

Solution Polymerization of Polybenzimidazole

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ABSTRACT: Polybenzimidazoles (PBI) are an important class of heterocyclic polymers that exhibit high thermal and oxidative stabilities. The two dominant polymerization methods used for the synthesis of PBI are the melt/solid polymerization route and solution polymerization using polyphosphoric acid as the solvent. Both methods have been widely used to produce high-molecular weight PBI, but also highlight the obvious absence of a practical organic solution-based method of polymerization. This current work explores the synthesis of high-molecular weight meta-PBI in *N,N*-dimethyl acetamide (DMAc). Initially, model compound studies examined the reactivity of small molecules with various chemical functionalities that could be used to produce 2-phenyl-benzimidazole in high yield with minimal side reactions. ¹H NMR and FTIR studies indicated that benzimidazoles could be efficiently synthesized in DMAc by reaction of an *o*-diamine and the bisulfite adduct of

an aromatic aldehyde. Polymerizations were conducted at various polymer concentrations (2–26 wt % polymer) using difunctional monomers to optimize reaction conditions in DMAc which resulted in the preparation of high-molecular weight m-PBI (inherent viscosities up to 1.3 dL g⁻¹). TGA and DSC confirmed that m-PBI produced via this route has comparable properties to that of commercial m-PBI. This method is advantageous in that it not only allows for high-polymer concentrations of m-PBI to be synthesized directly and efficiently, but can be applied to the synthesis of many PBI derivatives. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 1795–1802

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INTRODUCTION Polybenzimidazoles (PBIs) are an important class of heterocyclic polymers that were first reported in 1959¹ with the development of the first aromatic PBI reported shortly thereafter, in 1961.² Polybenzimidazole was originally synthesized and investigated as a thermally stable, oxidatively resistant material.³ Since the early development, numerous variations of PBI derivatives have been reported.^{4–6} Of all the derivatives of polybenzimidazoles, aromatic PBIs have received the most attention due to their excellent thermal stabilities and chemical resistance.^{7–17}

Fully aromatic PBIs exhibit very high decomposition temperatures (>500 °C), and do not show melting points due to their lack of crystallinity or have melting points above their decomposition temperatures.¹⁸ Since PBI demonstrates excellent thermal stabilities, it is especially suited for high-temperature fabric applications, and is commercially produced as a high-performance, thermally stable fiber.¹⁹

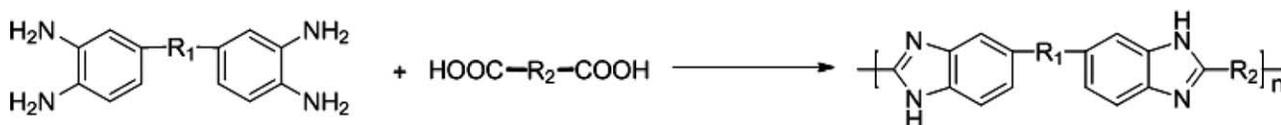
Polybenzimidazoles can be synthesized via a few different methods. One common synthetic route is through a polycon-

densation of diacid and tetra-amine monomers as shown in Scheme 1. A typical synthesis of bisbenzimidazoles involves a reaction between *o*-phenylenediamines with a diacid in hydrochloric acid or polyphosphoric acid.²⁰ Synthesis of 2-substituted benzimidazoles from the reaction of *o*-phenylenediamine with an imidate are also well known.²¹ Synthetic knowledge of these procedures can be applied to polymeric systems when di-functional monomers are incorporated, however, challenges arise when considering polymer solubility and degree of polymerization. Although PBI is a basic polymer (p*K*_a ~5.25)²² with both proton donor and acceptor sites that allow for specific interactions with polar solvents,^{23–25} fully aromatic PBIs are practically insoluble in most organic solvents.²⁶

Many polymerization techniques have been investigated to develop high-molecular-weight PBI including: Eaton's reagent as the polymerization solvent,²⁸ mixed solvent systems,²⁹ oxidative cyclization of corresponding polyamidines,³⁰ and Higashi phosphorylation techniques.³¹ More commonly, PBI is synthesized with polyphosphoric acid as a solvent and has proven to be quite advantageous for fuel cell applications.³²

Kayley J. Fishel and Alexander L. Gullede contributed equally to this work.

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SCHEME 1 Polybenzimidazole synthesis through polycondensation of diacid and tetra-amine monomers.

Although PBI can be successfully prepared using these methods, none of the techniques mentioned provide an efficient route to the synthesis of high-molecular weight PBI in a common organic solvent suitable for commercial production of fibers, films, or coatings. In 1970, Higgins and Marvel had reported the use of tetraamines with the bisulfite adducts of aldehydes to produce PBI directly in dimethyl acetamide (DMAc).²⁷ Though small molecule studies indicated this method was promising for the synthesis of PBI, the polymerizations were conducted at 1 wt % polymer and high inherent viscosity (IV) was never achieved. PBI is commercially produced by PBI Performance Products using a two stage melt/solid phase polymerization method by condensing diphenyl isophthalate (DPIP) with tetraaminobiphenyl (TAB) to produce poly(2,2'-m-phenylene-5,5'-bibenzimidazole) (m-PBI).³³ The polymerized powder product is then dissolved at high temperatures and pressures and used to produce a high-performance thermally stable fiber which is used for various fire-resistant applications.

