Linear High Molecular Weight Ladder Polymers by Optimized Polycondensation of Tetrahydroxytetramethylspirobisindane and 1,4-Dicyanotetrafluorobenzene†

Jingshe Song,‡ Naiying Du,‡ Ying Dai,‡ Gilles P. Robertson,‡ Michael D. Guiver,*,‡ Sylvie Thomas,§ and Ingo Pinnau§

Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada, and Membrane Technology and Research Inc., 1360 Willow Road, Suite 103, Menlo Park, California 94025-1516

Received May 2, 2008; Revised Manuscript Received August 13, 2008

ABSTRACT: A study on the optimization of conditions for polycondensation of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′,6,6′-tetrol, TTSBI, with 1,4-dicyanotetrafluorobenzene (DCTB) in dimethylformamide (DMF) at 50−70 °C is reported. A linear PIM-1 polymer (PIM = polymer with intrinsic microporosity) with high molecular weight was obtained by optimized reaction conditions. Of the solvents tested, DMF was the preferred solvent for this reaction. The optimized molar ratio TTSBI/DCTB/K_2CO_3 was 1/1/2.04. The mechanism of PIM-1 cross-linking during polymerization was studied, and gel-free, high molecular weight PIM-1 polymer was prepared. The physical properties of anhydrous K_2CO_3 significantly affected the reaction rate. Flexible tough polymer films were cast from PIM-1 solution in chloroform, and pure permeability data are reported for several gases.

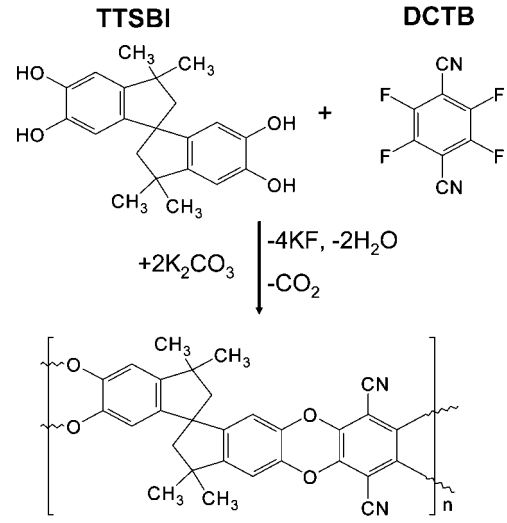
1. Introduction

Syntheses of aromatic polyethers are most often based on nucleophilic substitution polycondensation of activated fluoro-, chloro-, or nitroaromatics with sodium or potassium phenoxides.[1−3] Recently, Budd and co-workers reported[4−8] on the syntheses of high molecular weight linear ladder polymers by irreversible polycondensations of tetraphenols with activated tetrafluoro- or tetrachloroaromatics. The most widely studied example (structure 1 in Scheme 1) of these so-called "polymers with intrinsic microporosity" (PIMs) is based on polycondensation of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′,6,6′-tetrol (TTSBI) with 1,4-dicyanotetrafluorobenzene (DCTB). These studies were focused on the application of these ladder polymers for gas separation membranes, for adsorption of small molecules, or for heterogeneous catalysts based on an unusually high microporosity due to a high rigidity in combination with a loose chain packing generating a high free volume. However, these papers did not provide detailed information on the monomer purification, synthetic conditions, or reaction mechanism for this kind of ladder polymer.

Later the group of Kricheldorf[9] studied the condensation polymerization of the tetraphenoxide of TTSBI with DCTB in four different solvents at 70 °C. They determined that, when the reaction solvent was dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and sulfolane, cyclic polymers were formed exclusively as detected by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry up to masses of around 13 000 Da. When dimethyl sulfoxide (DMSO) was used, linear byproducts were also found. Higher temperatures caused degradation reactions catalyzed by potassium carbonate. In contrast with earlier reports by Budd, no linear PIM-1 with high molecular weight and narrow molecular weight distribution was prepared.

For the syntheses of normal linear aromatic polyethers, Schwarz et al. observed[10−12] that polycondensations involving silylated diphenols are cleaner and may yield higher conversions and molecular weights than analogous polycondensations employing the phenoxide route. Similar observations were made for cross-linked polyethers prepared from silylated triphenols.[13] Therefore, Schwarz et al.[14] studied polycondensations of silylated TTBSI with DCTB under various conditions of solvent temperature, reaction time, and monomer feed ratio. Unfortunately, linear ladder polymers with high molecular weight were not obtained. Under optimized reaction conditions, all products detectable by MALDI-TOF mass spectrometry (up to masses around 8000 Da) were shown to be mixtures of cyclic ladder oligomers and polymers. In NMP and DMSO, odd-numbered cycles were formed in addition to the prevailing even-numbered ones. However, in sulfolane, even-numbered cycles were obtained exclusively (detectable up to masses of around 10 000 Da), together with even-numbered linear chains. Temperatures above 100 °C were reported to increase the molecular weights by side reactions, which resulted in reduced solubility and broader molecular weight distribution.

Scheme 1. Synthetic Route to the Linear Ladder Polymer PIM-1



* To whom correspondence should be addressed. Phone: (613) 993-9753. Fax: (613) 991-2384. E-mail: Michael.Guiver@nrc-cnrc.gc.ca.

† NRCC Publication No. 49183.

‡ National Research Council of Canada.

§ Membrane Technology and Research Inc.

10.1021/ma801000u CCC: $40.75
Published on Web 10/04/2008

In view of the variability of the reported results, we have been exploring various ways to produce PIM-1 consistently with high molecular weight, low polydispersity, and linear structure.[15] Herein, we report on the optimization of the monomer purification and the low-temperature polycondensation, resulting in a PIM-1-type ladder polymer with number average molecular weight greater than 50 000 and with a narrow molecular weight distribution. We also investigated the cross-linking phenomenon that occurs during polymerization.

