Research artical Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Synthesis and Characterization of Novel Aromatic Poly (ester-imide)s ContainingBulkyPendant groupand Heterocyclic Moiety

ChristabelShaji Y.*, Rose G. Leema and Sinthuja S. Ajith

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil, Kanyakumari District, Tamil Nadu. INDIA.

ABSTRACT:

Tetrimide-dicarboxylic acids were synthesized from a commercially available monomer 2,6-diaminopyridine and a newly synthesized monomer bis(4-amino-3.5-dimethyl phenyl) 4′methoxynaphthyl methane, on treatment with pyromelliticdianhydride and *p*-amino benzoic acid.This on chlorination with excess of thionyl chloride, the corresponding diacidchlorides were obtained. These tetrimide- diacid chlorides on polycondensed with 1,4-dihydroxy benzene has resultedpoly(ester-imide)s. The synthesized polymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR and UV- visible spectroscopy. The properties of the poly(ester-imide)s such as thermal stability, inherent viscosity and solubility were also studied. The crystallinity of the polymer was evaluated by means of X-ray diffraction patterns. The newly synthesized poly(ester-imide)s exhibit high thermal stability, good solubility and processability.

KEYWORDS: 4′-methoxynaphthaldehyde, Tetrimide-dicarboxylic acids, pyromelliticdianhydride, tetrimidediacid chloride, Poly (ester-imide)s, inherent viscosity.

***Corresponding author:**

Christabel Shaji Y.

Department of Chemistry, Holy Cross College (Autonomous),

Nagercoil, Kanyakumari District, Tamil Nadu. INDIA.

1 INTRODUCTION

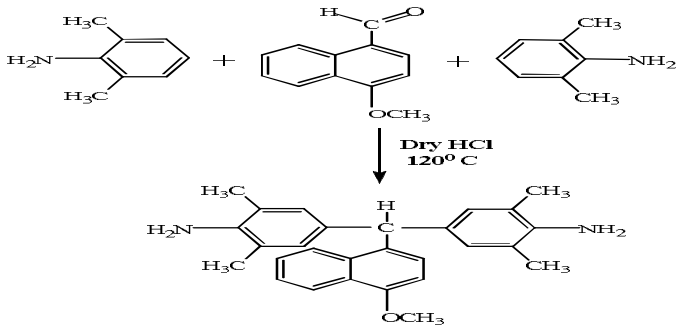
Polyimides are one of the high-performance materials with excellent thermal stability, dimensional stability and high electronic property. Poor solubility and processability are the major problems for wide the application of polyimides. Certain approaches are used to increase the solubility and processability of polyimides without sacrificing their thermal stability. This includes the synthesis of poly(ester-imide)s, poly(siloxane-imide)s, poly(urethane-imide)s, poly(amide-imide)s, the introduction of flexible linkages, non-planar asymmetric units and bulky pendent groups along the polymer backbone chain [1,2.] Aromatic poly(ester-imide)s (PEIs) are thermally stable polymers widely used in coatings for enameled wires, high strength fibers, hot melt adhesives, heat resistant films and printed circuit boards [3]. The present study focus the synthesis of PEIs from newly synthesized tetrimide-dicarboxylic acid chlorides and aromatic diol by solution polycondensation using nitro benzene as solvent and pyridine as hydrogen chloride trap [4].

2 MATERIALS AND METHODS

2,6-dimethyl aniline,pyromelliticdianhydride, (PMDA), 2,6-diamino pyridine, 4-methoxy naphthaldehyde, N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), *p*-amino benzoic acid, 1,4-dihydroxy benzene, concentrated hydrochloric acid, toluene, acetone, chloroform, m-cresol, dimethyl sulphoxide (DMSO), N-methyl pyrrolidone (NMP), xylene, tetrahydrofuron(THF) were purchased from Sigma Aldrich. The solvents used for polymerization were purified according to standard methods.

