recent data^{26–69} for polymers that perform close to, or exceed, the upper bound. The objective of much research is to generate polymers that perform in the upper right region of Fig. 2, and some of the most interesting materials achieved thus far are polymers of intrinsic microporosity (PIMs).

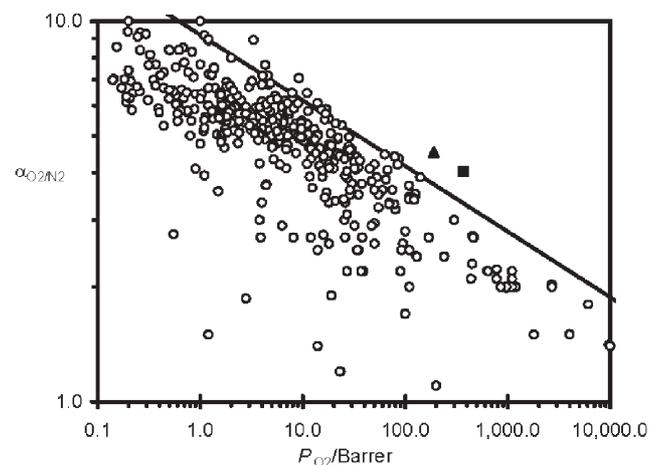


Fig. 2 Relationship between oxygen/nitrogen selectivity and oxygen permeability. (—) Robeson's 1991 upper bound.²⁵ (○) More recent results for a range of polymers.^{26–69} (■) PIM-1. (▲) PIM-7.

Polymers that perform in the vicinity of the upper bound are generally stiff-chain glassy polymers, whilst rubbery materials lie well below the upper bound. Polymers that function well with one pair of gases usually also perform well with other pairs of gases. The slope of the upper bound relates to the kinetic diameters of the gases involved. Freeman⁷⁰ has developed a theory to rationalize these observations and justify an empirical principle that to obtain the best permeability/selectivity properties, up to a limit, one needs to create a polymer structure with a stiff backbone (which enhances mobility selectivity at the expense of diffusivity) whilst also disrupting interchain packing (to improve permeability). This principle is taken to the extreme with PIMs, as is discussed later. Alentiev and Yampolskii⁷¹ showed that the trade-off behaviour could be predicted on the basis of a free volume model. Both Freeman⁷⁰ and Alentiev and Yampolskii⁷¹ indicate that one way to surpass the upper bound is for solubility selectivity (S_A/S_B) to be enhanced. It will be seen later that, even if the ratio S_A/S_B is unchanged, a significant improvement can be achieved through an overall increase in S , and hence P .

Ultra-high free volume polymers

In recent years, several glassy polymers have been developed that exhibit remarkably high gas permeability, attributed to extremely high excess fractional free volume. Notable amongst these are poly(1-trimethylsilyl-1-propyne) (PTMSP),^{65,72} poly(4-methyl-2-pentyne) (PMP),⁷³ and a 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole-tetrafluoroethylene copolymer (designated Teflon AF 2400 by Du Pont).^{60,74} The structures of these polymers, and their permeabilities, are indicated in Table 1.

Table 1 Typical values of oxygen permeability^a and oxygen/nitrogen selectivity for some ultra-high free volume polymers

Polymer	Structure	P_{O_2} / Barrer	α_{O_2/N_2}	Ref.
PTMSP		6100	1.8	65
PMP		2700	2.0	73
Teflon AF 2400		1600	2.0	60

$n = 0.87, m = 0.13$

^a Units of permeability coefficient: 1 Barrer = 10^{-10} cm³ [STP] cm cm⁻² s⁻¹ cmHg⁻¹ = 3.35×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹.

PTMSP is known as the most permeable of all polymers to gases. It has a backbone of alternating single and double bonds, like other polyacetylenes, but the double bonds are not significantly conjugated.⁶⁵ The bulky trimethylsilyl and methyl groups cause the polymer chain to be twisted. Furthermore, there is a very high barrier to rotation about the single bonds (170 kJ mol⁻¹),⁷⁵ so that at normal temperatures it cannot easily change its conformation. These twisted, inflexible polymer chains trap a considerable amount of excess free volume ($f_v = 0.32$, based on eqn. (1)).⁷⁶ Sorption measurements suggest that PTMSP is essentially porous, with a void fraction of about 0.25, leading to the suggestion that free volume elements are connected to give a micropore structure.⁷⁷ The permeability of PTMSP depends on the history of the sample and can decrease dramatically over time, which has been attributed in part to changes in the amount and distribution of free volume.⁷⁸

Polymers of intrinsic microporosity (PIMs)

A few years ago, a programme of research commenced in Manchester aimed at generating organic microporous materials through step-growth polymerization. The initial objective was a network polymer incorporating planar phthalocyanine units, with a microporous structure allowing access to a catalytically active transition metal ion within the central cavity of the macrocycle. Whilst phthalocyanines are potentially useful and versatile catalysts, and are utilised for the oxidative destruction of sulfurous impurities in crude petrochemicals, their application as heterogeneous catalysts is limited because of the strong tendency for the macrocycles to stack together through π - π and other non-covalent interactions. Previous attempts at network formation had resulted in non-porous solids.⁷⁹ We sought, therefore, to link the macrocycles together through rigid, nonlinear linking units that would inhibit cofacial association and prevent structural relaxation to a dense solid. A suitable linking unit is derived from the commercially available monomer 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (**A1** in Fig. 3). The fused ring structure gives rigidity and the spiro-centre (*i.e.*, a single tetrahedral C atom shared by two rings) makes it nonlinear (*i.e.*, provides a site of contortion). A double aromatic nucleophilic substitution reaction of **A1** with 4,5-dichlorophthalonitrile yields a bis(phthalonitrile) precursor that forms a phthalocyanine network, *via* a cyclotetramerization facilitated by a metal ion template (Fig. 3).⁸⁰ The network polymers are obtained as highly coloured, free-flowing, insoluble powders. Low-temperature N₂ adsorption measurements (discussed further below), indicate high apparent surface areas (500–1000 m² g⁻¹ by BET analysis), with significant adsorption at very low relative pressures ($p/p^\circ < 0.01$), suggestive of a microporous structure. Studies of the activity of the phthalocyanine networks as heterogeneous catalysts, using hydrogen peroxide degradation as a test case, demonstrate a substantial improvement when compared to precipitated low molar mass phthalocyanines (Fig. 4).

