Communications to the Editor

A Facile Synthesis and the Polymerization of Macrocyclic 1,4-Phenylene Sulfide (PPS) Oligomers

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Received February 21, 1996
Revised Manuscript Received April 18, 1996

Poly(1,4-phenylene sulfide) (PPS) is an excellent high-performance semicrystalline thermoplastic with many desirable characteristics, including outstanding thermal, oxidative and chemical resistance.[1,2] PPS is being increasingly used in structural components, e.g., as a matrix resin in fiber-reinforced composites and coatings in the electronic, automotive, and aerospace industries. Due to the high melting and crystalline nature of PPS, the conventional synthesis must overcome the insolubility of the polymer and therefore requires rigorous polymerization conditions, often limiting the molecular weight of the polymers formed. Traditionally, PPS is synthesized by polycondensation of 1,4-dichlorobenzene and sodium sulfide in polar solvents such as *N*-methylpyrrolidinone (NMP) at high temperature and pressure.[2] This process produces a large proportion of undesirable byproduct sodium chloride, which is difficult to completely remove by conventional washing with water. Furthermore, the polymers produced by this process generally contain chlorine and sodium atoms at the ends of the polymeric chains. Commercially available PPS usually has a sodium content in the range 1000−3000 ppm and a chlorine content in the range 2000−4000 ppm. The alkali metal salt residue at that level presents difficulties when the material is used, for example, for sealing or encapsulating electronic devices. Recently, several new synthetic methods for the preparation of PPS have been developed by several groups, including oxidative polymerization[3] of diphenyl disulfide in the presence of a Lewis acid, self-condensation of bis(4-iodophenyl) disulfide,[4] melt polymerization of *p*-diiodobenzene with sulfur,[5] self-condensation of methyl (*p*-thiophenoxyl)phenyl sulfoxide,[6] oxidative polymerization of methyl phenyl sulfide,[7] and polymerization of a cyclic disulfide with a *p*-dihalobenzene.[8]

Ring-opening polymerization is a well-known class of polymerization reactions. Using ring-opening polymerization to prepare high molecular weight polymers offers many advantages over other polymerization methods, including the elimination of the need for using solvents, the absence of volatile byproducts, and the capability of achieving very high molecular weights in a short reaction time. Recently, various reports have appeared concerning the use of low melt viscosity macrocyclic oligomers as intermediates for the preparation of high-performance linear condensation polymers via ring-opening polymerization.[9,10] The high melt viscosity of these high molecular weight polymers limits their potential in applications such as fabrication of long or continuous fiber-reinforced thermoplastic composites via reaction injection molding and melt pultrusion. The employment of macrocyclic 1,4-phenylene sulfide oligomers in the preparation of high molecular weight PPS could be extremely advantageous. It has been reported that cyclic phenylene sulfide oligomers undergo either free-radical ring-opening polymerization[11] or anionic and cationic ring-opening polymerization[12a] to form high molecular weight PPS. However, up to now, no simple and effective method for the synthesis of cyclic phenylene sulfide oligomers has been reported in the literature.[11,12] As part of an ongoing project dealing with the chemistry of aromatic macrocyclic oligomers, this communication reports an efficient synthesis of cyclic phenylene sulfide oligomers in two steps in excellent yield. Furthermore, the cyclic oligomers undergo ring-opening polymerization in the melt, in the presence of a catalytic amount of elemental sulfur, to form linear high molecular weight PPS with T_g up to 100 °C and T_m of 275 °C.

In a previous communication,[11b] we reported the synthesis of cyclic aryl ether sulfide oligomers via chemical reduction of the cyclic aryl ether sulfoxide oligomer precursors. It has also been found that poly(arylene sulfide)s can be prepared from masked bisthiophenols.[13] We have successfully combined these procedures for the preparation of cyclic phenylene sulfide oligomers (Scheme 1). Cyclic phenylene thioether sulfoxide oligomers **3** (see Scheme 1) were prepared, in high yield, by an aromatic nucleophilic substitution reaction from the potassium salt, prepared *in situ*, of the bisthiophenol *N*-propylcarbamates **2**[14] with bis(4-fluorophenyl)sulfoxide under high dilution conditions.[15] A concentrated solution (0.67 M) of the reactants **1** and **2a** or **2b** in *N*,*N*-dimethylformamide (DMF) was continuously added (via a syringe pump) to a mixture of DMF and anhydrous potassium bicarbonate ($KHCO_3$) at 150 °C under nitrogen over 5 h, which led to a final concentration of products as high as 80 mM. The reaction mixture was kept under reflux for another 2 h in the temperature range of 150−155 °C under nitrogen.

