Synthesis and thermal properties of polyimides containing azomethine linkage for processable high-performance engineering plastics

Rubbia Iqbal*, Muhammad Kaleem Khosa*,†, Muhammad Asghar Jamal*, and Mazhar Hamid**

*Department of Chemistry, Government College University, Faisalabad 38000, Pakistan
**National Engineering and Scientific Commission, P. O. Box 2216, Islamabad, Pakistan
(*Received 16 May 2014 • accepted 17 July 2014*)

Abstract−A new series of polyimides having azomethine functionality in backbone was synthesized by two-steps polycondensation method. Five substituted aromatic diamines--N-(4-aminobenzylidene)-2chloro-6-methylbenzene-1,4-diamine (DA1), N-(4-aminobenzylidene)-2-methoxybenzene-1,4-diamine (DA2), N-(4-aminobenzylidene)-2-methylbenzene-1,4-diamine (DA3), N-(4-aminobenzylidene)-3-methylbenzene-1,4-diamine (DA4) and N,(4-aminobenzylidene)-2-hydroxybenzene-1,4-diamine (DA5)--were prepared and condensed with 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) to obtain poly(azomethine imide). All synthesized polyimides PI(1-5) were fully characterized by elemental analyses, FTIR, ^{1}H-NMR, having amorphous nature and are soluble in dmac, dmf, and dmso, *m*-cresol due to presence of azomethine functionality. The inherent viscosities and moisture absorption of all polyimides lie in the range of 0.65-0.85 dL gm^{-1} and 0.68-0.82% respectively. Thermal stability was assessed by 10% weight loss temperature and the degradation temperature of the resultant polymers falls in the ranges from 480-535 °C in nitrogen. The glass transition temperature was in the range of 225-330 °C. Due to above mentioned attractive properties, polyimide-based material are attractive for processable high-performance engineering plastics and starting material for fabrication of new polymers.

Keywords: Polyimide, Diamines, Glass Transition Temperature, Schiff Base, Thermal Stability

INTRODUCTION

Polyimides are considered as part of high performance polymer materials class. Aromatic polyimides with extraordinary properties like excellent electrical, good mechanical behavior, incredible stability and outstanding chemical and heat resistance have a wide range of applications in electronics, composite materials, coatings and membranes [1,2]. However, their limited solubility, high glass transition and melting temperatures create difficulties in their processing. That is why limited applications of these rigid polyimides in technological and industrial applications are observed. The main reason for this behavior is the rigid structure and strong interaction among the polyimide chains. Extensive research has been done to improve their solubility without disturbing their excellent properties [3,4]. A large number of possibilities exist in altering chemical structures to synthesize polymeric material by maintaining their excellent level of thermal and mechanical properties. Several modifications have been made in their chemical structure by the incorporation of bulky alkyl side substitution, flexible aryl or alkyl ether linkages and asymmetric biphenyl moieties in the backbone of rigid polyimides [5-7]. Through incorporation of flexible linkages, an improvement in solubility and significant processability has been achieved by altering their crystallinity and intermolecular interactions [8,9]. The incorporation of aliphatic segments and non-copla-

nar structures also helps to improve the solubility of polyimides but is deleterious for thermal and mechanical properties [10-12]. To achieve best quality polyimides, there is a need to design new monomers (diamines and dianhydride) with structural modifications [13,14]. Many efforts have been pursued to design and synthesize new diamines and dianhydride monomers, thus to generate a wide range of polyimides with promising processability and solubility for various technological and industrial applications [15-17]. Polymers with a Schiff-base structure (polyazomethine) have been drawing the attention of researchers for more than 50 years. Studies on azomethine-based polymers have been conducted by many research groups and a great diversity of structures has been obtained. It is well-known that fully aromatic Schiff-base polymers are of high performance polymers presenting high thermal stability, good mechanical strength and semiconducting properties. Their poor solubility in simple organic solvents make it difficult to obtain high molecular weight polymers. Moreover, in many cases the transition temperature of conjugated polyazomethines is above the decomposition limit, and their technical applications are strongly limited by their sensitivity to acidic hydrolysis and thermal exchange reactions between different azomethine groups. The inclusion of polyazomethines in rotaxane architecture was already proposed as a useful method to improve their processability [18-20]. Generally, polyazomethines are synthesized by polycondensation reactions method that has some disadvantages, among them being a high reaction temperature and the use, in some cases, of specific catalysts [21-23]. The present work describes the synthesis and characterization of soluble aromatic polyazomethine. The monomers, aro-

