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Understanding the Topology of the Polymer of Intrinsic Microporosity PIM-1: Cyclics, Tadpoles, and Network Structures and Their Impact on Membrane Performance

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Supporting Information

ABSTRACT: The synthesis of PIM-1 is reported from stepgrowth polymerizations of 5,5',6,6'-tetrahydroxy-3,3,3',3'tetramethyl-1,1'-spirobisindane with the commercially cheaper monomer, tetrachloroterephthalonitrile. Nitrogen-purged polymerizations (100-160 °C) were quenched after a monitored increase in viscosity. A combination of multiple detector size exclusion chromatography, nuclear magnetic resonance, matrix-assisted laser desorption/ionization-time of flight (MALDI TOF) mass spectrometry, dynamic light scattering, and elemental analysis was used to elucidate



significant structural differences (cyclic, branched, tadpole, extended, and network topologies) in the polymers produced under different conditions. A significant proportion of the apparent surface area (up to $200 \text{ m}^2 \text{ g}^{-1}$) associated with PIM-1 can be attributable to whether its contorted polymer chains in fact link to form cyclic or other nonlinear structures. Membranes cast from solutions of polymer samples containing higher branching and network contents exhibited higher gas pair selectivities $(CO_2/CH_4 \text{ and } CO_2/N_2)$, above the Robeson 2008 upper bound. A toolbox approach to the characterization and production of topologically different PIM-1 samples has been developed which can be used to tune membrane performance for gas separation and other applications.

INTRODUCTION

Polymers of intrinsic microporosity (PIMs) have generated significant interest for membrane separations and other applications since their initial discovery in Manchester in 2004.^{1,2} PIMs in general are designed to have highly rigid and contorted backbone structures that cannot pack efficiently and thus exhibit microporosity.^{3,4} The polymers however remain solution processable, readily cast into films which display a combination of high permeability, and exhibit significant gas pair selectivities as membranes for important industrial CO₂ separations, such as carbon dioxide/methane (CO₂/CH₄) and carbon dioxide/nitrogen (CO2/N2).5-8 As with other glassy nonequilibrium materials, problems remain with mitigating physical aging in membrane performance over its lifetime, owing to reducing free volume and increasing densification as the polymer chains strive toward thermodynamic equilibrium.⁵

The original "low" and "high" temperature routes^{1,10,11} to the first recorded polymer of this type, PIM-1, from stepgrowth polymerizations, via double nucleophilic aromatic substitution, of tetrafluoroterephthalonitrile (TFTPN) and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) are outlined in Scheme 1. Early work on the synthesis of PIM-1, focused on "low-temperature" reactions with dimethylformamide at 50-70 °C, typically reacted over a couple of days.^{1,11} These heterogeneous reactions typically produced high molecular weight polymers exhibiting generally high dispersity values. Guiver et al.¹⁰ later reported a "hightemperature" synthesis of PIM-1 from the same monomers in a mixture of dimethylacetamide (DMAc) and toluene at 155 °C in only 8 min, producing narrower molecular weight distribution polymers. Generally small variations on this "high-temperature" method, typically at 160 °C for 40 min, are now employed.¹² Differences have been observed in the performance and aging behavior of PIM-1 films as membranes; some of these variations can be attributed to the processing and treatment of the films prior to testing⁹ but others may prove to be attributable to microstructural differences generated in the polymer during the synthesis.

There have been great advances in the array of complex polymeric architectures which can be synthesized, often from living polymerization routes.¹³ Well-defined star, comb/graft, cyclic, tadpole, branched and hyperbranched, and dendritic and multiblock multicomponent polymeric structures can deliver substantial differences in the polymer physical proper-

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^aS and C residue structures are derived from the tetrahydroxy spiro monomer, TTSBI and the tetrachloro monomer, TCTPN, respectively.

ties in applications. For example, the absence of chain ends in cyclic polymeric structures imparting properties that are substantially different to those of their linear analogues of similar molecular weight, including exhibiting increased glass transition temperatures (T_g), smaller hydrodynamic volumes, and lower intrinsic viscosities.¹⁴ Cyclic structures could be considered likely in this polymerization reaction from ring closure via homodifunctional bimolecular couplings if it exhibits a vastly larger rate constant for cyclization relative to the linear chain alternatives.¹⁵ Generally extensive purification processes are required to isolate the purely cyclic structures in low polydispersities from these types of reactions.

Stiff linear polymer chains were originally proposed to be even less prone to cyclization than more flexible polymer chains. Step-growth polymerizations can proceed either with kinetic control or thermodynamic control. The small molecule byproducts of this polycondensation (HCl and KCl) do not react with the linkages in the cyclic or linear products. Recent work has also indicated that cyclic structures can be the preferred outcome in polymerizations of other rigid rod-type structures with flexible joints if they can take up folded conformations.¹⁶

Kricheldorf et al.¹⁷ have previously reported that the PIM-1 produced from polymerizations of TTSBI and TFTPN in a range of solvents was mainly composed of cyclic structures, on

the basis of extensive matrix-assisted laser desorption/ ionization-time of flight (MALDI TOF) mass spectrometry analysis. Some doubts have remained that the window of cyclic series clearly captured in the mass spectra was representative of the overall structures present in the polymers, generally shown by size exclusion chromatography (SEC) analysis to be of significantly higher molecular weights. This study builds on some of their conclusions, but in terms of the polymerization conditions, replaces the fluoro monomer with its cheaper chloro analogue, tetrachloroterephthalonitrile (TCTPN) (Scheme 1), and utilizes a new solvent mixture of DMAc and 1,2 dichlorobenzene (DCB). These changes mean that the reactions are homogeneous throughout and run to very high conversions over a wide range of temperatures $(100-160 \ ^{\circ}C)$ in short reaction times (<3 h). The polymerization quenching points are in each case determined from rapid changes in viscosity assessed via monitoring the torque changes of the mechanical overhead stirrer throughout the reactions. Chlorine is also easier than fluorine to distinguish from OH in mass terms on the potential chain ends of any linear polymeric structures (Scheme 2). The progression of the reaction of TTSBI with the chloro monomer, TCTPN, was also predicted to be different, with model compound studies suggesting slower, monosubstituted steps toward the double nucleophilic aromatic-substituted structure of the polymer.¹⁸ The un-

Table 1. Step-Growth Polymerizations of TCTPN and TTSBI To Produce Chloro Monomer-Derived PIM-1 at a Range of Temperatures under Homogeneous Conditions^a

	temperature/°C									
PIM-1 reaction	set:average	reaction time ^b /min	yield/g (%)	network content ^c /wt %	$M_{\rm w}/{ m kg\ mol^{-1}}$	$M_{\rm n}/{ m kg}~{ m mol}^{-1}$	Ð	intrinsic viscosity, $[\eta]/cm^3 g^{-1}$	hydrodynamic radius, r/nm	BET surface area ^{d} /m ² g ⁻¹
1	160:121	33	4.40 (96)	0.7	115.3	57.2	2.02	27.6	7.50	614
2	140:124	54	4.50 (98)	0.3	47.5	30.6	1.55	13.4	4.46	899
3	120:110	65	4.43 (96)	3.0	58.5	31.3	1.87	21.7	5.56	776
3b	120:112	81	4.51 (98)	7.8	94.8	41.9	2.27	29.1	7.07	727
4	100:97	159	4.46 (97)	3.7	70.6	30.1	2.35	23.2	5.96	781
5	90:85	180	2.96 (64)	0	4.5	2.9	1.58	4.60	1.44	539
6	80:79	300	3.90 (85)	2.8	8.1	6.2	1.30	5.32	1.85	571