2.1. Synthesis of Monomer

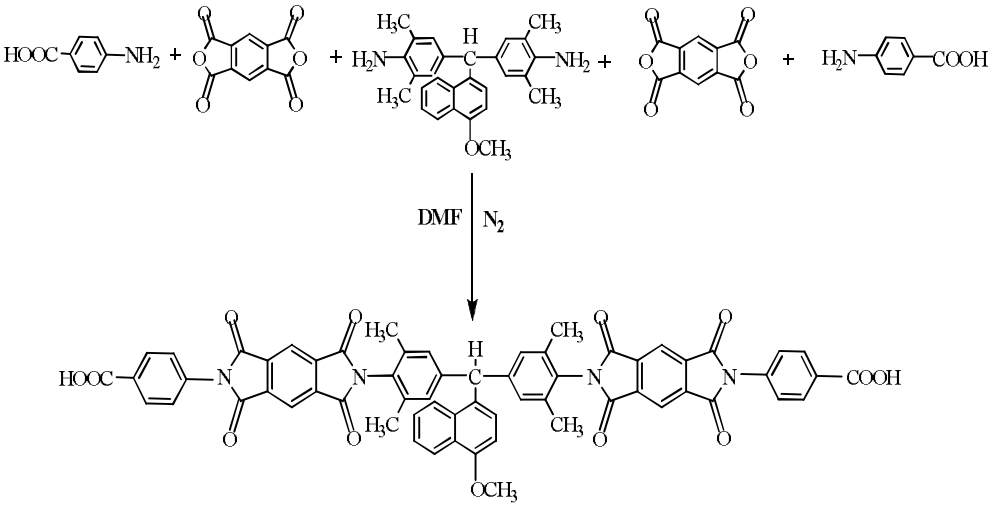
2,6-Dimethylaniline (12.1g, 0.1 mol) was charged into a 250 ml three necked round bottomed flask equipped with nitrogen inlet, an addition funnel and a reflux condenser. Concentrated hydrochloric acid (8 ml) was added drop-wise to the reaction vessel for 30 minutes. The solid substance obtained was melted by heating to 100 °C. To this4-methoxy naphthaldehyde (8.3 g, 0.05 mol) was added. After complete addition the temperature was raised to 120 °C and the reaction mixture was stirred at this temperature for 12 hrs, cooledand neutralized with sodium hydroxide solution. The solid product obtained was filtered, washed with methanol, recrystallized in ethanol and finally dried in vacuum at 70 °C for 12 hrs.(Sheme1).



Scheme 1. Synthesis of bis(4-amino-3,5-dimethylphenyl) 4'methoxynaphthylmethane(BADM)

2.2. Synthesis of Tetrimide-Dicarboxylic Acids

A three necked 150 ml RB flask equipped with nitrogen inlet and a reflux condenser was charged with bis(4-amino-3,5-dimethylphenyl) 4'methoxynaphthyl methane(BADM)(0.01 mole), *p*-amino benzoic acid (0.02 mole) and pyromelliticdianhydride (0.02 mole) in 20 ml DMF. The mixture was stirred at room temperature for two hrs. About 25 ml of toluene was then added and mixture was refluxed for 3 hrs. The water formed in the reaction was distilled off azeotropically using Dean-Stark trap. At the end of the reaction the residual toluene was distilled off under reduced pressure. After cooling, the obtained solution was trickled into water and the precipitated product was collected by filtration and dried in vacuum at 100°C for 12 hrs(Scheme 2). This experiment was repeated with same anhydride and acid but different monomer (i.e) 2,6-diamino pyridine.Figure1 represents the structure of tetimide-dicarboxylic acid from commercial monomer.