Herein, we report an efficient solution polymerization method for the synthesis of high-molecular weight m-PBI (IV's up to 1.3 dL g⁻¹) in *N,N*-dimethylacetamide suitable for commercial production of m-PBI which can be applied to the synthesis of a variety of PBI derivatives. Model compound studies were conducted and monitored via GC/MS analysis to determine suitable candidates for the synthesis of m-PBI in DMAc. Using the bisulfite adduct of isophthalaldehyde, m-PBI was polymerized in DMAc at reflux as shown in Scheme 2. Polymerization parameters were optimized and the resulting polymer was confirmed via ¹H NMR and FTIR analysis. Further comparisons of the solution-polymerized m-PBI product and the commercially produced m-PBI product were conducted via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to confirm that the solution polymerized m-PBI polymer was nearly identical to the polymer produced by the commercially used melt/solid-state polymerization route for m-PBI.

EXPERIMENTAL

Materials

Isophthalaldehyde (98%) was purchased from Combi-blocks. Sodium bisulfite (NaHSO₃) and sodium metabisulfite

(Na₂S₂O₅) were purchased from JT Baker. Diphenyl isophthalate (DPIP) was donated by PBI Performance Products. Isophthalic acid (99+%) was purchased from Amoco. Lithium chloride (LiCl, 99%) and phenyl benzoate (99%) were purchased from Acros. Benzaldehyde (99%) and *o*-phenylenediamine (99%) were purchased from Aldrich. TAB monomer, 3,3',4,4'-tetraaminobiphenyl (polymer grade, ~97.5%) was donated by Celanese Ventures (now, BASF). Common solvents (e.g., DMSO, MeOH, EtOH, etc.) and benzoic acid certified primary standard were purchased from Fisher Scientific. Sulfuric acid (96%) was purchased from Alfa Aesar. Dimethyl acetamide (DMAc) was purchased from Oakwood Products. All chemicals were used as received unless otherwise stated.

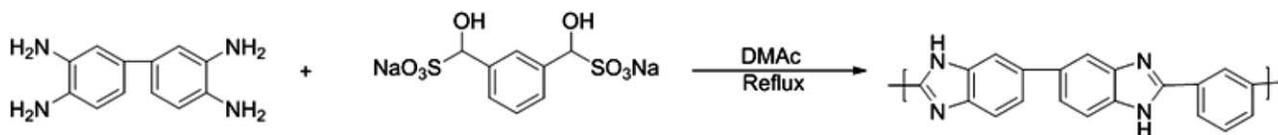
Preparation of Isophthalaldehyde Bisulfite Adduct

The procedure used for the synthesis of isophthalaldehyde bisulfite adduct (IBA) was adapted from Higgins et al.²⁷ Sodium bisulfite (22.5 g, 0.216 mol) was dissolved in 75 mL of deionized water. Isophthalaldehyde (14.5 g, 0.108 mol) was dissolved in 500 mL of MeOH. Once dissolved, the solutions were combined in a 1000-mL round-bottom flask and stirred at room temp for 24 h. After ~2 h, a white precipitate formed. This precipitate was confirmed via ¹H NMR to be the bisulfite adduct of isophthalaldehyde (yield: 11.36 g, 91.5%).

Analysis: FTIR: 1410w, 1350w, 1250w, 1175s, 1000s, 650s cm⁻¹. ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 7.7 (s, 1H), 7.5 (d, 1H, *J*=6.1), 7.3 (d, 1H, *J*=6.1), 6.0 (s, 1H), 5.1 (s, 1H).

Solution Polymerization of m-PBI

In a typical polymerization, 4.0 g (11.6 mmol) of IBA, 2.504 g (11.6 mmol) of tetraaminobiphenyl, and 17.5 mL of DMAc were added to a three-neck 100-mL round-bottom flask under nitrogen. The flask was equipped with a stir-rod and paddle and stir-rod adaptor in the center flask neck which was connected to an overhead mechanical stirrer. A reflux condenser with a nitrogen outlet was attached and the remaining flask neck was fitted with a nitrogen inlet. A slow nitrogen flow rate, monitored by oil filled bubblers, was then established. The nitrogen flow rate was maintained throughout the reaction. Once assembled, the apparatus was lowered into a temperature regulated silicone oil bath. The oil bath temperature was regulated with an IR² thermal controller.



SCHEME 2 Polymerization of poly(2,2'-m-phenylene-5,5'-bibenzimidazole) (m-PBI) in DMAc.