^{*a*}Equimolar amounts of the monomers, TCTPN (10 mmol) and TTSBI (10 mmol), were placed along with potassium carbonate (30 mmol) into a flask to which the solvent mixture of DMAc (20 mL) and DCB (10 mL) was then added. A strong positive pressure of nitrogen was maintained over the reaction mixture. The reaction mixtures were initially stirred at 200 rpm, with the stirring rate increased gradually, as appropriate, and torque readings were recorded at regular intervals (temperature and torque reading profiles are presented in Figure 1). ^{*b*}The higher temperature reactions, 1-4 (≥ 100 °C), were quenched hot into excess methanol when the solutions exhibited a sudden increase in viscosity (sharp rise in torque reading at maximum 500 rpm stirring rate). Reactions, 5 & 6, completed at 90 and 80 °C, respectively, did not exhibit sudden viscosity changes in the same manner (Figure 1b) and in fact in the case of reaction 5 in particular the viscosity decreased significantly toward the end of the reaction. Given that high yields of 96–98% were obtained in higher temperature reactions (≥ 100 °C) in just over 2 h, it was deemed appropriate to quench the lower temperature reactions (80 and 90 °C) after 5 and 3 h, respectively. ^cAll PIM-1 samples, at the very least, completely disperse in chloroform, but in some cases, significant colloidal network content was back calculated from solid content analysis of dilute chloroform solutions (1 mg mL⁻¹) of the polymer samples passed through a PTFE syringe filter with 0.45 μ m pore size. DLS analysis of unfiltered chloroform solutions suggested the colloidal content in each solution. ^dErrors of S–10% associated with BET surface area measurements.

expectedly short reaction times for the polymerizations minimized the potential for secondary reactions, often promoted by prolonged heating at high temperatures or the ever present base which could alter the polymer microstructure.¹⁷

Improvements in the gas separation membrane performances of PIM-1 films have been achieved by different post film formation approaches to thermal oxidative cross-linking of the polymer chains, either directly at intermediate temperatures (300–385 °C) or indirectly via functionalized PIM-1 (decarboxylation).^{19–21} These types of film treatment typically produce membranes exhibiting lower permeabilities but, particularly in the case of the direct cross-linking approaches, significantly higher selectivity values for important gas pairs such as CO₂/CH₄ and CO₂/N₂. This work has been carried out on free-standing thick films and often the extent of the heat treatment leaves these membranes brittle afterward. Recently, a tightly cross-linked network version of PIM-1 has been directly synthesized in a step-growth polymerization in which the tetrafluoro monomer was replaced by an equivalent octafluoro monomer.²² The network structures were characterized as nanosheets which, when incorporated as a filler at a very low loading (0.5 wt %) in mixed matrix membranes with PIM-1 itself, yielded improvements in both CO₂ permeability and CO_2/CH_4 selectivity.

If a mono-substitution-mediated polymerization of PIM-1 with TCTPN monomer can be tuned to produce increased levels of cyclic and branched microstructures, the hypothesis explored further here is that as the polymerization reaches very high conversion, more rigid interconnected polymeric structures (defined here as extended structures, with predicted connecting structures not dissimilar to end-linked network subgraphs²³) will be created which start to approach a full network structure. The developing polymer structure however remains soluble as the competing desire of reactive ends for cyclization lessens the likelihood of complete gelation of the reaction mixture, ultimately producing a structurally very

different polymer sample, which still dissolves in the typical solvents used to process PIM-1 into films. This would mean that potentially the improved molecular sieving properties delivered from in situ cross-linking of PIM-1 films could be generated directly in films cast from these structurally different PIM-1 samples without any heat treatment.

If the chloro monomer-derived PIM-1 polymer is to be scaled up to meet possible industrial membrane applications, better control of the polymerization process is required and understanding of the microstructure formed is needed. The slower reactivity toward fully fused PIM-1 structures when using the chloro monomer proved to deliver differences in the topological composition across the temperature range explored. A wide range of BET surface area values for PIM-1 $(600-900 \text{ m}^2 \text{ g}^{-1})$ have been previously reported in the literature.¹ The roles of reaction temperature, time, and monomer stoichiometry on the resultant PIM-1 topology are explored in this publication, with characterization of the polymers from solution primarily through nuclear magnetic resonance (NMR), multiple detector SEC analysis, and MALDI-TOF mass spectrometry, and in the bulk in relation to elemental analysis, surface area, and membrane film performance for gas separation. Correlations between polymer topology and membrane performance are used to develop a toolbox for PIM-1 synthesis which can develop high thin film performance in gas separation from the polymer itself.

EXPERIMENTAL SECTION

Materials. The monomers, TTSBI and TCTPN, were purchased from Alfa Aesar and Jinan Finer Chemical Co., Ltd (China), respectively, and were used as received at certified levels of purity, after drying in vacuum overnight at room temperature. Anhydrous potassium carbonate was purchased from Fisher Scientific Ltd, with the base ground into a fine powder and dried in a vacuum oven at 110 $^{\circ}$ C overnight before use. Anhydrous DMAc, anhydrous DCB, methanol, chloroform, tetrahydrofuran (THF), and 1,4-dioxane were purchased from Sigma-Aldrich and used as received.



Figure 1. Temperature and torque change profiles for stoichiometric step-growth polymerizations performed at (a) higher temperatures (reactions 1-3b, ≥ 120 °C) and (b) lower temperatures (reactions 4-6, 80-100 °C).

Typical Polymerization Procedure. The following procedure was used to produce PIM-1 polymer, designated as reaction 3 in Table 1. Equimolar amounts of the monomers, TCTPN (98.2%, 2.708 g, 10 mmol) and TTSBI (98.4%, 3.460 g, 10 mmol), were placed along with potassium carbonate (4.146 g, 30 mmol) into a 100 mL three-necked, round-bottom flask. The solvent mixture of DMAc (20 mL) and DCB (10 mL) was then added. The flask was equipped with a nitrogen inlet, a coil condenser, and a Heidolph RZR 2052 control mechanical stirrer (complete with digital rpmf and torque reading display) which was used to mix the reaction mixture. A strong positive pressure of nitrogen was maintained over the reaction mixture to remove small molecules. Heat was supplied via a hotplate equipped with a DrySyn aluminum heating block, with the flask inserted together with a temperature probe. The reaction mixture was heated from room temperature to 120 °C, initially stirred at 200 rpm, with the stirring rate increased gradually as appropriate and torque readings recorded at regular intervals (temperature and torque profiles for all reaction mixtures are presented in Figures 1 and S1). The viscosity of the reaction mixture facilitated increasing the stirrer rate to its maximum setting of 500 rpm after 54 min. The torque reading at 500 rpm then increased from 9.3 to 10.4 N cm during the next 10 min, as a consequence of a substantial increase in the viscosity of the reaction mixture. After 65 min, the hot viscous reaction mixture was quenched into excess methanol, precipitating as a yellow, thread-like PIM-1 polymer.

Purification of PIM-1 Polymer. The recovered filtered polymer was redissolved in chloroform at a concentration of ca. 5 g/120 mL and then reprecipitated by pouring slowly into methanol. The PIM-1 polymer was again collected via filtration and then refluxed in deionized water for 16 h. The filtered polymer was immersed in a minimal amount of 1,4-dioxane for 15 min (volume of dioxane used was just enough to cover the mass of the polymer in the beaker). The polymer was then filtered before washing further with copious amounts of acetone. The filtered polymer was then left to soak in methanol overnight to remove all traces of dioxane and acetone. It was filtered dry using a sintered glass funnel with vacuum before being dried in a vacuum oven at 120 °C for 2 days to completely remove all traces of the solvent. The polymer yields reported in Tables 1 and 2 are after this purification process.

