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The Effect of the Methyl Functional Group on the Physicochemical and Structural Properties of a Synthesized Semi-Aromatic Polyimides

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ABSTRACT

It is crucial to design and develop new polymers with desirable characteristics. Aromatic polyimides have been attracted more attention in comparison with other polymeric materials, because of their excellent properties, such as the high thermal stability, mechanical strength, and chemical resistance. In this work, two semi-aromatic polyimides (BCDA-mPDA and BCDA-Durene) were successfully synthesized from bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarbocylic dianhydride (BCDA), 1,3-phenylenediamine (mPDA), and 2,3,5,6-tetramethyl-1,4-phenylenediamine (Durene) to investigate the effect of methyl functional groups on the physicochemical and structural properties of the synthesized polyimides. The synthesized polyimides were characterized by the proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy, inherent viscosity measurement, and solubility test. FTIR and ^{1}H-NMR results confirmed the chemical structure of the synthesized polyimides. XRD results showed that the presence of bulky methyl groups has led to increasing amorphous regions in the polymer structure. In addition, these new polymers were soluble in various organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP). The inherent viscosity of the synthesized polyimides was 0.65 dl/g for BCDA-Durene and 0.96 dl/g for BCDA-mPDA, which indicates the moderate molecular weight of the polymers.

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1. Introduction

Usually, most of the commercially available glassy and rubbery polymers show weak physicochemical properties [1, 2]. Thus, it is

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crucial to design and develop new polymers with desirable characteristics. Aromatic polyimides have been attracted more attention in comparison with other polymeric materials, because of their excellent properties, such as the high thermal stability, mechanical strength, and chemical resistance [3-5]. Most aromatic polyimides are insoluble in common organic solvents and have high glass transition (T_g) and melting (T_m) temperatures due to the rigidity of their chain and strong intermolecular interactions. Their poor solubility and high melting temperature make it challenging to process them into different forms such as fibers and films. Recently, many studies have been carried out to prepare polyimides with high solubility and proper processibility without decreasing their excellent properties [6, 7].

Many factors such as molecular packing, molecular ordering, free volume, and rotational motions around a bond at the molecular level can affect the polyimide properties. On the other hand, these factors are mainly dependent on the polyimide structures and preparation conditions. It has been illustrated that there is a relationship between polyimide property and its structure that must be clarified to design a suitable polyimide for an application [8, 9]. In other words, the properties of polyimide can be significantly affected by a slight change in its structure, and at a higher level, by choosing two compartments of the polyimide monomer. For example, the presence of bulky groups and kink monomers in the backbone of the polyimide can increase the free volume and enhance the solubility of the polymer. Aromatic polyimides are synthesized from aromatic diamine and dianhydrides. Strong intra- and/or inter-chain interactions between the electron-withdrawing groups of aromatic dianhydride and the electron-donating moieties of aromatic diamine in these polyimides lead to the formation of charge transfer complexes (CTCs) [10-13]. The appearance of intra- and inter-chain CTCs can affect the solubility of the polymer and thus its processability. The formation of CTC increases chain packing, which leads to a lower solubility of the polymer. On the other hand, CTC can reduce the amorphous regions by inhibiting macromolecular mobility, which reduces the transparency property. Therefore, aromatic polyimides with high CTC often show deep yellow or brown colored films, which limit their optical applications [10, 14]. In general, there are three strategies to prevent the formation of CTCs and thus increase the optical transparency property: (1) the introduction of electronegative groups, (2) the introduction of alicyclic moieties, and (3) the introduction of sterically hindered groups (such as methyl groups) with twisted or bulky structures.