matic azomethine diamines, and polyimides, **PI (1-5)** were characterized by elemental analysis, FT-IR and ^{1}H-NMR spectroscopy. The aromatic diamines containing azomethine moiety were incorporated in polymer backbone to examine their structure-property relationship in terms of inherent viscosity, solubility in various solvents, thermal stability, glass transition temperature and nature of polyimides in terms of crystallinity/amorphous.
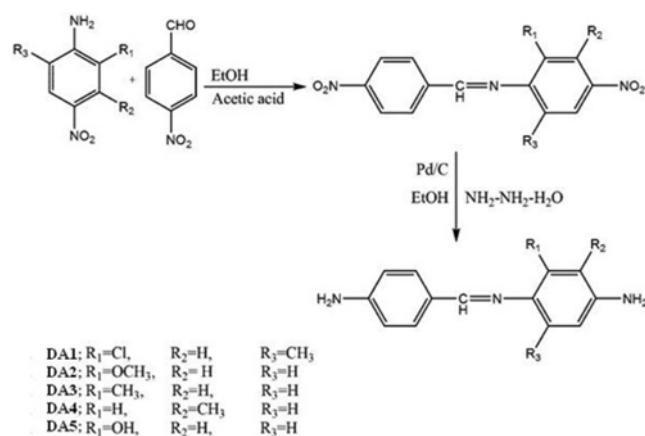
EXPERIMENTAL

1. Materials

2-Chloro-6-methyl-4-nitroaniline, 2-methoxy-4-nitroaniline, 3-methyl-4-nitroaniline, 2-methyl-4-nitroaniline, 2-hydroxy-4-nitroaniline, 4-nitrobenzaldehyde, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), acetic acid, dimethyl sulfoxide (dmso), dimethylformamide (dmf), N,N-dimethylacetamide (dmac), N-dimethylpyrolidone (nmp), *m*-cresol, methanol, ethanol, toluene, hydrazine monohydrate.

2. Measurements

^{1}H, NMR spectra were recorded by using deutrated dimethylsulfoxide (dmso-d_6) as an external solvent and tetramethylsilane as an internal reference. FT-IR spectra were recorded in the range 400-4,000 cm^{-1}. Melting points of monomers were noted on digital melting point apparatus. Viscosities were determined by a Gilmont falling ball viscometer in H_2SO_4. Solubility was determined in different solvents. Moisture absorption values were determined by change in weight of dried synthesized polymers before and after immersion in water at 25 ^{o}C for 24 hrs.

3. Synthesis of Monomers

A series of new diamine monomers--N-(4-aminobenzylidene)-2chloro-6-methylbenzene-1,4-diamine (DA1) N-(4-aminobenzylidene)-2-methoxybenzene-1,4-diamine (DA2), N-(4-aminobenzylidene)-2-methylbenzene-1,4-diamine (DA3), N-(4-aminobenzylidene)-3-methylbenzene-1,4-diamine (DA4) and N-(4-aminobenzylidene)-2-hydroxybenzene-1,4-diamine (DA5)--were synthesized in two steps as shown in Scheme 1, following a method reported in the literature [24,25]. In the first step dinitro monomer was synthesized by the condensation of nitroamines with 4-nitrobenzaldehyde. A two-neck flask equipped with condenser and magnetic stirrer was charged with 0.02 mol of nitroamine and 0.02 mol of 4-nitro-
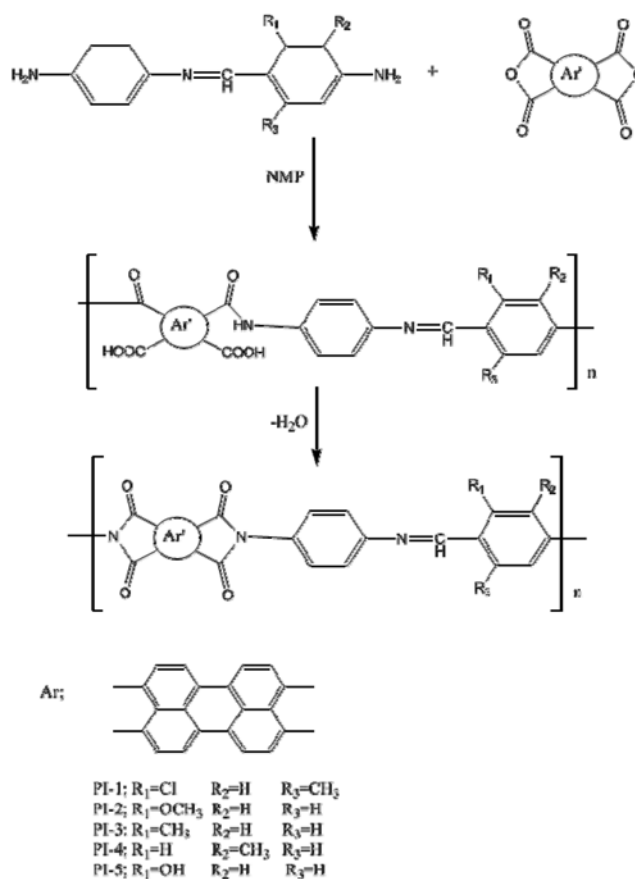
benzaldhyde in 20-25 ml of absolute ethanol. A few drops of glacial acetic acid were added that act as catalyst and the reaction mixture was stirred at room temperature for about an hour, then refluxed about 4-5 hrs. Completion of reaction was monitored by TLC. The reaction mixture was filtered and precipitates were collected. The crude product was washed with ethanol and recrystallized with methanol. In the second step, which was the reduction of the nitro compounds, 1 g of above synthesized dinitro compound was suspended in 250 ml of a two-neck flask with 10 ml of hydrazine monohydrate and 0.06 g of 5% palladium on carbon (Pd-C) and 60 ml of dry ethanol. The reaction mixture was refluxed for 16 hours and then filtered to remove Pd-C. Solvent was evaporated through rotary evaporator and the solid product obtained was recrystallized from ethanol.