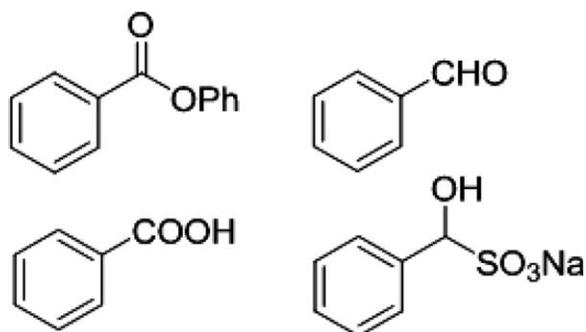


FIGURE 1 Chemical functionalities evaluated for the synthesis of 2-phenyl benzimidazole with *o*-phenylenediamine in DMAc.

Once the reaction was purged, the oil bath was heated to 180 °C, and maintained for the duration of the reaction. Upon refluxing of the solution, stirring was initiated at 60 rpm and maintained throughout the duration of the reaction. The polymerizations were allowed to proceed at reflux for 48–72 h with the exception of the trials performed to determine the effect of time on IV.

Polymerizations in which sodium metabisulfite was added to generate sulfur dioxide *in situ* were allowed to heat at reflux before the sodium metabisulfite was added. In these trials, 1 equivalent of sodium metabisulfite was added for every 3–6 equivalents of IBA (0.371–0.741 g, 1.95–3.90 mmol). The sodium metabisulfite was added over the duration of the polymerization (48–72 h).

Polymer Isolation

Upon completion of the reaction, the polymer product was isolated by precipitation in deionized water. The polymer was blended in water and vacuum filtered three times then blended in methanol and filtered three times. Powders were collected and dried under vacuum at 180 °C for 24 h. Once dried, the polymer powder was used for product analysis.

Characterization Techniques

FTIR spectra were recorded on a Perkin Elmer Spectrum 100. ¹H NMR spectra were recorded using a Varian Mercury 300 spectrometer. TGA of dried polymer samples was conducted using a TA Instruments Q5000 with nitrogen or air flow rates of 25 mL/min and a heating rate of 10 °C/min. TGA was performed from room temperature to 750 °C. GC/MS analysis was used to monitor reaction products of small molecule analogs using a Shimadzu GCMS-QP2010S equipped with a Shimadzu SHRX1-5MS column. Samples were prepared in DMAc. The temperature program for the GC column oven ramped the oven temperature from 150 to 300 °C at 30 °C/min and then held at 300 °C for 6 min. DSC was conducted using a TA Instruments Q2000 with 50 mL/min nitrogen flow and a heating rate of 5 °C/min.

IV measurements were conducted using a Cannon Ubbelohde (200 μm) viscometer at a concentration of 0.2 g/dL in sulfuric acid (H₂SO₄) at 30.0 °C. Samples were prepared by dis-

solving the dried polymer powders in sulfuric acid using a mechanical shaker. Reported IV values are an average of three separate measurements and were calculated as previously reported by Mader et al.²⁸

RESULTS AND DISCUSSION

Model Compound Studies

Model compound studies were conducted using GC/MS analysis to evaluate the reactivity of various chemical functionalities with *o*-phenylenediamine at 1:1 ratios in DMAc for the production of 2-phenyl benzimidazole as shown in Figure 1. All small molecule reactions were monitored over a 24-h period for consistency.

Initially, the reaction of phenyl benzoate with *o*-phenylenediamine was evaluated because of the commercial utilization of DPIP, however, even at reflux, the reaction was unsuccessful and did not produce any 2-phenyl benzimidazole. Studies were then conducted with benzoic acid, as PBIs are commonly synthesized using diacid monomers.^{7,14,29} GC/MS analysis of the reaction of benzoic acid and *o*-phenylenediamine showed multiple reaction products. After 48 h of reaction, <10% of the desired 2-phenyl benzimidazole product was obtained. Efforts then proceeded to evaluate the reaction of benzaldehyde and *o*-phenylenediamine as shown in Figure 2. A higher yield of the desired product was obtained (~30% after 24 h); however, the reaction system was quickly dominated by an *m/z* 284 signal which was later determined to be the bisimine or Schiff-base product *N*¹,*N*²-bis(phenylmethylene)-1,2-benzenediamine.

Previous literature reported the synthesis of low-molecular-weight PBI using an IBA and TAB when the polymerization was conducted in DMAc at low monomer concentration.²⁷ We studied the reaction of the bisulfite adduct of benzaldehyde with *o*-phenylenediamine in DMAc via GC/MS. GC/MS analysis revealed a very efficient reaction with high yield of 2-phenylbenzimidazole and no unwanted byproducts as shown in Figure 3. It is important to note that the bisulfite adduct of benzaldehyde and *o*-phenylenediamine were used in a 1:1 equivalent even though the early time data seems to indicate that less of the bisulfite adduct of benzaldehyde was used. This is due to the low solubility of the bisulfite adduct of benzaldehyde in DMAc.