2. Experimental Section

2.1. Materials. TTSBI (98%, Alfa Aesar) was purified by recrystallization from ethanol−dichloromethane solvent. DCTB (99%, Matrix Scientific) was purified by vacuum sublimation at 140−150 °C. Anhydrous potassium carbonate (EMD Chemical, EM Science) and anhydrous DMF (Aldrich) were used as received.

2.2. Equipment and Characterization. The molecular weight and molecular weight distributions were measured by GPC using Ultrastyragel columns and THF as the eluent at a flow rate of 1 mL/min. The values obtained were determined by comparison with a series of polystyrene standards. NMR analyses were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 376.276 MHz for ^{19}F, and the spectra were obtained using a 5 mm pulsed field gradient indirect detection probe. Samples were dissolved as a 2−5 wt % polymer solution in chloroform-d_6, and $CFCl_3$ (0 ppm) was used as a reference. MALDI-TOF mass spectra were recorded on a Voyager DE-Pro MALDI-TOF (Applied Biosystems, Foster City, CA) with the instrument set in the reflection positive ion mode. 1,8,9-Anthracenetriol (dithranol) was used as the matrix and KCl as the dopant.

2.3. Condensation Polymerization. The reactant ratios for the optimized condensation polymerization of TTSBI and DCTB to produce high molecular weight ladder polymer PIM-1 are presented below. These polymers were prepared from purified monomers using DMF as the solvent and K_2CO_3 as the base. All glassware was oven-dried prior to reaction to ensure anhydrous conditions. A mixture of anhydrous K_2CO_3 (8.292 g, 60 mmol), TTSBI (10.213 g, 30 mmol), and DCTB (6.003 g, 30 mmol) in anhydrous DMF (200 mL) was magnetically stirred in a 500 mL flask at room temperature for at least 20 min to make sure all the monomers dissolved in DMF. Air was removed from the reaction flask four times by application of a gentle vacuum and replaced with Ar gas. Then the reaction flask was immersed into a preheated 55 °C oil bath. The reaction was maintained at this temperature for 23 h at a stirring rate of 810 rpm.

On cooling, the mixture was added to water (300 mL), and the crude product was collected by filtration. It was then dissolved in chloroform and reprecipitated from methanol. A 75% yield of fluorescent yellow polymer (PIM-1) was obtained after complete drying; M_n = 101 400 and M_w = 337 500 by GPC, calculated against polystyrene standards.

2.4. Film Preparation and Gas Permeation. Films of PIM-1 were ring-cast from polymer solutions (2 wt % in chloroform, filtered through 0.45 μm pore size polypropylene syringe filters) onto glass plates and allowed to evaporate slowly over a period of one day under ambient conditions. The films were dried in an oven at 70 °C; the films were weighed periodically to ensure complete removal of solvent. Circular stamps (12.6 cm^2 diameter) with an average thickness of 53 μm were cut from the film for permeation tests.

Pure-gas permeabilities were determined at 25 °C at a feed pressure of 50 psig and atmospheric permeate pressure using the constant-pressure/variable-volume method. The order of gas permeation measurements was nitrogen, methane, oxygen, hydrogen, and carbon dioxide. The feed and permeate sides of the permeation cell were always purged with the test gas prior to any measurements. The permeate flow rate was measured using a soap-bubble flow meter. Previously reported pure-gas permeability data for PIM-1 are included for comparison.

3. Results and Discussion

As is true in most condensation polymerizations, pure reactants and stoichiometric control are crucial in attaining high molecular weight polymers. In the case of PIM-1, a TTSBI/DCTB stoichiometry of 1/1 is crucial to obtain molecular weights sufficiently high to provide polymer films with good mechanical properties. However, the commercially available monomers with various grades of purity are an obstacle in achieving high molecular weight ladder polymers. The initial part of our studies concerns important details about the purification of both monomers TTSBI and DCTB, which have not been discussed before.

3.1. Purification of Monomers. *3.1.1. Purification of TTSBI.* TTSBI is soluble in polar solvents such as THF, methanol, and ethanol and insoluble in nonpolar solvents such as dichloromethane, chloroform, and *n*-hexane. Pure TTSBI is white, and its solution is colorless. As is the general tendency for phenols, TTSBI is easily oxidized by exposure to air during normal laboratory handling. TTSBI solution in ethanol became yellow due to the oxidized impurities. The solution became darker with increasing levels of impurities.

3.1.1.1. Attempt To Decolorize the TTSBI Solution. Initially, attempts were made to remove the colored impurities by passing the solution through a fluorosil media column and by activated charcoal absorption. However, the color of this solution did not disappear, probably due to the strong interaction of TTSBI with ethanol.

3.1.1.2. Attempt To Recrystallize TTSBI in Pure Ethanol.

The solubility of TTSBI in ethanol at its boiling point is less than 50 g/L. This solution was cooled in a fridge overnight, but no crystal formation occurred. Most of the ethanol was removed by evaporation until the solution became cloudy, but too little ethanol remained, most ethanol was absorbed by TTSBI, and the suspension was difficult to filter. Most solvent and impurities were retained in the TTSBI when ethanol was used as the crystallization solvent.

3.1.1.3. Recrystallization of TTSBI in Methanol/CH_2Cl_2. A 10 g sample of TTSBI was dissolved in 80 g of hot methanol, and then half of the methanol was evaporated by heating. CH_2Cl_2 was added to the hot solution slowly until the solution became cloudy. The solution was allowed to stand for 2 h. The resulting white solid was collected by vacuum filtration. Because the methanol and CH_2Cl_2 used for recystallization are not anhydrous, water absorbed by TTSBI must be removed. Purified TTSBI was dried at 60 °C under vacuum for 2 days until there was no further weight reduction. The yield was 80%. It is crucial in condensation polymerization to use pure monomers to obtain polymers with high molecular weights.