4. Synthesis of Polyimide (PI)

A novel series of polyimides was synthesized by polycondensation of diamine monomers DA1, DA2, DA3, DA4 and DA5 with PTCDA by a reported method [29]. A three-neck flask equipped with nitrogen inlet and mechanical stirrer was charged with 1.2 mol of diamine in 5-10 ml of nmp. Then 1.2 mol of 3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA) was added slowly in the dissolved diamine in nmp. The reaction mixture was stirred for 24 hrs at room temperature to produce polyamic acid in inert conditions. The resulting polyamic acid solution was converted into polyimides through chemical imidization method. In polyamic acid solution, equimolar pyridine and acetic anhydride were added. The reac-

DA1: R_1=Cl, R_2=H, R_3=CH$_3$
DA2: R_1=OCH$_3$, R_2=H R_3=H
DA3: R_1=CH$_3$, R_2=H, R_3=H
DA4: R_1=H, R_2=CH$_3$ R_3=H
DA5: R_1=OH, R_2=H, R_3=H

Scheme 1.

PI-1; R_1=Cl R_2=H R_3=CH$_3$
PI-2; R_1=OCH$_3$ R_2=H R_3=H
PI-3; R_1=CH$_3$ R_2=H R_3=H
PI-4; R_1=H R_2=CH$_3$ R_3=H
PI-5; R_1=OH R_2=H R_3=H

Scheme 2.

tion mixture was stirred at room temperature for one hour and then heated at 100 °C for 3 hrs. The resulting solution was poured into methanol and fibrous precipitates of polyimides were collected and dried as shown in Scheme 2.

RESULTS AND DISCUSSION

Five different polyimides were synthesized by polycondensation method. All the synthesized diamines were characterized by elemental analysis, FT-IR and ^{1}H-NMR. FT-IR and NMR spectroscopic techniques confirmed the structures of diamines monomers and polyimides. Physical data of diamines is presented in Table 1.

1. IR Spectroscopy

Chemical structures of the synthesized diamines and polyimides were identified by FT-IR analysis and spectral data of the investigated monomers, diamines (DA1-DA5) and their respective polyimides **PI(1-5)** is shown in Tables 2 and 3. The formation of polyamic acid (PAA) was confirmed by the presence of absorption bands in the region of 3,500-3,200 cm^{-1} due to the amino (NH) and hydroxyl (OH) groups and amide carbonyl absorption at 1,690 cm^{-1}. The dehydration cyclization of PAA to an imide ring was confirmed by the disappearance of the band at 1,690 cm^{-1} (related to C=O of amic acid), N-H vibration at 3,500 and 3,200 cm^{-1}, and the appearance of a new characteristic absorption of the imide ring at 1,785-

Table 1. Physical data of diamines

Diamines	Molecular formula	Melting point °C	Yield (%)	Solubility	Elemental analyses		
					%C (Found)	%H (Found)	%N (Found)
DA1	$C_{14}H_{15}N_3Cl$	152±1	78	CH$_3$OH C$_2$H$_5$OH DMSO CH$_2$Cl$_2$	73.00 (72.54)	6.16 (6.15)	19.9 (19.7)
DA2	$C_{14}H_{15}N_3O$	148±1	75	CH$_3$OH, C$_2$H$_5$OH DMSO CH$_2$Cl$_2$	70.00 (70.05)	6.25 (6.3)	17.5 (17.4)
DA3	$C_{14}H_{15}N_3$	162±1	85	CH$_3$OH DMSO, CH$_2$Cl$_2$	75.00 (74.85)	6.69 (6.5)	18.7 (18.5)
DA4	$C_{14}H_{15}N_3$	185±1	87	CH$_3$OH DMSO CH$_2$Cl$_2$	75.00 (74.5)	6.69 (6.70)	18.7 (18.45)
DA5	$C_{13}H_{13}N_3O$	175±1	80	CH$_3$OH DMSO CH$_2$Cl$_2$	68.7 (68.5)	5.72 (5.70)	18.5 (18.41)