Here we report semi-alicyclic/semi-aromatic polyimides synthesized from alicyclic dianhydride, BCDA, and aromatic diamines, mPDA or Durene. BCDA is a non-coplanar monomer that can reduce the chain packing and intermolecular interactions and increase the solubility of the polymer. In other words, BCDA dianhydride has a weaker electron-withdrawing effect compared to aromatic dianhydrides; therefore colorless films with low CTC are expected to be produced. The mPDA monomer can increase the porosity of the polymer by preventing the formation of linear chains. In addition, mPDA is an asymmetrical diamine with meta substitutions [15]. The presence of asymmetrical structures in the main chain of the polymer has the following advantages: (1) increasing the penetrant diffusivity, (2) enhancing the solubility of the polymer, and (3) reducing inter-chain packing and intermolecular interactions without changing the rigidity of the chain and thermal properties of the polymer [3]. The sterically hindered methyl groups of Durene diamine can improve the penetrant diffusivity by reducing the CTC formation and increasing free volume. In addition, these bulky groups can improve polymer-solvent interactions or, in turn, the solubility of the polymer by preventing inter-chain interactions and chain packing [16]. It should be noted that aromatic diamines are used here because aliphatic diamines have much higher basic cites than aromatic diamines. Therefore, the polymerization of the polyimide derived from aliphatic diamines often undergoes strong gelation or the salt formation in the initial reaction stage, and thus polymerization is prevented.

2. Experimental

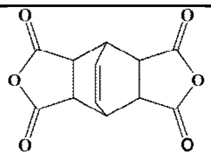
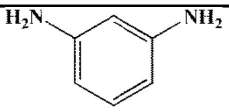
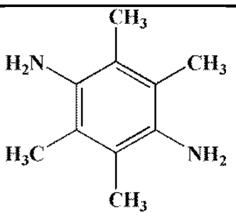
2.1. Materials

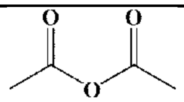
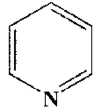
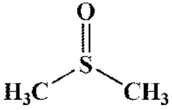
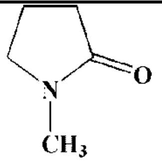
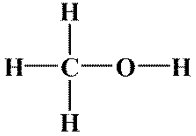
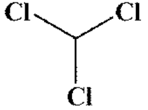
Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarbocylic dianhydride (BCDA), and 2,3,5,6-tetramethyl-1,4-phenylenediamine (Durene) were purchased from Sigma-Aldrich company. BCDA and Durene monomers were purified by the recrystallization method using dimethyl sulfoxide (DMSO) and methanol solvents respectively. Also, 1,3-phenylenediamine (mPDA) was obtained from Merck company and recrystallized by chloroform before use. Acetic anhydride and pyridine were obtained from PARS Chemie and Daejung companies respectively and used without purification. N-methyl-2-pyrrolidone (NMP) and Dimethylformamide (DMF) were obtained from Merck Company.

It should be noted that the diamine monomers were highly sensitive to oxygen as they could be easily oxidized in the presence of air. Therefore, they are purified before use in the synthesis of polymers. In addition, dianhydride monomers are highly sensitive to moisture and need to be purified before polymerization. The presence of impurities in primary monomers reduces the molecular weight of the final polymer. Table 1 summarizes all the materials in this research.

Table 1

The chemical formula, structures and some physical properties of the materials used in this study.

Material	Chemical formula	2D chemical structure	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Density (g/cm^3)
BCDA monomer	$C_{12}H_8O_6$		248.19	> 300	-	-
mPDA monomer	$C_6H_8N_2$		108.14	64-66	282-284	1.139
Durene monomer	$C_{10}H_{16}N_2$		164.25	150-155	192	0.868

Acetic anhydride	$C_4H_6O_3$		102.09	-73.1	139.8	1.08
Pyridine	C_5H_5N		79.1	-41.6	115	0.982
DMSO solvent	C_2H_6OS		78.13	19	189	1.1
NMP solvent	C_5H_9NO		99.133	-24.2	204	1.03
MeOH solvent	CH_3OH		32.04	-97.6	64.7	0.792
Chloroform solvent	$CHCl_3$		119.38	-63.5	61.2	1.49

2.2. Polymer synthesis

The two-step chemical method was used to synthesize the polymers in this study. At first, 2 mmol of diamine (0.2163 g of mPDA or 0.3285 g of Durene) was dissolved in the NMP solvent (25 wt % of solution) under nitrogen atmosphere and at room temperature. A transparent and homogenous solution was obtained after 30 min. Then, 2 mmol (0.4964 g) of BCDA dianhydride was added rapidly to the reaction mixture and stirred at 0 °C for 24 h to produce the poly (amic acid) solution. Next, 8 mmol (0.8167 g) of acetic anhydride and 8 mmol (0.6328 g) of pyridine were added to the reaction medium to convert poly (amic acid) into polyimide at 80 °C under vigorous stirring for 24 h. Finally, the resulting viscous solution was cooled to room temperature, followed by precipitation in methanol. White polymer powders were separated by filtration and washed with methanol several times. The resultant powder was dried at 80 °C for 24 h and stored in a desiccator before being used.

