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Synthesis and characterization of Poly (p-phenylenediamine) and its derivatives using aluminium triflate as a co-catalyst

Ismael Amer¹* and Sonja Brandt¹

Abstract: A series of p-phenylenediamine (pPD), 2,5−dimethyl-p-phenylenediamine (dMe-pPD) and 2,3,5,6−tetramethyl-p-phenylenediamine (tMe-pPD) polymers were successfully synthesized in different polymerization conditions, using ammonium persulfate as an oxidant and aluminium triflate (Al(OTf)₃) as a co-catalyst. The poly(p-phenylenediamine) (P(pPD)), poly(2,5−dimethyl-p-phenylenediamine) (P(dMe-pPD)) and poly(2,3,5,6−tetramethyl-p-phenylenediamine) (P(tMe-pPD)) polymers obtained were characterized by UV−vis, FT-IR, ¹H and ¹³C NMR, WAXD, DSC and TGA. The addition of Al(OTf)₃ to the polymerization reaction improved the polymerization yield of some polymers. In most solvents, significantly improved solubility of P(dMe-pPD) and P(Me-pPD) polymers was obtained compared to the P(pPD) polymers as a result of methyl side groups effects. The yield, structure and solubility of the polymers were shown to depend to a large extent on the polymerization conditions. The polymers displayed crystallization and melting transitions on DSC. The P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers were found to have good thermal stability, as indicated by TGA results, and to decompose above 400°C in nitrogen.

Subjects: Materials Chemistry; Materials Science; Polymers & Plastics; Polymer Science; Polymer Technology

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Sonja Brandt completed MSc in Biochemistry in 2012 from Stellenbosch University and subsequently pursued a degree in medicine, which was obtained in 2017. She is interested in the synthesis and characterization of polymers.

PUBLIC INTEREST STATEMENT

In the last few decades, poly(p-phenylenediamine) (P(pPD)) as a typical conductive polymer has attracted a large attention from researchers because of its varied structure, high environmental and thermal stability, adsorption of heavy metal ions, and attractive application in technology. Unfortunately, the P(pPD) homopolymers are slightly soluble in most of the common organic solvents and have poor mechanical properties which cause difficulties in the determination of the molecular structures and restrict them from widely practical use. Therefore, this study focused on improving the solubility, maintaining the original functionalities and providing novel interesting performances of P(pPD) polymers. This was done by introducing longer side-substituents in the polymer chain which greatly improved the solubility, fusibility, processability, environmental stability and optical properties without substantially losing conductivity of the P(pPD) polymer materials.
1. Introduction
The distinctive multifunctionality of aromatic polyphenylenediamine polymers, which include strong electroactivity, variable conductivity, good optical and magnetic activity, colourful electrochromism, significant performance in electronic, electrical, thermal, adsorption of heavy metal ions, and high environmental and thermal stability, has resulted in significant interest from researchers (Boehme, Mudigonda, & Ferraris, 2001; Huang, Lu, & Li, 2012; Li, Huang, Duan, & Yang, 2002; Li, Li, & Huang, 2007; Li, Liu, & Huang, 2005; Liu, Huang, & Li, 2007; Lu, Smela, Adams, Zuccarello, & Mattes, 2004; Torres-Gomez, Tejada-Rosales, & Gomez-Romero, 2001; Virji, Kaner, & Weiller, 2005). Polyaniilne (PAN) is one of the conducting polymers which have garnered the most attention as a result of its easy preparation and outstanding stability in comparison to other similar conducting polymers (Li et al., 2002). However, some research groups have attempted to make polymers with enhanced thermal stability, electrical conduction and processing properties compared to PAN (Li et al., 2002). Novel conjugated polymers have been made using phenylenediamines (para, ortho and meta derivateis) (Li et al., 2003, 2002; Zane, Raffaele, Curulli, Appetecchi, & Passerini, 2007; Zhou et al., 2004). Ladder and ladder-like structures with highly aromatic nitrogenous heterocycles and remarkably high thermostability have reportedly been obtained when potassium, sodium or ammonium persulfate was used as oxidants in the chemical oxidative polymerization of polyphenylenediamines ( Cataldo, 1996; Huang, Li, & Yang, 2001; Li, Huang, Chen, Jin, & Yang, 2001; Sestrem, Ferreir, Londers, Temperini, & Do Nascimento, 2009, 2010). The nitrogenous heterocyclic ladder structure is thought to greatly assist in the synthesis of advanced membranes for air separation (Li & Huang, 1997). The first description of p-phenylenediamine (pPD) in chemical oxidative polymerization was as an additive of aniline (AN) polymerization with the aim of enhancing the rate and yield of polymerization (Li et al., 2002). Earlier Chan, Rawat, and co-workers had reported on the use of persulfate as the oxidant in chemical oxidative polymerization of various aromatic diamines from 0 °C to room temperature with in acidic aqueous solution (Rawat, Kansara, & Rama, 1991). The design of functional materials has resulted from advances in techniques involving the synthesis and characterization of the structure and properties of phenylenediamine polymers (Huang, Peng, & Li, 2006; Li et al., 2002; Li, Ma, Sun, & Huang, 2009; Li, Wang, & Huang, 2007). However, the poor mechanical properties and only slightly soluble nature of phenylenediamine homopolymers in most of the common organic solvents have limited their practical use and made determination of the molecular structures difficult ( Cataldo, 1996; Grigoros & Antonoaia, 2005; Li, Huang, & Yang, 2001). Improvements in the processability of the P(pPD) polymer, by enhancing the fusibility and solubility, have thus been challenging.