Table 2. FTIR and ^{1}H NMR of diamines

| Compound	IR (KBr)/cm^{-1}	^{1}H NMR (dmso-d_6, δ, ppm) (s: singlet, m: multiplet)
DA1	3405, 3315 (NH$_2$) 1650 (C=N)	2.14 (s, 3H, CH$_3$); 5.96 (-NH$_2$); 6.48-7.60 (m, 7H, aromatic); 8.76 (s, 1H, azomethine)
DA2	3400, 3326 (NH$_2$) 1635 (C=N)	3.83 (3H, OCH$_3$); 6.15 (-NH$_2$); 6.88-7.90 (m, 7H, aromatic); 8.21 (s, 1H, azomethine)
DA3	3410, 3330 (NH$_2$) 1628 (C=N)	2.14 (s, 3H, CH$_3$); 5.88 (-NH$_2$); 6.61-7.30 (m, 7H, aromatic); 8.52 (s, 1H, azomethine)
DA4	3400, 3328 (NH$_2$) 1655 (C=N)	2.14 (s, 3H, CH$_3$); 5.64 (-NH$_2$); 6.55-7.86 (m, 7H, aromatic); 8.16 (s, 1H, azomethine)
DA5	3404, 3365 (NH$_2$) 1675 (C=N), 3150 (OH)	5.91 (-NH$_2$); 6.38-7.10 (m, 7H, aromatic); 8.44 (s, 1H, azomethine); 9.68 (OH)
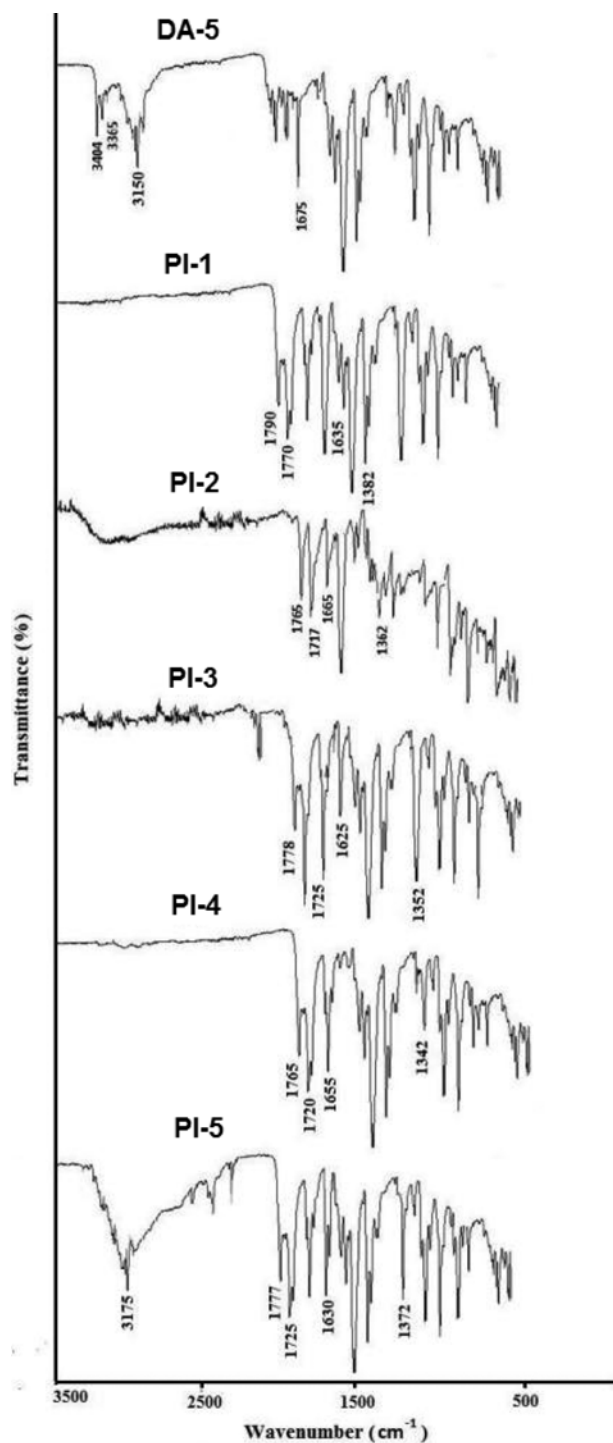
Fig. 1. IR spectra of DA-5 and polyimides (PI-1 to PI-5).