It should be noted that in this procedure, the progress of the reaction is strongly influenced by the pre-reaction conditions, even the molecular weights of the product are changed by the purity of monomers.

Inherent viscosity is a suitable property for the evaluation of polymer’s molecular weight. This property was measured using an Ubbelohde viscometer at the temperature of 25 °C and concentration of 0.5 g/dl using NMP as the solvent. In addition, the solubility of the synthesized polyimides in various organic solvents was investigated experimentally.

2.3. Polymer characterization

The fourier transform infrared (FTIR) spectra of the materials were obtained using a spectrophotometer (Galaxy Series 5000, Mattson Instruments Inc., Madison, WI, USA) in the scan range of 400-4000 cm^{-1} to investigate the changes in polyimides’ chemical structures. The proton nuclear magnetic resonance (^1H-NMR) spectra of the synthesized polyimides were collected by Bruker 400 MHz (Bruker Biospin, Rheinstetten, Germany) spectrometer using the DMSO solvent. The X-ray diffraction (XRD) patterns of the polymers were analyzed to investigate their microstructural properties. The XRD analysis was carried out by a PANalytical X′Pert Pro diffractometer (PANalytical BV, Almelo, The Netherlands) with the accelerating voltage of 40 kV, anode material of Cu Kα (λ = 0.15406 nm), tube current of 40 mA, and at the step size increment of 0.0260 $°s^{-1}$.