Polymerization Trials

The model compound studies provided further motivation to conduct polymerization trials using difunctional monomers corresponding to those used in the model compound studies. As suggested by the model compound studies, the polymerization of DPIP and TAB did not produce any polymer product. Polymerizations using isophthalic acid and TAB yielded some reaction products; however, polymer was not obtained. Polymerizations involving isophthalaldehyde and TAB quickly resulted in cross-linked products which were insoluble in all solvents tested. This was attributed to the formation of the imines which were previously observed and reported by Higgins and Marvel.²⁷ Finally, polymerization experiments using

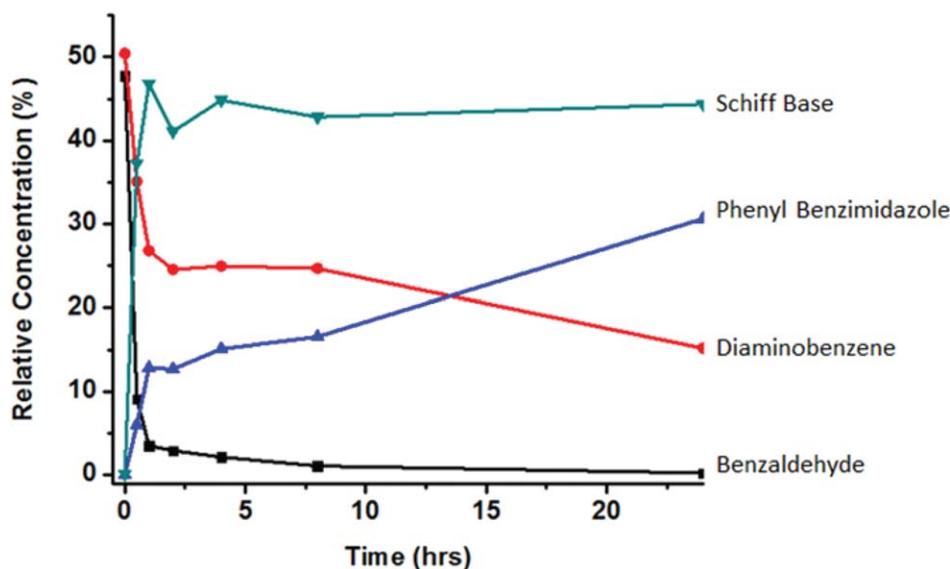


FIGURE 2 GC/MS analysis for the reaction of benzaldehyde and *o*-diaminobenzene in DMAc at 160 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

IBA and TAB were conducted and shown by ^1H NMR, TGA, and DSC to produce m-PBI which was studied in further detail and reported herein.

Synthesis of Isophthalaldehyde Bisulfite Adduct

IBA was synthesized using mild reaction conditions as described previously. Monomer scale-up was achieved on the kilogram scale to allow for detailed polymerization studies. This was performed by dissolving 498.64 g of isophthalaldehyde in 17.5 L of MeOH in a 7-gallon plastic pail. An overhead stirrer was used at a stir rate of approximately 250 RPM. Sodium bisulfite (781.0 g) was then dissolved in 2.6 L of distilled water. Once both the sodium bisulfite and the isophthalaldehyde were dissolved, the sodium bisulfite

solution was added to the bucket over a 5-min period and vigorous stirring was continued. After 5 h, a large amount of white precipitate was obtained in high yield (>90%) and purity (>98%). Monomer was purified via a methanol wash to remove residual isophthalaldehyde before drying under vacuum at 80 °C. Purity was assessed by monitoring the aldehyde peak at 9.9 ppm in the ^1H NMR spectrum. It was found that monomer batches containing <3% aldehyde resulted in the highest IV polymers. To be certain that additional salt was not present from the sodium bisulfite reactant, TGA was performed to assess the char yield. Monomer batches that contained <33% char at 400 °C yielded the highest IV polymer. It is important to note that impurities in monomer can affect the IV of the polymer by disrupting

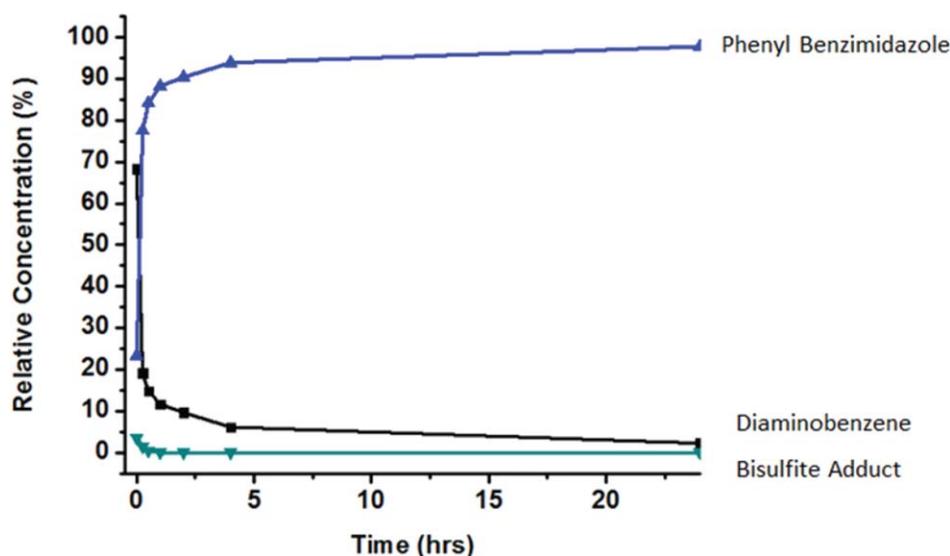


FIGURE 3 GC/MS analysis for the reaction of the bisulfite adduct of benzaldehyde and *o*-diaminobenzene in DMAc at 160 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