Scheme 2. Synthesis bis [(N-carboxy phenyl) 4-pyromellitimido 3,5 dimethyl phenyl] 4'-methoxynaphthyl methane (BCPMM)

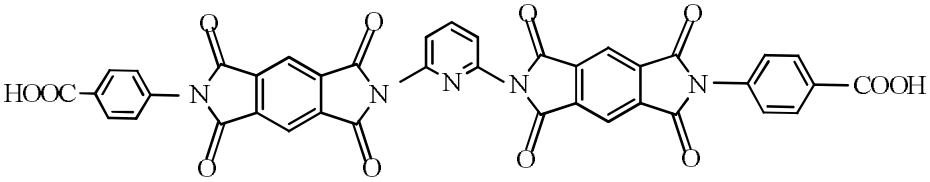
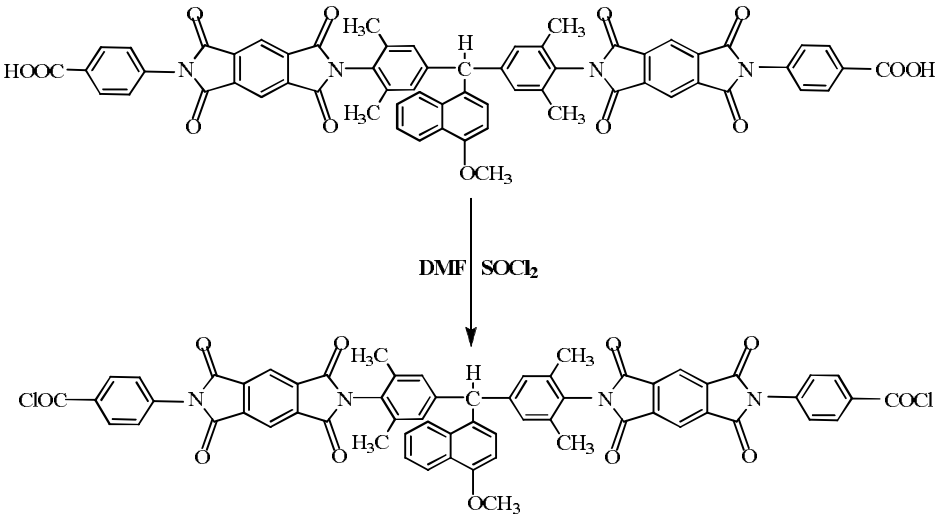


Figure 1.Structure of bis [(N-carboxy phenyl) 2-pyromellitimido] pyridine (BCPP)

2.3. Synthesis of Tetrimide-Diacid Chlorides

The synthesizedtetrimide-dicrboxylicacids (BCPMM and BCPP) were refluxed with an excess of thionyl chloride using DMF as a catalyst. The viscous solution obtained were cooled and trickled into excess methanol with vigorous stirring. The precipitates were filtered off, washed several times with hot methanol and dried in vacuum oven at 100°C for 7 hrs. The yields of the reactions were 83% and 85%(Scheme3). Figure 2 represents the structure of diacid chloride from pyridine monomer.



Scheme 3 Synthesis of bis [(N- benzoyl chloro) 4-pyromellitimido 3,5 dimethyl phenyl] 3'-methoxynaphthyl methane (BBCPMM)