The next objective was to establish a more general route to microporous network polymers. The remarkably efficient double aromatic nucleophilic substitution (*i.e.*, dioxane-forming

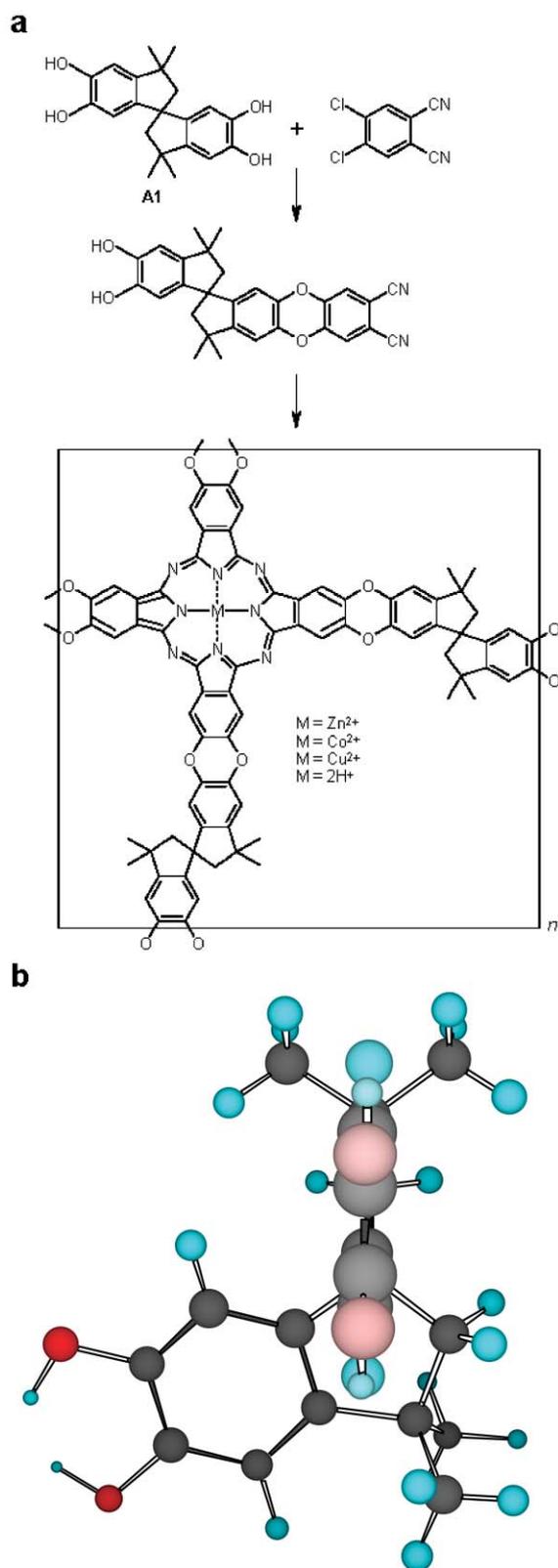


Fig. 3 (a) Preparation of spiro-linked phthalocyanine network polymer. (b) Model of monomer A1 showing the site of contortion.

reaction)^{81,82} between an aromatic monomer bearing multiple hydroxyl groups and an aromatic monomer bearing multiple fluorines (or chlorines) proved eminently suitable (Fig. 5).

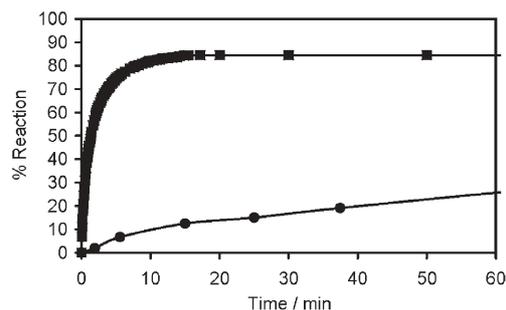


Fig. 4 Dependence of extent of reaction on time for the degradation of H_2O_2 (0.74 mol dm^{-3} , $T = 30 \text{ }^\circ\text{C}$) with (●) low molar mass Co phthalocyanine and (■) spiro-linked Co phthalocyanine network as catalyst (1 mol% Co). Oxygen evolution measured with a gas burette. Data obtained by Helen Kingston (University of Manchester). Phthalocyanine network prepared by Verena Maffei (University of Manchester).

We were thus able to generate network polymers with high apparent surface areas incorporating pre-formed phthalocyanine (monomers A1 + B3, Fig. 5), porphyrin (monomers A1 + B1, Fig. 5),⁸³ hexaazatrinaphthylene (monomers A1 + B2, Fig. 5)⁸⁴ and other units with ligands capable of binding to metal ions or with cavities able to host organic molecules. To obtain an intrinsically microporous polymer, at least one of the monomers must contain a *site of contortion* such as a spiro-centre (monomer A1, Fig. 5), a non-planar rigid skeleton (monomers A2, A4, A7, Fig. 5) or a single covalent bond about which rotation is severely hindered (monomers A5, B1, Fig. 5). For network formation, the average functionality of the pair of monomers should be greater than two, with each pair of adjacent hydroxyl groups or fluorines counting as a single functional group for dioxane formation.

Having established a general approach to microporous networks, we explored the potential of non-network polymers formed from pairs of bifunctional monomers. Reaction of monomer A1 with tetrafluorophthalonitrile (monomer B4, Fig. 5) was found to give a fluorescent yellow polymer of high molar mass ($M_w = 140\,000 \text{ g mol}^{-1}$ by gel permeation chromatography with light scattering detector).^{85,86} This polymer (termed PIM-1) is soluble in solvents such as tetrahydrofuran and chloroform, and can be precipitated as a powder or cast from solution to form a robust membrane. Low-temperature N_2 adsorption–desorption analysis (see below) indicates that PIM-1 in powder or membrane form has a high apparent surface area and exhibits microporous character. Dynamic mechanical analysis of a PIM-1 membrane shows a tensile storage modulus of 0.9 GPa, decreasing only marginally up to its decomposition temperature ($>350 \text{ }^\circ\text{C}$).⁸⁶ There is no evidence of crystallinity or a glass transition below the decomposition temperature. The rigid but highly contorted molecular structure of PIM-1, that frustrates efficient packing in the solid state, is illustrated in Fig. 6.

