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Effect of Heating Methods and Immersion Times on the Physicochemical Properties of Polyimide Based on 3,3′,4,4′-Benzophenone Tetracarboxylic Dianhydride and 4,4′-Methylene Diphenyl Diisocyanate (BTDA-MDI)

(Kesan Kaedah Pemanasan dan Masa Rendaman terhadap Sifat Fisikokimia Polimida Berdasarkan 3,3′,4,4′-Benzofenon Tetrakarboksilat Dianhidrida dan 4,4′-Metilena Difenil Diisosianat (BTDA-MDI))

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ABSTRACT

Aromatic polyimides (PIs) derived from diisocyanates can be synthesized through one-step polycondensation process, either by stepwise heating with controlled temperature increments or by direct heating, in which the reaction mixture is exposed immediately to the final target temperature. However, the impact of these heating method on the resulting PIs properties remains underexplored. In this study, PIs were synthesized from the reaction of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4′-methylene diphenyl diisocyanate (MDI) using both heating methods. Additionally, the effect of longer and shorter immersion times in distilled water applied after the thermal reaction during the precipitation process was examined to determine their influence on polymer properties. The combined effects of heating protocol and immersion duration on precipitation behaviour, solubility, and thermal stability were evaluated. Structural characterization was performed using FTIR and NMR spectroscopy. Thermogravimetric analysis (TGA) confirmed high thermal stability, with degradation temperatures ranging from 574 °C to 585 °C. Solubility tests showed that all BTDA-MDI-based PIs were partially soluble in N-methyl-2-pyrrolidone (NMP), while a comparative PIs synthesized from 6FDA-MDI was fully soluble in various organic solvents. These findings suggest that monomer structure has a stronger influence on solubility than on thermal or crystalline properties. Overall, the study provides valuable insights into how synthesis and post-reaction conditions influence PIs characteristics, supporting their optimization for advanced material applications.

Keywords: Diisocyanate; direct heating; one-step polycondensation; polyimide; stepwise heating

ABSTRAK

Poliimida aromatik (PIs) terbitan diisosianat dapat disintesis melalui proses polikondensasi satu langkah, sama ada menerusi pemanasan berperingkat dengan peningkatan suhu terkawal atau pemanasan langsung pada suhu sasaran. Walau bagaimanapun, kesan cara pemanasan ini terhadap sifat PIs yang terhasil masih kurang dikaji. Dalam kajian ini, PI telah disintesis daripada 3,3′,4,4′-benzofenon tetrakarboksilat dianhidrida (BTDA) dan 4,4′-metilena difenil diisosianat (MDI) menggunakan kedua-dua kaedah pemanasan. Di samping itu, kesan tempoh rendaman yang berbeza (lama dan singkat) dalam air suling selepas tindak balas terma semasa proses pemendakan turut dikaji bagi menilai pengaruhnya terhadap sifat polimer. Kesan gabungan protokol pemanasan dan tempoh rendaman terhadap tingkah laku pemendakan, keterlarutan dan kestabilan terma telah dianalisis. Pencirian struktur dilakukan menggunakan spektroskopi FTIR dan NMR. Analisis termogravimetri (TGA) menunjukkan kestabilan terma yang tinggi dengan suhu penguraian antara 574 °C hingga 585 °C. Ujian keterlarutan menunjukkan bahawa semua PIs berasaskan BTDA-MDI adalah separa larut dalam N-metil-2-pirolidon (NMP) manakala PIs perbandingan yang disintesis daripada 6FDA-MDI menunjukkan keterlarutan penuh dalam pelbagai pelarut organik. Keputusan ini menunjukkan bahawa struktur monomer memberikan pengaruh yang lebih ketara terhadap keterlarutan berbanding sifat terma atau kekristalan. Secara keseluruhan, kajian ini memberikan keputusan penting mengenai pengaruh kaedah sintesis dan keadaan pasca-tindak balas terhadap ciri PIs, yang dapat menyokong pengoptimuman bahan ini untuk aplikasi berprestasi tinggi.

Kata kunci: Diisosianat; pemanasan berperingkat; pemanasan langsung; poliimida; satu langkah polikondensasi

INTRODUCTION

Polyimide (PI) is a high-performance plastic widely used in preparation of flexible films in aerospace, electronics, and other industries because of its flexibility and heat resistance. Its structure, which consists of aromatic and heterocyclic rings, provides outstanding properties such as resistance to corrosion, radiation, oxidation, and high temperatures, as well as good mechanical strength. These characteristics make PI one of the most commonly used heat-resistant polymers (Liu et al. 2023; Zhou et al. 2023). The synthesis of polyimides involves a one-step polycondensation reaction using diisocyanate and dianhydride, during which carbon dioxide gas is produced as a by-product and removed through bubbling (Mustaffa et al. 2023a). This polycondensation can be carried out using either stepwise or direct heating methods with controlled temperature increments or direct heating to the target temperature.