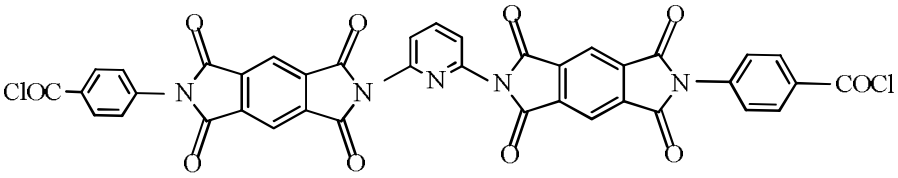
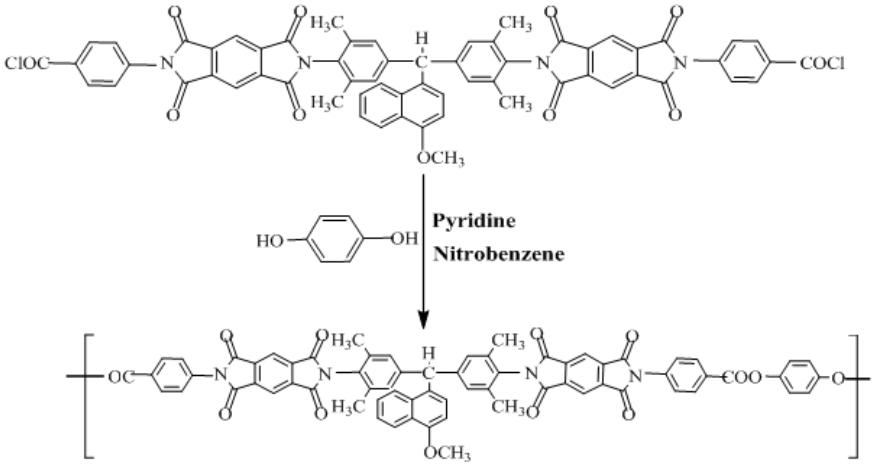


Figure 2 Structure of bis[(N-benzoyl chloro) 2-pyromellitimido] pyridine(BBCPP)

2.4. Synthesis of PEIs

1,4-dihydroxy benzene (0.02 mole), tetrimidediacid chlorides **(**BBCPMM and BBCPP) (0.01 mole), pyridine and nitrobenzene were homogenized at room temperature and subjected to a heating temperature of 170°C for 10 hrs. After the completion of the reaction, the mixture was allowed to cool, filtered and washed several times with water. The products were filtered off and dried at 100°C for 8 hrs in a vacuum oven. The yield of the reaction were 86 and 81% (Scheme 4).Structure of PEI-2 is given by Figure3.



Scheme 4. Synthesis of poly(ester-imide)s (PEI-1)

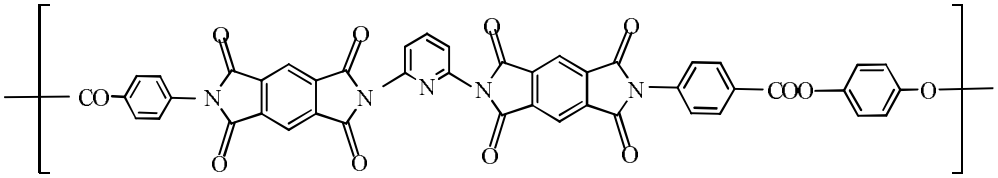


Figure 3. Structure of PEI-2

3 CHARACTERIZATION TECHNIQUES

3.1. Elemental Analysis

The elemental analysis data of poly(ester-imide)s are in good agreement with the calculated values. The values are given in Table 1.

Table1.Physico-chemical characteristics of PEIs

S. No.	Polymer code	Molecular Formula	% Yield	Elemental analysis (wt %)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1.	PEI-1	$(C_{68}H_{42}O_{13}N_4)_n$	86	72.72	72.15	3.74	3.53	4.99	5.35
2.	PEI-2	$(C_{45}H_{19}O_{12}N_5)_n$	81	65.77	65.10	2.31	2.70	8.52	9.12

3.2 IR Spectral Studies

FTIR spectroscopic technique is an important method in determining the structure of the polymers. The absorption peaks at 1726 and 1779 cm^{-1} correspond to symmetric and asymmetric stretching of the imide carbonyl group.The peak at 1364 cm^{-1} is due to the C-N-C stretching vibration of the imide ring. The peaks at 1115 and 731 cm^{-1} correspond to the imide ring deformation. The absorption peak at 2922 cm^{-1} corresponds to

C-H stretching of the methyl group. In addition to these characteristic vibrations, all the polymers show absorption peak around 1400-1460 cm^{-1} and 1540-1600 cm^{-1}, corresponding to aromatic ring vibrations. A strong characteristic absorption peak around 1715 and 1705cm^{-1}corresponds to aryl ester carbonyl stretching vibration and the peak around 1250 and 1212 cm^{-1} is due to the asymmetrical C-O-C stretching vibration of the ester group[5]. Figure 4 and 5 represents the IR spectrum of PEI-1 and PEI-2.