3.1.2. Purification of DCTB. Due to its symmetrical structure, DCTB could be purified readily by vacuum sublimation. A key point is to control the temperature in the range of 140−150 °C. Higher temperature resulted in DCTB being attached to the bottom of the flask, which affected the overall quality of the purified DCTB. Another detail to prevent decomposition of DCTB during recovery is to maintain Ar flow in the flask.

3.2. Condensation Polymerization. Our initial small-scale reactions were based on literature reports.[4] However, rather than high molecular weight polymers, only linear or cyclic oligomers were obtained, similar to the results of the German group.[9,11] In an attempt to increase the reaction rate and molecular weight, a higher ratio of K_2CO_3 to monomer was used. The following experiment was performed: All glassware was oven-dried prior to reaction, to ensure anhydrous conditions. A mixture of reagent-grade anhydrous K_2CO_3 (30 g, 217 mmol), TTSBI (29.4 mmol), and DCTB (29.4 mmol) in anhydrous DMF (200 mL) was magnetically stirred at 60 °C for 7 days. A steady reaction

Table 1. Reaction Conditions and Results of Condensation Polymerization[a]

expt no.	reagent ratio,[b] molar ratio	T, °C	time, h	results [c]	comments
1	1/1/8	60	24	insoluble in THF and CH_2Cl_2	cross-linked, T higher than 100 °C for the first 15 min
2	1/1/8	60	24	insoluble in THF and CH_2Cl_2	cross-linked
3	1/1/8	40	24	no solid polymer precipitated from methanol	low MW
		then 60	24	insoluble in THF and CH_2Cl_2	cross-linked
4	1/1/8	60	24	insoluble in THF and CH_2Cl_2	cross-linked
5	1/1/8	50	24	partly soluble in THF and CH_2Cl_2	partly cross-linked
6	1/1/2.2	50	24	M_n = 72 300, M_w = 258 000, and PDI = 3.57	less than 5% insoluble
			48	more polymer insoluble in THF and CH_2Cl_2	more polymer cross-linked
7	1/1/2.04	50	17	M_n = 19 700, M_w = 36 200, and PDI = 1.84	soluble
			22	M_n = 23 200, M_w = 51 400, and PDI = 2.22	soluble
			43	M_n = 33 100, M_w = 107 600, and PDI = 3.25	soluble
			92	M_n = 211 900, M_w = 1 095 000, and PDI = 5.43	soluble
8	1/1/2.00	55	11	M_n = 38 200, M_w = 71 400, and PDI = 1.87	soluble
			18	M_n = 63 500, M_w = 159 300, and PDI = 2.51	soluble
			23	M_n = 101 400, M_w = 337 500, and PDI = 3.33	soluble
			37	M_n = 89 100, M_w = 391 600, and PDI = 4.40	partly insoluble

[a] The solid content for all reactions is about 5 wt %. [b] Reagent molar ratio TTSBI/DCTB/K_2CO_3. [c] PDI = M_w/M_n.

temperature was maintained using a temperature-controlled oil bath. On cooling, the mixture was added to water (300 mL) and the crude product collected by filtration. Fluorescent yellow polymer (PIM-1) was obtained by repeated reprecipitation from methanol. The molecular weights of the resulting PIM-1 were low, with M_n from 8000 to 20 000 and PDI from 4 to 7, and the resulting films cast from these samples were brittle.

Following the initial unsuccessful experiments, polycondensations were run using purified monomers and fresh K_2CO_3 powder, using the same recipe and procedure (experiments 1 and 2 in Table 1). The polycondensation reaction was sampled at different reaction times, the first being after one day. All the obtained polymer samples were insoluble in any solvent, suggesting that cross-linking had occurred. To gain insight into this reaction and prepare PIM-1 with high molecular weight, the effects of different reaction parameters on the reaction rate and molecular weights were investigated in more detail.

Due to the nature of this reaction, it is difficult to prevent the formation of oligomers and cyclic polymers, their presence being inferred from GPC curves. To remove these oligomers and cyclic polymers, Budd et al.[5] used a process of repeated reprecipitation from methanol, which is tedious and costly. A convenient and simplified method for purification was developed as follows. When a 1−2-fold amount (volume over DMF) of THF was added to the reaction flask after the reaction was terminated, the dispersed PIM-1 particles coagulated and precipitated at the bottom of the reaction flask. The oligomers and cyclic polymers were soluble in the mixture of THF and DMF. In some cases, when the resulting polymer had very low molecular weight, no precipitate formed in the mixture of THF and DMF, indicating that this method preferentially coagulates high molecular weight polymer and removes low molecular weight fractions. The coagulated and precipitated solid was recovered and redissolved in THF. Salts (KF and unreacted K_2CO_3) and cross-linked (or highly branched, in the case of partly cross-linked) polymer were removed by filtration. The resulting clear solution was used for molecular weight measurement by GPC. The clear solution was poured into water to remove traces of salt. The precipitates were collected by filtration, and methanol was used to rinse this solid. The solid was dried under vacuum until its weight became constant. The yield was calculated according to the weight of the dry PIM-1.

3.2.1. Effects of the Reaction Temperature. Initially, the experiments were conducted by fixing the TTSBI/DCTB/K_2CO_3 molar ratio to 1/1/8, the K_2CO_3 being present is in high molar excess. It was considered that K_2CO_3 is not only a reaction reagent but also a drying agent that could promote the polymerization reaction.

Five experiments (experiments 1−5 in Table 1) were carried out using the same recipe and procedure but at different temperatures. If the reaction temperature was 60 °C or higher, and when the reaction time was 24 h or longer, the resulting polymer was insoluble in THF or CH_2Cl_2 (both THF and CH_2Cl_2 are good solvents for PIM-1), which indicated that cross-linking occurred. When the reaction temperature was decreased to 40 °C, the resulting polymer was soluble in methanol, which indicated that its molecular weight was too low to precipitate in methanol and also indicated that the reaction rate at 40 °C was very slow. When the reaction was conducted for 24 h and at a temperature of 50 °C, the resulting polymer had very high molecular weight and contained a small amount of cross-linked material. This temperature was then selected for studying the effects of the K_2CO_3 concentration.