The one-step method is particularly advantageous for producing polyimides in powder form. However, assessing the solubility of powdered polyimides is crucial to enhance their processability and broaden their applications. Several factors, including monomer structure, influence polyimide solubility (Avadhani & Chujo 1997; Mustaffa et al. 2023a). Despite employing similar monomers with anhydride (BTDA, PMDA, 6FDA) and diisocynate (MDI, TDI), studied have shown variations in solubility, even when polyimides contain bulky or flexible groups like hexafluoroisopropylidene diphthalic anhydride (6FDA) in their polymer backbone (Avadhani & Chujo 1997; Mustaffa et al. 2023b; Sarkar et al. 2009).

Mustaffa et al. (2023b) and Sarkar et al. (2009) employed direct heating methods and found that their synthesized polyimides (MDI-6FDA) and (aromatic diisocyanate with alkoxy flexible-6FDA) were soluble in organic solvents like dimethylformamide (DMF) and dimethylacetamide (DMAc). In contrast, Avadhani and Chujo (1997) utilized stepwise heating and discovered that their MDI-6FDA PIs were insoluble in the same solvents. Therefore, this study aims to explore how heating methods impact the solubility and thermal behavior of PIs and identify the optimal immersion time required for producing PI.

Chao (2018) found that residual solvents remained in PI synthesized with BTDA and 4,4′-oxydianiline (ODA) after a short immersion period in methanol. Conversely, Goh et al. (2015) demonstrated that immersing the material in distilled water for an optimal period produced exceptionally pure bis(2-hydroxyethyl) terephthalate (BHET) crystals, completely free of residual solvents. In this study, we aim to investigate the effects of both heating methods and immersion time on the properties of PIs synthesized from 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4’-methylene diphenyl diisocyanate (MDI) as monomers.

MATERIALS AND METHODS

MATERIALS

3,3’,4,4’-Benzophenone tetracarboxylic dianhydride (BTDA), 4,4’-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), methylene diphenyl diisocyanate (MDI), dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich Chemie GmbH, Germany. Dimethyl sulfoxide (DMSO) and methanol were obtained from Systerm, Malaysia. All chemicals were used as received.

CHARACTERIZATION METHODS

Fourier transform infrared spectroscopy (FTIR) was conducted using an Agilent instrument to identify the functional group present in the PIs, with a scanning resolution of 2 cm^{-1}. Nuclear magnetic resonance (NMR) spectroscopy was carried out using a Bruker Avance III HD 400 MHz spectrometer and dimethyl sulfoxide (DMSO)-d_6 as the solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed at a heating rate of 10 °C/min in nitrogen using NETZSCH DSC 214 Polyma calorimeter and a Perkin Elmer TGA 4000 analyzer, respectively. Both thermal analyses involved two heating cycles: the first cycle ranged from 30 °C to 350 °C for removal of any residual solvent, and the second cycle ranged from 30 °C to 600 °C. X-ray diffraction (XRD) analysis was conducted using a Bruker D8 Advance diffractometer to characterize the crystallinity of the polyimide samples.

SYNTHESIS OF POLYIMIDE POWDER

The direct synthesis of PIs was carried out in a glovebox under a nitrogen atmosphere. The PI was synthesized using BTDA powder, MDI, and DMAc solvent in a molar ratio of 1:1:1. MDI and BTDA were separately dissolved in DMAc solvent in 50 mL flasks at room temperature until fully dissolved. The BTDA solution was then added to the MDI solution and stirred until homogeneous. After 1 h, the reaction mixture was heated to 130 °C for 3.5 h. The resulting PI solutions was poured into distilled water for precipitation. To examine the effect of immersion duration, the PI solutions was left in distilled water for either 5 or 17 h. The precipitate was collected, washed with distilled water, rinsed with methanol, and left in a desiccator for 24 h. The resulting powder was then dried in a vacuum oven at 150 °C for 3 h.