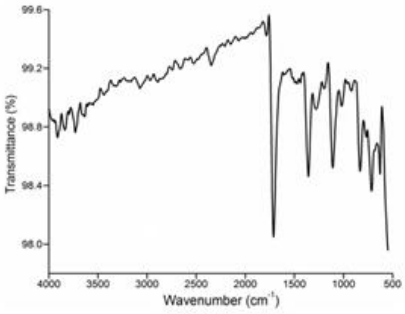


Figure 4IR spectrum of PEI-1

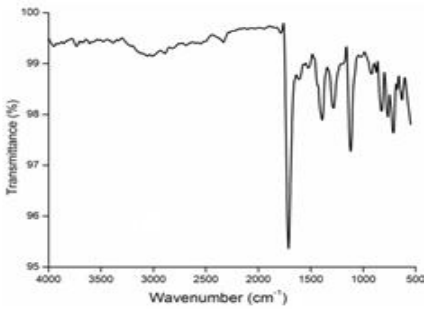


Figure 5 IR spectrum of PEI-2

3.3. ^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of the polymers are shown in Figures 6 and 7. The aromatic protons of the polymers resonate at varying δ values between 6.90 and 8.5 ppm depending on the polymer backbone structure. The aromatic protons of PMDA containing polymers appear in the farthest downfield region (8.6-8.8 ppm) due to the presence of electron withdrawing imide C=O group. The methyl proton of PEI-1 and PEI-2 appear in the region around 2.03 and 2.13 ppm.

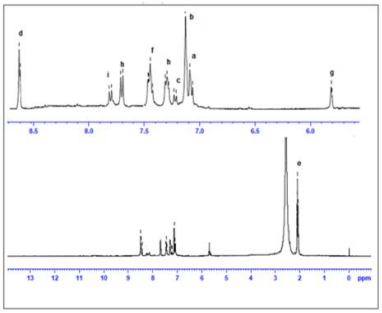


Figure6.^{1}H NMR spectrum of PEI-1

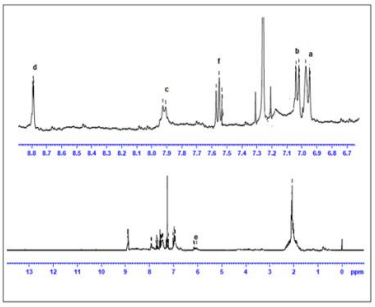


Figure7.^{1}H NMR spectrum of PEI-2

3.4. Solubility

The solubility of the PEIs were tested qualitatively in various organic solvents such as N-methyl pyrrolidone (NMP), dimethyl sulphoxide(DMSO), dimethyl acetamide (DMAc), chloroform ($CHCl_3$), tetrahydrofuran (THF), toluene, m-cresol and xylene. The results are reported in Table 2.

Table 2. Solubility of the PEIs

Polymer	NMP	DMSO	DMAc	$CHCl_3$	THF	toluene	*m*-cresol	Xylene
PEI-1	++	++	++	++	++	++	++	-
PEI-2	++	++	++	++	++	+-	+	-

Solubility keys: (++) soluble; (+) soluble on heating; (+-) partly soluble; (-) insoluble.

The newly synthesized PEIs show high solubility in solvents such as NMP, DMSO, DMAc, $CHCl_3$, toluene, m-cresol and xylene. The excellent solubility of PEI-1may be due to the presence of methyl group in the polymer backbone, which would decrease the packing density and intermolecular interactions of the macromolecular chain[6]. The PEI-2 shows lower solubility in the less polar solvents than PEI-1 because of the molecular symmetry of the pyridine moiety, which allows better packing and strongerinter chain interactions[7].