3.2.2. Effects of the K_2CO_3 Concentration. To prevent the resulting polymer from cross-linking, smaller K_2CO_3 stoichiometric ratios were used in experiments 6 and 7 compared with experiment 5. When 10% excess K_2CO_3 was used (experiment 6), less than 5% cross-linked material was produced after 24 h. The longer the reaction time, the greater the amount of cross-linked polymer produced. When the K_2CO_3 was only in 2% excess (experiment 7), no insoluble polymer was detected after a 92 h reaction time and the weight average molecular weight reached 1 million. The polymerization reaction was not continued beyond this time.

From the above results, it was concluded that the molar ratio of K_2CO_3 is crucial to reduce the presence of cross-linked polymer. It was also found that the polycondensation reaction rate was higher with higher K_2CO_3 stoichiometric ratios. In the following experiments, the molar ratio of K_2CO_3 to monomers was carefully controlled.

3.2.3. Effects of the Reaction Time. Reaction time is an important parameter to control the molecular weight and to prevent or reduce cross-linking. The effect of the reaction time under different molar ratios of K_2CO_3 was studied. When K_2CO_3 was in 10% excess (experiment 6), a 24 h reaction time resulted in soluble polymer with M_n = 72 300, M_w = 258 000, and PDI = 3.57 and containing less than 5% insoluble polymer. However, an extended reaction time of 48 h led to more than 50% insoluble polymer.

When the K_2CO_3 was in slight (2%) excess (experiment 7), no insoluble fraction of polymer was detected. This molar ratio of K_2CO_3 was subsequently used to study the effects of the reaction time on the molecular weights and molecular weight distributions. The experiments showed that, with an increase in reaction time, both M_n and M_w increased. However M_w increased faster than M_n, indicating that the molecular weight distributions become broader (shown in Figure 1). GPC curves

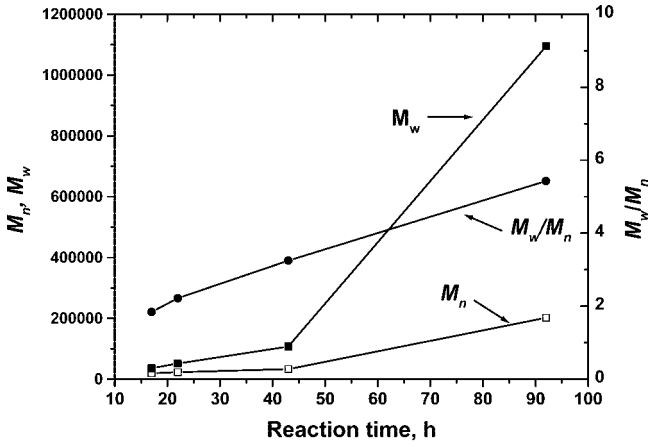


Figure 1. Effects of the reaction time on the molecular weights and molecular weight distributions (experiment 7 in Table 1).

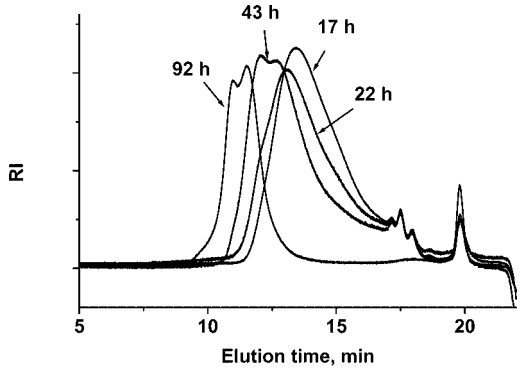


Figure 2. GPC curves of the resulting polymer at different reaction times (experiment 7 in Table 1).

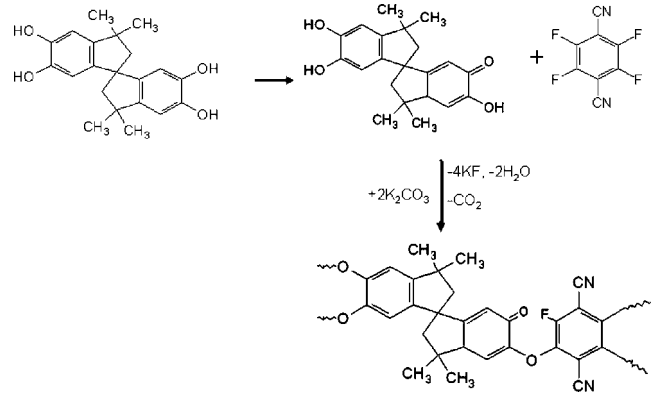
of the resulting polymer at different reaction times are shown in Figure 2.

3.2.4. Effects of the Solvent. The choice of solvents for aromatic nucleophilic substitution reactions is somewhat complex, wherein several factors need to be considered. These include (1) the reactivity of the monomers, (2) the solvation power of the solvent for the monomers and growing polymer chains, which may affect the temperature necessary to achieve a useful molecular weight in a reasonable time, (3) the solubility of the high molecular weight polymer under the reaction conditions, (4) the choice of base, either carbonate or hydroxide, and (5) the solvation of the cation. Among the dipolar aprotic solvents, those most frequently used are DMSO, DMAc, NMP, sulfolane, dimethyl sulfone, and diphenyl sulfone.

Schwarz et al.[9] performed a series of polycondensations under apparently the same reaction conditions as those described by Budd and co-workers.[4] However, in addition to the solvent DMF, three other solvents were used: NMP, DMSO, and sulfolane. The highest molecular weight was obtained using DMF, which had an M_n of 18 000 and a polydispersity of 5.2. Thus, DMF appears to be the optimum solvent for this type of polycondensation.