The same procedure was followed for the stepwise synthesis, with the exception that the reaction mixture was gradually heated at 40 °C for 1 h, 90 °C for 1 h, and 130 °C for 3.5 h. For structural comparison in the solubility test, PI based on 6FDA-MDI was synthesized using the same method. PIs produced through the direct heating

method are referred to as ST, while those obtained through the stepwise heating method are designated as SB. The product yields obtained for all BTDA-MDI-based PIs were 86.45% (PI ST_{R5}), 81.53% (PI ST_{R17}), 84.63% (PI SB_{R5}), and 85.88% (PI SB_{R17}).

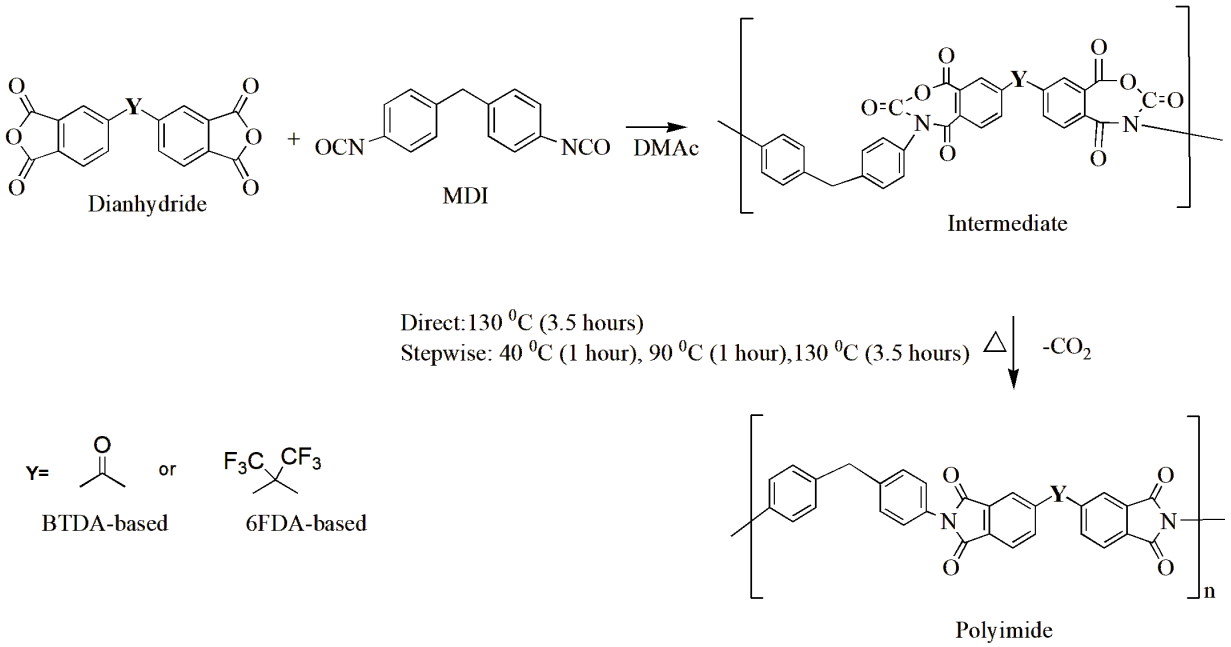
RESULTS AND DISCUSSION

BTDA-MDI POLYIMIDE POWDER

The polyimide synthesis reaction was carried out following established protocols from the literature (Avadhani & Chujo 1997; Mustaffa et al. 2023b; Sarkar et al. 2009). Referencing these prior methods ensures methodological consistency and reproducibility. The synthesis was performed via one-step polycondensation between diisocyanates and dianhydrides in DMAc solvent. This reaction involves the nucleophilic attack of amine groups on the anhydride carbonyls, leading to the formation of imide linkages and the concurrent release of CO_2, as depicted in Scheme 1. The reaction initiated with CO_2 evolution at approximately 100 °C, serving as a clear indicator of reaction progress (Mustaffa et al. 2023b). To ensure complete CO_2 removal and drive the reaction to completion, a temperature of 130 °C was employed for both direct and stepwise heating methods, as illustrated in Scheme 1. This temperature effectively maximized polymer yield. These results support the conclusion that moderate heating is sufficient for the one-step polycondensation of diisocyanates and dianhydrides in DMAc solvent, with both heating strategies demonstrating comparable effectiveness.