Fig. 2. ^{1}H nmr of PI-1, PI-2 and PI-5.

1,710 cm^{-1} for (CO)$_{asym}$ and (CO)$_{sym}$ stretching, respectively, as shown in Fig. 1. An absorption band at 1,628-1,655 cm^{-1} corresponding to the Schiff base group (-CH=N-) is observed. The disappearance of the amide and carbonyl bands indicated a virtually complete conversion of the imide ring in polyimides [26].

2. ^{1}H-NMR Spectroscopy

Formation of diamines and respective polyimides also confirmed by ^{1}H-NMR and data is presented in Table 3 and Table 4. ^{1}H NMR
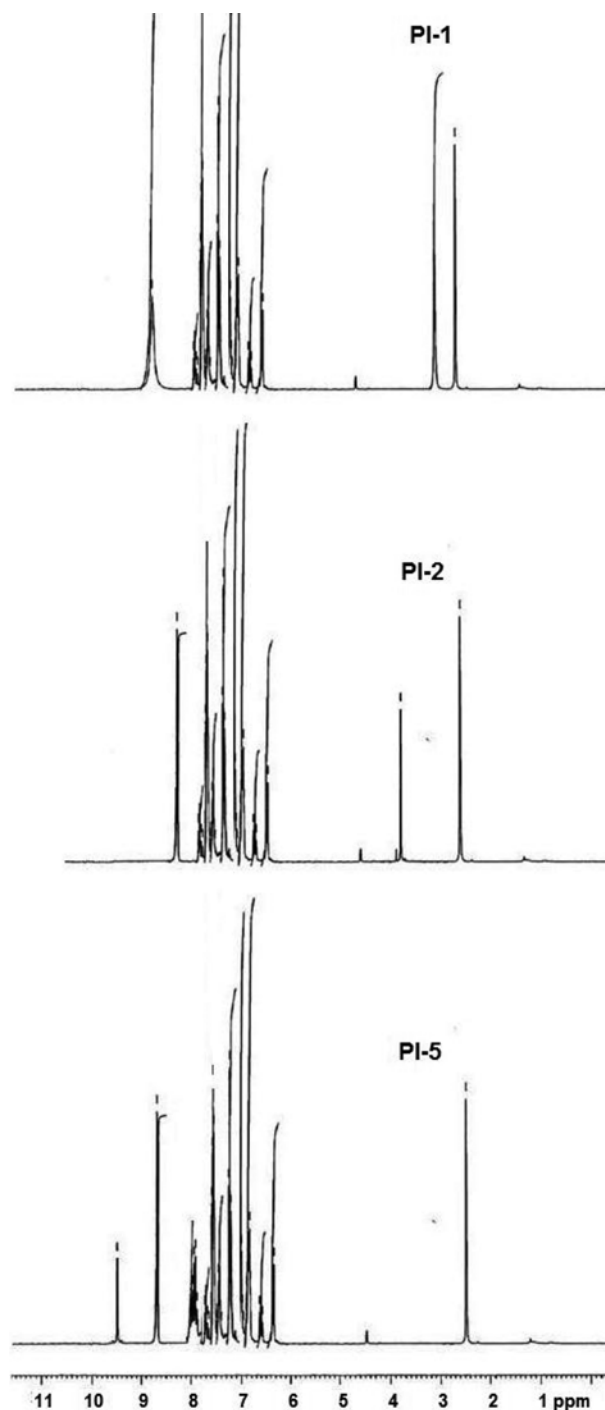
confirmed the reduction of nitro compounds into amines by high field shift of aromatic protons from 8.33 to 6.68 and 7.43. Signals at range 5.64-6.15 are due to NH$_2$ protons. Characteristic signals of C=N- at 8.16-8.76 in ^{1}H NMR spectra of diamines and poly-mer confirmed the of azomethine moiety. The signals at 2.14 and 3.83 ppm correspond to methyl and methoxy protons in the mono-mers as well as in polymer. The phenolic protons always give a sin-glet at high δ values (ca 9.68 ppm). The aromatic protons at about 6.00-8.50 ppm in the ^{1}H NMR spectra confirmed the imidic struc-

Table 3. FTIR, ^{1}H NMR of polyimides (PI-1-PI-5)