DMF and DMAc can dissolve low molecular weight PIM-1, whereas NMP and DMSO are nonsolvents for PIM-1. In the present study, the efficacies of DMF and DMAc solvents were compared in PIM-1 synthesis. The experiments were conducted by fixing the TTSBI/DCTB/K_2CO_3 molar ratio to 1/1/2.04 and the reaction temperature to 60 °C. When DMF was used as the solvent, a 3 h reaction time resulted in a polymer with an M_n of 43 600 and a polydispersity of 1.7. However, when DMAc was used as the solvent, the molecular weight of the resulting polymers after a 3 h reaction was too low to precipitate in

Scheme 2. Possible Chain Defects Leading to Branching or Cross-Linking of PIM-1 during Condensation Polymerization



methanol and a 20 h reaction gave PIM-1 polymer with an M_n of 19 200 and a polydispersity of 2.2. Using DMF as the solvent gave a faster reaction rate, higher molecular weight, and narrower polydispersity.

DMF is a nonsolvent for high molecular weight PIM-1, so DMF would appear not to be the ideal solvent for PIM-1 synthesis. However, because the solubility of K_2CO_3 and tetraphenolate salts in DMF is comparatively high, DMF is still effective as a reaction solvent. The initially clear reaction mixture became cloudy and yellow several minutes after the flask containing all the reagents was immersed into a 50−70 °C oil bath. This phenomenon indicates that the polymerization reaction is very fast and the resulting polymer is not soluble in DMF. However, since the precipitates dispersed well in DMF in the form of fine particles, probably in a swollen state, this does not appear to hinder further polymerization.

3.3. Mechanism of Cross-Linking of PIM-1 during Polymerization. Gel-free ladder polymer relatively free of cross-linked material is important for casting defect-free membranes for separation applications. To study the mechanism of cross-linking of PIM-1 polymer during polymerization, two experiments were designed. The reaction temperature was maintained at 60 °C, and the molar ratio of TTSBI/DCTB/K_2CO_3 was 1/1/2.04 (K_2CO_3 in 2% excess). A sample was taken from the flask when the reaction time was 3 h. GPC results showed that M_n = 30 400, M_w = 65 600, and PDI = 2.2. This suspension was separated into two parts. Into one part was added excess phenol (same molar quantity as DCTB) and additional K_2CO_3 (half-molar amount of the original addition). Nothing was added in the other part, and the reactions were continued for another 21 h.

When the added K_2CO_3 was in 2% excess and the reaction temperature was 60 °C, a 24 h reaction time resulted in insoluble polymer, which indicated that the resulting PIM-1 polymer was cross-linked. However, when excess phenol was added after 3 h of reaction, the molecular weight and molecular weight distribution of the resulting polymer did not show an evident increase during further reaction after phenol addition, since the polymer had an M_n of 34 500 and a PDI of 2.3 after 24 h. No insoluble polymer was detected in this reaction.

We believe that a likely mechanism of cross-linking is similar to the reaction leading to the formation of the polyether. In common with all phenolics, we make the assumption that some phenol groups in TTSBI are susceptible to oxidation into a benzoquinone-type structure (Scheme 2). Polymerization incorporating oxidized TTSBI would lead to single-bond chain defects and unreacted fluorine groups in the ladder polymer. This residual −F is amenable to reaction with phenolate chain ends of another PIM-1 chain, resulting in branched or cross-linked structures. The addition of excess phenol consumes the

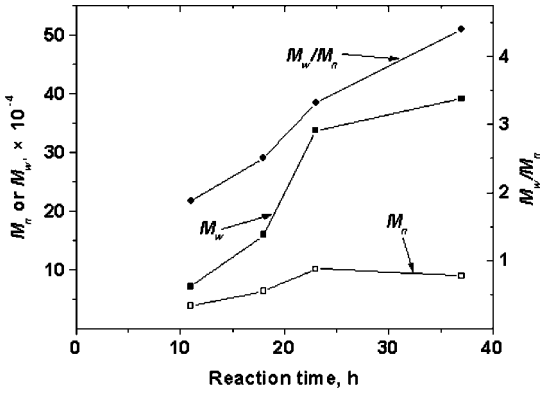


Figure 3. Effects of the reaction time on the molecular weights and molecular weight distributions at a reaction temperature of 55 °C (experiment 8 in Table 1).

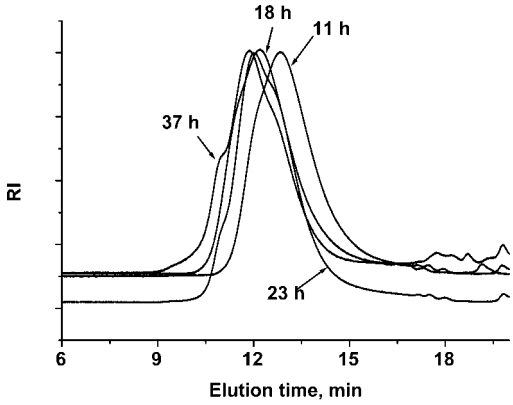


Figure 4. GPC curves of the resulting polymer at different reaction times (experiment 8 in Table 1).

residual fluorine groups including those on the ends of the growing chains, preventing further chain growth, branching, or cross-linking.

3.4. Scale-Up Experiment for Condensation Polymerization. To prepare larger amounts of PIM-1 for membrane studies, scale-up reactions were investigated. Initially, an attempt was made to increase the reaction rate by increasing the polymerization temperature, while controlling the degree of cross-linking by decreasing the molar ratio of K_2CO_3 to monomer. Experiment 8 (Table 1) was carried out at 55 °C with a K_2CO_3/monomer ratio of exactly 2/1 (i.e., 1/1 mol equiv of $-OH/K^+$). The effects of the reaction time on the molecular weights and molecular weight distributions are shown in Figure 3, and the GPC curves of the resulting polymer samples are shown in Figure 4. Compared with the reaction temperature of 50 °C (experiment 7), 55 °C (experiment 8) gave a much faster reaction rate (Figure 5). The results of experiment 8 showed that the reaction time was crucial, with an optimal time beyond which M_n began to decline and the molecular weight distribution became much broader.