Membranes of PIM-1 were tested for the removal of organic compounds from aqueous solution by pervaporation.⁸⁶ The membranes are organophilic, the permeate being enriched in the organic component (*e.g.*, a feed of 5 wt% phenol in water gave a permeate of nearly 50 wt% phenol), and the

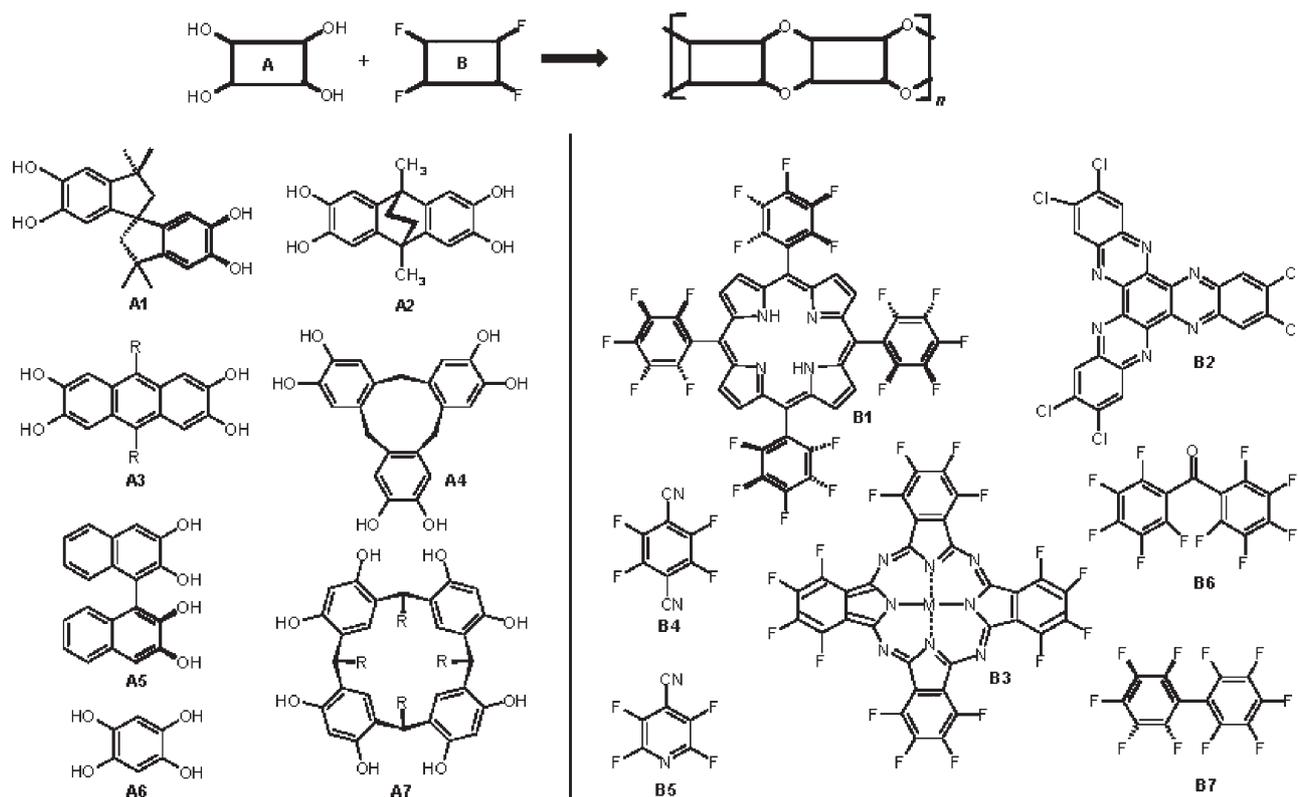


Fig. 5 Preparation of PIMs by the dioxane-forming polymerization of appropriate hydroxylated aromatic monomers (e.g., A1–A7) with fluorinated or chlorinated aromatic monomers (e.g. B1–B7). For microporosity at least one monomer must contain a site of contortion.

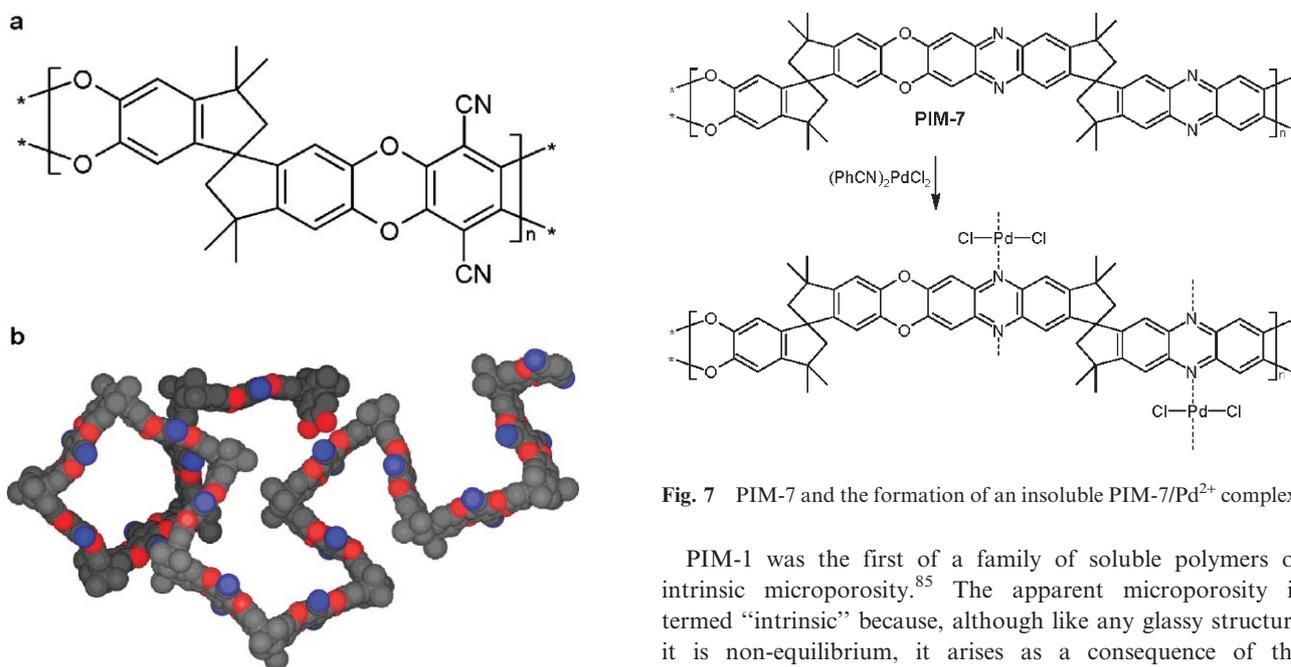


Fig. 6 (a) Chemical structure of PIM-1. (b) Molecular model of PIM-1 showing its highly contorted, rigid structure.

fluxes achieved were comparable to the rubbery polymer poly(dimethyl siloxane). This is unusual for a glassy polymer, with the notable exception of PTMSP.⁸⁷

Fig. 7 PIM-7 and the formation of an insoluble PIM-7/Pd²⁺ complex.