Characterization. ¹H and ¹³C NMR spectra of PIM-1 polymers were recorded using a Bruker AVANCE II 500 MHz instrument. Polymer solutions (50 mg mL⁻¹) in CDCl₃ were prepared for the NMR analysis (Schemes S1 and S2, Figures S2–S25 in the Supporting Information). Signal peaks for the solvent were used as references. Average molar masses of the PIM-1 polymers (numberaverage M_{n} , weight-average M_{w} , and dispersity $D = M_w/M_n$) were measured by triple detector SEC. Analysis was performed in chloroform from 1 mg mL⁻¹ polymer solutions (injection volume 100 μ L) at a flow rate of 1 mL min⁻¹ using a Viscotek VE2001 SEC solvent/sample module with two PL Mixed B columns and a Viscotek TDA 302 triple detector array (refractive index, light scattering, and viscosity detectors). The data were analyzed using OmniSec software. A polystyrene (PS) standard of known molar mass (110 kg mol⁻¹) was used for system calibration. MALDI-TOF mass spectrometry analysis was carried out on a Shimadzu Biotech AXIMA Confidence instrument. Each sample of approximately 5 mg was dissolved in chloroform (100 μ L). The chloroform solution was then mixed with a matrix solution (dithranol in THF, 10 mg mL⁻¹) in a 1:10 ratio (sample/matrix). This resultant mixture was then spotted onto a plate using the layered method with sodium iodide solution (10 mg mL^{-1}). Calibration was completed using a spherical peptide mix at a range of 1600-3500 Da. Samples were run with the instrument in the linear mode with the pulse extraction optimized at 7000 kg mol⁻¹. UV-vis absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer from polymer solutions prepared in THF (0.09 mM) at room temperature. Dynamic light scattering (DLS) analysis of PIM-1 sample dispersions (50 ppm) in chloroform at 25 °C was carried out on a Malvern Zetasizer Nano ZS instrument. A Micromeritics ASAP 2020 sorption analyzer was used to obtain N2 adsorption/desorption isotherms at 77 K and to measure the Brunauer-Emmett-Teller (BET) surface area. Samples were accurately weighed and about 0.10 g of the polymer was degassed at 120 °C for 16 h under high vacuum (10^{-5} bar) before starting the analysis at 77.3 K. After cooling, degassed samples were reweighed and placed in the analysis port. Nitrogen adsorption/desorption isotherms were undertaken at 77 K. Helium was used for the freespace determination before sorption analysis.

Self-Standing Film Preparation. Thick PIM-1 sample films were each cast in a glass Petri dish from their respective 3% w/v solutions in chloroform (0.3 g of the polymer in 10 mL of CHCl₃). Each solution was left for 4 days at room temperature in a positive nitrogen atmosphere cabinet to allow the film to slowly form and dry. The formed film was detached from the Petri dish surface and immersed in methanol overnight. Excess methanol was then removed and the film was replaced in the cabinet for further 2 days at room temperature. The films were placed in a vacuum oven overnight at 100 °C to complete drying. Film thicknesses of typically 60–80 μ m were recorded for all the samples (measured with a Mitutoyo digimatic micrometer).

Mixed Gas Permeation Measurements. Sample films were then prepared for mounting in a membrane testing rig for mixed gases.²⁴ The membrane testing time, t = 1, refers to a film being prepared and tested immediately after methanol soaking and ovendrying steps. CO₂/CH₄ mixed gas permeability measurements were completed as follows. A binary feed mixture (30 mL min⁻¹ each gas) was used in a permeation apparatus²⁴ with the standard variable volume method. The total feed side pressure was set to 3 atm at T =25 °C and the permeate side was at atmospheric pressure. Alicat Scientific mass flow controllers with the operating flow range of 0– 100 ccm were used for the preparation of binary mixtures. Flat sheet membranes were masked between two aluminum-tape donuts, and the membrane–aluminum interface was sealed using two-part potting epoxy (Araldite Rapid, Industrial MTCE Suppliers). Samples of 1 cm diameter were placed in the stainless steel permeation cell, where the two parts of the cell were sealed with rubber O rings. Helium (60 mL min⁻¹) was used as the sweep gas for the analysis of the permeate. The sweep was at atmospheric pressure and was used to dilute the permeate gases and direct them to a microgas chromatograph (GC, Agilent technologies 490) for automated on-line analysis of the permeate composition. The GC utilized a PoraPLOT U (PPU) column, coupled to a thermal conductivity detector for detection of CO_2 -containing mixtures. After measuring the flux of each gas, the permeability was calculated using the following equation

$$P_{i} = \frac{N_{i}l}{(p_{i,1} - p_{i,2})}$$

in which P_i is the permeability coefficient for the component *i* in barrer [1 barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹], N_i is the steady state flux of the penetrant *i* (cm³ cm⁻² s⁻¹), *l* is the membrane thickness (cm), and $p_{i,1}$ and $p_{i,2}$ are the partial pressures of the component *i* in the feed (1) and permeate (2) side (in cmHg), respectively.

The selectivity $\alpha_{A/B}$ was then calculated as the ratio of the permeabilities of the two gases A and B, using the following equation

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Thin-Film Composite Membrane Preparation. Thin-film membranes of the PIM-1 samples [$\leq 2 \mu m$ thickness, determined by transmission electron microscopy (TEM) analysis] were kiss-coated on to a polyacrylonitrile (PAN) support (Sepro PA350 ultrafiltration membrane) from 3% w/v solutions in chloroform (CHCl₃) using a roller coater.²⁵ The electric motor for the coater was set at 7 V which equated with the roller completing a full revolution in approximately 5 s. A piece of the PAN support $(25 \times 60 \text{ mm})$ was adhered to the top of the roller, with the edges sealed with aluminum tape, to ensure that only the PAN-coated side of the support came into contact with the coating solution. The roller completed one full rotation with the PAN support in direct contact with the underlying solution for about 2 s. The thin-film composite (TFC) membranes were rested on a horizontal surface for 24 h in a nitrogen atmosphere storage cabinet and then maintained under vacuum at room temperature in a desiccator for 2 h, in order to ensure the removal of any remaining residual solvent. This constituted 1 day aging of a film, after which single gas permeation measurements proceeded. Further testing of the sample films was completed after 7 and 28 days, and no additional vacuum treatment was applied prior to the later aging tests.

Transmission Electron Microscopy Preparation and Analysis of Thin-Film Composite Membranes. TEM analysis was carried out using an FEI Tecnai G2 20 microscope. Thin-film membrane samples were embedded in epoxy resin and further underwent ultramicrotomy with the aim of obtaining ultrathin specimens of 100 nm. An Ultracut E ultramicrotome (Reichert-Jung, USA) and a diamond knife purchased from Diatome (Switzerland) were used for the process described below. An Araldite resin AY103-1 and Aradur hardener HY951 were used as resin precursors, both were mixed in the same ratio and poured into a silicone rubber mold. Finally ultrathin specimens were obtained using the diamond knife positioned perpendicular to the face of the membrane specimen. During the cutting process, the diamond knife was tilted at an angle of 6° and the speed was set at 1 mm s⁻¹. The specimens were removed from the water by means of a lacey carbon film on a mesh copper grid and further dried at room temperature for 2 h.

Single Gas Permeation Measurements. The permeability measurements using pure gases $(CO_2 \text{ and } N_2)$ were carried out by the standard variable volume method²⁶ at an upstream gas pressure of

approximately 2 atm and at ambient temperature (\sim 298 K), while maintaining the permeate side at atmospheric pressure. Membrane samples (25 mm in diameter), were immediately mounted in the permeation cell. The gas permeance was calculated using the following equation

$$K = \frac{Q}{tA(p_1 - p_2)} \times 10^{-6}$$

where *K* is the permeance in gas permeation units $[1 \text{ GPU} = 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} = 3.348 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}]$, *Q* is the volume of the permeated gas $[\text{cm}^3, \text{ adjusted to STP} (0 \, ^\circ\text{C}, 1 \, \text{atm})]$, *t* is the permeation time (s), *A* is the membrane area (cm²), and p_1 and p_2 are the feed and permeate side pressures (cmHg), respectively. Gas permeability was calculated using the following equation

$$P = \frac{Ql}{tA(p_1 - p_2)} \times 10^{-10}$$

where *l* is the membrane thickness (cm) and *P* is the permeability coefficient expressed in barrer [1 barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹ = 3.348×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹].