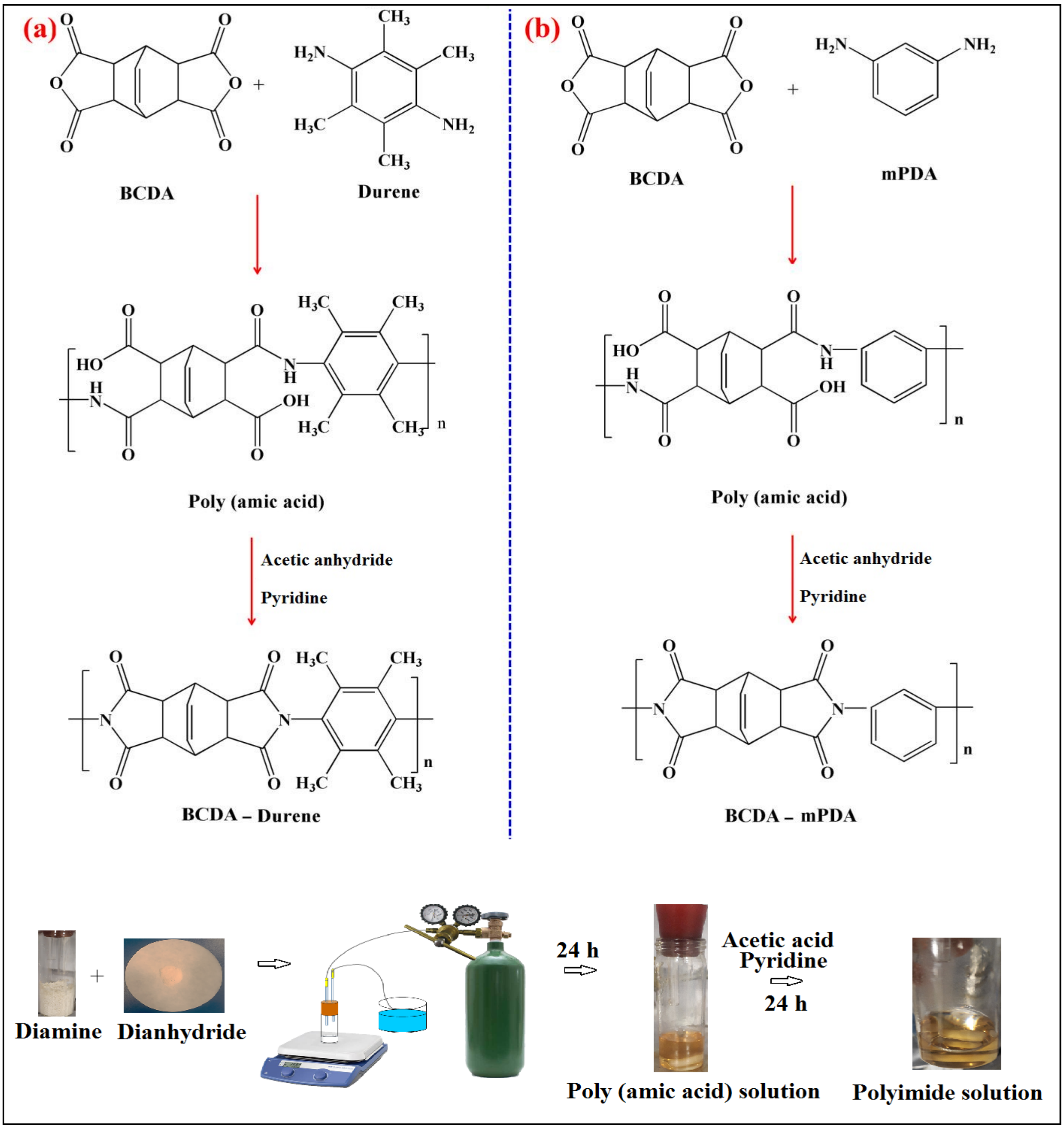


Figure 1. General scheme for the synthesis of the polyimide: (a) BCDA-Durene, and (b) BCDA-mPDA.

3. Results and discussion

3.1. Inherent viscosity and solubility of polyimides

The inherent viscosities of the synthesized polyimides were 0.65 and 0.96 dl/g for BCDA-Durene and BCDA-mPDA respectively, which indicate moderate molecular weights. The solubility of the synthesized polyimides in various organic solvents was investigated experimentally. The results are summarized in Table 2.

Table 2

Solubility of the synthesized polyimides in various solvents at room temperature.

Solvent	BCDA-mPDA	BCDA-Durene
Dimethylformamide (DMF)	+	+
Dimethylsolfoxide (DMSO)	+	+
N-methyl-2-pyrrolidone (NMP)	+	+
Tetrahydrofuran (THF)	±	±
Trichloromethane (Chloroform)	±	±
Methanol (MeOH)	±	±
Water (H_2O)	±	±

+: Soluble ±: Partially soluble

3.2. FTIR

As shown in the FTIR spectra (Figure 2), the absorption bands of C–N–C stretching vibration and C=O (carbonyl) asymmetric and symmetric vibrations appeared, respectively, at 1195-1380, 1780, and 1708 cm^{-1}, that confirm the imides formation [17-19]. Also, the disappearance of the –NH absorption band between 3180-3500 cm^{-1} and that for the carboxylic –OH at 2933 cm^{-1} confirm a complete poly (amic acid) conversion into polyimides [20]. The absorption band at the 2958 cm^{-1} wavenumber is associated with cycloaliphatic moieties [21]. The absorption band at 703 cm^{-1} confirms the deformation of the imide carbonyl group or imide ring [22, 23]. In addition, the absorption band that appeared around 1461 cm^{-1} characterized the C–C stretching in aromatic rings [23]. For BCDA-Durene polyimide, typical aliphatic C-H absorption bands have appeared at 2866-2926 cm^{-1} which are attributed to the CH_3 substitutes of Durene diamine [24].