3.5 Optical Studies

The pyridine containing polymer (PEI-2) showshigher cut off wavelength than the PEI-1 because of their rigid closely packed structure which increases the electronic conjugation between the polymer chains. The polymer (PEI-1) exhibits shorter cut off wavelength because of the presence of bulky pendant group in the polymer chain. The bulky pendant unit inhibits chain-chain interaction between the polymer chains by increased entropy mechanism and thereby, it decreased the CTC formation.

3.6. Inherent Viscosity

The viscosity values of the PEIs depend on the reactivity of the diamine, the anhydride and with the extent of polymer chain mobility [8].The presence of bulkygroups on the benzene ring increases the segmental rigidity of the polymer backbone resulting in increased solution viscosity. The results are tabulated in Table 3.

Table-3 Viscosity and optical properties of PEIs

S.No	Polymer Code	Inherent viscosity (dL/g)	λ_0 nm	Transmittance %
1	PEI-1	1.06	370	78
2	PEI-2	0.83	401	71

3.7. X-RAY Diffraction Studies

The X-ray diffraction patterns shows PEIs are almost amorphous or semi-crystalline. This could be attributed to the introduction of the bulky pendant group (naphthyl) which resulted in increased chain distance and decreased chain-to-chain interactions there by leading to decrease in crytallinity[9]. The amorphous diffraction patterns of PEIs may be due the presence of bulky pendant napthyll group that loosen the chain packing and decrease the intra molecular forces between the polymer chains causing a decrease in crystallinity [10].The pyridine based PEI shows slightly sharp diffraction peaks, indicative of moderate level of crystallinity.

This may be due to the absence of pendant group and high density of hydrogen bonding between polymer chains of highly symmetric pyridine ring.

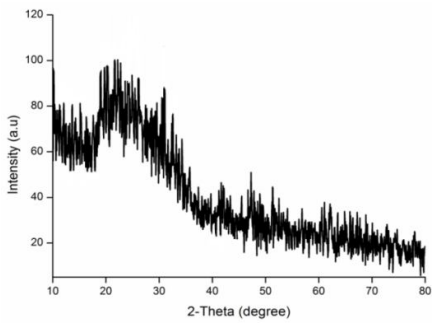


Figure-8.XRD patterns of PEI-1

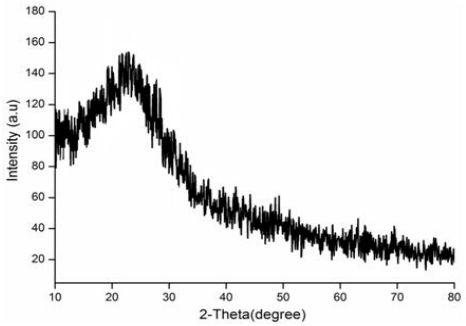


Figure-9.XRD patterns of PEI-2

3.8. Thermal Analysis

The synthesized PEIs are stable up to 420^{0}C, indicating high thermal stability. The high thermal stability of the polymers could be attributed to the incorporation of imide and ester groups and phenylation of backbone[9].Thermograms of synthesized PEIs exhibit two-stage decomposition behavior at elevated temperature. The first stage of weight loss occurs in the range of 420-450^{0}C and it might be attributed to the early degradation of less stable ester groups, and second weight loss occurring in the range 470-550^{0}C is most probably due to the degradation of rigid imide segments [10,11].