Figure 1 shows that each PI sample from both heating methods demonstrates distinctive peaks corresponding to the characteristic imide functional group. The peaks at 1778 cm^{-1} and 1710 cm^{-1} represent the asymmetric stretching and symmetric stretching of the C=O bond, respectively. In addition, the peaks at 1377 cm^{-1} and 719 cm^{-1} are associated with C-N bond stretching and the bending of the C=O group (Ni et al. 2022; Li et al. 2023; Long et al. 2022). The peak at 1658 cm^{-1} corresponds to the vibrations of the carbonyl C=O group within the BTDA structure (Avci & Sirin 2014; Liu et al. 2023). These distinctive peaks provide conclusive evidence of the successful synthesis of the PIs, with no significant differences in wavenumbers observed between the PIs synthesized using different heating methods. However, residual DMAc solvent remains present in the sample, even after the immersion processes were carried out for 5 and 17 h. The peaks corresponding to solvent residues include alkane C-H stretching (3033 cm^{-1}), amide C=O stretching (1621 cm^{-1}), N-CH_3 deformation (1210 cm^{-1}), and C-N stretching around 1094 cm^{-1} (Gottlieb, Kotlyar & Nudelman 1997; Guo et al. 2014; Verma, Singh & Mankhand 2017).

It is also noted that the symmetric stretching of the C=O group in the PIs synthesized via the stepwise heating method and immersed for 5 and 17 h, appears slightly lower compared to those obtained through direct heating. A similar pattern is observed for the wavenumbers corresponding to the C=C group. These findings suggest that the presence of solvent residues is more pronounced in the PI sample immersed for 5 h than in the one immersed for 17 h (Huang, Yang & Chou 2006). The interaction



SCHEME 1. Reaction scheme of the polyimide synthesis

between the solid material and the solvent results in a reduction of molecular vibration frequencies, leading to the appearance of peaks at lower wavenumbers, as observed in previous studies (Gottlieb, Kotlyar & Nudelman 1997; Guo et al. 2014).

The ^{1}H and ^{13}C NMR analyses were conducted to further confirm the successful synthesis of the BTDA-MDI based PI using different heating methods and immersion times, as shown in Figure 2(a)-2(d). The ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) displays peaks at 7.43-7.53 ppm (H1-H2), 4.13 ppm (H3), and 8.0-8.25 ppm (H4-H6). The peaks in the ranges of 7.34-7.53 ppm and 8.0-8.25 ppm are indicative of the proton hydrogen on phenyl groups from MDI and BTDA, respectively. The phenyl group of BTDA exhibits higher hydrogen peak values, influenced by the presence of neighboring carbonyl (C=O) groups (Wang, Huang & Lei 2020). Additionally, a peak at approximately 4.13 ppm corresponds to the hydrogen atoms in the –CH_2– group of the MDI structure (Huang, Yang & Chou 2006). Figure 2(b) shows the presence of residual traces of the DMAc solvent. The residual solvents, DMSO-d_6 and water, are observed at 2.51 ppm and 3.4 ppm, respectively, consistent with previous reports (Guo et al. 2014). Furthermore, hydrogen peaks at 2.74 (i), 2.93 (iii), and 3.03 ppm (ii) are observed. The peak at 2.74 ppm is attributed to the hydrogen atoms in the methyl group near the carbonyl group, while the peaks at 2.39 and 3.03 ppm correspond to hydrogen atoms from methyl groups bonded to nitrogen atoms (Gottlieb, Kotlyar & Nudelman 1997; Khaki, Namazi & Amininasab 2021; Verma, Singh & Mankhand 2017).

Based on the ^{13}C-NMR spectrum (400 MHz, DMSO-d_6), the following chemical shifts were observed: 118.64-143.02 ppm (C1-C4, C7-C12), 166.48 ppm (C6), 193.46 ppm (C13), and 40.72 ppm (C5). The peaks observed in the range of 118.64 ppm to 143.02 ppm in Figure 2(c) correspond to the aromatic rings of the BTDA and MDI monomers, while the peak at 166.48 ppm is attributed to the imide group (Avci & Sirin 2014; Khaki, Namazi & Amininasab 2021; Subramani et al. 2000). The peak at 40.72 ppm corresponds to the methylene group in the MDI monomer (Arunkumar & Ramachandran 2017). A residual DMSO-d_6 solvent peak was detected around 39.61 ppm. A detailed analysis of Figure 2(d) shows carbon peaks corresponding to the residual DMAc solvent. These peaks appear at 21.26 ppm (i), 36.10 ppm (ii), 34.56 ppm (iii), and 167.82 ppm (iv). The peak at 167.82 ppm is assigned to the carbonyl group, while the peaks at 36.10 ppm and 34.56 ppm are attributed to methyl groups bonded to nitrogen atoms. The peak at 21.26 ppm is associated with methyl groups bonded to carbonyl groups (Subramani et al. 2000; Verma, Singh & Mankhand 2017).