RESULTS AND DISCUSSION

"High-Temperature" Step-Growth Polymerizations with TCTPN To Produce PIM-1. The modified "hightemperature" route at 160 °C¹² (Scheme 1) now favored to produce PIM-1 is a very rapid reaction with the end point of the reaction (quenching into methanol) governed by the significant change in viscosity observed, associated with an indication of high molecular weight and conversion in the stepgrowth polymerization. Even with high shear mixing provided with an overhead stirrer, it is difficult to ensure polymer structural reproducibility in this short reaction time. A series of polymerizations were performed at progressively lower temperatures (Table 1) in which changes in torque readings from the stirrer were recorded at regular intervals to provide a better guide to the increase in viscosity. The polymerization reaction 1, set at 160 °C, exhibited a sharp spike in viscosity after only 33 min (reaction mixture had not in fact reached the set temperature). Reactions 2 and 3 carried out at 140 and 120 °C exhibited sharp increases in viscosity and were quenched after 54 and 65 min, respectively (temperature and torque change profiles throughout the durations of these reactions are presented in Figure 1a). These initial higher temperature reactions $(1-3, \geq 120 \ ^{\circ}C)$ all exhibited narrow molecular weight distribution PIM-1 polymers ($D \le 2.0$) in multiple detector SEC analysis after overall reaction times \leq 65 min, with high yields recovered between 96 and 98%, even after the extensive polymer purification procedures outlined in Experimental Section. Multiple detector SEC analysis utilizes both refractive index (to determine concentration, refractive index increment dn/dc = 0.196 for PIM-1) and light scattering detection for absolute determination of molecular weight, as opposed to conventional calibration from RI detection with PS standards. A basic problem with solely relying on RI detection is that the molecular weights are "as if" PS. However, molecular weight determination via light scattering also has some drawbacks, notably restricted sensitivity toward smaller polymer molecules²⁷ which results in rather low reported dispersity (D) values (1.3-2.3) in comparison with D values of 1.8-7.1 derived solely from PS calibration of RI detection (Table S1). Both reactions, 1 & 3, at 120 and 160 °C produced polymer samples with D values around 2.0, typical for high conversion step-growth polymerizations. Reaction 2 at 140 °C

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produced a polymer sample with a narrower molar mass distribution (D of 1.6).

MALDI mass analysis captured lower molecular weight material produced in all these high-temperature reactions, revealing almost exclusively the cyclic series, defined as cSC_n in Scheme 2. The mass distribution obtained of the polymer recovered from reaction 1 (160 °C), presented in Figure 2



Figure 2. MALDI mass spectrum of the PIM-1 polymer recovered from the stoichiometric reaction at 160 $^{\circ}$ C (1).

(Table S2), indicated no evidence of peaks attributable to any of the predicted linear series $(SC_n, CC_n, or SS_n)$ under 12 kg mol⁻¹ (MALDI spectra of polymers 2 & 3 are presented in Figures S26 and S27 of the Supporting Information). Changes in the theoretical carbon to nitrogen ratio (C/N = 12.44) in elemental analyses are a direct indicator of whether there is an excess of C or S residues in the PIM-1 polymeric structures (Table 3). The ratios of C to S residues determined from the C/N ratios indicate only very small variations away from the starting feed mixtures ($\leq 2\%$) in the high yield stoichiometric reactions; very few reactions in general produce a polymer with any excess of S residues. Predicted end groups (H and Cl) on SC_n structures or present internally on other possible structures will not influence this particular elemental ratio in the samples. This is discussed more in relation with polymers synthesized at lower temperatures (≤ 100 °C) and in nonstoichiometric reactions later.

Mark-Houwink plots obtained from multiple detector SEC analysis of the polymers in chloroform (presented in Figure 3) indicate that polymer 2 exhibited a markedly lower intrinsic viscosity than the other two polymers, 1 & 3, otherwise measured by light scattering to inhabit similar molecular weight ranges (Figure S28). This suggests structural differences in the particular polymer sample produced in high yield at 140 °C. Cyclic structures are asserted to be more compact than their linear counterparts of similar molecular weight (predicted to elute later from the SEC column) and would be expected to exhibit lower intrinsic viscosities in solution.¹⁴ Theoretical calculations^{28–31} have proposed that the proportion of cyclics will increase substantially as the conversion draws closer to 100%. The "cyclic" polymer 2 sample (13.44 cm³ g⁻¹) exhibited a lower intrinsic viscosity in solution to that of a similar molecular weight polymer 3 (21.70 cm³ g⁻¹). The ratio of intrinsic viscosity, $[\eta]_{\rm C}/[\eta]_{\rm L}$, of a cyclic polymer compared to that of a linear polymer at the same molecular weight in a



Figure 3. Mark–Houwink plots obtained in multiple detector SEC analysis of PIM-1 polymers produced in stoichiometric reactions (1–3, 5, and 6) compared against 4 mol % TCTPN excess reaction "linear" polymer (8).

theta or good solvent, termed g' factor, has been calculated theoretically by different groups at 0.56^{32} or between 0.65 and $0.67.^{33-35}$ A range of g' factor values, 0.56-0.76, have been reported experimentally for PS, differences influenced by the polymer molecular weight range and choice of the solvent. The g' factor comparison of the intrinsic viscosities of the "cyclic" polymer sample **2** versus polymer sample **3** in chloroform is 0.62. The intermediate molecular weight, cyclic-rich polymer **2** would be proposed to pack more inefficiently (higher free volume) in the bulk, and this was further suggested by a BET surface area measurement of 899 m² g⁻¹, the highest recorded from the series of PIM-1 polymer samples. It could also still be cast into a viable self-standing film from a chloroform solution for thick film membrane testing.

A longer duration reaction (3b, 81 min) was carried out at 120 °C, in which the mixture viscosity was allowed to increase further (Figure 1a) before the reaction was guenched into methanol. A higher molecular weight PIM-1 polymer in a higher yield (98%) to that obtained in reaction 3 was recovered, exhibiting in solution the highest intrinsic viscosity of the series. The cyclic series (cSC_n) was again the only distribution in the low molecular weight fraction captured in MALDI analysis (Figure S29). The very high molecular weight section of the Mark–Houwink ($[\eta] = KM^a$) plot for polymer 3b (Figure 4) was not unlike that evident for the high molecular weight polymer 1 prepared at 160 °C. The linear plot regions evident in lower molecular weight ranges exhibit slopes (a) of 0.62–0.69, values typically associated with flexible polymers in a good solvent; however, slopes of ca. 2.0 are evident in the high molecular weight regions. In the case of the polymer 1, an a value of 1.9 was determined, which is typically associated with rigid rods. The presence of more rigid polymeric structures in the soluble fraction suggested that further reaction toward network-type structures was evident in other materials not amenable to SEC analysis within the samples. Indeed a network content of almost 8% (Table 1) was determined for the polymer prepared at 120 °C in the longer duration polymerization (3b).

"Low-Temperature" Step-Growth Polymerizations with TCTPN To Produce PIM-1. A further stoichiometric



Figure 4. Mark–Houwink plots obtained in multiple detector SEC analysis of high molecular weight PIM-1 polymers produced in 120 °C reactions (3, 3b) compared against the 160 °C reaction (1).

reaction was undertaken at 100 °C (4) in which quenching was only completed after the change in torque (+3.9 N cm) matched that measured in the reaction 3b at 120 °C. The torque change profiles during all the lower temperature reactions (4–6, 80–100 °C) are presented in Figure 1b. The

polymer recovered in reaction 4 again predominantly exhibited the cyclic cSC_n series, along with some evidence of the linear CC_n series (Table S3), in MALDI analysis (Figure S30).