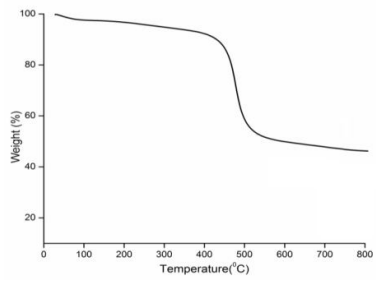


Figure 9.TGAThermogram of PEI-1

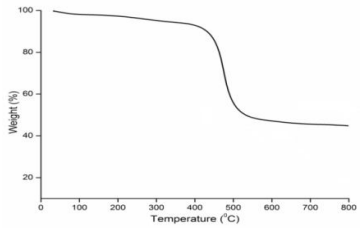


Figure 10.TGAThermogram of PEI-2

4 CONCLUSION

The new poly(ester-imide)s (PEIs) were synthesized from the precursor tetrimidediacid chlorides with 1,4-dihydroxy benzene in the presence of pyridine and nitrobenzene. The elemental analysis and the spectral studies confirm the structure of the PEIs. The introduction of heterocyclic moiety in the polymer backbone has effectively enhanced the thermal stability. The incorporation of the flexible ester linkage and pendant group in the polymer backbone has increased the solubility of the PEIs and hence, the processability may also be increased .Therefore the newly synthesized PEIs can be used as high performance polymers.

REFERENCES

1. Banihashemi, A and Behniafar, H., "Synthesis and characterization of novel aromatic poly(amide-imide)s derived from2,2′-bis(4-trimellitimidophenoxy)biphenyl or 2,2′-bis(4-trimellitimidophenoxy)-1,1′-binaphthyl and various aromatic diamines" Polymer International.2003;52:1136-1144.
2. Kricheldorf, H.R., "Liquid-crystalline polyimides".Adv. Polym.Sci.1999; 141:83-188.
3. Liaw, D.J., Chang, F. C., Leung, M.K., Chou, M.Y and Muellen, K.,"High thermal stability and rigid rod of novel organosoluble polyimides and polyamides based on bulky and noncoplanar naphthalene-biphenyldiamine". Macromolecules.2005; 38:4024-4029.
4. Liaw, D.J., Fan, C.H., Lin, C.C and Wang, K.L., "Synthesis and characterization of new soluble poly(ester-imide)s containing noncoplanar 2,2′-dimethyl-4,4′-biphenylene unit".J.Appl. Polym. Sci., 2004;92:2486-2493.
5. Li, F., Fang. S., Ge, J.J., Hongifort, P.S., Chen, J.C., Harris, F.W and Cheng, S.Z.D., "Diamine architecture effects on glass transitions, relaxation processes and other material properties in organo-soluble aromatic polyimide films".Polym.,1999;40:4571-4583.
6. Hsiao, S.H., Chung, C.L and Lee, M.L., "Synthesis and characterization of soluble polyimides derived from 2′,5′-bis(3,4-dicarboxyphenoxy)-p-terphenyldianhydride".J. Polym. Sci.Part A:Polym. Chem.,2004;42:1008-1017.
7. St.Clair, T.L., St. Clair, A.K., Smith, E.N., "In Structure–Solubility Relationships in Polymer" Harries, F. W.; Seymour, R. B., Eds.; Academic Press: New York.1977, 199.
8. Wang, C.S and Leu, T.S., "Synthesis and characterization of polyimides containing naphthalene pendant group and flexible ether linkages".Polymer, 2000;41:3581-3591.
9. Ataei, S.M., Laleh, N,B and Amirshaghaghi, A., Polym. Degrad. Stabil.,2006;91:2622-2631.
10. Hsiao, S.H and Dai, L.R.,"Synthesis and properties of poly(ether imide)s based on the bis(ether anhydride)s from hydroquinone and its derivatives"J. Polym. Part A: Polym. Chem.,1999;37:665-675.
11. Wang, C.S and Shieh, J.Y., "Synthesis and properties of epoxy resins containing 2-(6-oxid-6*H*-dibenz[c,e] [1,2]oxaphosphorin-6-yl)1,4-benze-nediol". Polymer,1998;39:5819-5829.