Compound	IR (KBr)/cm^{-1}	^{1}H NMR (dmso-d_6, δ, ppm) (s: singlet, m: multiplet)
PI-1	1710, (CO)$_{sym}$, 1785 (CO)$_{asym}$ 1635 (C=N) 1382 (C-N)	2.11 (s, 3H, CH$_3$); 6.45-7.80 (m, aromatic protons); 8.71 (s, 1H, azomethine)
PI-2	1717, (CO)$_{sym}$, 1765 (CO)$_{asym}$ 1665 (C=N) 1362 (C-N)	3.61 (3H, OCH$_3$); 6.55-7.82 (m, aromatic protons); 8.11 (s, 1H, azomethine)
PI-3	1725, (CO)$_{sym}$, 1778 (CO)$_{asym}$ 1625 (C=N) 1352 (C-N)	2.14 (s, 3H, CH$_3$); 6.61-7.30 (m, aromatic protons); 8.33 (s, 1H, azomethine)
PI-4	1725 (CO)$_{sym}$, 1780 (CO)$_{asym}$ 1655 (C=N) 1342 (C-N)	2.13 (s, 3H, CH$_3$); 6.25-7.98 (m, aromatic protons); 8.15 (s, 1H, azomethine)
PI-5	1725 (CO)$_{sym}$, 1777 (CO)$_{asym}$ 1630 (C=N), 1372 (C-N), 3175 (OH)	6.61-8.10 (m, aromatic protons); 8.72 (s, 1H, azomethine); 9.55 (OH)

Table 4. Solubility and Inherent viscosity of polyimides (PI-1-PI-5)

Polyimide	DMSO	DMAc	DMF	THF	m-cresol	H$_2$SO$_4$	η_{inn} (dl/gm) (H$_2$SO$_4$)	Moisture absorption %
PI-1	++	++	+	−	++	+++	0.65	0.68
PI-2	+	+	−	−	+	+++	0.69	0.77
PI-3	++	+	+	+	+	++	0.78	0.71
PI-4	++	+	+	−	+	++	0.72	0.75
PI-5	+	++	+	+	++	+++	0.85	0.82

+++=soluble at room temperature, ++=soluble on heating, +=slightly soluble on heating, −=insoluble

ture of the polymers. The conversion of polyamic acid into polyimides was confirmed by deprotonation of amino group showed the complete imidization [27]. All the protons in the polyimides have been identified by their multiplicity pattern, and the total number of protons calculated from the integration curve is in agreement with the expected molecular composition of synthesized polyimides (PI-1-PI-5) (Fig. 2).

3. Viscosity Measurement

Viscosities were obtained by Gilmont falling ball viscometer. Values of inherent viscosities determined in H$_2$SO$_4$ of synthesized polyimides were calculated in the range of 0.65-0.85 dl·g^{-1} indicating higher molecular weight of polyimides [28,29]. The average molecular weights (Mw) of the polyimides determined from inherent viscosity were in the range of 65,517 to 85,676 g mol^{-1}.

4. Organosolubility of Polyimides

The solubility of polyimides was determined in different solvents like DMSO, DMAc, DMF, m-cresol and THF, and the data is listed in the Table 4. Some polyimides are soluble at room temperature and some are soluble on heating. Most of the polyimides show better solubility in most of the polar aprotic solvents. This progress in solubility might be due to the incorporation of aliphatic substituents like -Cl, -CH$_3$, -OCH$_3$, -OH in the backbone along with azomethine linkage. These substituted structures are responsible for minimizing the chain-to-chain interaction, increasing the free volume, hindering the dense chain packing and increasing polymer polar

solvent molecule interaction in the polymer chain. As a result, the solubility of azomethine polyimides from other reported polyazomethines is improved [31-33].

5. Moisture Absorption

Moisture absorption of polyimides was determined by weight changes of the dried compounds before and after immersion in ionized water at 25 °C. The moisture absorption of the polyimides ranges from 0.68-0.82%. The moisture absorption property of polyimides is mainly due to the chemical structure of polyimides, which might be increase the dielectric constant and decrease the mechanical strength [34].

6. Thermal Behavior

The thermal stability of the polymers was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It is clear that the thermal properties of the compounds strongly depended on their chemical structure, as a different behavior of polyimides was observed. The glass transition temperature Tg as a second-order endothermic transition could be considered as the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone. The flexible linkages decrease the energy of internal rotation, lowering the Tg [30]. Different intra- and intermolecular interactions including hydrogen bonding, electrostatic, ionic forces, chain packing efficiency and chain stiffness affected the T$_g$. The T$_g$ of the polyimides (PI-1-PI-5) was observed in the range of 225-330 °C, depending
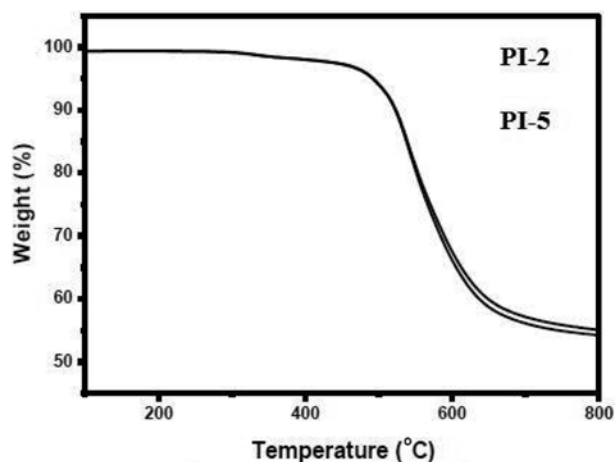
Fig. 3. TGA curves of PI-2 and PI-5.