The reactions (5, 6) carried out at 90 and 80 °C, respectively, were quenched before any significant increase in viscosity (torque change) was observed, indeed conversely in the case of reaction 5, the viscosity of the mixture did in fact decrease toward the end of the reaction time. It proved useful in structural analysis terms to have quenched these reactions early as it allowed the capture of the prevalent microstructures at lower conversions, with and without end groups, and minimized the added complication of structures produced through occurrence of secondary reactions.¹⁷ Lower polymer yields were obtained in these reactions, 64 and 85% for 5 and 6, respectively.

The oligomeric PIM-1 material ($M_n = 2.9 \text{ kg mol}^{-1}$) produced in low yield (64%) and containing no network material in reaction 5 after 3 h at 90 °C clearly showed resonances associated with end groups in aromatic NMR spectral analysis (reaction 5 in Figure 5). The proton resonances associated with TCTPN monomer residue (C)terminated chain ends (aromatic protons c and d, $\delta = 6.9$ and 6.5 ppm) are about 13 times more intense than that attributed to TTSBI monomer residue (S) ends (resolved aromatic proton f, $\delta = 5.9$ ppm) in polymeric structures generated in this stoichiometric reaction. This is far removed from the ratio of 2:1:1 of linear SC_n, CC_n, and SS_n residue structures



Figure 5. Aromatic NMR (¹H and ¹³C, left and right) resonance regions of key PIM-1 samples synthesized in stoichiometric reactions (1, 2, 5, and 6) and the 4 mol % TCTPN excess reaction (8).

predicted for a step-growth polymerization, where monomers, oligomers, and polymers possess identical reactivities.³⁶ The number of PIM-1 residues (defined predominantly from main aromatic proton resonances, **a** and **b**, $\delta = 6.9$ and 6.5 ppm, respectively) per end group, calculated from comparing respective integral band areas of assigned aromatic proton NMR resonances, was determined at 12 residues, which equates to a higher apparent polymer $M_{\rm p}$ of 5.5 kg mol⁻¹. However, this calculation assumes that only linear polymer chains are present, that is, there are two end groups per polymer chain, which does not take account of the possibility of cyclic polymer structures. This overall analysis suggests that S residues formed on a chain end are very prone to react further in a number of ways, including cyclization and branching, which is explored and rationalized further in the MALDI analysis of this sample and generally in nonstoichiometric reactions discussed later.

By comparison, the marginally higher molecular weight of the polymer with narrow dispersity $(M_n = 6.2 \text{ kg mol}^{-1}, D =$ 1.30) obtained in higher yield (85%) in the longer duration reaction 6 at 80 °C showed much less evidence of these types of end groups, particularly in carbon NMR analysis (reaction 6 in Figure 5). A high total of 33 PIM-1 residues are evident per end group $(M_n = 15.2 \text{ kg mol}^{-1})$ in the proton NMR analysis, which again suggests that a significant proportion of the residues are to be found in cyclic structures with either no or less chain ends. The proton NMR spectrum has a pair of resonance bands, centered at 6.7 and 6.3 ppm (labeled g and h), which are even more intense than the bands associated with aromatic hydrogens (c, d, or f) present next to chain ends in linear polymeric structures. These minor bands are tentatively assigned to aromatic protons, g and h, in various structures in which two S residues are partially attached to the same side of a C residue in the main polymer chain (defined in Scheme 3 as part of either an underreacted PIM-1 residue structure, $urSC_n$, or, with further reaction, as a branched structure bSC_n). Recent studies of model compounds in similar reactions³⁷ have indicated that at a low temperature (50 °C), products originating from successive monosubstitutions of 1,2-dihydroxybenzene to a multifluoro aromatic compound, rather than the full disubstitution reaction to form a fully fused ring, form a significant proportion of the yielded material. In addition, the rate of the reaction of specifically the chloro monomer, TCTPN, with 1,2-dihydroxybenzene in model studies at 65 °C is significantly slower than that of TFTPN, only 16% of the fully fused product is formed in a reaction time of 4 h, with the remaining material either only monosubstituted or unreacted material.¹⁸ These minor bands are present in the proton NMR spectra of all PIM-1 samples to varying degrees, with their prominence relative to the main aromatic proton residue bands, a and b, at 6.8 and 6.4 ppm, often allied with the cyclic content of each particular sample, as assessed from interpretation of intrinsic viscosity measurements as part of SEC analysis. The best example is in the case of polymer 2, whose proton NMR spectrum is also presented in Figure 5. This cyclic-rich polymer has a high proportion of these structures relative to the main PIM-1 residue structures. Given the relatively high molecular weight of this particular polymer, the resonance bands cannot be associated with end group structures.

Elemental analyses of both samples (5 & 6) indicated the presence of a significant amount of chlorine (2-3 wt %) (Table 3) but differences in the elemental ratios would suggest





Figure 6. MALDI mass spectrum of PIM-1 polymer recovered from a stoichiometric reaction at 90 $^{\circ}$ C (5).

that the chlorine was present in different locations on the polymer chains in each case. The C/N ratio is virtually unchanged in the case of polymer 6 (only 0.1% excess of C residues) which means that the chlorine can only be present either in one end of SC_n residue structures or, much more likely included in, $urSC_n$, or certain bSC_n residue structures, given the molecular weight and relatively high chlorine content (2.5%). In contrast, a lower C/N ratio (coupled with higher C/H and N/H ratios) for polymer 5 is consistent with polymer chains containing an excess of C residues (4.3%) which are

Table 2. Nonstoichiometric Step-Growth Polymerizations of TCTPN and TTSBI To Produce PIM-1 under Homogeneous Conditions

PIM-1 reaction	reaction conditions	monomer in excess/mol %	yield/g (%)	$M_{\rm w}/{ m kg}~{ m mol}^{-1}$	$M_{\rm n}/{\rm kg}~{ m mol}^{-1}$	Ð	intrinsic viscosity, $[\eta]/cm^3 g^{-1}$	hydrodynamic radius, <i>r</i> /nm	BET surface area/m ² g ⁻¹
3	120 °C, 65 min	—, 0	4.43 (96)	58.5	31.3	1.87	21.70	5.56	776
7	120 °C, 65 min	TCTPN, 2	4.36 (94)	36.8	23.3	1.58	15.06	4.25	684
8	120 °C, 65 min	TCTPN, 4	4.39 (94)	12.3	7.6	1.62	8.92	2.48	376
9	120 °C, 65 min	TTSBI, 4	4.35 (92)	28.3	20.8	1.36	13.32	3.77	643
10	160 °C, 33 min	TTSBI, 50	$1.23 (20)^a$	6.6	4.8	1.38	6.58	1.84	455

^aOnly 20% yield of 10 after the entire purification process. However, a further 33% of the polymer of similar molecular weight (NMR spectra presented in Figures S24 and S25) was recovered from the filtrate in the prefinal treatment step with 1,4-dioxane.