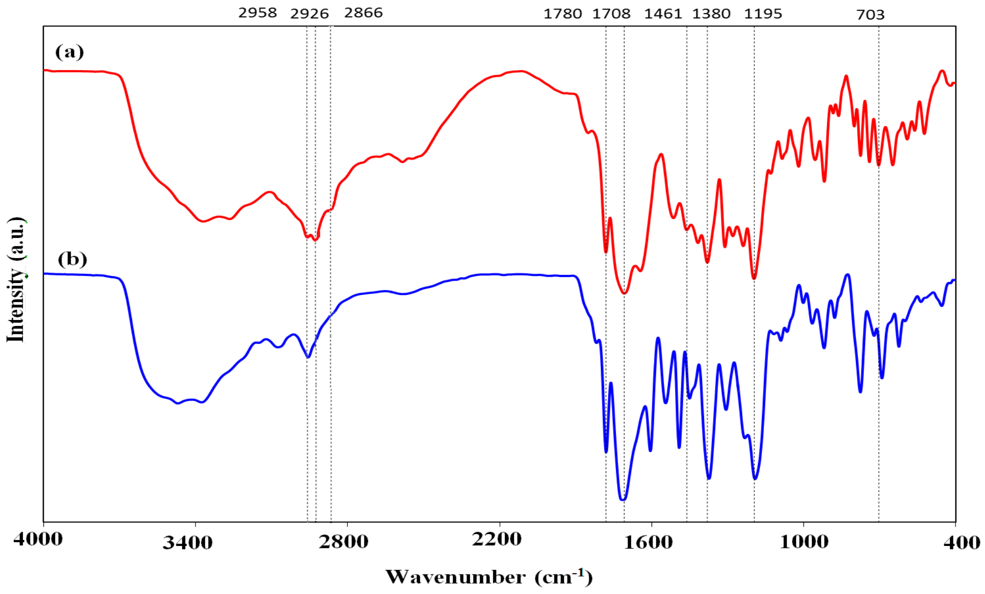


Figure 2. FTIR spectra of (a) BCDA-Durene and (b) BCDA-mPDA.

3.3. ^{1}H-NMR

Figures 3 a,b show the 1H-NMR spectra of BCDA-mPDA and BCDA-Durene polyimides respectively. For BCDA-mPDA polyimide (Figure 3a), the peak at 7.19 ppm (1H) appeared as singlet and was attributed to the aromatic proton, which was present between nitrogens of imide groups. Aromatic protons, which are ortho to nitrogen of the imide group, have appeared as the doublet in the range of 6.96-7.05 ppm (2H). Also, the peaks in the range of 7.45-7.57 ppm (1H) are appeared as the triplet and are attributed to the aromatic proton, which is meta to both the imide group nitrogens [25]. In addition, ^{1}H-NMR signals at δ: 2.68 (4H), 2.49 (2H), and 6.3 (2H) ppm correspond to the aliphatic and alkene protons of dianhydride respectively [26, 27]. In the ^{1}H-NMR spectra of BCDA-Durene polyimide (Figure 3b), the peak that appears at 2.05 ppm (12H) is assigned to the methyl groups of the Durene diamine [28]. Also, the peaks of aliphatic (4H and 2H) and the alkene moiety of dianhydride appear at δ: 3.34-3.36, 3.15, and 6.23-6.24 ppm respectively [4, 29].