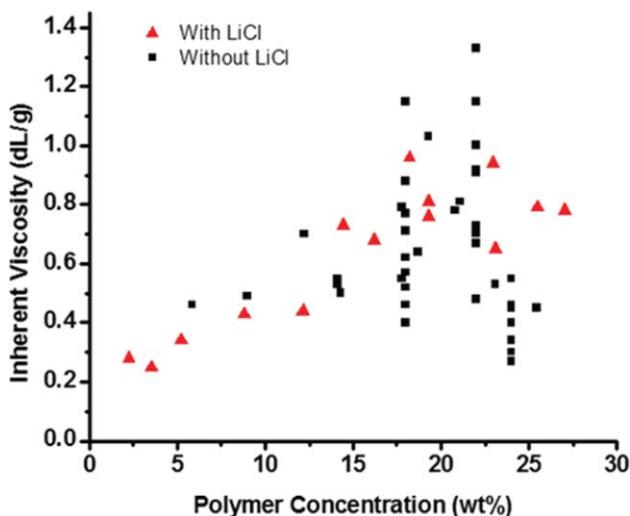


FIGURE 4 Polymer IV's from the synthesis of m-PBI in DMAc with and without the presence of LiCl. A solution of 2% LiCl in DMAc was used when indicated. The graph contains comprehensive data for the polymerization at different polymerization times and multiple monomer lots. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stoichiometry during weighing, as explained via Carother's equation.³⁰

Polymerization Studies for m-PBI

Detailed polymerization experiments were conducted for the polymerization of m-PBI using IBA and TAB in DMAc to study the effects of LiCl addition, monomer concentration, and polymerization time on final polymer molecular weight as indicated by IV measurements. Investigations were conducted with and without the addition of LiCl, a solution stabilizer for m-PBI in DMAc, at various polymer concentrations as shown in Figure 4. Polymerizations were conducted with varying monomer lots and over a range of 24–48 h. Although variability in IV was observed across the many experiments, the highest IV's were found when polymerizations were conducted between 18 and 22 wt % polymer.

Experiments were also performed to assess the effect of time on IV at various polymer concentrations as seen in Figure 5. No direct correlation was observed between IV and time when polymerizations were conducted for greater than 30 h. At 18 and 24 wt % polymer, the IVs did not appear to correlate with polymerization time. Initially, the polymer IVs for polymerizations conducted at 22 wt % appeared to correlate with polymerization time, however, when polymerizations were repeated at 48 h, the results were not reproducible. Remarkably, when using purified monomer and high (18–22 wt %) polymer concentrations, the polymer IVs obtained under these conditions were significantly higher than previously reported.²⁷ Additionally, polymerizations could be conducted at much higher monomer charges without polymer precipitation. The higher final polymer solution concentrations are in the range of polymer concentrations

used in commercial processes for coating, casting and fiber spinning, thus allowing the direct processing of polymerization solutions without polymer isolation, purification, or lengthy re-dissolution procedures.

Due to the variation in polymer IV values obtained in polymerizations that were performed under similar reaction