The reproducibility of the experiments is very important for scale-up experiments. There are many factors affecting the polymer reproducibility such as monomer purity, stirring efficiency, reagent fluctuation, temperature fluctuation, etc. Two experiments were conducted with anhydrous K_2CO_3 from different suppliers. The reaction temperature was maintained at 60 °C, and the molar ratio TTSBI/DCTB/K_2CO_3 was 1/1/2.04. When fresh anhydrous powder K_2CO_3 (EMD CAPX1390-1) was used, the reaction rate was high. A sample taken from the reaction flask after 3 h had an M_n of 43 600 and a PDI of 1.7 by GPC. However, when fresh anhydrous granular K_2CO_3

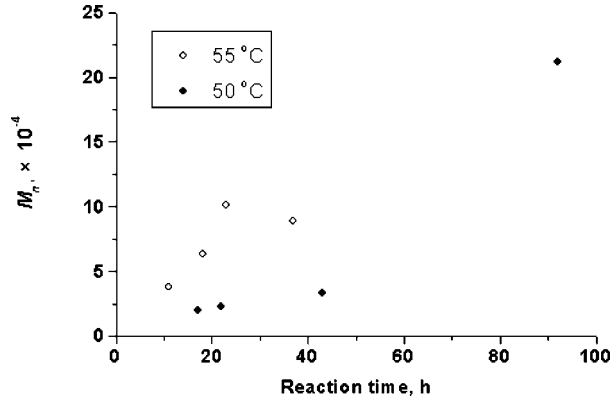


Figure 5. Polymerization rate at different reaction temperatures (experiments 7 and 8 in Table 1).

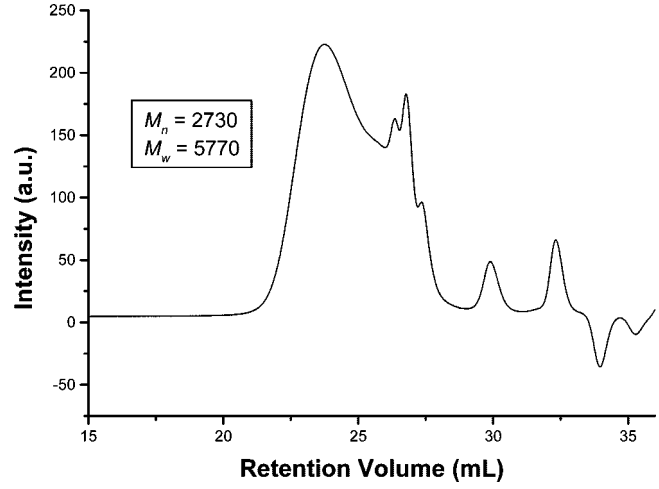


Figure 6. GPC curve of the PIM-1 oligomers collected from methanol solution (25 wt % of the total PIM-1) from experiment 8-11 h.

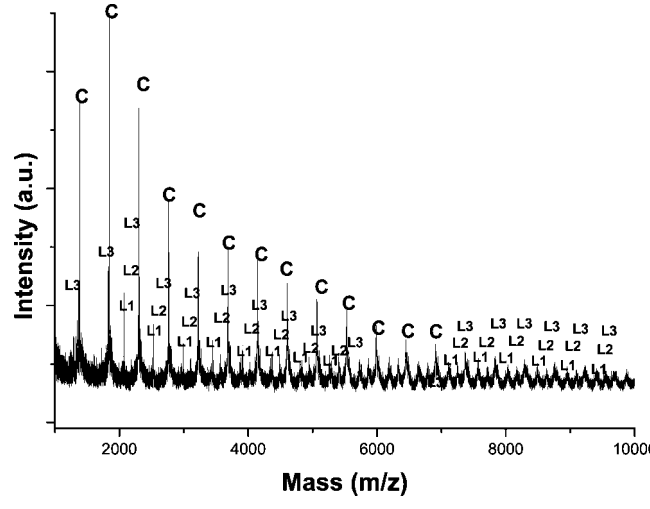


Figure 7. MALDI-TOF mass spectrum of the PIM-1 oligomer fraction collected from methanol solution (25 wt % of the total PIM-1) from experiment 8-11 h.

(J. Baker) was used, the reaction rate was extremely low, resulting in a polymer having an M_n of only 8000 and a PDI of 1.7 after 24 h. This K_2CO_3 was ground into a fine powder to increase the surface area, but it did not result in a significant improvement in the reaction rate. An older sample of anhydrous K_2CO_3 powder (EMD CAPX1390-1) and regenerated anhydrous powder K_2CO_3 were also tested. The reaction rate was very sensitive to the physical shape and quality of the K_2CO_3.

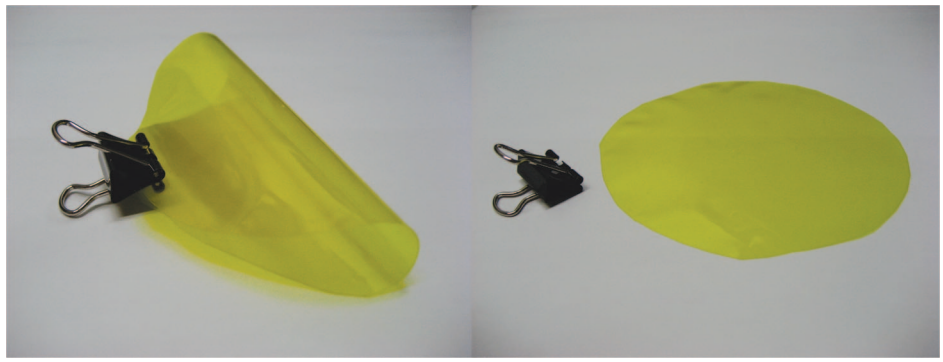


Figure 8. Flexible transparent PIM-1 film (M_n = 30 000, PDI = 1.9, thickness 80 μm).