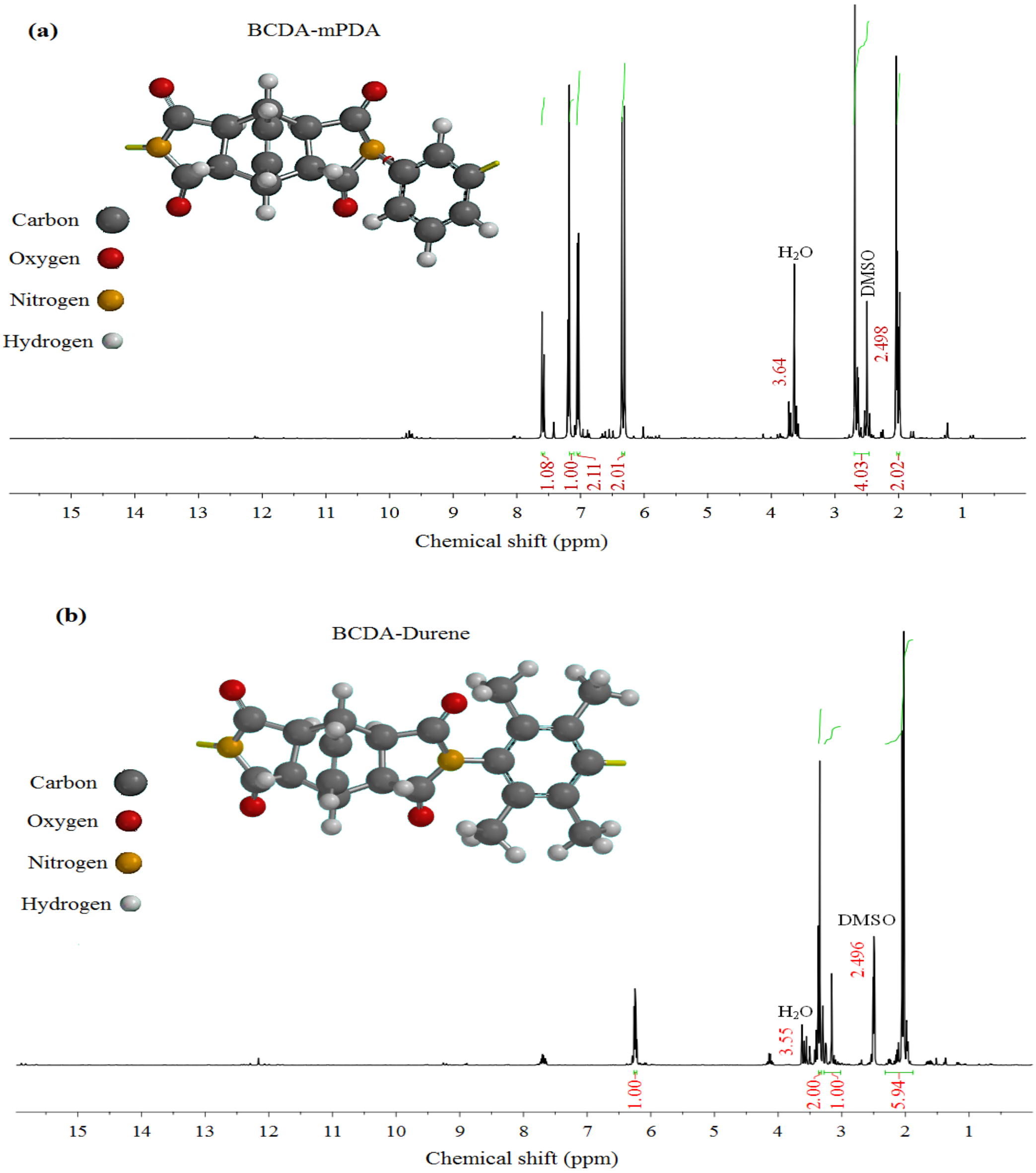


Figure 3. ^{1}H-NMR spectra of (a) BCDA-mPDA, and (b) BCDA-Durene.

3.4. XRD

The crystallinity of two polymers was analyzed by XRD to investigate the influence of methyl groups on the arrangement of polymer chains. Figure 4 represents the XRD patterns of BCDA-mPDA and BCDA-Durene polymers at 2θ ranging from 10° to 100°. Two characteristic broad peaks at the 2θ of 26.335° and 71.987° are observed in the XRD pattern of BCDA-mPDA polyimide, which confirm the semi-crystalline structure of this polymer. On the other hand, the XRD pattern of BCDA-Durene displays two broader peaks at the 2θ of 20.887° and 68.224°, which signifies the more amorphous structure of BCDA-Durene compared to the BCDA-mPDA. The presence of more bulky methyl groups in the Durene diamine can decrease the intra and inter-chain interactions, which is resulted in the increased chain mobility, and hence, more disordered or amorphous regions in the polymer structure.