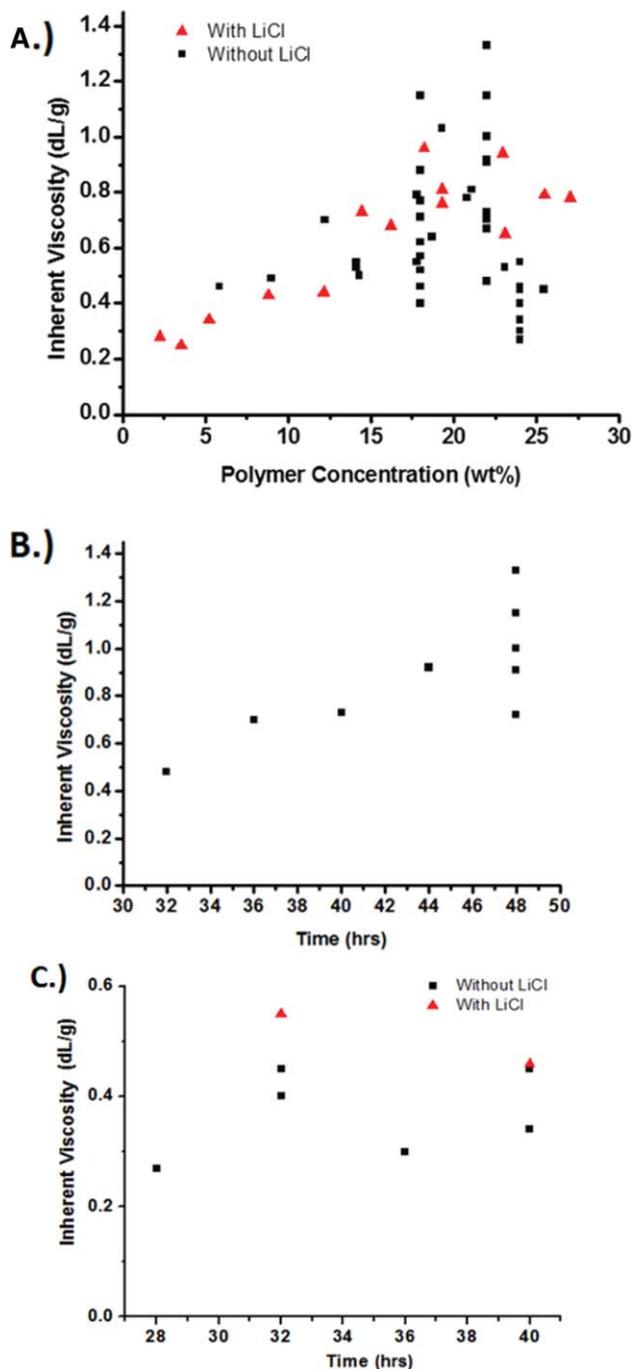


FIGURE 5 Inherent viscosity as a function of time using various monomer lots for (A) 18 wt % polymer, (B) 22 wt % polymer, and (C) 24 wt % polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

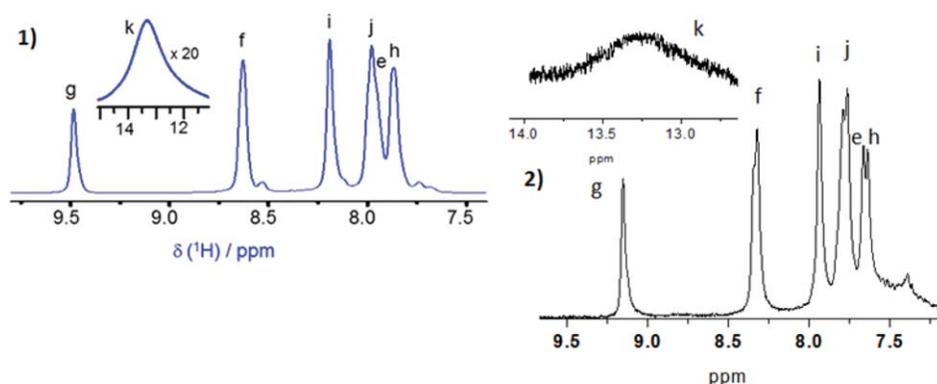


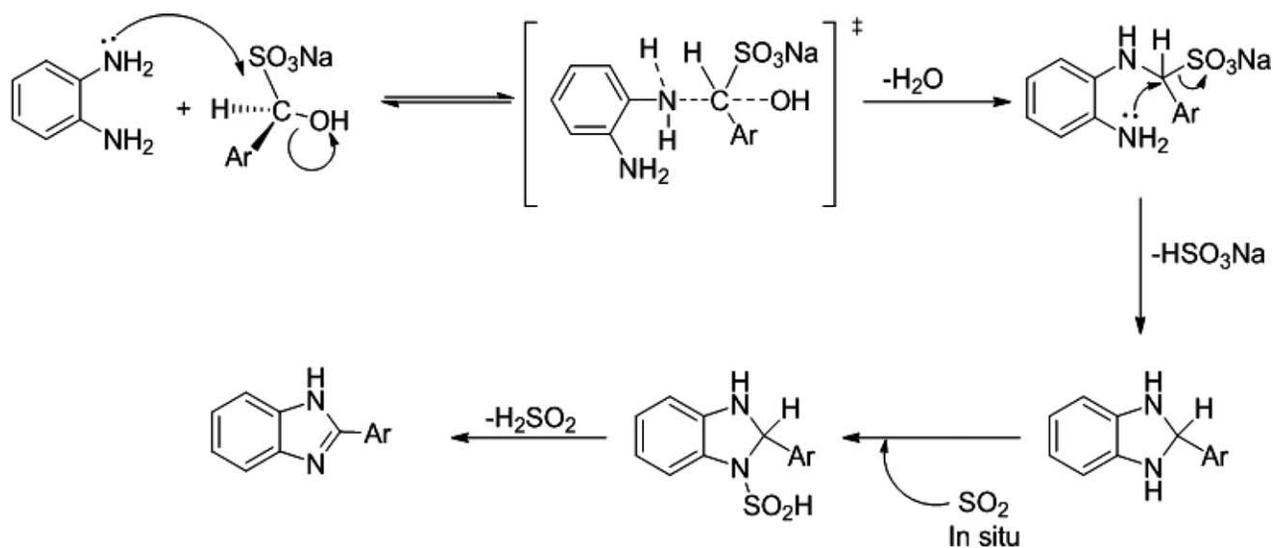
FIGURE 6 (1) Reported literature for the ^1H NMR of m-PBI in DMAc with D_2O standard³⁶ and (2) ^1H NMR of solution polymerized m-PBI in $\text{DMSO}-d_6$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conditions, the monomer purity of IBA was reassessed. Variations in monomer purity were found among different monomer batches and thus, a more dilute monomer synthesis procedure than previously reported was followed (as reported in the experimental section) that produced high-purity monomer (see scale-up discussion). These inconsistencies in monomer purity can cause the variation in IV when polymerizations were conducted under identical conditions except for monomer lot. Multiple points at the same time on the IV curve indicate identical polymerization conditions with the exception of IBA monomer lot. The m-PBI product was characterized via ^1H NMR and compared to a reported literature spectrum for m-PBI³¹ as shown in **Figure 6**. FTIR spectral comparisons (not shown) of the solution polymerized product and commercially produced m-PBI also confirmed the synthesis of m-PBI.