The cyclization reaction led to essentially quantitative yield of low molecular weight oligomers (Table 1). The oligomeric materials are soluble in solvents such as DMF, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and 1,1,2,2-tetrachloroethane (TCE). GPC analysis[16] of the whole area of the curves (Figure 1A) shows that **3a** and **3b** consist of oligomeric mixtures with M_n of 1000 and 800, respectively, and M_w of 3600 of and 1500, respectively (against polystyrene standard). ^1H, ^{13}C, and ^{19}F NMR spectroscopy give no indication of the presence of any fluoro or thiophenolic end groups, which suggests that the low molecular weight oligomeric mixtures are macrocycles. Direct confirmation of the cyclic nature of these oligomers was provided by employing matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). MALDI-TOF-MS analysis[17] indicates that the cyclic oligomers

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Scheme 1

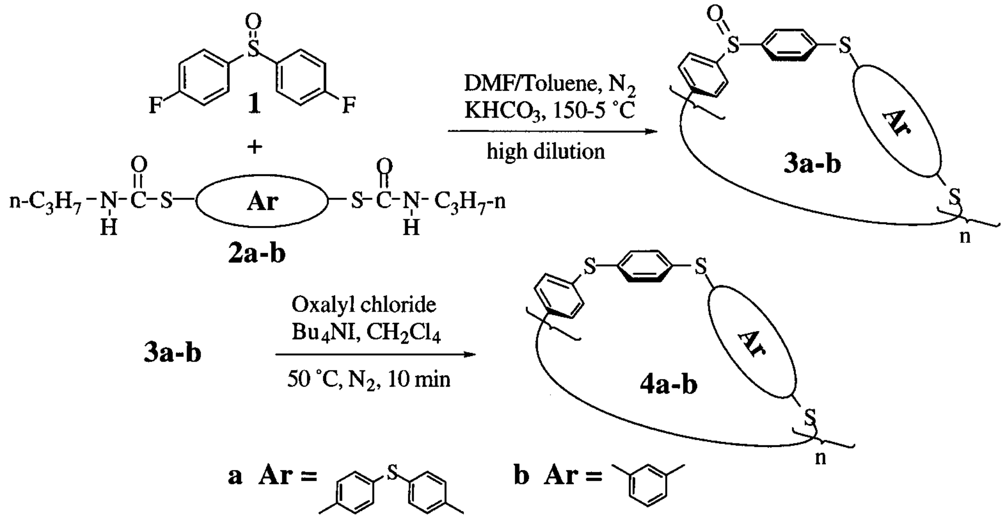

Table 1. Yields and Physical Properties of Macrocyclic Oligomers 3 and 4

cyclic oligomer	isolated yield (%)	M_n^{a}	M_w^{a}	T_g (°C)^b	T_m (°C)^b	ΔH_m (J/g)^c	$T_{-5\%}$ (°C)^d
3a	98	1000	3600	133	242	14.2	386
3b	95	800	1500	121	254	19.4	356
4a	96	*e*	*e*	*f*	256	36.4	484
4b	92	700	2000	69	198	29.9	495

[a] Measured by GPC and calibrated against polystyrene standards. [b] Measured by DSC under nitrogen (a flow rate of 100 mL/min) at a heating rate of 20 °C/min. [c] Enthalpy change of the melting endotherm, measured by DSC and calibrated against indium. [d] 5% weight loss temperature, measured by TGA under nitrogen (a flow rate of 100 mL/min) at a heating rate of 20 °C/min. [e] Not available due to the limited solubility of **4a**. [f] Not detected.