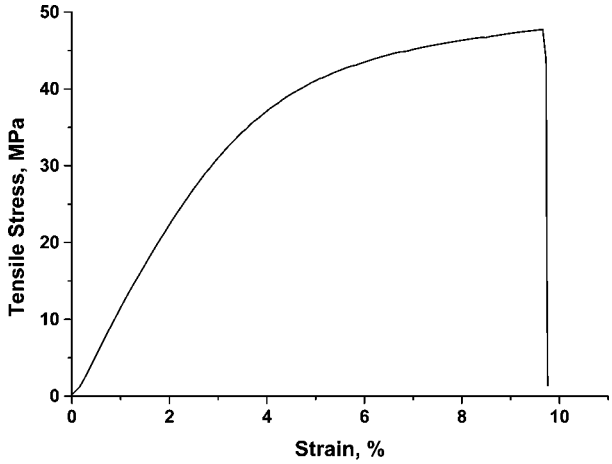


Figure 9. Stress−strain curve of a typical PIM-1 film (M_n = 30 000 and PDI = 1.9).

Table 2. Pure-Gas Permeabilities of the PIM-1 Film at 25 °C[a]

	permeability (barrer[b])			selectivity (gas/N_2)		
gas	this work	ref 16	ref 17	this work	ref 16	ref 17
N_2	270	92	238			
CH_4	350	125	360	1.3	1.4	1.5
O_2	990	370	786	3.6	4.0	3.3
H_2	1900	1300	2332	7.0	14	9.8
CO_2	4030	2300	3496	15	25	15

[a] The feed pressure was 65 psi and the permeate pressure 15 psi. The film of ref 16 was tested at a feed pressure of 4.5 psi, a permeate pressure of ~0 psi, and T = 30 °C. The film of ref 17 was tested at a feed pressure of 59 psi, a permeate pressure of ~0 psi, and T = 35 °C. [b] 1 barrer = 10^{-10} [cm^3(STP)·cm]/(cm^2·s·cmHg).

Regenerating K_2CO_3 by heating in a vacuum sometimes resulted in lower reaction rates.

The packing density of K_2CO_3 may affect its solubility and dissolution rate in DMF, which ultimately affects the reaction rate. Fresh anhydrous powder K_2CO_3 may be porous or open. The regenerating process could remove the absorbed water but may not regenerate the original porous or open structure. This result could explain that, under seemingly the same reaction conditions, we obtained high molecular weight PIM-1 or cross-linked PIM-1, but Schwarz et al.[11] obtained only oligomeric PIM-1.

3.5. Characterization of the Ladder Polymer PIM-1. *3.5.1. NMR Spectroscopy.* ^{19}F NMR spectroscopy was used to investigate the presence of any fluorine in the backbone structure of PIM-1 polymer. The sample from experiment 8-11 h (experiment 8 with 11 h of reaction time, shown in Table 1) was selected. The GPC result showed that M_n = 38 200, M_w = 71 400, and M_w/M_n = 1.87. The original consideration for choosing this sample was that the reaction time was not very long and the molecular weights for this sample were not too high, making it feasible to investigate the polymer structure or end groups.

^{19}F NMR is a very sensitive nucleus for detecting the presence of fluorine in the structure of the polymer. If the ladder structure is not fully formed or has defects, a significant amount of F should be detectable in the ^{19}F NMR spectrum. The ^{19}F NMR spectrum of experiment 8-11 h (not shown here) did not show any sharp signals, which indicated that no F was detectable, suggesting that the ladder structure was fully formed. Although the sensitivity of ^{19}F NMR is high, it may not be sufficient for end group analysis or to detect the level of branching when the molecular weights are higher than 10 000.

3.5.2. MALDI-TOF Spectroscopy. MALDI-TOF MS is useful for detecting cyclic and linear oligomers.[9] Polymers with M_n higher than 10 000 were difficult to detect. The purified PIM-1 from experiment 8-11 h by reprecipitation from methanol did not show any peak in the MALDI-TOF mass spectrum (not shown here). The PIM-1 oligomer fraction collected from the methanol solution, accounting for 25 wt % of the total PIM-1, was used for MALDI-TOF MS measurement. The GPC curve of this sample (Figure 6) showed that M_n = 2730, M_w = 5770, and PDI = 2.1. Figure 7 shows the MALDI-TOF mass spectrum of this sample. There are three series of linear ladder polymers, having four −F end groups (L1, MW = 460.7n + 200.1), four −OH end groups (L2, MW = 460.7n + 340.4), two −OH and two −F groups (L3, MW = 460.7n + 40.4), and a series of cyclics (C). This is consistent with the hypothesis illustrated in Scheme 1. In Figure 7, it is seen that, in the low molecular weight region, the intensity of the main peaks corresponding to cyclic species decreases quickly after 2000 Da and almost disappears around 7000 Da. There are also few low molecular weight L1, L2, and L3 species, suggesting that most linear oligomers polymerize and move to the high molecular weight region. It is estimated that less than 10% of the polymers have a cyclic structure. After purification, experiment 8-11 h resulted in PIM-1 with an M_n of 38 200 and a PDI of 1.87 in 75% yield.

3.5.3. Mechanical Properties. PIM-1 with moderate molecular weight and a narrow molecular weight distribution gave flexible transparent films when cast from chloroform solutions, as observed in Figure 8. This film was mechanically strong and flexible enough to record gas permeability data. The stress−strain curve (Figure 9) of a typical PIM-1 film showed that PIM-1 had good mechanical properties with a tensile strength of 47.8 MPa and a strain of 10%.