PIM-1 was the first of a family of soluble polymers of intrinsic microporosity.⁸⁵ The apparent microporosity is termed “intrinsic” because, although like any glassy structure it is non-equilibrium, it arises as a consequence of the molecular structure and is not generated solely through processing. The common features of a PIM are (i) no, or very highly restricted, rotational freedom about all bonds in the backbone and (ii) the inclusion of sites of contortion such as spiro-centres.

The gas permeation properties of membranes formed from PIM-1 (Fig. 6) and PIM-7 (Fig. 7) were investigated at the

Table 2 Gas permeation data^a at 30 °C for a PIM-1 membrane (46 μm thick) and a PIM-7 membrane (28 μm thick)⁸⁸

PIM	Gas	P_X/Barrer	$D_X/10^{-8} \text{ cm}^2 \text{ s}^{-1}$	$S_X/10^{-3} \text{ cm}^3 \text{ cm}^{-3} \text{ cmHg}^{-1}$	α_{X/N_2}	D_X/D_{N_2}	S_X/S_{N_2}
PIM-1	N ₂	92	22	42	—	—	—
PIM-1	O ₂	370	81	46	4.0	3.7	1.1
PIM-1	H ₂	1300	1700	7.6	14	77	0.2
PIM-1	CO ₂	2300	26	880	25	1.2	21
PIM-1	CH ₄	125	6.8	180	1.4	0.3	3.9
PIM-7	N ₂	42	16	26	—	—	—
PIM-7	O ₂	190	62	31	4.5	3.9	1.2
PIM-7	H ₂	860	1100	8	20	69	0.3
PIM-7	CO ₂	1100	21	520	26	1.3	20
PIM-7	CH ₄	62	5.1	120	1.5	0.3	4.6

^a P_X is permeability coefficient; units: $1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \text{ [STP]} \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} = 3.35 \times 10^{-16} \text{ mol m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. D_X is diffusion coefficient. S_X is solubility coefficient, calculated on the basis of the solution–diffusion model from $S_X = P_X/D_X$. Overall selectivity α_{X/N_2} , mobility selectivity D_X/D_{N_2} and solubility selectivity S_X/S_{N_2} are for the gas relative to N₂. The data are for measurements at 200 mbar feed pressure.

GKSS Research Centre.⁸⁸ In the permeation experiment, a membrane is held between two evacuated chambers. Gas at a particular pressure is then admitted to one chamber and the pressure in the other chamber monitored. D and P are calculated from the time-lag and the steady permeation rate, respectively. Results are given in Table 2 for a 46 μm thick PIM-1 membrane and a 28 μm thick PIM-7 membrane. The permeabilities are higher than for most glassy polymers, only exceeded by ultra-high free volume polymers such as PTMSP, PMP and Teflon AF 2400 (Table 1). However, whilst the latter polymers fall beneath Robeson's upper bound, the PIMs exhibit selectivities substantially above it for important gas pairs such as O₂/N₂ (Fig. 2). It can be seen in Table 2 that the O₂/N₂ separation for the PIMs is dominated by the mobility selectivity. The solubility selectivity is small, but the values of solubility, derived by application of the solution–diffusion model, are extraordinarily high, significantly higher than the values encountered with other polymers.⁷¹ Thus, the improved performance of PIMs over Robeson's upper bound is linked to large apparent solubilities, boosting the permeability whilst maintaining selectivity. The high apparent solubility of gases in PIMs may be attributed to the microporous character of PIMs, which provides a high capacity for gas uptake, coupled with chemical functionality that strengthens intermolecular interactions and encourages sorption. In contrast, for the ultra-high free volume polymer PTMSP the high permeability arises largely from very high diffusion coefficients.⁷⁷ Differences in behaviour between PIMs and PTMSP are likely to relate in part to differences in the distribution of free volume, as discussed below.

For commercial gas separations, very thin polymer films are necessary, to maximise the flux through the membrane. These need to be coated onto a more permeable support, for structural stability. Thin-film composite membranes have been prepared at the GKSS Research Centre by dip-coating dilute solutions of PIM-1 onto an asymmetric porous polyacrylonitrile support (Fig. 8). Composite membranes with a range of active layer thicknesses and permeation properties were obtained by varying the concentration of the coating solution, the solvent composition, and pre-treatment of the support.

In PIM-7 (Fig. 7), the phenazine unit can act as a ligand for the coordination of metal ions. For example, the addition of bis(benzonitrile)palladium(II) dichloride to a yellow solution

of PIM-7 results in immediate precipitation of a red solid, which has an apparent surface area of 650 m² g⁻¹ and contains >20 wt% Pd²⁺. This material is insoluble in all solvents tested, presumably because Pd²⁺ is acting as a crosslink between PIM-7 macromolecules, giving a network structure. We have found the palladium-containing material to be an effective heterogeneous catalyst for aryl–aryl coupling Suzuki reactions. Furthermore, a solvent-cast film of PIM-7 can be crosslinked with Pd²⁺ ions, opening up possibilities for catalytic membrane systems.