3 consist principally of macrocycles with repeating units of 2−10. A typical positive MALDI-TOF-MS spectrum of **3a** (Figure 2), using 1,8,9-anthracenetriol (dithranol) as matrix and lithium bromide as cationization agent, clearly gives the correct molecular ion signals for lithium adducts $[M_n + Li]^+$ of the desired macrocyclic oligomers with excellent signal-to-noise ratio. In the mass range (m/z up to 5000), there is no indication of the presence of linear oligomers. We have observed that, in the mass range 1−500 m/z, the MALDI-TOF mass spectra are very often complicated by the matrix; therefore, it is difficult to identify molecules that have mass below 500. In an effort to identify the presence of any monomacrocycles, EI mass spectroscopy analysis was employed. EI mass indicates that cyclic oligomers **3a** also contain monomacrocycle ($n = 1$, 448 m/z), which correlates to the peak at elution volume of 49.5 mL of the GPC trace of **3a** (Figure 1A). Based on the integration of the peak area, GPC analysis indicates that macrocyclic oligomers **3a** contain 5% cyclic monomer, 28% cyclic dimer, 13% cyclic trimer, 8% cyclic tetramer, 5% cyclic pentamer, 4% cyclic hexamer, and 37% higher member of cyclic ($n > 6$). Macrocyclic oligomers **3b** contain 41% cyclic dimer, 16% cyclic trimer, 9% cyclic tetramer, 6% cyclic pentamer, and 29% higher member of cyclic ($n > 5$). It is interesting to note that there is a higher percentage of cyclic dimer and a lower percentage of cyclics higher than hexamer in **3b** than **3a**. This is likely due to the special configuration (i.e., the *meta* position of the dithiol) of monomer **2b**, which favors the formation of cyclics.

DSC analysis[18] shows that the cyclic oligomers **3** are semicrystalline. In general, the cyclics show a moderate T_g and a melting endotherm followed by an intense exothermic peak. TGA measurements[18] show that cyclics **3** undergo a sharp weight loss corresponding to 4% around 340 °C under nitrogen. Although the true nature of the exothermic reaction associated with the sharp weight loss at 340 °C is unknown, we speculate that it involves reaction of the sulfoxide group. The thermal properties of **3** are tabulated in Table 1.

The cyclic arylene sulfide oligomers **4** were prepared in excellent yield (see Table 1) by the chemical reduction of cyclic sulfoxides **3** with oxalyl chloride and tetrabutylammonium iodide (see Scheme 1) according to the previously reported method.[19] The resulting cyclic oligomers **4a** are only partially soluble in organic solvents such as THF, chloroform, and TCE, although they are soluble in hot 1-chloronaphthalene (at about 100 °C). However, cyclic PPS oligomers with repeating units from 4 to 15 are very soluble in most organic solvents.[11b] The limited solubility of oligomers **4a** might be due to the fact that they only have an even number of repeating units ($4n$, $n = 1−10$), which might make them tend to crystallize more readily. It is also likely due to the relatively large ring size of macrocyclic **4a** (from 4 to 40 repeating units) as, with large ring sizes, the physical properties of cyclics tend to be more like those of the linear homologues. Due to the limited solubility of **4a**, molecular characterization methods such as solution NMR and GPC analyses cannot be performed. DSC analysis shows that oligomers **4a** are highly crystalline, and there is only a melting endotherm at 256 °C, with an onset temperature of 214 °C and an offset temperature of 275 °C. The fact that there is no exothermic peak in the temperature range of 300−360 °C indicates the absence of any sulfoxide functional group in **4a**. Direct proof of quantitative reduction of sulfoxide to sulfide was provided by MALDI-TOF-MS analysis. The MALDI-TOF mass spectrum of the soluble fraction of **4a** in TCE clearly gives the correct molecular ion signals for protonated PPS cyclic oligomers with repeating units of 8, 12, 16, 20, 24, 28, and 32, with excellent signal-to-noise ratio (see Figure 2). In the mass range up to 3600 m/z, there is no indication of the presence of the molecular ion of **3a** in **4a**. The MALDI-TOF mass spectrum of **4a** was obtained under the same conditions as **3a**, and there are no molecular ion signals corresponding to the lithium adducts $[M_m$