Various aromatic amines, including o-phenetidine, xylidine and sulfonic monomers have been utilized in oxidative copolymerization as co-monomers in order to enhance the solubility of P(pPD) polymers, but maintain the original functionalities and partial phenazine structure, and enable new interesting performances (Amer et al., 2016; Amer, 2017; Amer, Mokrani, Jewell, Young, & Vosloo, 2015; Li et al., 2001, 2002). However, although an in increase the solubility is obtained using copolymerization, the polymerization yield is still low and solubility is less than satisfactory. Luckily, it is known that steric hindrance in the polymer chain may cause greater distortions in polymer chains with longer side-substituents, likely increasing the solubility through reduced hydrogen bonding interactions between the polymer chains and reduced inter-chain van der Waals forces. Solubility is also enhanced by the display of more solvation sites on side groups in the polymer chains (Li et al., 2003).

The role of metal triflates as Lewis acids in various reactions has garnered much attention (Chaminade, Chiba, Narasaka, & Dunach, 2008; Gohain, Marais, & Bezuidenhoudt, 2012a; Williams & Lawton, 2008; Williams, Shaw, Green, & Holzapfel, 2008; Williams, Simelane, Lawton, & Kinfe, 2010). Since water-tolerant metal triflates can easily be recycled, they are of particular interest from both an economic and environmental perspective (Gohain, Marais, & Bezuidenhoudt, 2012b). The
reusable catalyst, aluminium triflate (Al(OTf)₃), is stable in aqueous medium and effectively tolerates water (Bradley, Williams, & Lawton, 2006). Despite being more affordable, Al(OTf)₃ has not been extensively explored, compared to other metal triflates, such as the rare earth metal triflates (Bradley et al., 2006; Gohain et al., 2012b). Our study made use of Al(OTf)₃ as co-catalyst, instead of protic acids which are typically used, to polymerize various phenylenediamines (Amer & Young, 2013; Amer, Young, & Vosloo, 2013, 2014). The use of Al(OTf)₃ affected the molecular weight of phenylenediamine polymers differently, compared to polymerization reactions utilizing protic acids, and resulted in a significant improvement in the polymerization yield (Amer & Young, 2013).

This study describes the synthesis of soluble substituted P(pPD) polymers by chemical oxidative polymerization. The manner in which oxidants, acidic medium polymerization, temperature and time affect the solubility, structure, thermal properties and polymerization yield of the P(pPD) polymers were systematically investigated.

2. Experimental

2.1. Materials

The reagents, solvents, Al(OTf)₃, pPD, 2,3,5,6-tetramethyl-p-phenylenediamine (tMe-pPD) and 2,5-dimethyl-p-phenylenediamine (dMe-pPD) were used as obtained from Fluka (Johannesburg, South Africa) or Aldrich.

2.2. General polymerization procedure

Oxidative polymerization was performed according to the methods described in Ref [14]. Typically, polymers were prepared in the following manner: Al(OTf)₃ (1.0 g) and/or ammonium persulfate ((NH₄)₂S₂O₈) (4.0 g) was added to 20 mL of water in a flask in preparation of the oxidant solution. Hydrochloric acid (150 mL) or water in a separate 500-mL round-bottomed flask was placed in an oil bath at certain temperatures (Table 1). Phenylenediamine monomer (1.7 g) (pPD, dMe-pPD or tMe-pPD) was added and the mixture was magnetically stirred. Oxidant solution was added in a dropwise manner, at a rate of one drop every 3 s, into the monomer solution over a 30 min period. Since the polymerization reaction is highly exothermic, dropwise addition of oxidant solution allowed the reaction to be well controlled, while simultaneously producing high molecular weight polymers with a particular narrow molecular weight distribution. The colour of the reaction solution changed, after the first few drops of oxidant were added, to the colour of the polymer powders shown in Table 1. Vigorous stirring of the reaction solution for at least 24 h followed. After filtration of the reaction mixture, distilled water was used to wash the filtrate several times in order to remove excess oligomers and oxidant. The resulting powder products were then dried for 1 week in ambient air.