SOLUBILITY TEST

All PIs synthesized using different heating methods or immersed for varying durations exhibited partial solubility in the NMP solvent, as shown in Table 1. This suggests that the rigid nature of BTDA increases chain stiffness, thereby reducing the solubility of the PIs. Moreover, the symmetrical structure of MDI enhances the rigidity of the polyimide, promoting the formation of compact chains and facilitating interchain interactions within the polymer (Zhuang, Seong & Lee 2019). To further evaluate the role of monomer structure, PI based on 6FDA-MDI were synthesized (Supplementary Data S1). PI derived from 6FDA-MDI, synthesized by both methods, were completely soluble in all tested solvents. The enhanced solubility of 6FDA-based polyimides is primarily attributed to the bulky trifluoromethyl groups and the non-coplanar structure introduced by the hexafluoroisopropylidene moiety in Scheme 1. These structural features disrupt intermolecular packing and reduce chain rigidity, thereby facilitating better interaction with organic solvents (Mustaffa et al. 2023a). This further reaffirms the significant impact of monomer selection on the solubility properties of PI.

THERMAL PROPERTIES OF POLYIMIDES

A consistent two-step degradation pattern was observed in all PIs, as shown in Figure 3(a)-3(b). The first degradation step (218-238 °C) is attributed to the presence of residual solvents in the polyimide powder, while the second degradation step corresponds to the degradation of the polyimide's backbone (Kuhire et al. 2018; Purushothaman & Bilal 2014). The strong interaction between the polyimide and residual solvents necessitates higher temperatures to fully eliminate the remaining solvent residues, despite the boiling point of DMAc being only 165 °C (Joshi & Adhikari 2019; Kaba et al. 2005).

A decrease in solvent residue was observed for PIs synthesized through the stepwise heating method and subjected to longer immersion periods (e.g., PI SB_{R17}: 3.1% < PI ST_{R5}: 6.0%). Conversely, PIs synthesized using the direct heating method exhibited a slightly higher solvent residue content when immersed for longer durations, with a marginal difference of 1.4% (e.g., PI ST_{R17}: 3.4% > PI SB_{R5}: 2%). This suggests that extended immersion periods led to reduced degradation temperatures in the PIs, indicating a weaker interaction between the solid polyimide and residual solvents (Goh et al. 2015).

Polyimides synthesized using stepwise heating and immersed for 17 h showed slightly higher degradation temperatures compared to others (PI SB_{R17}: 585 °C, PI SB_{R5}: 574 °C, PI ST_{R17}: 577 °C, PI ST_{R5}: 575 °C). All synthesized polyimides experienced weight losses ranging from 43% to 52%. Although the differences are not substantial, PIs immersed for longer durations exhibit slightly enhanced thermal stability, as evidence by a lower weight reduced compared to the 5-h immersion (PI ST_{R17}: 47%, PI ST_{R5}: 52%, PI SB_{R17}: 43%, PI SB_{R5}: 46%).

The DSC analysis in Figure 3(c) showed the presence of residual solvent, as indicated by peaks around 75 °C during the initial heating cycle (Esmaeilpour et al. 2015).