Table 3. Element	al Analyses	of PIM-1	Polymer	Samples	(1 - 10))
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PIM-1 polymer	reaction conditions	C/%	N/%	H/%	Cl/%	C/N^{a}	C/H	N/H	$r(C/S)^{b}$
cSC _n	(cyclic PIM-1 composition)	75.64	6.08	4.38	0	12.44	17.27	1.388	1.000
1	160 °C, 33 min	74.20	5.98	4.36	< 0.30	12.41	17.02	1.372	1.002
2	140 °C, 54 min	73.90	5.93	4.34	< 0.30	12.46	17.03	1.366	0.995
3	120 °C, 65 min	73.58	5.97	4.30	0.89	12.32	17.11	1.388	1.012
3b	120 °C, 81 min	74.25	6.06	4.38	< 0.30	12.25	16.95	1.384	1.020
4	100 °C, 159 min	73.61	5.92	4.33	0.40	12.43	17.00	1.367	0.999
5	90 °C, 180 min	70.90	5.88	4.08	3.36	12.06	17.38	1.441	1.043
6	80 °C, 300 min	70.65	5.69	4.24	2.49	12.42	16.66	1.342	1.001
7	120 °C, 65 min, 2 mol % TCTPN	72.37	5.96	4.26	< 0.30	12.14	16.99	1.399	1.033
8	120 °C, 65 min, 4 mol % TCTPN	71.47	6.32	4.00	2.38	11.31	17.87	1.580	1.142
9	120 °C, 65 min, 4 mol % TTSBI	73.11	5.88	4.31	< 0.30	12.43	16.96	1.364	0.999
10	160 °C, 33 min, 50 mol % TTSBI	69.00	5.12	4.35	0.80	13.48	15.86	1.177	0.896
urSC _n	(under-reacted PIM-1 composition)	70.09	5.64	4.26	7.14	12.43	16.45	1.324	1.000

^aSignificant deviation of the C/N ratio from theoretical (12.44) is indication of excess of one particular residue in the polymer structures. ^bRatios of TCTPN to TTSBI monomer-derived residues [r(C/S)] present in samples, determined from these C/N ratios, suggest no significant excess of S residues in most of the samples, with the exception of the polymer produced from the 50 mol % excess TTSBI reaction (10).

conditions.

found on the chain ends with associated chlorine atoms attached. MALDI TOF mass analysis of polymer 5 (Figure 6) confirmed the primacy of linear CC_n residue structures (Table S3) in an overall molar mass distribution approaching that indicated in SEC analysis. The secondary series present in the spectrum, when considered in isolation from other analysis, would appear to correlate in mass terms with the SC_n series presented in Scheme 2 (Table S4). However, as mentioned previously, this assignment does not tally with, in particular, the end group proton NMR analysis of this particular sample or in the context of further results obtained from the nonstoichiometric reactions where TTSBI is in excess.

Both cyclic and further reacted branched structures, which each originate from one under-reacted $urSC_n$ residue (Scheme 3), generate the same numerical mass series (Tables S5 and S6). The secondary series is tentatively assigned to a tadpole polymeric structure based around a cyclic branched structure terminated by a chloro residue. The low yield for reaction 5 and lesser proportion of cyclics in analysis could be a reflection that a reaction time of 3 h at 90 °C was not sufficient for step-growth and cyclization to commence. The MALDI TOF mass spectrum of polymer 6 presented in Figure S31 indicates a much more complex mixture of distributions, between 10 and 15 different series apparent, each with peak spacings which equate to the PIM-1 residue mass (460.49 g mol⁻¹). The even lower temperature employed in reaction 6 is predicted to

amounts of TCTPN (2 and 4 mol %, respectively, Table 2) to disrupt the formation of cyclics and provide samples of solely linear polymers for a comparative study in multiple detector SEC analysis. The reaction time of 65 min employed in the stoichiometric reaction 3 was maintained for these extra

further increase the degree of monosubstitution occurring

between the TTSBI and TCTPN monomers, creating all

manner of cyclic and branched species. The CC_n series is the only linear series clearly identified in this complex mixture of

structures. The molar mass distribution ranges demonstrated in MALDI analysis across these samples would suggest that if

any linear species had been prevalent in the lower molecular

weight fractions of the higher temperature synthesized PIM-1

polymers, they would have been readily captured under similar

with Excess TCTPN Monomer. The inference from the

stoichiometric reactions at a range of temperatures was that the

synthesized PIM-1 polymers contained a significant amount of

nonlinear polymeric structures, particularly evident from

combination of proton NMR and multiple detector SEC

analysis. Nonstoichiometric reactions, 7 and 8, were under-

taken at 120 °C from reaction mixtures containing excess

reactions and the torque changes recorded at regular intervals

(Figure S1). The 2 mol % excess reaction mixture (7) generally

exhibited a gradual increase in torque throughout the reaction

Nonstoichiometric Step-Growth Polymerizations

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Figure 7. MALDI mass spectra of PIM-1 polymers recovered from (a) 2 and (b) 4 mol % TCTPN excess reactions at 120 °C (7, 8).

time, without reaching the heights in viscosity of the stoichiometric reaction at a stirring speed of 500 rpm at the end of the reaction. The percentage polymer yield was only marginally negatively affected (94%) and the reduction in molecular weight of the polymer sample observed in SEC analysis could be correlated with the stoichiometric imbalance in the reaction (Table 2).

The 4 mol % excess reaction mixture (8) initially exhibited a similar increase in torque readings to that observed in the first 25 min of reaction 7. However, in the later stages of the reaction, the viscosity of the reaction mixture subsequently plummeted to such an extent that the stirrer speed had to be reduced from 400 to 350 ppm. A more significant drop in the molecular weight of the polymer recovered was observed $(M_{\rm p}/$ $M_{\rm w} = 7.6/12.3 \text{ kg mol}^{-1}$ in this case, although the overall yield (94%) remained high. Changes were observed in the aromatic region of the proton NMR spectra as the chloro monomer excess in the reactions was increased (Figures S16 and S18) and the molecular weight of the products decreased. The sharp bands centered at 6.9 and 6.5 ppm both increased in intensity relative to the main aromatic proton bands, a and b, at 6.8 and 6.4 ppm, confirming that these bands were associated with the outermost aromatic protons (labeled, c and d, respectively in Figure 5) on spiro monomer (S) residues next to a chloro monomer (C) residue on a chain end.

Elemental analyses (Table 3) of particularly polymer 8 indicated a substantial decrease in the C/N ratio and increases in C/H and N/H ratios, all consistent with the presence of shorter polymer chains at the very least terminated on both ends by C monomer-associated residues (CC_n) (large 14.2%) excess of C residues in this sample). The MALDI mass distributions of PIM-1 polymer structures obtained from the 2 and 4 mol % TCTPN excess reactions (7, 8) are presented in Figure 7a,b MALDI mass spectrum of the polymer from the corresponding stoichiometric reaction (3) is presented in the Supporting Information, Figure S27]. The mass analysis of the three polymers produced at 120 °C for 65 min, first in the stoichiometric reaction (3) and then from reaction mixtures with an increasing stoichiometric imbalance (7, 8), exemplify a transition from cyclic series (cSC_n) structures toward predominantly linear structures terminated on both ends with TCTPN monomer-derived (C) residues, defined as CC_n (Scheme 2). Given the large excess of C residues suggested by the elemental analysis, the secondary series evident toward the higher mass end of the MALDI spectrum obtained of the 4 mol % TCTPN reaction polymer is more likely to be

associated with a tadpole polymer structure terminated with a C residue, rather than simply a conventional SC_n residue series. The evident prevalence of CC_n structures in MALDI analysis, when coupled with number average molecular weights of polymer 8 obtained in SEC analysis, would suggest that the most abundant linear residue structure equates to approximately the $C-[S-C]_{16}$ polymer chain (17 C + 16 S units per average polymer chain), not very much removed from the stoichiometric imbalance in the overall reaction mixture (104 C for every 100 S present in the starting feed). Increasing the stoichiometric imbalances with TCTPN in the reactions at 120 °C reduced the molecular weight and cyclic content and significantly reduced the BET surface area of the resultant polymers (from 776 to 376 m² g⁻¹). The low surface area recorded for "linear" polymer 8 compares favorably with grand canonical Monte Carlo (GCMC) simulations of N₂ loading, using packing models of linear structures of similar molecular weight, which have estimated the PIM-1 surface area at 435 m² g^{-1}