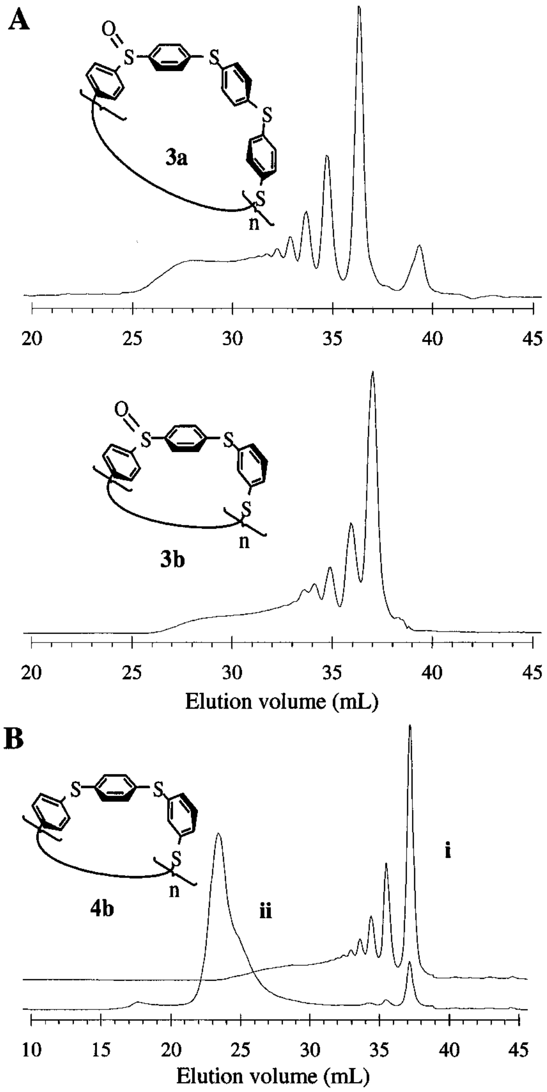

Figure 1. (A) GPC traces of cyclic oligomers **3**, using THF containing 0.5 wt/v % LiBr as the eluent with detection at 254 nm. (B) GPC traces of cyclic oligomers **4b** (i) and the resulting polymer (ii) from melt ring-opening polymerization of cyclic **4b** at 300 °C under N_2 for 30 min in the presence of 1.0 mol % S.

+ Li]$^+$ of the cyclics, although LiBr was deliberately added as a cationization agent.

Cyclic oligomers **4b** are very soluble in most organic solvents, such as THF, chloroform, and TCE. GPC analysis[20] shows that oligomers **4b** have M_n of 700 and M_w of 2000. This analysis indicated no change (within the GPC's experimental error of 10%) in molecular weight upon chemical reduction of sulfoxide to sulfide (see Table 1). A typical GPC trace of **4b** is shown in Figure 1B (trace i). Based on the integration of the peak areas, macrocyclic oligomers **4b** contain 40.5% cyclic dimer, 16.2% cyclic trimer, 8.9% cyclic tetramer, 5.5% cyclic pentamer, 3.7% cyclic hexamer, 2.8% cyclic heptamer, and 22.3% higher member of cyclics ($n > 6$). The quantitative conversion of the sulfoxide **3b** to sulfide **4b** was established by ^1H and ^{13}C NMR analyses. The protons *ortho* to the sulfoxide ring centered at 7.5 ppm in the ^1H NMR spectrum (in TCE-d_2) of **3b** have shifted quantitatively upfield after reduction. The MALDI-TOF mass spectrum of **4b** clearly gives the correct molecular ion signals for protonated cyclic oligomers with repeating units from 2 to 12, with excellent signal-to-noise ratio, and there is no indication of the presence of the molecular ion of **3b**. DSC analysis indicated that oligomers **4b** are semicrystalline and have a T_g of 69 °C and a melting endotherm centered at 198 °C, with an onset temperature of 133 °C and an offset temperature of 209 °C. There is also no exothermic peak in the temperature range of 300−360 °C, which indicates the absence of any sulfoxide functional groups in **4b**.