Table 1. Chemical oxidative polymerization conditions for the polymerization of pPD and derivatives using (NH₄)₂S₂O₈ as oxidant for 24 h

<table>
<thead>
<tr>
<th>Run</th>
<th>Polymer</th>
<th>Powder colour</th>
<th>Co-catalyst/solvent</th>
<th>T° (°C)</th>
<th>Yield (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(pPD)</td>
<td>Dark brown</td>
<td>H₂O</td>
<td>100</td>
<td>93.0</td>
</tr>
<tr>
<td>2</td>
<td>P(pPD)</td>
<td>Black</td>
<td>HCl/H₂O</td>
<td>30</td>
<td>55.0</td>
</tr>
<tr>
<td>3</td>
<td>P(pPD)</td>
<td>Black</td>
<td>Al(OTf)₃/H₂O</td>
<td>100</td>
<td>95.0</td>
</tr>
<tr>
<td>4</td>
<td>P(dMe-pPD)</td>
<td>Dark brown</td>
<td>H₂O</td>
<td>100</td>
<td>34.0</td>
</tr>
<tr>
<td>5</td>
<td>P(dMe-pPD)</td>
<td>Yellow</td>
<td>HCl/H₂O</td>
<td>30</td>
<td>47.0</td>
</tr>
<tr>
<td>6</td>
<td>P(dMe-pPD)</td>
<td>Brown</td>
<td>Al(OTf)₃/H₂O</td>
<td>100</td>
<td>30.0</td>
</tr>
<tr>
<td>7</td>
<td>P(tMe-pPD)</td>
<td>Light brown</td>
<td>H₂O</td>
<td>100</td>
<td>17.0</td>
</tr>
<tr>
<td>8</td>
<td>P(tMe-pPD)</td>
<td>Yellow</td>
<td>HCl/H₂O</td>
<td>30</td>
<td>61.0</td>
</tr>
<tr>
<td>9</td>
<td>P(tMe-pPD)</td>
<td>Brown</td>
<td>Al(OTf)₃/H₂O</td>
<td>100</td>
<td>23.0</td>
</tr>
</tbody>
</table>

° Reaction temperature.
2.3. Equipment

The molecular structures of aromatic diamine polymers were characterized using Fourier-transform infrared spectroscopy (FT-IR). A Bruker VERTEX 80 FT-IR spectrometer recorded the infrared spectra of the polymer samples at room temperature using ATR. Results were based on an average of 40 scans, in which a resolution of 2 cm$^{-1}$ was used to analyse samples between 500 and 4000 cm$^{-1}$.

A Bruker Avance 600MHz NMR spectrometer was used to record $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy ($^1$H and $^{13}$C-NMR) at room temperature. Deuterated dimethyl sulfoxide (DMSO-d$_6$) was used to dissolve samples (20–30 mg) for NMR analyses.

A Bruker AXS D8 Advance diffractometer was used to perform wide-angle X-ray diffraction (WAXD) analyses with filtered CuK$_\alpha$ radiation at room temperature. A sampling width of 0.02° was used to scan all samples at 20 angles, where 20 is the diffraction angle, from 0–80°.

A TA Instruments Q100 DSC was used for Differential Scanning Calorimetry (DSC) analyses. Crimped aluminium pans were used to conduct measurements under a nitrogen atmosphere, at a 50 mL/min purge gas flow rate. Each sample was subjected to three cycles. The samples were first heated at a rate of 10°C/min from 25 to 450°C. Cooling of samples from 450 to 25°C followed. The samples were then heated to 450°C, at rate of 10°C/min, for a second time.

A TA Instruments TGA Q100 was used to perform thermogravimetric analyses (TGA) in a nitrogen atmosphere at a resolution of 0.1 mg. Each sample (5–10 mg) was heated at a rate of 10°C/min from 20–800°C.