Comparison of the solution behavior in chloroform of the lower molecular weight polymers obtained from stoichiometric reaction 6 and reaction 8 in multiple detector SEC analysis is also of particular interest. The full characterization of polymer 6 (paucity of end groups evident in NMR analysis) suggests a predominantly cyclic sample, whereas the 4 mol % stoichiometric imbalance in the reaction 8 mixture ensured that its polymer chains remained almost exclusively linear in form. Right angle light scattering (RALS) and viscosity detector responses of these two polymers, 6 and 8, across their elution volumes, also compared against the oligomeric linear sample, 5, are presented in Figure S32. Mark Houwink plots of all three polymers in solution are included in Figure 3. The cyclic-rich polymer 6 sample (5.32 $\text{cm}^3 \text{ g}^{-1}$) exhibited an intrinsic viscosity in solution closer to the oligomeric sample 5 $(4.59 \text{ cm}^3 \text{ g}^{-1})$ than the linear polymer 8 (8.92 cm³ g⁻¹) of similar molecular weight. The g' factor calculated from the intrinsic viscosities of the "cyclic" polymer sample 6 versus "linear" polymer sample 8 in chloroform yielded a value of 0.63, again suggesting significant differences in the topological content of the two samples. The cyclic-rich polymer 6 sample also exhibits a much higher BET surface area of 571 m² g⁻¹ than the linear polymer sample 8 (376 $\mbox{m}^2\mbox{ g}^{-1})$ of similar molecular weights.

Nonstoichiometric Step-Growth Polymerizations with the Excess TTSBI Monomer. A nonstoichiometric reaction (9) containing 4 mol % excess of TTSBI at 120 °C produced a narrow molar mass distribution polymer of relatively high molecular weight ($M_{\rm p} = 20.8 \text{ kg mol}^{-1}$, D =1.36, Table 2) in a yield of 92%. Both the lower yield obtained and elemental ratio analyses (unchanged C/N ratio in Table 3) suggest that the excess TTSBI does not get significantly incorporated onto the chain ends of the polymeric structures. The calculated number of PIM residues evident per chain end derived from proton NMR analysis equates to an $M_{\rm p}$ of 25.8 kg mol^{-1} . The carbon NMR spectrum of polymer 9 (Figure S21) only presents hints of resonances (143.6 and 144.9 ppm) which could be feasibly attributed to aromatic carbons next to the chain ends of the expected SS_n residue structures. MALDI mass analysis shows predominantly the presence of the cyclic series, cSC_n , up to 7 kg mol⁻¹ (Figure S33), with only a few CC_n linear polymeric structures present. These findings are similar to those observed in reactions to produce PIM-1 from TTSBI and the fluoro equivalent monomer, TFTPN.¹⁷ An additional new series is evident which is attributed to a single branching unit associated with two S residues, rather than one, adding to one side of the C residue in larger linear polymeric structures, derived from bSC_n as shown in Scheme 3 (Table S7). This linear series is not evident in MALDI analysis of any other polymer sample and its presence is not perhaps unexpected in this particular sample, given the imbalance toward TTSBI in stoichiometry. These findings would appear to confirm that S residues are very seldom found on chain ends and almost always react further to form cyclic or other more complex structures.

A further reaction (10) completed at 160 °C for 33 min with a huge excess of TTSBI (50 mol %) further tested this hypothesis. The higher temperature was selected to maximize the probability that the monomers would react together in the conventional fully fused manner in the polymerization and the expectation from the monomer excess was that this would produce oligomers (maximum possible degree of polymerization, $\overline{X}_n = 5$ monomer units, $M_n = 1.3$ kg mol⁻¹) doubly end capping with TTSBI-associated (S) residues. This very nontypical starting point for a step-growth polymerization still produced a polymer with number average molecular weight in SEC analysis approaching 5 kg mol⁻¹ in a significant yield (approximately 53% in total). The proton NMR spectrum of the fully purified portion of polymer 10 (Figure S22) most closely resembled that obtained from the stoichiometric reaction at 80 °C (6). Although the aromatic proton peak, f (δ = 5.9 ppm), associated with free spiro residue (S) ends is further enhanced, it is still minor in intensity in comparison with structures based around under-reacted urSC, residues or further reacted structures as part of branched bSC_n or even network points. The fully purified portion of the polymer (20%) still has approximately twice as many chloro residue (C) ends present as spiro residue (S) end type structures. The calculated number of PIM-1 residues evident per end group in proton NMR analysis equates to the polymer with number-average molecular weight, $M_{\rm n} = 11.1$ kg mol⁻¹, just over double the SEC measured absolute molecular weight, and is again indicative of a polymer sample containing a very high proportion of cyclic structures. This is further exemplified by the simple carbon NMR spectrum of this sample, devoid of end group resonances and remarkably similar to that obtained for much higher molecular weight PIM-1 (Figure S23). The MALDI mass spectrum obtained of polymer 10 is presented in Figure 8. The main species (indicated by blue numbers) present in the lower molecular weight region would at first



Figure 8. MALDI mass spectrum of PIM-1 polymer recovered from the 50 mol % excess TTSBI stoichiometric reaction at 160 $^\circ C$ (10).

numerical examination be predicted to be associated with SS_n residue structures (Table S8). However, in the context of the proton NMR analysis, the two series evident are tentatively assigned to tadpole-type polymeric structures (Scheme 3). The main series (blue) is attributed to uneven residue (spiro rich) structures of this type defined as terminated with a spiro residue structure (Table S9). The secondary series (purple), which gains more prominence in the higher molecular weight detection range, is attributed to even residue structures of this type terminated with a chloro residue structure (Table S6).

Optical Properties of PIM-1 Samples. The fully fused aromatic ring structure of PIM-1 gives rise to some interesting optical absorption properties which are attributed to the isolated 6,13-dicyanobenzo-1,2,4',5'-bis-1,4-benzodioxane chromophores insulated at each end by spirocyclic carbons^{18,39,40} (Figure 9). A significant reduction in intensity



Figure 9. UV-vis absorption spectra of similar molecular weight PIM-1 polymers (6 & 8) obtained in THF solutions (0.09 mM).

of the main absorption peak at 433 nm for polymer **6** in THF solution was observed in comparison with similar solutions of all other PIM-1 samples, including the oligomeric sample **5** (Figures S34 and S35). This observation is consistent with the low-temperature synthesis (80 °C) of polymer **6** producing a significant number of under-reacted residue structures (**urSC**_n), which progress to branch points, which will reduce the rigidity/planarity (hypochromic effect) of the contributing

Macromolecules



Figure 10. Mixed gas (CO₂/CH₄, 1/1, v/v) permeation performances of self-standing films (60–80 μ m) cast from 3 wt %/v PIM-1 chloroform solutions (methanol-treated).

chromophores in the polymer chains. Comparing the solution absorption spectra of polymer **6** with polymer **8** (sample of similar molecular weights characterized to be in contrast both linear and fully fused in higher temperature nonstoichiometric reactions) indicated an 18% decrease in the molar attenuation coefficient calculated from the peak maxima (Table S10).

Membrane Testing of Self-Standing PIM-1 Films. Robust thick films (60–80 μ m) were prepared for mixed gas $(CO_2/CH_4, 1/1, v/v)$ permeation studies (Figure 10, Tables S11 and S12) from PIM-1 samples, 1, 2, 3b, and 4. The initial CO₂ permeabilities (8-10 000 barrer) obtained compare favorably to data typically reported for PIM-1. The decline in performance upon aging of the thick films prepared from PIM-1 samples, 1 & 2, in particular, was very slow, with these films still exhibiting CO₂ permeabilities > 8000 barrer after 96 days (Table S11), much higher than those typically reported from fresh fluoro monomer-derived PIM-1 sample films.⁴¹ Some additional films were prepared and heat-treated for longer in a vacuum oven at 100 °C prior to initial testing to accelerate the aging process (Table S12). Increased CO_2/CH_4 selectivities were generally observed from these PIM-1 sample films, to match their lower permeabilities, in line with the inverse trajectory of the 2008 Robeson upper bound line. Films cast from PIM-1 samples synthesized at lower temperatures generally outperformed the "high-temperature" (1, 160 °C) PIM-1 sample in the mixed gas testing, often in the process far exceeding the Robeson 2008 upper bound.