To further understand the factors involved in obtaining high molecular weight PBI via the solution polymerization method,

the final step of the mechanism (dehydrogenation) leading to imidazole formation was investigated. Starshikov and Romero both reported the synthesis of heterocyclic aromatic molecules that are similar in structure to benzimidazole.^{32,33} In both cases, sulfur dioxide is generated *in situ* and used as the oxidant for the final dehydrogenation step with the concomitant generation of sulfurous acid.^{32,33} To test the effects of sulfur dioxide on imidazole formation and final polymer IV, polymerizations were conducted with the *in situ* generation of sulfur dioxide. Sodium metabisulfite, which thermally decomposes into sulfur dioxide and sodium sulfite, was added to these polymerizations over the duration of the reaction. Scheme 3 shows the proposed reaction mechanism in which sulfur dioxide is generated *in situ*. The highlighted area shows how the SO_2 oxidizes the heterocyclic ring to the benzimidazole while the sulfur dioxide is reduced to sulfurous acid.

Figure 7 shows the results of polymerizations conducted at 22 wt % polymer content with and without additions of



SCHEME 3 Proposed mechanism of ring closure in the presence of sulfur dioxide.

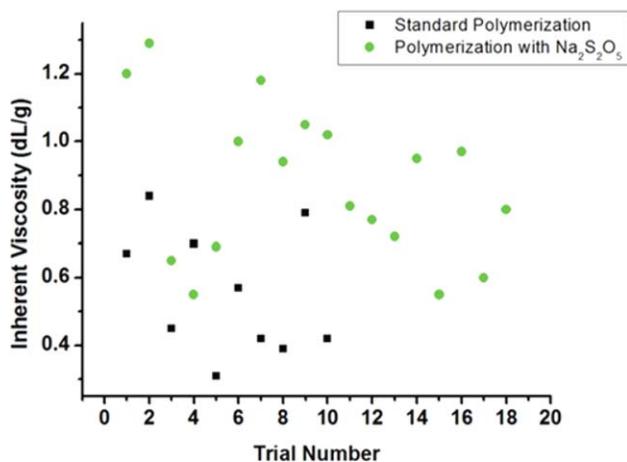


FIGURE 7 Polymerization trials with and without the addition of sodium metabisulfite for *in situ* SO₂ generation at 22 wt % polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

metabisulfite. The trials performed with sodium metabisulfite were conducted using 1 mol of sodium metabisulfite to 3–6 mol of IBA that was added ~10 g at a time over the 48- to 52-h reaction duration. Polymerizations conducted without sodium metabisulfite had a reaction duration of 72–120 h. The overwhelmingly major correlation on final polymer IV was the introduction of sodium metabisulfite during the polymerization. Polymer IVs in excess of those found commercially (>0.5–0.7 dL g⁻¹) were routinely prepared under different conditions.

Thermal Analysis

Thermal analyses of the solution polymerized m-PBI and the commercially produced m-PBI were conducted via DSC and TGA. Modulated DSC was conducted from ambient tempera-

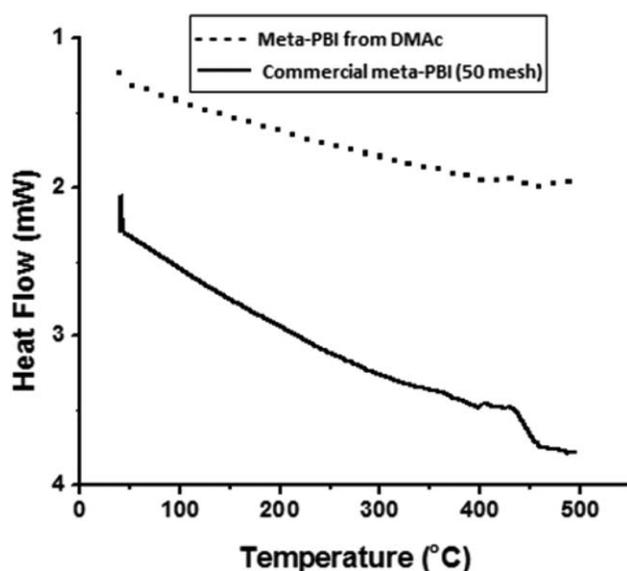


FIGURE 8 Modulated DSC analysis for the solution polymerized m-PBI and commercially produced m-PBI.