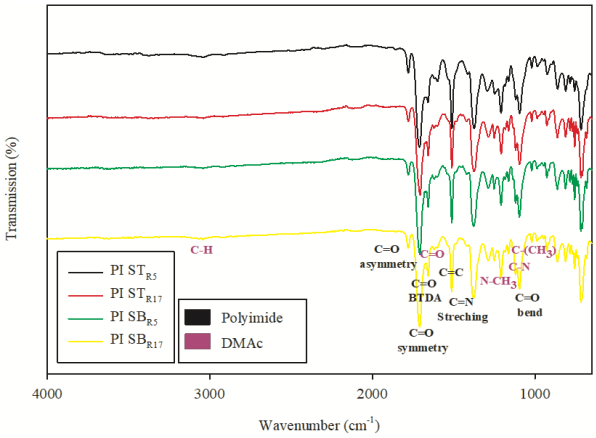


FIGURE 1. Fourier Transform Infrared (FTIR) spectrum of the polyimide BTDA-MDI

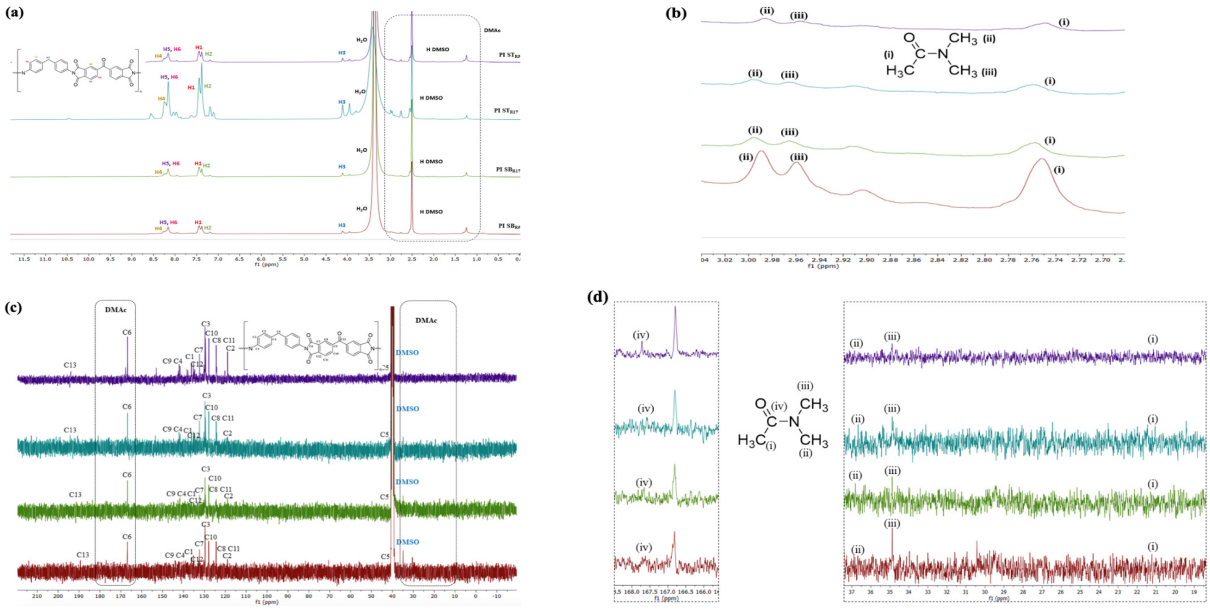


FIGURE 2. Spectra: (a) ^{1}H NMR spectrum of PI, (b) magnified spectrum of residual DMAc in PI, (c) ^{13}C NMR spectrum of PI, and (d) ^{13}C NMR spectrum of residual DMAc in PI

TABLE 1. Solubility test of polyimide samples based BTDA-MDI and 6FDA-MDI at ambient temperature

Samples	Solvents			
	DMAc	NMP	DMF	THF
PI BTDA-MDI ST_{R5}	--	-+	--	--
PI BTDA-MDI ST_{R17}	--	-+	--	--
PI BTDA-MDI SB_{R5}	--	-+	--	--
PI BTDA-MDI SB_{R17}	--	-+	--	--
PI 6FDA-MDI ST	++	++	++	++
PI 6FDA-MDI SB	++	++	++	++

Solubility: (- -) = not soluble after 24 h; (- +) = partially soluble after 24 h; (++) = completely soluble after 24 h; Solubility was tested using 20 mg of PI and 2 mL of solvent for 24 h

Furthermore, Figure 3(d) shows that all samples exhibited notable endothermic melting (T_m) peaks, ranging from 423 °C to 428 °C. Remarkably, polyimides immersed for 17 h, such as PI SB_{R17} (T_m: 428 °C) and PI ST_{R17} (T_m: 428 °C), exhibited higher T_m values compared to those immersed for 5 h, like PI SB_{R5} (T_m: 425 °C) and PI ST_{R5} (T_m: 423 °C). This observation can be attributed to the formation of stronger molecular interactions in polyimide subjected to extended immersion periods (Chao 2018).