The best-performing outlier film sample in terms of selectivity ($CO_2/CH_4 = 56.6$) was associated with the PIM-1 sample, **3b**, synthesized at 120 °C. A range of other films exhibited mixed gas selectivities approaching 30 at high CO_2 permeabilities (4000–6000 barrer), which compare favorably with recent data reported for films cast from a very high molecular weight PIM-1 polymer ($M_w = 348$ kg mol⁻¹, D = 2.4).⁴² Generally, aging thick PIM-1 films closely follow the Robeson 2008 upper bound trajectory,²¹ but the performance may be influenced by the structural nature of the particular PIM-1 sample or indeed whether the casting polymer solution was passed through a poly(tetrafluoroethylene) (PTFE) syringe filter prior to coating, which this work shows

potentially removes all colloidal network material. These thick films in fact more closely match the improved initial performance only reported after post film cross-linking of PIM-1 at elevated temperatures (\geq 300 °C, 24 h).^{19,21} The PIM-1 polymer samples synthesized at lower temperatures do indeed contain more complex branched and network type materials. A new upper bound (2019) for this gas pair has been recently proposed to reflect the performances achieved by benzo-triptycene-based PIMs.⁴³ The promising membrane performance of the lower temperature synthesized PIM-1 polymers cast in thick films suggested that these materials can approach this new target from topological variations of the original PIM polymer. The overall promising performance of these lower temperature PIM-1 polymers cast in thick films suggested that testing of these materials in TFCs should also be explored.

Membrane Testing of PIM-1 Thin-Film Composites. Single gas (CO_2, N_2) permeation studies were undertaken (Figure 11 and Table S13) on TFC membranes with a PIM-1



Figure 11. Single gas (CO_2, N_2) permeation performances of TFCs ($\leq 2 \mu m$ selective layer) prepared from the PIM-1 samples (1–4).

separation layer ($\leq 2 \mu m$) kiss-coated from chloroform solutions (3 wt %/v) onto a commercial PAN support material. The initial CO₂ permeance values were in general significantly higher than those reported for films prepared recently from kiss-coating fluoro monomer-derived PIM-1 sample solutions onto the same support material.⁴⁴ If we take account of the respective film thicknesses determined by TEM analysis (examples of cross-sectional images obtained are presented in Figures 12 and S36-39), initial CO₂ permeabilities of around 11 000 barrer were achieved for a number of the films. Large decreases (70-82%) in both CO_2 and N_2 permeances were recorded between 1 and 7 day aging measurements. The fall in N2 was always slightly larger than that for CO₂, which meant that slight increases in overall selectivities were evident in this early aging period. This trend was reversed on further aging between 7 and 28 days, with lower final selectivities recorded. The highest CO_2/N_2 selectivities of 20-21 for this series were recorded for thin films prepared from PIM-1 samples, 3b & 4, synthesized at the lower temperatures (120, 100 °C). The high initial permeances and selectivities determined from TFCs prepared from these PIM-1 samples are among the best obtained for the polymer.



Figure 12. Cross-sectional image of the TFC prepared from PIM-1 polymer sample 3 obtained in TEM analysis.



Figure 13. Correlation between the polymer network content and initial selectivity (CO_2/N_2) observed in TFCs.

A positive correlation between increasing initial selectivity values (at constant permeances) and the increasing colloidal network content in TFCs prepared from polymer samples synthesized at lower temperatures was evident and is presented in Figure 13. It is unclear on the basis of analysis of these samples alone whether this improvement was directly associated with the extra network content alone or also the branched structures which would constitute the building blocks of the network structures. Given the typical aging behavior observed with the thick films, initially it was unclear why both permeability and selectivity of the TFCs decreased between 7 and 28 days for this batch of samples. However, the molar mass distributions of the polymers (1-4) used to cast these TFCs were not particularly high in the context of thin film-forming polymeric materials, which may contribute to nontypical aging performance.

CONCLUSIONS

Nitrogen-purged PIM-1 polymerizations starting from the chloro equivalent monomer, TCTPN, in a new solvent system over a wide range of temperatures $(80-160 \ ^{\circ}C)$ in short reaction times (<5 h) were undertaken. A combination of multiple detector SEC analysis, NMR, elemental analysis, and

MALDI-TOF mass spectrometry was used to exemplify the structural differences in the PIM-1 polymers prepared under these different conditions. Cyclic structures were identified, particularly in MALDI analysis of the polymers synthesized at higher temperatures, but when polymerization temperatures were dropped further (<100 °C), a significant amount of branching occurs, which generally reduces the overall molecular weight of the soluble material obtained. The relative differences in intrinsic viscosities (g' factor) observed between polymer sample solutions with similar measured molar mass distributions would suggest that the proportion of cyclics varied substantially (0-100%) in some of these step-growth polymerizations. The suggestion, from the lower temperature reactions with the tetrachloro monomer, is that the reaction proceeds to some extent in monosubstituted steps. The added flexibility of polymer chains initially containing some partially reacted ring structures may indeed enhance further the likelihood of cyclization. The natural progression from branching is that chains can react together to form tadpole structures, extended rigid structures (still soluble and observed in Mark Houwink plots), and eventually colloidal network structures (insoluble for SEC analysis but still fully dispersible in chloroform). The failure of low-temperature polymerizations (<100 °C) under standard nitrogen purging to reach high conversion is most likely because of excessive cyclization, branching, and network formation.

Results from nonstoichiometric polymerizations exemplified that the spiro residue terminated polymer chain ends are very reactive and end up being incorporated into cyclic and other more complex structures. The proportion of cyclic structures produced can only be reduced in stoichiometric imbalanced reactions, containing excess TCTPN, producing predominantly linear polymer chains of lower molecular weight which also exhibited progressively lower surface areas in the bulk. A significant proportion of the apparent bulk surface area of PIM-1 (up to 200 m² g⁻¹) can be attributable to contorted polymer chains in fact linking to form cyclic structures. Nonstoichiometric polymerization reactions with an excess of TTSBI can be used to produce polymer mixtures virtually entirely cyclic or tadpole in the topological content.

Self-standing films prepared from topologically rich PIM-1 polymers, synthesized at temperatures of 120-140 °C, exhibited CO₂/CH₄ selectivities approaching the new 2019 upper bound for the gas pair. Highly selective CO₂/N₂ performances in early stages of aging in TFCs cast from these same PIM-1 polymer samples were also apparent. In general, higher gas pair selectivities were achieved with films cast from highly branched and network-containing PIM-1 samples, compared to those more structurally conventional PIM-1 samples synthesized at 160 °C, at equivalent permeabilities.

This work presents a series of characterization tools which should be employed to classify structurally every PIM-1 polymerization product and which ultimately will give insight into what topological structures contribute to the performance of a typical PIM as a membrane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02185.

NMR spectra and assignments (¹H and ¹³C) of PIM-1 polymers; SEC analysis of polymers; MALDI spectra and comparison tables of predicted adduct masses of different topological structures; UV–vis absorption spectra of the polymer solutions; mixed gas permeation testing results of self-standing films and single gas permeation testing results of TFCs; and cross-sectional images of TFCs obtained in TEM analysis (PDF)

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The experimental work was completed by A.B.F., with some assistance from Z.L. and M.T. TEM analysis was completed by J.M.L. The article was written by A.B.F. and edited by P.M.B. Other authors provided minor contributions to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MALDI-TOF MS, matrix-assisted laser desorption/ionizationtime of flight mass spectrometry; BET, Brunauer–Emmett– Teller; PAN, polyacrylonitrile; PIM, polymer of intrinsic microporosity; SEC, size exclusion chromatography

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