Fig. 4. XRD patterns of PI-2 and PI-5.

Table 5. Thermal stability of the polyimides (PI-1-PI-5)

Polymer code	T_g (^{o}C)	Thermal stability			
		T_5 (^{o}C)[a]	T_{10} (^{o}C)[b]	T_{max} (^{o}C)[c]	Char yield (%)[d]
PI-1	245	438	485	500	45
PI-2	310	480	520	570	57
PI-3	290	455	480	495	44
PI-4	225	462	495	510	51
PI-5	330	495	535	590	58

[a]T_5%
[b]T_{10}%: temperatures at 5, 10% weight loss, respectively
[c]Temperature at which rate of decomposition is maximum
[d]Residual weight when heated to 600 ^{o}C in nitrogen

on the structure of diamine component and decreased with change in rigidity of the polymer backbone. The obtained polyimides began to decompose at 438-495 ^{o}C, 5% wt loss and show 10% wt loss in the range of 480-535 ^{o}C (Fig. 3). The prepared polyimides were thermally stable up to about 440 ^{o}C according to T_{10} and drastic degradation (T_{max}) occurred in the range of 470-510 ^{o}C. TGA analysis showed that the presented polyimides possessed good thermal stability without significant weight loss up to 380 ^{o}C. Data presented in Table 5 show that no thermal decomposition occurred below that temperature and the onset decomposition temperature was as high as 400 ^{o}C for all the polyimides. The glass transition temperature (Tg) of PIs samples, which is one of the key parameters of polymers when considering high-temperature device fabrication and the long-term heat releasing environment, was determined by the DSC analysis. All studied polyimides gave similar DSC profiles with no melting endotherms and a clear Tg transition. It can be concluded that by introduction of substituent along with -C=N-, polyimides having better solubility and higher thermal stability can be prepared as compared to other reported polyazomethines [31,32].

7. X-ray Diffraction

Wide angle X-ray diffraction analysis showed that all polyimides exhibited amorphous nature. In wide angle X-ray diffraction inte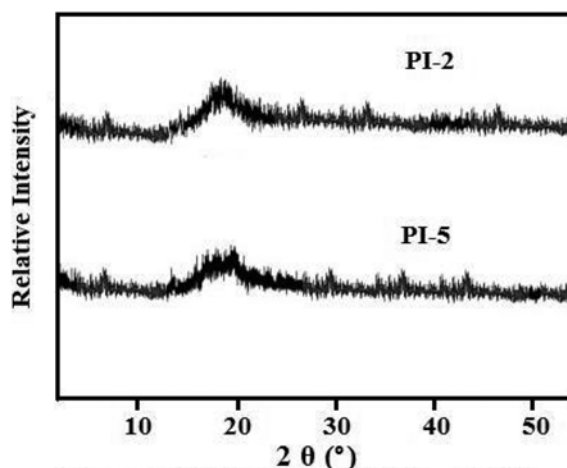nsity curve of all polyimides broad peaks were observed indicating the amorphous nature of polyimides. This might be due to the -C=N- group which inhibited the polymer chain packing, interactions and resulted in amorphous nature of polyimides and lack of crystalline morphology. This amorphous nature of polyimides is also reflected by the progress in solubility of polyimides Fig. 4.

CONCLUSION

An aromatic diamine-containing azomethine linkage, methyl, methoxy and hydroxyl side groups in the main chain were used to prepare a series of Schiff-base PIs in a two-step procedure via the reaction between diamine and commercially available aromatic dianhydride (3, 4, 9, 10-perylenetetracarboxylic dianhydride). The PIs were characterized and their physical properties, such as the solubility and viscosity, thermal properties, and thermal stability, were studied. The introduction of phenyl groups containing methyl and hydroxyl groups into the structures of the diamine monomers resulted in amorphous PIs with improved solubility in organic aprotic solvents such as dmso, dmac, dmf, m-cresol and thf. The results from DSC and TGA measurements indicated that the prepared PIs possess good thermal stability without significant weight loss up to 380 ^{o}C. The presence of an azomethine linkage in the polymer backbone could be responsible for the good thermal stability by increasing the initial and maximum degradation temperatures. Amorphous nature of polyimides was determined by XRD. Therefore, these polymers can be a potential candidate as processable high performance polymeric materials and used to synthesize certain blends having electrical conducting properties.