3. Results and discussion

The structures of $p$PD, dMe-$p$PD and tMe-$p$PD monomers that were polymerized in this study are shown in Figure 1. However, the synthesis conditions, yield and colours of the P($p$PD), poly(2,5-dimethyl-$p$-phenylenediamine) (P(dMe-$p$PD)) and poly(2,3,5,6-tetramethyl-$p$-phenylenediamine) (P(tMe-$p$PD)) polymers produced in our experiments are summarized in Table 1.

3.1. Polymerization yield

The oxidative polymerization yield (grams of oxidation polymers per grams of phenylenediamine monomers) obtained was generally higher for P($p$PD) polymers than for P(dMe-$p$PD) and P(tMe-$p$PD) polymers (Table 1). Steric hindrance of the methyl groups on the aromatic rings likely caused the lower yields of P(dMe-$p$PD) and P(tMe-$p$PD) polymers compared to P($p$PD) polymers (Li et al., 2003).
The use of water as a solvent and ammonium persulfate as an oxidant (runs 4 and 7 in Table 1) resulted in lower polymerization yields of P(dMe-pPD) and P(tMe-pPD) polymers being obtained, compared to the yields of P(dMe-pPD) and P(tMe-pPD) polymers obtained when aqueous HCl solution (runs 5 and 8 Table 1) was used. This contrasts findings in P(pPD) polymers, in which a higher polymerization yield was obtained with water as solvent than with aqueous HCl solution (Amer & Young, 2013). Depending on the experimental conditions, different coloured powdered precipitates were obtained for P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers (Table 1). The use of ammonium persulfate and Al(OTf)$_3$ as oxidants in water-enabled preparation of pPD, dMe-pPD and tMe-pPD polymers (Table 1).

Unfortunately, the yields of P(dMe-pPD) and P(tMe-pPD) polymers were low compared to P(pPD) polymers obtained in this study and to poly(o-phenylenediamine), poly(m-phenylenediamine), poly(4,4′-diaminodiphenylmethane) and poly(benzidine) polymers obtained in our previous studies (Amer & Young, 2013; Amer et al., 2013, 2014). The low yield of P(dMe-pPD) and P(tMe-pPD) polymers probably resulted from steric hindrance of the methyl groups as explained above. Interestingly, however, P(pPD) polymer prepared using a mixture of Al(OTf)$_3$ and ammonium persulfate as oxidant in water showed the highest yield (run 3 in Table 1). The fact that no monomer salts, which lower the polymerization yield, are formed by Al(OTf)$_3$, as is the case with the application of protic acids, likely account for this finding (Amer & Young, 2013; Amer et al., 2013, 2014).

### 3.2. Solubility of polymers

100 mg of polymer sample was added to 10 mL of solvent and dispersed thoroughly in order to measure solubility. Following several hours of continuous stirring at room temperature, quantitative characterization of the solubility was performed for all solvents. The effect that the conditions of polymerization had on the solubility of P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers in different solvents are displayed in Table 2. The P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers were generally found to be soluble in Sulfuric acid ($H_2SO_4$), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), Dimethylformamide (DMF) solvents, as illustrated in Table 2, which are also good solvents of PAN polymers (Huang, Li, & Duan, 2005; Li et al., 2003, 2002). P(pPD) polymers, however, were only partially soluble in chloroform ($CHCl_3$) and tetrahydrofuran (THF) solvents, however, while P(dMe-pPD) and P(tMe-pPD) polymers were largely soluble in $CHCl_3$ and THF solvents (Table 2). This corresponds to findings for P(pPD) homopolymers by Li et al. (Li et al., 2001, 2002).

Table 2 clearly illustrates that the introduction of side-substituents in the polymer chain enhanced solubility of P(pPD) polymers. The solubility is enhanced due to side group steric hindrance, which reduces the inter-chain van der Waals forces, allowing greater polymer chain distortions. Furthermore, the substituents could serve as internal solubilizers and plasticizers of the polymers (Li et al., 2003, 2002). The molecular structure rather than the molecular weight largely determines the solubility of the polymers, as was put forward by Tsuchida et al., provided that the

| Run | Polymer  | NMP | DMSO | DMF | $H_2SO_4$ | THF | $CHCl_3$
|-----|----------|-----|------|-----|----------|-----|-------
| 1   | P(pPD)   | 100 | 92   | 83  | 100      | 38  | 36    |
| 2   | P(pPD)   | 100 | 91   | 87  | 100      | 31  | 29    |
| 3   | P(pPD)   | 95  | 92   | 90  | 100      | 47  | 33    |
| 4   | P(dMe-pPD) | 100 | 100  | 100 | 100      | 81  | 74    |
| 5   | P(dMe-pPD) | 100 | 100  | 100 | 100      | 83  | 77    |
| 6   | P(dMe-pPD) | 100 | 100  | 100 | 100      | 84  | 82    |
| 7   | P(tMe-pPD) | 100 | 100  | 100 | 100      | 90  | 90    |
| 8   | P(tMe-pPD) | 100 | 100  | 100 | 100      | 93  | 89    |
| 9   | P(tMe-pPD) | 100 | 100  | 100 | 100      | 91  | 83    |
molecular weight is not too low (Tsuchida, Kaneko, & Kurimura, 1970). Polymer solubility, however, was virtually independent of the polymer synthesis reaction time (Li et al., 2002).