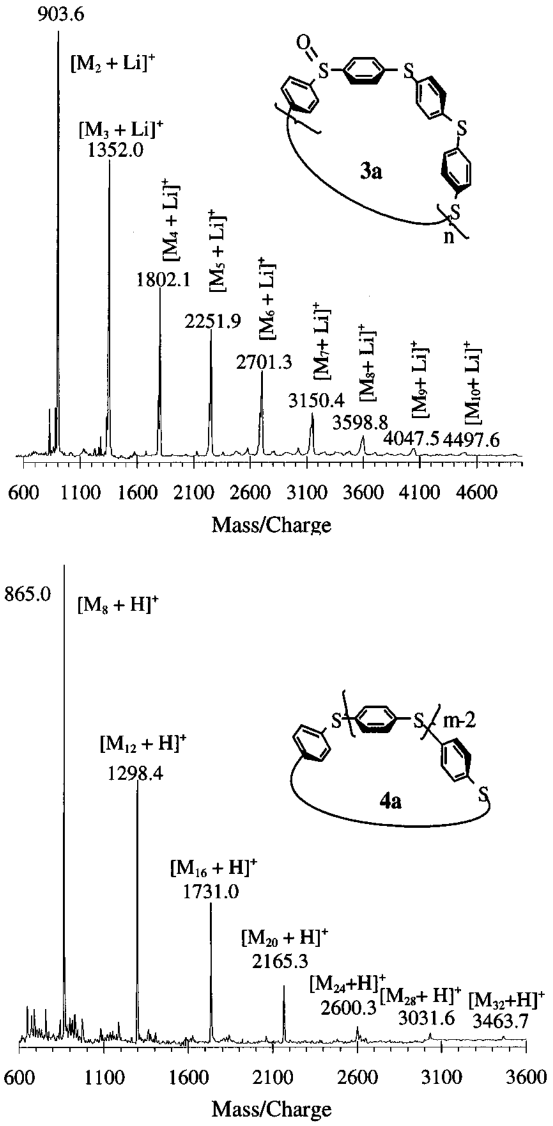

Figure 2. Positive ion MALDI-TOF mass spectra of cyclic oligomers **3a** and **4a**. The data were acquired in the reflectron mode using dithranol as the matrix and LiBr as the cationization agent (dithranol/cyclics/LiBr = 20:1:1 by weight).

Melt polymerization[21] of cyclic oligomers **4a** at 300 °C under nitrogen for 30 min, in the presence of 1.0 mol % elemental sulfur, led to the formation of high molecular weight PPS via a free-radical ring-opening polymerization reaction. The free-radical ring-opening polymerization of macrocyclic oligomers containing an aromatic sulfide linkage has been described previously.[11b,22] The resulting polymer is tough and flexible and only soluble in boiling 1-chloronaphthalene. DSC analysis revealed that the resulting polymer is highly crystalline and readily recrystallizes upon heating after quenching without the need of annealing. The first scan does not show a glass transition temperature, but a melting endotherm is observed. The melting endotherm has a peak temperature of 275 °C, with an onset temperature of 224 °C and an offset temperature of 298 °C, and has a melt enthalpy change of 3.7 kJ/mol. After quenching the sample from 330 °C to room temperature, a T_g of 99 °C, a T_c of 144 °C and a T_m of 275 °C are observed. Melt polymerization of cyclic **4b** under the same conditions led to the formation of a tough and flexible polymer which has a T_g of 75 °C and is soluble in common organic solvents such as chloroform. The polymerization is complete in 30 min, with only less than 8% cyclic oligomers (mainly cyclic dimer) remaining. GPC analysis[20] (trace ii in Figure 1B) shows that the resulting material has M_n of 31 000 and M_w of 73 000.

In conclusion, a convenient and efficient synthetic route for the preparation of macrocyclic phenylene sulfide oligomers has been described. Cyclic 1,4-phenylene sulfide oligomers **4a** undergo a facile ring-opening polymerization in the presence of 1.0 mol % S at 300 °C to form linear high molecular weight PPS, which has a T_g of 99 °C and a T_m of 275 °C. Polymerization of cyclic phenylene sulfide oligomers **4b** led to the formation of very high molecular weight poly(phenylene sulfide), which, in contrast to PPS, is very soluble because of the *meta* linkages. The polymerization is complete in 30 min at 300 °C in the presence of 1.0 mol % S, with less than 8% cyclic oligomers remaining.