X-RAY DIFFRACTION (XRD) ANALYSIS

Figure 4 shows the presence of sharp peaks at 2θ = 18°, indicating that all the synthesized PIs are semi-crystalline (Chao 2018). All the synthesized PIs have degree of crystallinity ranging from 28.7% to 28.9%, except for PI SB_{R5} (17.7%). No significant differences in crystallinity were observed between the polyimides synthesized directly with immersion times of 5 and 17 h (PI ST_{R5}: 28.7% and PI ST_{R17}: 28.9%). However, for the stepwise-synthesized

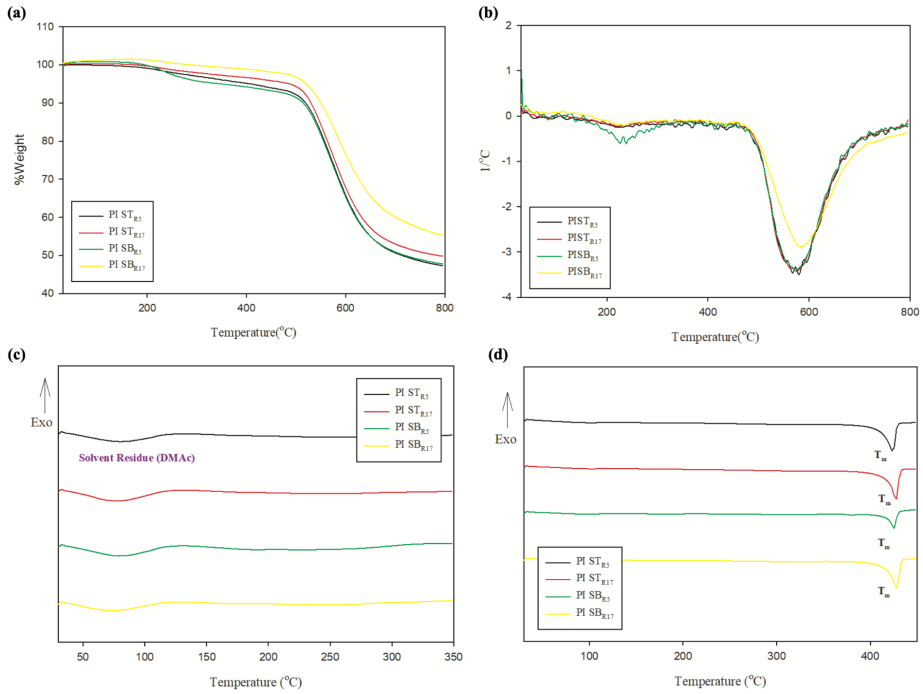


FIGURE 3. (a) Thermogravimetric (TG) curve, (b) derivative thermogravimetric (DTG) curve, (c) first-cycle differential scanning calorimetry (DSC) curve, and (d) second-cycle differential scanning calorimetry (DSC) curve

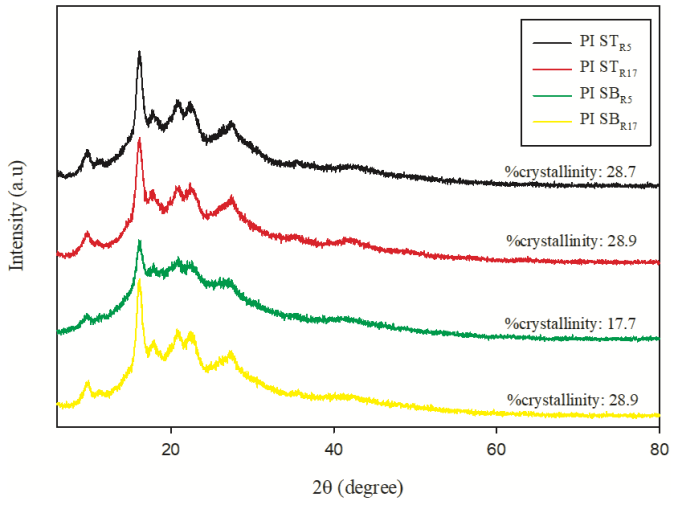


FIGURE 4. X-ray diffractogram of BTDA-MDI

polyimide, PI SB_{R5} exhibited a lower crystallinity percentage compared to PI SB_{R17}. The higher amount of residual solvents in PI SB_{R5} appears to significantly disrupt its crystal formation (Meenan, Anderson & Klug 2002; Poornachary 2008).

CONCLUSION

Polyimides synthesized from BTDA-MDI using both direct and stepwise heating methods demonstrated excellent thermal stability, with degradation temperatures ranging from 574-585 °C. However, the solubility test showed no significant differences between the two heating methods, as all polyimides displayed partial solubility in NMP while remaining insoluble in DMAc, DMF, and THF solvents at room temperature. In contrast, polyimides based on 6FDA-MDI were completely soluble in NMP, DMAc, DMF, and THF. This highlights that the choice of monomer structure has a more pronounced effect on solubility properties than the heating method employed. Furthermore, the study found that longer immersion durations reduced solvent residue within the polyimides. In conclusion, both the selection of monomer structure and the immersion duration during precipitation processing are crucial factors for enhancing the processability and thermal properties of polyimides, particularly when tailored for specific application requirements.