3.5.4. Gas Permeabilities. The pure-gas permeability data of PIM-1 are shown in Table 2; previously reported pure-gas permeability data are included for comparison.[16,17] As expected for a high-free-volume, microporous glassy polymer, PIM-1 has very high gas permeabilities. For example, the oxygen permeability in our study was 990 barrer. On the other hand, the

selectivities of PIM-1 are relatively modest for most gas pairs. However, the polymer has a selectivity of 3.6 for oxygen over nitrogen, which when combined with its high oxygen permeability is a remarkable result. It is interesting to note that our permeability values are significantly higher than those reported by Budd et al., whereas our gas selectivities are lower.[16] It is well-known that the permeability of highly rigid glassy polymers can vary significantly depending on the film formation protocols.[18] For example, the type of solvent and drying conditions can influence the polymer chain packing, which, in turn, affects the gas permeability and selectivity. As described above, our films were made from chloroform solution and dried in an oven at 70 °C. The permeability data reported by Budd et al. were determined for a PIM-1 film, which was made from tetrahydrofuran and dried at ambient temperature with a nitrogen purge. It is suggested that these differences in PIM-1 film formation caused the differences in gas permeability and selectivity. Recent data reported by Staiger et al. support our hypothesis; the pure-gas permeabilities and selectivities of a PIM-1 film made from methylene chloride are similar to our data for a chloroform-solution-cast PIM-1 film.[17] Current work is directed at investigating the effects of the solvent type and drying conditions on the permeability and selectivity of microporous PIM-1 in more detail. We will report the results in a future paper.

4. Conclusions

A series of experimental variables was studied to determine optimized conditions to prepare ladder-type PIM-1 polymer with high molecular weight with minimal cross-linking or branching. DMF was the best solvent for a maximized reaction rate and molecular weight. When DMAc was used as the solvent, the reaction rate was much slower than with DMF. The reaction was surprisingly sensitive to the quality and molar ratio of K_2CO_3 used. Anhydrous fine K_2CO_3 powder resulted in much higher polycondensation rates than when granular K_2CO_3 was used. When the molar feed ratio of K_2CO_3 to monomer was greater than 2%, branched or cross-linked polymer was formed. Reaction rates were very sensitive to temperature and increased with increasing temperature (40−70 °C). However, higher reaction temperatures (≥60 °C) led more readily to cross-linked polymers, while the rate of polycondensation at lower temperature (40 °C) was too slow. The optimal temperature range was 50−55 °C. The reaction time was also an important parameter, with extended reaction times leading to increased polydispersity or cross-linking. Careful control of the reaction time gave polymers with suitable molecular weight and molecular weight distribution. It is believed that the mechanism of cross-linking occurs through the reaction of the salt of −OH on one polymer chain with residual −F on another chain. Gel-free PIM-1 was prepared by adding excess potassium phenoxide after polymerization. GPC and MALDI-TOF MS indicate that the polymers contained few macrocyclic oligomers and cross-linked fractions. Flexible tough PIM-1 films were cast from chloroform solution with PIM-1 with M_n from 30 000 to 90 000. PIM-1 exhibited very high gas permeabilities and modest selectivities, as expected for a high-free-volume, microporous glassy polymer.

Acknowledgment. This work was supported primarily by the U.S. Department of Energy (SBIR Contract Number DE-FG02-05ER84243). Additional support was provided by the CCTII GHG (Climate Change Technology and Innovation Initiative, Greenhouse Gas) project. We are grateful to Dr. Li Jian Jun and Mr. Jacek Stupak, Institute for Biological Sciences, National Research Council, for the MALDI-TOF MS measurements.

References and Notes

(1) Cotter, R. J. Engineering Plastics. *A Handbook of Polyarylethers*; Gordon and Breach: London, 1995.
(2) Kricheldorf, H. R. In *Handbook of Polymer Syntheses*, 1st ed.; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1982; Chapter 9.
(3) Kricheldorf, H. R. In *Handbook of Polymer Syntheses*, 2nd ed.; Kricheldorf, H. R., Nuyken, O., Swift, G., Eds.; CRC Press: Boca Raton, FL, 2004; Chapter 7.
(4) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230.
(5) Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D. *Adv. Mater.* **2004**, *16*, 456.
(6) Budd, P. M.; McKeown, N. B.; Fritsch, D. *J. Mater. Chem.* **2005**, *15*, 1977.
(7) Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanema, E. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005**, *251*, 263.
(8) McKeown, N. B.; Budd, P. M.; Msayib, K. J.; Ghanem, B. S.; Kingston, H. J.; Tattershall, C. E.; Makhseed, S.; Reynolds, K. J.; Fritsch, D. *Chem.—Eur. J.* **2005**, *11*, 2610.
(9) Kricheldorf, H. R.; Lomadze, N.; Fritsch, D.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5344–5352.
(10) Kricheldorf, H. R. *Silicon in Polymer Syntheses*; Kricheldorf, H. R., Ed.; Springer: Berlin, 1956; Chapter 5.
(11) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. *Macromolecules* **2003**, *36*, 4337.
(12) Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *36*, 4337.
(13) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 354.
(14) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. *Macromol. Chem. Phys.* **2005**, *206*, 2239.
(15) Du, N.; Song, J.; Robertson, G. P.; Pinnau, I.; Guiver, M. D. *Macromol. Rapid Commun.* **2008**, *29*, 783.
(16) Budd, P. M.; Msayeb, K. J.; Tattershall, C. E.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005**, *251*, 263.
(17) Staiger, C. L.; Pas, S. J.; Hill, A. J.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2606.
(18) Moe, M. B.; Koros, W. J.; Hoehn, H. H.; Husk, G. R. *J. Appl. Polym. Sci.* **1988**, *36*, 1833.

MA801000U