3.3. Molecular structure of polymers

3.3.1. FT-IR spectroscopy

FT-IR spectra of P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers prepared in different solvents are shown in Figure 2. Two or three broad bands at 3400–3200 and 3150–3100 cm$^{-1}$ were generally displayed on the FT-IR spectra of all polymers, signifying N–H stretching vibrations of —NH and —NH$_2$ groups, respectively (Cataldo, 1996; Li et al., 2001, 2002; Sestrem et al., 2010). The weak broad peak centred at 2990–2920 cm$^{-1}$ presented in P(dMe-pPD) and P(tMe-pPD) polymers spectra (Figure 2(c), (d), (e) and (f)), are possibly due to aliphatic C–H stretching vibrations of the methyl groups (Huang et al., 2005; Li, Duan, Huang, & Yang, 2001; Li et al., 2003). Strong peaks were observed in the region between 1610 and 1690 cm$^{-1}$, as well as between 1490 and 1550 cm$^{-1}$, which were attributed aromatic ring stretching. Quinonoid rings are responsible for the peak at 1690–1610 cm$^{-1}$, while benzenoid rings caused the peak at 1550–1490 cm$^{-1}$ (Huang et al., 2001; Li et al., 2001). Note that the intensity of the peaks attributed to the quinonoid rings at 1690–1610 cm$^{-1}$ increased significantly in the case of P(tMe-pPD) polymers (Figure 2(e) and (f)) compared to P(pPD) and P(dMe-pPD) polymers (Figure 2(a), (b), (c) and (d)), suggesting that the content of quinonoid and benzenoid units in the polymers are not similar, resulting in different polymer ladder structures (Huang et al., 2006; Li et al., 2002).

C–N stretching vibration in quinonoid imine units likely accounts for the two medium peaks at 1400–1370 and 1100–1040 cm$^{-1}$, whereas C–N stretching in the benzenoid unit is responsible for the peak centred at 1240–1220 cm$^{-1}$ (Li et al., 2001, 2002). The C–H of 1,2,4,5-tetrasubstituted benzene nuclei of phenazine units out-of-plane bending vibrations probably account for the peaks at 870–820 and 580–570 cm$^{-1}$. The peaks at 870–820 and 580–570 cm$^{-1}$ became weaker and broader in the P(tMe-pPD) polymers (Figure 2(c) and (d)), and completely disappeared in the P(tMe-pPD) polymers (Figure 2(e) and (f)), because there were not any C–H substitutions on the benzene ring of P(tMe-pPD) polymers. The differences in the final polymer structures as indicated by the FT-IR spectra of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers was also found in a study by Li X-G (Li et al., 2002). The FT-IR spectra of P(pPD), P(dMe-pPD) and

Figure 2. FT-IR spectra of different polymers prepared by chemical oxidative polymerization using (NH$_4$)$_2$S$_2$O$_8$ as oxidant (a) P(pPD) prepared in water, (b) P(pPD) prepared in Al(OTf)$_3$ solution, (c) P(dMe-pPD) prepared in water, (d) P(dMe-pPD) prepared in Al(OTf)$_3$ solution, (e) P(tMe-pPD) prepared in water and (f) P(tMe-pPD) prepared in Al(OTf)$_3$ solution.
P(tMe-pPD) polymers indicate that these polymers have different contents of benzenoid and quinonoid units in their backbone structures (Li et al., 2001, 2002).

3.3.2. NMR spectroscopy

3.3.2.1. $^1$H NMR of the polymers. The $^1$H NMR spectra of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers in deuterated DMSO prepared in hydrochloric acid solution and water, are shown in Figure 3(a), (b) and (c), respectively. Some differences were observed in the $^1$H NMR spectra of respective polymers. Four major peaks were displayed on the $^1$H NMR spectrum of the P(pPD) polymer (Figure 3(A)), which correlated to the four types of protons on the polymer chains. The $^1$H NMR spectrum of the P(pPD) polymer displayed the strongest doublet peak at 5.6 ppm due to $^2$NH protons; four doublets centred at 6.6–7.1 ppm due to $^2$NH protons; and broad weak peaks at 7.3, 7.5–7.8 and 9.1–9.2 ppm due to the protons on 1,2,4,5-tetrasubstituted benzene rings (Li et al., 2001, 2002).