Distribution of free volume/micropores

The concept of free volume has proved extremely useful despite, as discussed earlier, the difficulty in deciding where the boundary lies between “occupied” and “free” volume. This difficulty is compounded by the likelihood that effective free volume is different for different penetrants. Furthermore, not only the amount of free volume but also its distribution (or the distribution of effective micropore size if the free volume elements are interconnected) is likely to have a significant

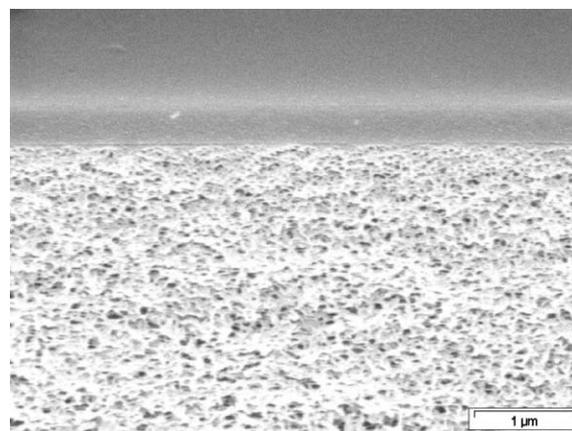


Fig. 8 Scanning electron micrograph (30° tilted) of a thin-film composite membrane of PIM-1 on an asymmetric polyacrylonitrile support. This membrane exhibits a selectivity $\alpha_{O_2/N_2} = 3.8$ and an O₂ permeance (*i.e.* permeability divided by thickness) of 0.48 m³ m⁻² h⁻¹ bar⁻¹. The 0.36 μm thick PIM-1 layer was dip-coated from tetrahydrofuran (1 wt%). SEM courtesy of Michael Schossig (GKSS Research Centre).

influence on polymer properties. A number of techniques have been used to investigate free volume in polymers, including ^{129}Xe NMR,⁸⁹ spin probe methods,⁹⁰ inverse gas chromatography⁹¹ small-angle X-ray scattering⁹² and molecular modelling.^{93,94} One of the most extensively applied techniques for determining the distribution of free volume is positron annihilation lifetime spectroscopy (PALS). Low-temperature gas adsorption methods are now also being applied to certain polymer systems. These last two methods are discussed further below.

Positron annihilation lifetime spectroscopy (PALS)

Positrons (e^+), the antiparticles of electrons (e^-), are generated by the decay of many radioactive isotopes, such as ^{22}Na . A positron may react with an electron to give a metastable positronium (Ps) particle. There are two forms of Ps which differ significantly in their average lifetimes. Antiparallel spins give *para*-positronium, *p*-Ps, which has an average lifetime in vacuum of 0.125 ns, whilst parallel spins give *ortho*-positronium, *o*-Ps, which has a much larger average lifetime in vacuum (142 ns). Within dense matter the lifetime of *o*-Ps is reduced, because it can “pick off” electrons from surrounding molecules and annihilate. In a polymer, *o*-Ps tends to be localized in free volume elements (FVE) and the lifetime may be related to the concentration, size and distribution of FVE.⁹⁵ PALS studies of the ultrapermeable polymers PTMSP and Teflon AF 2400 indicate a bimodal size distribution of FVE, with small microvoids of diameter in the range 0.5–0.8 nm and larger microvoids of diameter in the range 1–1.5 nm.⁹⁶ On moving to less and less permeable polymers, there is a loss of the larger FVE and the bimodal distribution converges ultimately on a unimodal distribution. Similar results have been obtained from molecular modelling studies.^{93,94}

Low-temperature gas adsorption

Analysis of the adsorption and desorption of N_2 at liquid N_2 temperature (77 K) is a classic method for determining the surface area and pore structure of porous materials.^{97,98} The technique has only rarely been applied to polymers, since they usually have low specific surface areas. In principle, a molecule such as N_2 can be used as a probe of microporosity, or interconnected free volume, in polymers. However, micropore filling is associated with the very low relative pressure region of the adsorption isotherm, so extremely high vacuum and very effective sample outgassing procedures are needed if suitable data are to be obtained.

Ilinitch *et al.*⁹⁹ investigated phenylene oxide polymers by low-temperature N_2 adsorption–desorption. They observed a broad hysteresis, with the desorption curve lying above the adsorption curve down to very low relative pressures. Whilst hysteresis at higher relative pressures is associated with mesoporosity (*i.e.*, containing pores of dimensions 2–50 nm),¹⁰⁰ low pressure hysteresis is generally linked to microporosity. It may arise where there is a network structure of micropores, with constrictions leading to larger cavities, or alternatively where the penetrant causes a microporous material to swell. For the phenylene oxide polymers, a series of experiments demonstrated that the adsorption process did not lead to permanent

structural changes in the polymers and that N_2 was completely removed from the samples on evacuation at ambient temperature. It was also found that the slightly smaller O_2 molecule (kinetic diameter of $\text{O}_2 = 0.346$ nm, *cf.* $\text{N}_2 = 0.364$ nm) gave higher sorption capacities and higher apparent surface areas. On the basis of these results, it was suggested that phenylene oxide polymers possess some intrinsic microporosity with effective pore diameters at 77 K around 0.4 nm.

Polymers designed to possess intrinsic microporosity, as discussed above, and ultrapermeable polymers such as PTMSP, exhibit similar low pressure hysteresis to the phenylene oxide polymers studied by Ilinitch *et al.*, but have much higher