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SUPPLEMENTARY DATA

Both produced samples, 6FDA-MDI-ST and 6FDA-MDI-SB, show peaks corresponding to the characteristics of imide groups as depicted in Figure S1 and Table S1. However, there is one distinct peak observed at a wavenumber of 1253 cm^{-1}. This peak represents the trifluoromethyl (CF_3) group present in the structure of 6FDA (Purushothaman & Bilal 2014). The analysis of the present peaks indicates that PI 6FDA-MDI was successfully synthesized as well.

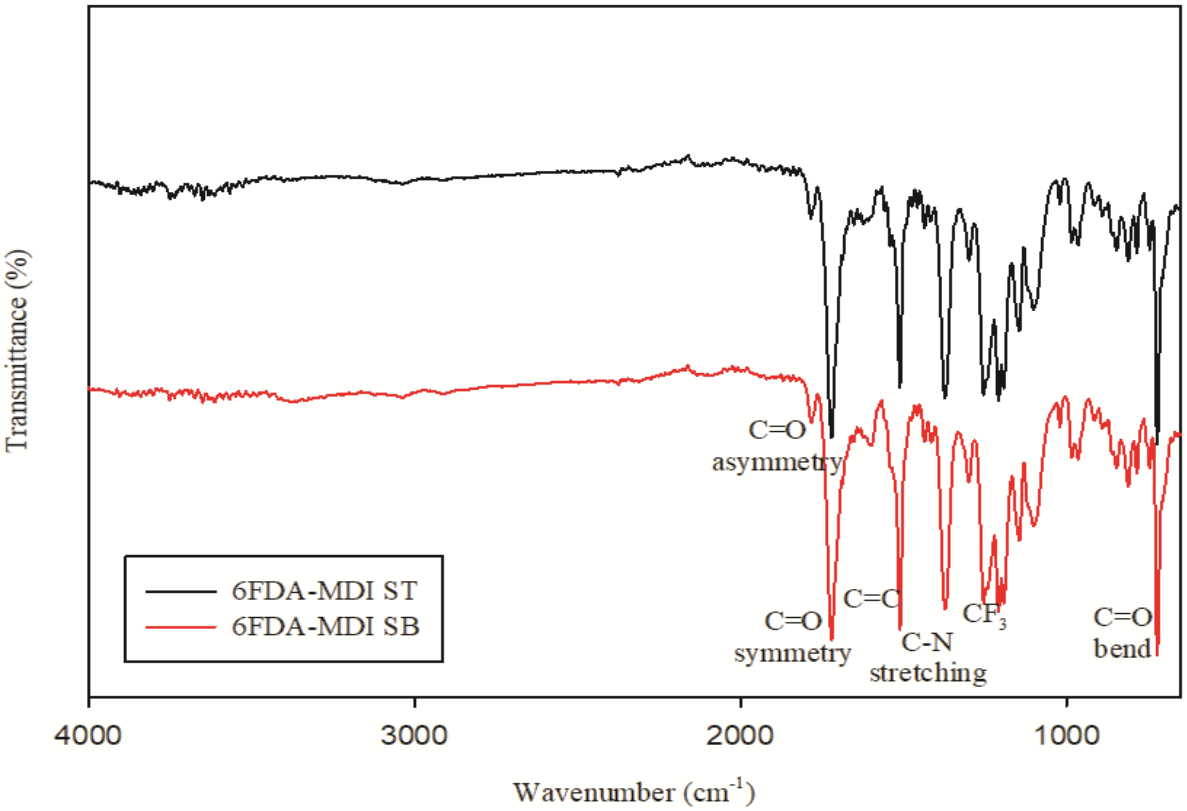

FIGURE S1. Fourier Transform Infrared (FTIR) spectrum of 6FDA-MDI

TABLE S1. Fourier Transform Infrared (FTIR) peaks of 6FDA-MDI

Polyimide/Functional group	6FDA-MDI ST cm^{-1}	6FDA-MDI SB cm^{-1}
C=O asymmetry	1784	1783
C=O symmetry	1720	1720
C=C	1511	1511
C-N stretching	1373	1373
CF_3 (6FDA)	1253	1253
C=O	721	721