Furthermore, the $^1$H NMR spectra of P(dMe-pPD) polymer (Figure 3(b)) and P(tMe-pPD) polymer (Figure 3(c)) exhibited weak peaks at 6.0 and 7.5 ppm, respectively, which correspond to $^2$NH protons. In addition, the $^1$H NMR spectra of P(dMe-pPD) and P(tMe-pPD) polymers showed weak peaks centred at 6.4–7.2 ppm due to $^2$NH protons. Note that $^1$H NMR spectrum of P(tMe-pPD) did not show any peaks due to the protons on 1,2,4,5-tetrasubstituted benzene rings, while $^1$H NMR spectrum of P(dMe-pPD) showed very weak peaks at 7.4, 7.9 and 9.1 ppm due to the protons on 1,2,4,5-tetrasubstituted benzene rings. The peaks located in a range from 1.0 to 2.2 ppm are the result of methyl protons on the benzenoid units of P(dMe-pPD) and P(tMe-pPD) polymers (Figure 3(b) and (c)) (Huang et al., 2005; Li et al., 2001, 2002).

3.3.2.2. $^{13}$C NMR of the polymers. The $^{13}$C NMR spectra of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers are displayed in Figure 4(a), (b) and (c), respectively. The strongest peak on the $^{13}$C NMR spectrum of the P(pPD) polymer (Figure 4(a)), observed at 116 ppm, is the result of the hydrogen-bonded carbon (C–H) in the benzenoid unit. The intensity of this peak decreased in the P(dMe-pPD) polymer (Figure 4(b)), and completely disappeared in the P(tMe-pPD) polymer (Figure 4(c)), because there were
not any C–H substitutions on the benzene ring of the P(tMe-pPD) polymer. Nitrogen-bonded carbon (C–NH) in the benzenoid units of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers accounts for the peaks at 125 and 140 ppm in the $^{13}C$ NMR spectra (Li et al., 2001, 2002; Sapurina et al., 2000). C = N in the quinonoid unit is probably responsible for the peak at 150 ppm (Figure 4(a)), while methyl groups on the benzenoid units likely accounts for other peaks centred at 14–18 ppm (Figure 4(b) and (c)) (Sapurina et al., 2000).

3.3.3. WAXD of polymers
WAXD of P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers are shown in Figure 5. Clear differences were visible between the XRD patterns of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers. P(pPD) polymers (Figure 5(a) and (b)) displayed the strongest diffraction intensity at $2\theta \leq 6^\circ$, which could be related to the presence of a few large crystalline structure in the polymer (Huang et al., 2001; Li...
et al., 2001, 2001). P(dMe-pPD) and P(tMe-pPD) polymers (Figure 5(c), (d), (e) and (f)) did not exhibit any diffraction peaks at \(2\theta \leq 6^\circ\).

Furthermore, P(dMe-pPD) and P(tMe-pPD) polymers showed the strongest peaks positioned at \(2\theta = 12\text{–}13^\circ\), which are attributed to diffraction by the small content of the crystalline structures as well as to the amorphous nature of the polymers (Li et al., 2002). P(pPD) and P(dMe-pPD) polymers showed additional strong diffraction peaks at \(2\theta = 24\text{–}26^\circ\) as well as a medium broad peak at \(2\theta = 17^\circ\) in the case of P(pPD) polymer prepared in Al(OTf)₃ solution (Figure 5(b)), which may be attributed to the amorphous structures of the P(pPD) and P(dMe-pPD) polymers (Li et al., 2002). Therefore, it can be concluded that the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers have different crystalline structures, which could be as a result from relatively different macromolecular chain structures, as shown in Figure 5, which was verified by the FT-IR and NMR spectra (Amer & Young, 2013; Li et al., 2001, 2001, 2002).

3.3.4. UV–vis spectra of polymers

The UV–vis spectra of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers are shown in Figure 6(a), (b) and (c), respectively. The UV–vis spectra of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers in Figure 6 exhibited two strong absorption bands centred at 240–290 and 400–470 nm.