ACKNOWLEDGEMENTS

REFERENCES

1. M. K. Ghosh and K. L. Metal, *Polyimides: fundamentals and appli-*

cations, Marcel Dekker, New York (1996).

2. F. Li, S. Fang, J. J. Ge, P. S. Honigfort, J. C. Chen and F. W. Harris, *Polymer*, **40**, 4571 (1999).

3. K. H. Choi, K. H. Lee and J. G. C. Jung, *J. Polym. Sci Part A: Polym. Chem.*, **39**, 3818 (2001).

4. H. S. Li, J. G. Liu, J. M. Rui, L. Fan and S. Y. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 2665 (2006).

5. C. P. Yang, Y. Y. Su and F. Z. Hsiao, *Polymer*, **45**, 7529 (2004).

6. D. J. Liaw, F. C. Chang, M. K. Leung, M. Y. Chou and M. Klaus, *Macromolecules*, **38**, 4024 (2005).

7. B. Liu, W. Hu, T. Matsumoto, Z. Jiang and S. J. Ando, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 3018 (2005).

8. S. Tamai, A. Yamaguchi and M. Ohta, *Polymer*, **37**, 3683 (1996).

9. C. P. Yang, S. H. Hsiao and M. F. Hsu, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 524 (2002).

10. C. P. Yang, R. S. Chen and K. H. Chen, *J. Appl. Polym. Sci.*, **95**, 922 (2005).

11. T. M. Moy, C. D. Deporter and J. E. McGrath, *Polymer*, **34**, 819 (1993).

12. J. Xu, C. He and T. S. Chung, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 2998 (2001).

13. H. B. Zhang and Z. Y. Wang, *Macromolecules*, **33**, 4310 (2000).

14. D. M. Hergenrother, K. A. Watson, J. G. Smith, J. W. Connel and R. Yokota, *Polymer*, **43**, 5077 (2002).

15. X. Z. Fang, Q. X. Li, Z. Wang, Z. H. Yang, L. X. Gao and M. X. J. Ding, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 2130 (2004).

16. S. H. Hsiao and K. H. J. Lin, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 331 (2005).

17. Y. Shao, Y. F. Li, X. Zhao, X. L. Wang, T. Ma and F. C. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 6836 (2006).

18. D. S. Reddy, C. H. Chou, C. F. Shu and G. H. Lee, *Polymer*, **44**, 557 (2003).

19. S. Utkarsh, K. V. Rao and A. K. Rakshit, *J. Appl. Polym. Sci.*, **88**, 152 (2003).

20. A. Farcas and M. Grigoras, *High Perform. Polym.*, **13**, 201 (2001).

21. M. Grigoras and C. O. Catanescu, *Polym. Rev.*, **44**, 131 (2004).

22. M. Grigoras and G. Colotin, *Macromol. Chem. Phys.*, **202**, 2262 (2001).

23. C. H. Li and T. C. Chang, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 361 (1991).

24. C. J. Yang and S. A. Jenekhe, *Chem. Mater.*, **3**, 878 (1991).

25. S. Xie, Z. Zhang and W. Wei, *J. Korean Phy. Soc.*, **51**, 1536 (2007).

26. Y. Zheng, Y. Zhai, G. Li, B. Guo, X. Zeng, L. Wang, H. Yu and J. Guo, *J. Appl. Polym. Sci.*, **121**, 702 (2011).

27. D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to spectroscopy*, Harcourt Brace College Publishers, New York, 211 (1996).

28. H. S. Hsiao, C. P. Yang and C. L. Chung, *J. Polym. Sci., Part A Polym. Chem.*, **41**, 2001 (2003).

29. S. J. Zhang, Y. F. Li, X. L. Wang, D. X. Yin, Y. Shao and X. Zhao, *Chinese Chem. Lett.*, **16**, 1165 (2005).

30. R. Hariharan, S. Bhuvana and M. Sarojadevi, *High Perform. Polym.,* **18**, 163 (2006).

31. O. Catenescu, M. Grigoras, G. Colotin, A. Dobreanu, N. Hurduc and C. I. Simionescu, *Eur. Polym. J.*, **37**, 2213 (2001).

32. B. J. Vasanthi and L. Ravikumar, *Eur. Polym. J,* **43**, 4325 (2007).

33. G. Yu, C. Liu, H. Zhou, J. Wang, E. Lin and X. Jian, *Polym.*, **50**, 4520 (2009).

34. P. Boinard, W. M. Banks and R. A. Pethrick, *Polym.*, **46**, 2218 (2005).