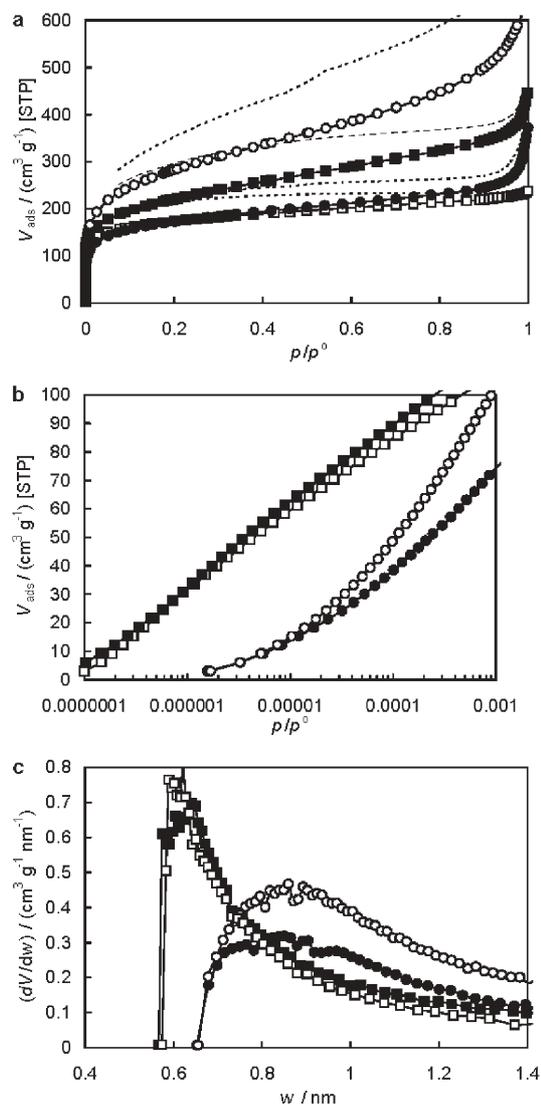


Fig. 9 Low-temperature N_2 adsorption–desorption analysis of (□) a spiro-linked Co phthalocyanine network, (■) PIM-1, (○) freshly precipitated PTMSP and (●) aged PTMSP. (a) N_2 adsorption and (---) desorption isotherms. (b) Expansion of the very low relative pressure region of the adsorption isotherms. (c) Pore size distributions calculated by the Horvath–Kawazoe method (slit-pore, carbon-graphite model). PTMSP supplied by Prof. V. Khotimskiy (Institute of Petrochemical Synthesis, Moscow). Data obtained by Carin Tattershall and Jia He (University of Manchester) using a Micromeritics ASAP 2020 analyser.

sorption capacities, indicating a more fully developed microporous structure. N₂ adsorption–desorption isotherms are shown in Fig. 9a for powder samples of a phthalocyanine network polymer, of the non-network polymer PIM-1, and of PTMSP both as received (*i.e.* an aged sample) and freshly reprecipitated. For PTMSP the sorption capacity decreases on aging, consistent with the known decrease in permeability. The very low relative pressure region of the adsorption isotherms for the four samples is expanded in Fig. 9b. Whilst the low pressure adsorption behaviour of the phthalocyanine network polymer and PIM-1 are similar to each other, for PTMSP the N₂ uptake commences at a higher relative pressure, suggesting a larger effective pore size. Fig. 9c shows pore size distributions for the four samples, calculated by the method of Horvath and Kawazoe,^{98,101,102} who related the relative pressure at which a micropore of particular size is filled to an average interaction energy within the pore. The results in Fig. 9c were obtained assuming a slit-pore geometry and using a carbon-graphite potential. Other models give qualitatively similar results, but different numerical values. Low-temperature gas adsorption shows clear differences between the PIMs and PTMSP, the latter exhibiting a greater proportion of larger micropores in the pore size distribution, consistent with the differences in gas permeability. There is a lower limit to the micropore size detectable by N₂ adsorption, determined ultimately by the size of the N₂ molecule. The procedures used here were not able to resolve a bimodal distribution for PTMSP, as obtained by PALS and molecular modelling. Further work is required to develop the most appropriate models for polymer systems and to provide proper comparison with results from other techniques.

Conclusions

The ability to tailor the molecular structure of a polymer so as to manipulate the amount and distribution of free volume enables materials to be fashioned that combine the characteristics of a conventional polymer and a microporous solid. Polymers of intrinsic microporosity (PIMs) are obtained by forming a backbone that has no freedom to change conformation, yet that is sufficiently contorted so as to prevent efficient packing. PIMs, which include both insoluble networks and soluble non-network polymers, represent a new class of microporous material, generated through polymer chemistry and offering processability combined with control over surface functionality and properties. PIMs offer unrivalled scope as bespoke materials for membrane separations, heterogeneous catalysis and other applications.

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Peter M. Budd,*^a Neil B. McKeown^b and Detlev Fritsch^c

^a*School of Chemistry and the Organic Materials Innovation Centre, The University of Manchester, Manchester, UK M13 9PL.*

E-mail: Peter.Budd@manchester.ac.uk; Fax: +161 275 4598; Tel: +161 275 4711

^b*School of Chemistry, Cardiff University, PO Box 912, Cardiff, UK CF10 3TB. E-mail: MckeownNB@cardiff.ac.uk*

^c*Institute of Chemistry, GKSS Research Centre, Max-Planck-Strasse 1, D-21502, Geesthacht, Germany. E-mail: Detlev.Fritsch@gkss.de*

References

- 1 Lucretius, *The Nature of Things*, W. W. Norton, New York, 1977.
- 2 H. Eyring, *J. Chem. Phys.*, 1936, **4**, 283–291.
- 3 A. K. Doolittle, *J. Appl. Phys.*, 1951, **22**, 1471–1475.
- 4 T. G. Fox, Jr. and P. J. Flory, *J. Appl. Phys.*, 1950, **21**, 581–591.
- 5 M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, 1955, **77**, 3701–3707.
- 6 R. Simha and R. F. Boyer, *J. Chem. Phys.*, 1962, **37**, 1003–1007.
- 7 A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, 1968.
- 8 D. W. van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1997.
- 9 A. Thran, G. Kroll and F. Faupel, *J. Polym. Sci., Part B: Polym. Phys.*, 1999, **37**, 3344–3358.
- 10 J. S. Vrentas and J. L. Duda, *Encycl. Polym. Sci. Eng.*, 1986, **5**, 36–68.
- 11 L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, New York, 1992.
- 12 U. W. Gedde, *Polymer Physics*, Chapman & Hall, London, 1995.
- 13 *Membrane Technology in the Chemical Industry*, ed. S. P. Nunes and K.-V. Peinemann, Wiley-VCH, Weinheim, 2001.
- 14 P. Meares, *J. Am. Chem. Soc.*, 1954, **76**, 3415–3422.
- 15 J. H. Petropoulos, *J. Polym. Sci., Polym. Phys. Ed.*, 1970, **8**, 1797–1801.
- 16 D. R. Paul and W. J. Koros, *J. Polym. Sci., Polym. Phys. Ed.*, 1976, **14**, 675–685.
- 17 W. R. Vieth, J. M. Howell and J. H. Hsieh, *J. Membr. Sci.*, 1976, **1**, 177–220.
- 18 Y. Tsujita, *Progr. Polym. Sci.*, 2003, **28**, 1377–1401.
- 19 M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, 1959, **31**, 1164–1169.
- 20 H. Fujita, *Fortschr. Hochpolymer. Forsch.*, 1961, **3**, 1–47.
- 21 S. A. Stern, S. M. Fang and H. L. Frisch, *J. Polym. Sci., Polym. Phys. Ed.*, 1972, **10**, 201–219.
- 22 S. M. Fang, S. A. Stern and H. L. Frisch, *Chem. Eng. Sci.*, 1975, **30**, 773–780.
- 23 J. S. Vrentas and C. M. Vrentas, *J. Polym. Sci., Part B: Polym. Phys.*, 1992, **30**, 1005–1011.
- 24 J. S. Vrentas and C. M. Vrentas, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 785–788.
- 25 L. M. Robeson, *J. Membr. Sci.*, 1991, **62**, 165–185.
- 26 Y. P. Yampolskii, A. P. Korikov, V. P. Shantarovich, K. Nagai, B. D. Freeman, T. Masuda, M. Teraguchi and G. Kwak, *Macromolecules*, 2001, **34**, 1788–1796.
- 27 K. Tanaka, H. Kita, M. Okano and K. Okamoto, *Polymer*, 1992, **33**, 585–592.
- 28 M. Al-Masri, D. Fritsch and H. R. Kricheldorf, *Macromolecules*, 2000, **33**, 7127–7135.
- 29 M. Al-Masri, H. R. Kricheldorf and D. Fritsch, *Macromolecules*, 1999, **32**, 7853–7858.
- 30 K. Tanaka, M. Okano, H. Toshino, H. Kita and K. Okamoto, *J. Polym. Sci., Part B: Polym. Phys.*, 1992, **30**, 907–914.
- 31 M. A. Tlenkopatchev, J. Vargas, M. d. M. Lopez-Gonzalez and E. Riande, *Macromolecules*, 2003, **36**, 8483–8488.
- 32 Z. K. Xu, M. Boehning, J. D. Schultze, G. T. Li, J. Springer, F. P. Glatz and R. Muelhaupt, *Polymer*, 1997, **38**, 1573–1580.
- 33 Y. P. Yampolskii, N. B. Bepalova, E. S. Finkelshtein, V. I. Bondar and A. V. Popov, *Macromolecules*, 1994, **27**, 2872–2878.