The absorption bands between 240 and 290 nm were attributed to \(\pi\text{—}\pi^*\) transition between quinonoid and benzenoid rings (Ayad, Rehab, El-Hallag, & Amer, 2007; Li, Duan, Huang, Yang, & Zhao, 2003; Yang & Liao, 2012). The absorption bands located in the range 400–470 nm may be the result of electronic transition of quinononeimine (quinonoid) structures in the polymer chains (Li, Li, Peng, Qin, & Chen, 2013). Similar electronic spectra have been detected for pernigraniline, which is a fully oxidized form of PAN and contains a quinononeimine structure (Li et al., 2003; Rani, Ramachandran, & Kabilan, 2010). However, small absorption bands at 900 nm in P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers were observed, suggesting the presence of a small amount of highly conjugated and oxidized structures in the polymers as was reported by Li et al. (Li et al., 2003, 2002). The different quinonoid contents and oxidative degrees of the polymer structures are thought to be responsible for the differences in the wavelength and intensity ratio of the absorption bands of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers in Figure 6 (Huang et al., 2005).

3.4. Electrical conductivity

A UT 70A multi-metre was used to measure the bulk electrical conductivity of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers at ambient temperature using a two-disc method. The conductivity...
of most P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers were less than \(1 \times 10^{-7}\) S/cm. Unfortunately, estimation of the effect of the methyl side groups on the ability of P(dMe-pPD) and P(tMe-pPD) polymers to conduct electricity presented some difficulty. Bulky —NH\(_2\) substituents which cause twisting of the main-chain, reducing its coplanarity and presenting a barrier to inter-chain jumping and transfer of electrons, which shortens the length of conjugation, likely accounts for the low electrical conductivity of phenylenediamine polymers (Huang et al., 2012; Li et al., 2002, 2009, 2007; Virji et al., 2005). The presence of bulky substituents can unfavourably affect the inter-chain electrical transport, leading to poor electrical conductivity as was reported by Goyette et al. (Goyette & Leclerc, 1995). However, electrical conductivity may be enhanced by copolymerization of phenylenediamines with other co-monomers with different functional groups (Huang et al., 2012; Li et al., 2002, 2009, 2007; Virji et al., 2005).

3.5. Thermal analysis of polymers

3.5.1. DSC of the polymers

The thermal data and DSC scans of P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers are shown in Table 3 and Figure 7(a), (b) and (c), respectively. Table 3 and Figure 7(a), (b) and (c) demonstrate that all the polymers displayed glass transition temperatures (\(T_g\)) in the range of 264–271°C. The midpoint of the change in slope of the DSC cooling curve baseline (as shown in Figure 7(A)) served as the glass transition temperature. The high rigidity of the polymer chains possibly account for the high glass transition temperatures of P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers (Hsiao & Chen, 2002). Crystallization and melting temperatures ranging from 422–428°C and 424–431°C, respectively, were observed for P(dMe-pPD) and P(tMe-pPD) polymers, but the DSC heating and cooling profiles did not show any crystallization and melting transitions of P(pPD) polymers.

Generally, P(dMe-pPD) polymers exhibited slightly higher crystallization and melting heats than P(tMe-pPD) polymers, which could be due to the greater distortions of the polymer chains in the P(tMe-pPD) polymers, as a result of the higher content of methyl substituents on the P(tMe-pPD) chains. Thus, P(dMe-pPD) polymers can be considered to have higher crystalline structures than P(tMe-pPD) polymers. The good thermal stability (no decomposition up to 400°C) displayed by (pPD), P(dMe-pPD) and P(tMe-pPD) polymers on DSC translates into easy processing and extreme usefulness of these polymers in applications by the engineering industry (Songa, Meng, Wang, Sun, & Tan, 2002).

3.5.2. TGA of the polymers

The TGA curves of polymer powders in flowing nitrogen of P(pPD), P(dMe-pPD) and P(tMe-pPD) are presented in Figure 8(a), (b) and (c), respectively. Two weight loss stages were observed for all the polymers (except P(dMe-pPD) polymer prepared in Al(OTf)\(_3\) solution, which exhibited three weight loss stages as illustrated in Figure 8(b)). Evaporating water molecules trapped in the polymer chains is responsible for the initial weight loss of 4–9% at 100–120°C, while thermal degradation of the polymer chains likely accounts for the second weight loss, which starts at about 250–340°C. Different thermal behaviours were observed between the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers due to the differences in molecular structures. The P(pPD) polymers exhibited better thermal stability than the P(dMe-pPD) and P(tMe-pPD) polymers (Figure 8(a), (b) and (c)). The initial