Acknowledgment. The authors acknowledge the financial support of this work by the Natural Sciences and Engineering Research Council of Canada.

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(11) (a) Hay, A. S.; Wang, Y.-F. U.S. Patent application 08/419,112, 1995. (b) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules* **1995**, *28*, 6371. In the patent application, cyclic 1,4-phenylene sulfide oligomers were prepared by the self-condensation reaction of copper(I) *p*-bromothiophenoxide in quinoline at 195−200°C under high dilution. In a typical reaction, copper(I) *p*-bromothiophenoxide solid (0.60 g) was periodically added to a quinoline solution (400 mL) at 195−200 °C every 8 h until, overall, 3.60 g (14.31 mmol) of the copper salt was added, to give a final concentration of product of 35.8 mM. This process led to formation of cyclic oligomers containing 4−15 monomeric units in 50% yield. The cyclic oligomers showed a melting point of 217 °C.

(12) (a) Miyata, H.; Inoue, H. U.S. Patent 5,384,391, 1995. (b) Ash, C. E.; Laurent, W. A. U.S. Patent 5,440,009, 1995. In both patents, cyclic 1,4-phenylene sulfide oligomers were extracted from PPS. In a typical process, only 1.2 g of cyclic oligomers containing 7−15 monomeric units was obtained from 200 g of PPS. The cyclic oligomers showed a melting point of 260 °C.

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(14) The bisthiophenol N-propylcarbamates **2** (**a** and **b**) were prepared by treating 4,4′-thiobis[benzenedithiol] and 1,3-benzenedithiol, respectively (both from Aldrich), with a slight excess (20% equivalent) of *n*-propyl isocyanate in DMF with addition of a few drops of pyridine at room temperature for 1 h. The corresponding carbamates were obtained in high yields (>92%) as crystalline, odorless, and colorless solids which were easily recrystallized from methyl ethyl ketone (MEK).

(15) A typical example of the cyclization reaction is as follows: to a 2 L, three-neck, round-bottom flask equipped with mechanical stirring, Dean−Stark trap and condenser, a thermometer, and a nitrogen inlet were added potassium bicarbonate ($KHCO_3$, 40 g, 0.4 mol), *N,N*-dimethylformamide (DMF, 1100 mL), and toluene (150 mL). The mixture was mechanically stirred and heated to reflux under nitrogen. The temperature of the mixture was kept at 150−155 °C by continually removing toluene. A concentrated solution of the reactants **1** (23.825 g, 0.100 mol) and **2a** (42.060 g, 0.100 mol) in DMF (150 mL) was then added over 5 h via a syringe pump. After the addition was complete, the reaction mixture was kept under reflux for another 2 h.

(16) The GPC analysis was carried out on a Waters 510 HPLC using four phenogel 5 μm columns arranged in series (each 300 mm × 7.8 mm i.d., one linear and three 500 Å). HPLC grade THF containing 0.5 wt/v % LiBr was used as the eluent, with a flow rate of 1.0 mL/min, the UV detector was at 254 nm, and polystyrene standards were used for the calibration.

(17) MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 μm diameter spot). The MALDI instrument was operated in a positive reflectron mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. An external calibration using bovine insulin and angiotension was used; this provides mass accuracy within 0.02% for this instrument.

(18) Thermal analyses of macrocyclic oligomers were carried out on Seiko 220 DSC and 220 TGA/DTA instruments under nitrogen (a flow rate of 100 mL/min), with a heating rate of 20 °C/min.

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(20) The GPC analysis was carried out as in note 16, except that chloroform was used as the eluent.

(21) A typical polymerization procedure is as follows: cyclics **4a** (2.0 g) were mechanically mixed with elemental sulfur (6.0 mg) in a 50 mL dry test tube. After sweeping with nitrogen for a few minutes, the test tube was sealed with a septum that was equipped with a nitrogen inlet and outlet. The test tube was then placed into a preheated salt bath at 300 °C for 30 min. The resulting polymer was removed by breaking the test tube.

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MA9602740