- 34 M. R. Pixton and D. R. Paul, *J. Polym. Sci., Part B: Polym. Phys.*, 1995, **33**, 1353–1364.
- 35 M. R. Pixton and D. R. Paul, *Polymer*, 1995, **36**, 3165–3172.
- 36 A. Alentiev, E. Drioli, M. Gokzhaev, G. Golemme, O. Ilinich, A. Lapkin, V. Volkov and Y. Yampolskii, *J. Membr. Sci.*, 1998, **138**, 99–107.
- 37 C. M. Zimmerman and W. J. Koros, *J. Polym. Sci., Part B: Polym. Phys.*, 1999, **37**, 1235–1249.
- 38 K. Ghosal, R. T. Chern, B. D. Freeman and R. Savariar, *J. Polym. Sci., Part B: Polym. Phys.*, 1995, **33**, 657–666.
- 39 S. L. Liu, R. Wang, T. S. Chung, M. L. Chng, Y. Liu and R. H. Vora, *J. Membr. Sci.*, 2002, **202**, 165–176.
- 40 Z. K. Xu, M. Bohning, J. Springer, F. P. Glatz and R. Mulhaupt, *J. Polym. Sci., Part B: Polym. Phys.*, 1997, **35**, 1855–1868.
- 41 R. L. Burns and W. J. Koros, *Macromolecules*, 2003, **36**, 2374–2381.
- 42 M. Heuchel and D. Hofmann, *Desalination*, 2002, **144**, 67–72.
- 43 D. Ayala, A. E. Lozano, J. de Abajo, C. Garcia-Perez, J. G. de la Campa, K. V. Peinemann, B. D. Freeman and R. Prabhakar, *J. Membr. Sci.*, 2003, **215**, 61–73.
- 44 A. Morisato, K. Ghosal, B. D. Freeman, R. T. Chern, J. C. Alvarez, J. G. de la Campa, A. E. Lozano and J. de Abajo, *J. Membr. Sci.*, 1995, **104**, 231–241.
- 45 Y. Hirayama, T. Yoshinaga, Y. Kusuki, K. Ninomiya, T. Sakakibara and T. Tamari, *J. Membr. Sci.*, 1996, **111**, 169–182.
- 46 W.-H. Lin, R. H. Vora and T.-S. Chung, *J. Polym. Sci., Part B: Polym. Phys.*, 2000, **38**, 2703–2713.
- 47 K. Ghosal, B. D. Freeman, R. T. Chern, J. C. Alvarez, J. G. de la Campa and J. de Abajo, *Polymer*, 1995, **36**, 793–800.
- 48 M. S. McCaig, E. D. Seo and D. R. Paul, *Polymer*, 1999, **40**, 3367–3382.
- 49 C. M. Zimmerman and W. J. Koros, *Polymer*, 1999, **40**, 5655–5664.
- 50 L. Yang, J. Fang, N. Meichin, K. Tanaka, H. Kita and K. Okamoto, *Polymer*, 2000, **42**, 2021–2029.
- 51 H. Kita, T. Inada, K. Tanaka and K. Okamoto, *J. Membr. Sci.*, 1994, **87**, 139–147.
- 52 C. T. Wright and D. R. Paul, *Polymer*, 1997, **38**, 1871–1878.
- 53 Y. Nagasaki, Y. Hashimoto, M. Kato and T. Kimijima, *J. Membr. Sci.*, 1996, **110**, 91–97.
- 54 G. Maier, *Angew. Chem., Int. Ed.*, 1998, **37**, 2961–2974.
- 55 C. L. Aitken, D. R. Paul and D. K. Mohanty, *J. Polym. Sci., Part B: Polym. Phys.*, 1993, **31**, 983–989.
- 56 Y. Dai, M. D. Guiver, G. P. Robertson, Y. S. Kang, K. J. Lee and J. Y. Jho, *Macromolecules*, 2004, **37**, 1403–1410.
- 57 E. Tocci, E. Bellacchio, N. Russo and E. Drioli, *J. Membr. Sci.*, 2002, **206**, 389–398.
- 58 Y. Dai, M. D. Guiver, G. P. Robertson, F. Bilodeau, Y. S. Kang, K. J. Lee, J. Y. Jho and J. Won, *Polymer*, 2002, **43**, 5369–5378.
- 59 L. M. Robeson, *Curr. Opin. Solid State Mater. Sci.*, 2000, **4**, 549–552.
- 60 I. Pinnau and L. G. Toy, *J. Membr. Sci.*, 1996, **109**, 125–133.
- 61 F. Piroux, E. Espuche, R. Mercier and M. Pineri, *Desalination*, 2002, **145**, 371–374.
- 62 Y. Liu, C. Pan, M. Ding and J. Xu, *Polym. Int.*, 1999, **48**, 832–836.
- 63 L. M. Robeson, C. D. Smith and M. Langsam, *J. Membr. Sci.*, 1997, **132**, 33–54.
- 64 L. M. Robeson, W. F. Burgoyne, M. Langsam, A. C. Savoca and C. F. Tien, *Polymer*, 1994, **35**, 4970–4978.
- 65 K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman and I. Pinnau, *Progr. Polym. Sci.*, 2001, **26**, 721–798.
- 66 S. Matsui, H. Sato and T. Nakagawa, *J. Membr. Sci.*, 1998, **141**, 31–43.
- 67 K. Matsumoto, P. Xu and T. Nishikimi, *J. Membr. Sci.*, 1993, **81**, 15–22.
- 68 Y. Li, X. Wang, M. Ding and J. Xu, *J. Appl. Polym. Sci.*, 1996, **61**, 741–748.