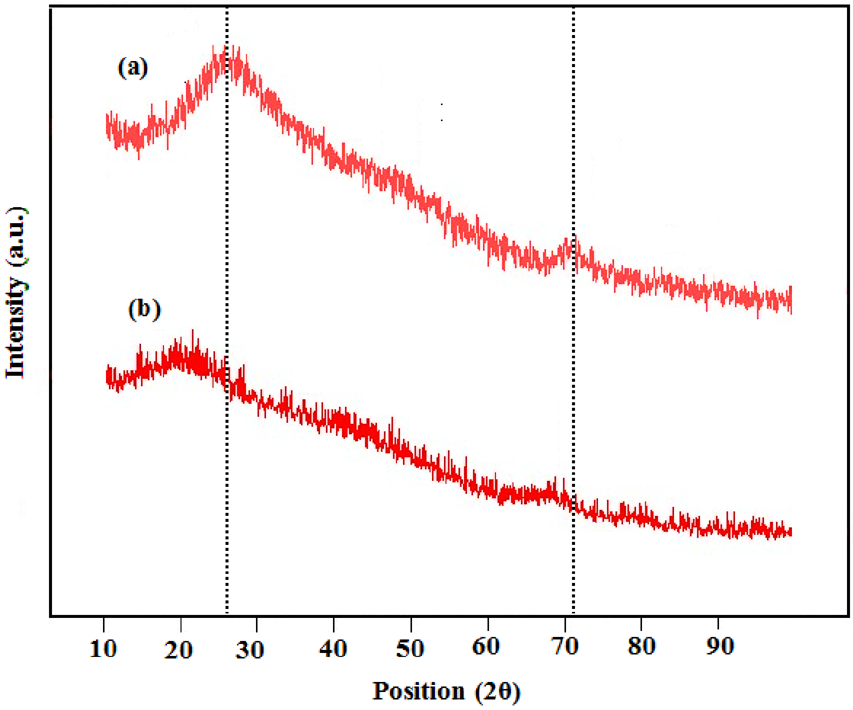


Figure 4. XRD patterns of (a) BCDA-mPDA, and (b) BCDA-Durene.

The interlayer spacing (d-spacing) between polymer chains can be determined by Bragg's equation [30]:

$$n\lambda = 2d \sin\theta \qquad (1)$$

where n, λ, 2θ, and d are the refractive index which takes integer values, the wavelength of the incident beam (Cu Kα, λ = 0.15406 nm), the diffraction angle between the incident and scattered X-ray wave vectors, and the interlayer spacing of lattice planes respectively. Moreover, the degree of crystallinity (X_C) can also be investigated by the XRD results. In this case, X_C is determined by the areas under crystallization peaks divided into the total sum of the areas under the crystalline and amorphous regions. Table 3 demonstrates the percentage of the crystallinity and d-spacing values of BCDA-mPDA and BCDA-Durene polyimides. It can be seen in Table 3 that BCDA-Durene polyimide has higher d-spacing values than BCDA-mPDA polyimide. This is due to the presence of methyl groups in Durene diamine which are bulkier than hydrogen atoms in mPDA that can positively affect the transport of species through the polymer film. The lower d-spacing value of BCDA-mPDA, and thus, a denser chain packing of the polymer confirm its higher density than that of BCDA-Durene polyimide. Breaking the CTCs or bonds due to the presence of $-CH_3$ groups in Durene diamine decreases the close packing, and thus, the density of BCDA-Durene polyimide.

Table 3

Crystallinity percent and d-spacing values of BCDA-mPDA and BCDA-Durene polyimides.

Polymer	Peak position (2θ°)	d-spacing (Å)	X_c (%)
BCDA-mPDA	24.335	5.430	13.250
	71.987	1.947	
BCDA-Durene	22.887	5.769	11.220
	68.224	2.041	

4. Conclusions

In this study, two new polyimides were synthesized by the two-step polymerization method. The characteristics of the prepared polymers were determined by proton nuclear magnetic resonance (^{1}H-NMR), Fourier transform infrared (FTIR), and X-ray diffraction (XRD) analyses. Moreover, the inherent viscosity measurement and solubility test were performed. The FTIR and ^{1}H-NMR results confirmed the synthesized polyimide structures. In addition, XRD patterns showed that incorporating of bulky methyl groups into polyimides could enhance their flexibility. The inherent viscosity of the polyimide solutions showed the moderate molecular weight of the polymers. Also, the solubility test showed that these synthesized polymers were soluble in various organic solvents such as DMSO, DMF, and NMP. The presence of methyl groups in Durene diamine can improve the flexibility, decrease the density, and therefore, enhance the solubility of the polymer of BCDA-Durene polyimide.

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