ture to 500 °C with 50 mL/min nitrogen flow and a heating rate of 5 °C/min. The glass transition temperature (T_g) of the solution polymerized m-PBI was determined to be ~430 °C as indicated by a baseline shift and compared to the commercially produced m-PBI as shown in Figure 8. The T_g s of these meta PBIs found using DSC were similar to the previously reported meta-PBI T_g of 427 °C.³⁴ PBI type polymers are well known for their high thermal stabilities resulting from their fully aromatic structure and polymer chain rigidities.^{35–37} TGA was conducted from ambient temperature to 800 °C at a heating rate of 10 °C/min for both solution polymerized and commercially produced m-PBI (Figure 9). Both materials exhibited more than 90% weight retention at 600 °C, which is typical behavior of aromatic PBIs.³⁸ The commercially produced m-PBI sample showed water loss between 100 and 200 °C, as expected since PBI is very hygroscopic and has been shown to absorb and retain up to 15% (by weight) of water even during short handling times.³⁹ Although, the solution polymerized m-PBI was washed with water and dried under vacuum before testing, the product showed gradual weight loss between 200 and 500 °C which was attributed to residual DMAc within the polymer sample and to the degradation of end groups.

CONCLUSIONS

Model compound studies were conducted with monofunctional reagents and monitored via GC/MS to determine chemical functionalities that would be suitable for benzimidazole formation in DMAc. Studies on the reaction of phenyl ester, carboxylic acid, aldehyde, and a bisulfite adduct of the aldehyde functionalities with *o*-phenylenediamine in DMAc showed that only the bisulfite adduct was capable of producing a high yield of the desired 2-phenylbenzimidazole.

Polymerizations were conducted with all difunctional counterparts and confirmed that the reaction of the bisulfite adduct of isophthalaldehyde with TAB was the only pair of

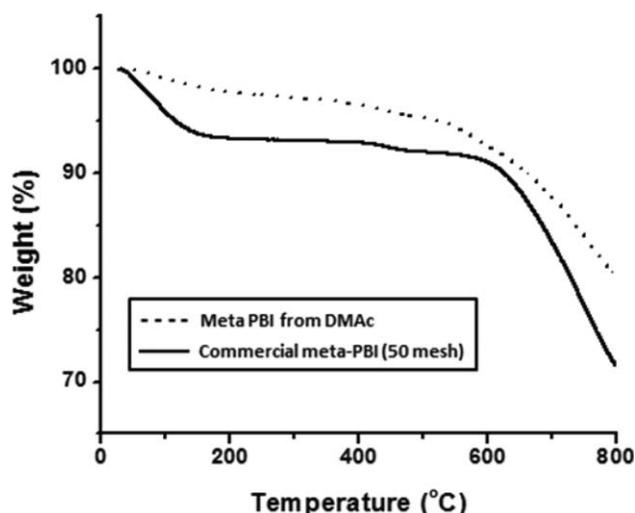


FIGURE 9 TGA analysis of the solution polymerized m-PBI and commercially produced m-PBI.

monomers that showed successful conversion to m-PBI. Monomer scale-up was conducted for the IBA to allow for further polymerization studies. Detailed polymerization experiments with IBA and TAB were conducted in DMAc for concentrations ranging from 2 to 26 wt % polymer which indicated that monomer produced under modified, more dilute conditions was important for obtaining high IV polymers. These studies established polymerization conditions that produced high IV polymers (up to 1.3 dL g⁻¹) at high polymer concentrations in the range suitable for the direct processing of solutions into films, coatings, and fibers. Additional mechanistic studies on the benzimidazole ring formation showed that *in situ* generation of sulfur dioxide (to ensure complete oxidative dehydrogenation) led to routine and consistent syntheses of high IV polymers.

The chemical structure of the solution polymerized m-PBI was confirmed via ¹H NMR and FTIR analyses. DSC showed the *T*_g of both the solution polymerization product and the commercially produced m-PBI to be approximately 430 °C. The thermal stability of the solution polymerized m-PBI was also comparable to that of the commercially produced m-PBI. Overall, a new, convenient, commercially viable solution polymerization method was developed for the synthesis of m-PBI in DMAc solutions. This new polymerization method is reported as a viable means for both laboratory scale and large scale production of high-molecular weight m-PBI and is applicable to the synthesis of a variety of PBI derivatives.

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