- 69 Y. P. Yampolskii, E. S. Finkelshtein, K. L. Makovetskii, V. I. Bondar and V. P. Shantarovich, *J. Appl. Polym. Sci.*, 1996, **62**, 349–357.
- 70 B. D. Freeman, *Macromolecules*, 1999, **32**, 375–380.
- 71 A. Y. Alentiev and Y. P. Yampolskii, *J. Membr. Sci.*, 2000, **165**, 201–216.
- 72 T. Masuda, E. Isobe, T. Higashimura and K. Takada, *J. Am. Chem. Soc.*, 1983, **105**, 7473–7474.
- 73 A. Morisato and I. Pinnau, *J. Membr. Sci.*, 1996, **121**, 243–250.
- 74 A. Y. Alentiev, Y. P. Yampolskii, V. P. Shantarovich, S. M. Nemser and N. A. Plate, *J. Membr. Sci.*, 1997, **126**, 123–132.
- 75 S. B. Clough, X. F. Sun, S. K. Tripathy and G. L. Baker, *Macromolecules*, 1991, **24**, 4264–4269.
- 76 D. S. Pope, W. J. Koros and H. B. Hopfenberg, *Macromolecules*, 1994, **27**, 5839–5844.
- 77 R. Srinivasan, S. R. Auvil and P. M. Burbhan, *J. Membr. Sci.*, 1994, **86**, 67–86.
- 78 G. Consolati, I. Genco, M. Pegoraro and L. Zangerighi, *J. Polym. Sci., Part B: Polym. Phys.*, 1996, **34**, 357–367.
- 79 N. B. McKeown, *J. Mater. Chem.*, 2000, **10**, 1979–1995.
- 80 N. B. McKeown, S. Makhseed and P. M. Budd, *Chem. Commun.*, 2002, 2780–2781.
- 81 G. C. Eastmond and J. Paprotny, *Chem. Lett.*, 1999, 479–480.
- 82 G. C. Eastmond, J. Paprotny, A. Steiner and L. Swanson, *New J. Chem.*, 2001, **25**, 379–384.
- 83 N. B. McKeown, S. Hanif, K. Msayib, C. E. Tattershall and P. M. Budd, *Chem. Commun.*, 2002, 2782–2783.
- 84 P. M. Budd, B. Ghanem, K. Msayib, N. B. McKeown and C. Tattershall, *J. Mater. Chem.*, 2003, **13**, 2721–2726.
- 85 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, 230–231.
- 86 P. M. Budd, E. S. Elabas, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall and D. Wang, *Adv. Mater.*, 2004, **16**, 456–459.
- 87 T. Masuda, B. Z. Tang and T. Higashimura, *Polym. J.*, 1986, **18**, 565–567.
- 88 P. M. Budd, K. J. Msayib, C. E. Tattershall, B. S. Ghanem, K. J. Reynolds, N. B. McKeown and D. Fritsch, *J. Membr. Sci.*, in press.
- 89 G. Golemme, J. B. Nagy, A. Fonseca, C. Algieri and Y. Yampolskii, *Polymer*, 2003, **44**, 5039–5045.
- 90 Y. P. Yampolskii, M. V. Motyakin, A. M. Wasserman, T. Masuda, M. Teraguchi, V. S. Khotimskii and B. D. Freeman, *Polymer*, 1999, **40**, 1745–1752.
- 91 Y. P. Yampolskii, N. E. Kaliuzhnyi and S. G. Durgar'yan, *Macromolecules*, 1986, **19**, 846–850.
- 92 R. J. Roe and J. J. Curro, *Macromolecules*, 1983, **16**, 428–434.
- 93 D. Hofmann, M. Entrialgo-Castano, A. Lerbret, M. Heuchel and Y. Yampolskii, *Macromolecules*, 2003, **36**, 8528–8538.
- 94 D. Hofmann, M. Heuchel, Y. Yampolskii, V. Khotimskii and V. Shantarovich, *Macromolecules*, 2002, **35**, 2129–2140.
- 95 *Principles and Applications of Positron & Positronium Chemistry*, ed. Y. C. Jean, P. E. Mallon and D. M. Schrader, World Scientific, Singapore, 2003.
- 96 V. P. Shantarovich, I. B. Kevdina, Y. P. Yampolskii and A. Y. Alentiev, *Macromolecules*, 2000, **33**, 7453–7466.
- 97 F. Schuth, K. S. W. Sing and J. Weitkamp, *Handbook of Porous Solids*, Wiley-VCH, Weinheim, 2002.
- 98 P. A. Webb and C. Orr, *Analytical Methods in Fine Particle Technology*, Micromeritics, Norcross, 1997.
- 99 O. M. Ilinitch, V. B. Felonov, A. A. Lapkin, L. G. Okkel, V. V. Terskikh and K. I. Zamaraev, *Microporous Mesoporous Mater.*, 1999, **31**, 97–110.
- 100 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniowska, *Pure Appl. Chem.*, 1985, **57**, 603–619.
- 101 G. Horvath and K. Kawazoe, *J. Chem. Eng. Jpn.*, 1983, **16**, 470–475.
- 102 J. Kurdi and A. Y. Tremblay, *Desalination*, 2002, **148**, 341–346.