<table>
<thead>
<tr>
<th>Table 3. Polymer powder thermal data obtained using DSC</th>
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<tbody>
<tr>
<td><strong>Polymer</strong></td>
</tr>
<tr>
<td>P(pPD)</td>
</tr>
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</table>
decomposition temperature ($T_0$) and the temperature for 10% weight loss ($T_{10}$) ranged from 180–250°C and 280–320°C, respectively. The polymers displayed of char yields of about 22–57% at 600°C. The $P(p\text{PD}), P(d\text{Me-}p\text{PD})$ and $P(t\text{Me-}p\text{PD})$ polymer TGA results are similar to those obtained for PAN, demonstrating the possible versatility of $P(p\text{PD}), P(d\text{Me-}p\text{PD})$ and $P(t\text{Me-}p\text{PD})$ polymers (Moravkova, Trchova, Tomsik, Zhigunov, & Stejskal, 2013; Trchova, Konyushenko, Stejskal, Kovanova, & Marjanovic, 2009).

TGA results of the $P(p\text{PD}), P(d\text{Me-}p\text{PD})$ and $P(t\text{Me-}p\text{PD})$ polymers are summarized in Table 4. The good thermal stability and heat resistance displayed by the $P(p\text{PD}), P(d\text{Me-}p\text{PD})$ and $P(t\text{Me-}p\text{PD})$ polymers on TGA are the result of their rigid chain structure. The engineering industry could therefore benefit from the use of $P(p\text{PD}), P(d\text{Me-}p\text{PD})$ and $P(t\text{Me-}p\text{PD})$ polymers.
in applications such as in structural components of advanced high speed aircraft, in the electrical application where higher temperature insulation is required, in space vehicles and in weapon systems (Trchova et al., 2009).
Table 4. Polymer powder thermal data obtained using TGA

<table>
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<tr>
<th>Polymer</th>
<th>T₀  (°C)</th>
<th>T₁₀ (°C)</th>
<th>Tmax,°C (°C)</th>
<th>Char yield at 600°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(pPD)</td>
<td>190–210</td>
<td>280–300</td>
<td>480–540</td>
<td>22–51</td>
</tr>
</tbody>
</table>

° Maximum decomposition temperature.

4. Conclusion
This study successfully prepared P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers with a chemical oxidative polymerization technique which utilized a mixture of Al(OTf)₃ and (NH₄)₂SO₄ as oxidant in water, obtaining a good polymerization yield. The solubility of P(dMe-pPD) and P(tMe-pPD) polymers improved, compared to P(pPD) polymers, despite a slightly lower yield, illustrating that it is possible to improve solubility of the P(pPD) by introducing side substituents on the P(pPD) polymer’s benzenoid rings. Relatively small differences were observed between the FT-IR, UV-vis, ¹H and ¹³C NMR spectra results of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers, which indicated that both quinonoid and benzenoid units are contained in the main structures of these polymers. Most of the P(pPD), P(dMe-pPD) and P(tMe-pPD) polymers were found to be amorphous by WAXD, but some crystalline structures were revealed in P(dMe-pPD) and P(tMe-pPD) polymer DSC results. No crystalline structures were found in P(pPD) polymers, however. This likely resulted from the methyl groups positioned on the benzenoid rings of P(dMe-pPD) and P(tMe-pPD) polymers, which limit the formation of ladder structures and lead to a higher content of linear structured polymers. Although the polymers displayed different thermal behaviours due to differences in their molecular structures, all the polymers were found to exhibit good thermal stability.

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Songa, Y.-J., Meng, S.-H., Wang, F.-D., Sun, C.-X., & Tan, Z.-C. (2002). Thermochemical study on the properties of

Statement of Novelty
The manuscript entitled: Synthesis and Characterization of Poly(p-phenylenediamine) and its Derivatives Using Aluminium Triflate as a Co-catalyst. The author is Ismael Amer who has read and approved the article. Ismael Amer will be responsible for correspondence.

Amer and Brandt did the experimental work and wrote the paper. This article describes the polymerization of different aromatic diamines using ammonium persulfate ((NH4)2S2O8) as a catalyst and aluminium triflate Al(OTf)3 as a co-catalyst. Al(OTf)3 was used for the first time for the polymerization of p-phenylenediamine derivatives. I have not only determined the structures of these polymers, but also demonstrated that they are unusually stable at high temperatures, which make these polymers suitable materials for high temperature applications. I have also showed that the solubility and the fusibility of these polymers were improved by introducing side-substituents in the polymer chains. I declare that this is my own work. I have chosen to submit the article as an original article to your Journal because of its distinguished publishing record and its high-quality polymer science journal that covers the characterization, and processing of advanced polymeric materials.

Ismael Amer 09–03–2018