Synthesis, Characterization, and Properties of Poly(amide-imide)s from a New Diimide-Diacid by Direct Polycondensation with Various Diamines

Mousa Ghaemy, Nasim Movagharnezhad, Soheila Khajeh

Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

ABSTRACT: A new diimide-diacid, 2,2′-(5-(4-(4-(4,5-diphenyil-1*H*-imidazol-2-yl)phenoxy)phenylcarbam-oyl)-1,3-phenylenebis(1,3-dioxoisoindoline-5-carboxylic-acid)(DADA), was synthesized from the reaction between trimellitic anhydride and a new diamine, *N*-(4-(4-(4-(4,5-diphenyl-1H-imidazole-2-yl)phenoxylphenyl)-3,5-diaminobenzamide(NIDA). The direct polycondensation of DADA with various diamines was carried out in NMP in the presence of triphenylposphite and pyridine as condensing agents. The resulting poly(amide-imide)s (PAIs) were amorphous, readily soluble in many polar aprotic solvents and showed inherent viscosities of 0.35–0.47 dL/g.

According to thermal analysis, these polymers exhibited glass transition temperatures (T_gs) in the range of 207–271°C, and their initial decomposition temperature (T_i) varied from 260 to 330°C and temperature of 10% weight loss (T_{10}) from 325 to 520°C in N_2. These polymers in NMP solution exhibited strong UV–vis absorption maxima at 320 nm and their fluorescence emission peaks appeared around 425–450 nm. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3679–3688, 2011

Key words: poly(amide-imide); direct polycondensation; solubility; thermal properties

INTRODUCTION

Aromatic polyimides are well recognized as a class of high-performance materials due to their remarkable thermal-oxidative stability, excellent electrical, and mechanical properties.[1,2] However, poor thermoplastic fluidity and solubility due to interaction between polyimide chains and their rigid structure, much emphasis was placed on the synthesis of polyimides by the incorporation of flexible groups or bulky groups to improve their solubility without much sacrifice in thermal characteristics.[3–6] To overcome the difficulties in processing, various co-polyimides such as poly(amide-imide)s (PAIs), Poly(amide-ester-imide)s, and poly(ester-imide)s were developed.[7–10] PAIs are well known as a class of polymers with good compromise between thermal stability and processability.[11–13] There is a growing interest in PAIs for a variety of applications as they retain good mechanical properties at high temperatures when compared with other aromatic thermostable polymers.[14] Imidazole ring is a useful *n*-type building block with high-electron affinity and good thermal stability and has been successfully incorporated in small molecules and polymers as the electron-transport component of OLEDs.[15–21] Moreover, lophine, 2,4,5-triphenylimidazole, and its derivatives are well-known potential chemiluminescence compounds and have significant analytical applications using their fluorescence and chemiluminescence properties.[22,23] One of convenient and efficient ways of synthesis of high-molecular weights PAIs, is the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by means of the Yamazaki–Higashi phosphorylation technique.[24–26] The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides, or isocyanates.[27–29]

This study explores the synthesis and basic characterization of several novel PAIs having pendent triaryl imidazole moiety by direct polycondensation of a new synthesized diimide-diacid, 2,2′-(5-(4-(4-(4,5-diphenyil-1*H*-imidazol-2-yl) phenoxy)phenylcarb-amoyl)-1,3-phenylene bis(1,3-dioxoisoindoline-5-carboxylic acid), with various aromatic and aliphatic diamines. This new diimide-diacid and the intermediates were characterized by FTIR and NMR spectroscopy, and elemental analysis. The presence of the bulky pendent triaryl imidazole moiety not only hinders close packing and between chains interactions, which will improve polymer solubility through interaction with solvent molecules, but also preserves their structural rigidity. The poly(amide-imide)s were characterized

Correspondence to: M. Ghaemy (ghaemy@umz.ac.ir).

by FT-IR and ^{1}H-NMR spectroscopy and their properties such as viscosity, solubility, X-ray diffractograms (XRD), thermal, and photophysical were measured.

EXPERIMENTAL

Materials

All materials and solvents were purchased either from Merck or from Fluka Chemical Co. Benzil, 4-hydroxybenzaldehyde, 3,5-dinitrobenzoylchloride, p-fluoronitro benzene, ammonium acetate, hydrazine monohydrate, Pd/C, potassium carbonate, trimellitic anhydride, triphenyl phosphite (TPP), triethylamine (NEt$_3$), acetic acid, and reagent-grade aromatic diamines such as 4,4′-diaminodiphenyl ether, 4,4′-diaminodiphenyl methane, 4,4′-diaminodiphenyl sulfone, 1,4-diaminoanthraquinone, 1,6-diamino hexane, and solvents such as DMF, DMSO, ethanol, methanol, acetone, hexamethylphosphoramide (HMPA), and tetrahydrofuran (THF) were used without further purification. N-methyl-2-pyrrolidone (NMP), N,N-Dimethyl acetamide (DMAc), and pyridine were purified by distillation over calcium hydride under reduced pressure. LiCl and CaCl$_2$ were dried at 180°C in vacuum for 14 h.

Measurements

FTIR measurements were performed on a Bruker-IFS 48 spectrometer (Ettlingen, Germany). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in dimethyl sulfoxide-d_6 (DMSO-d_6) solution using a Bruker Avance 500 MHz instrument (Germany). Differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses were recorded on a Stanton Redcraft STA-780 (London, UK) at heating rate of 10°C/min under N$_2$. Inherent viscosity was measured by using an Ubbelohde viscometer in a concentration of 0.5 g/dL in NMP at 25°C. UV–visible and fluorescence emission spectra were recorded on a Cecil 5503 and Perkin-Elmer LS-3B spectrophotometers, respectively. X-ray diffraction patterns were obtained with Cu Kα radiation using a Simens D-500 diffractometer (Simens, Madison, WI). The scanning rate was 1.0°/min over the range of 2θ = 8–40°.

Monomer synthesis

4-(4,5-Diphenyl-1H-imidazol-2-yl) phenol (DIP)

In a 500 mL round-bottomed, two-necked flask equipped with a condenser, magnetic stirrer bar, and a nitrogen gas inlet tube, a mixture of (12.21 g, 0.1 mol) 4-hydroxy benzaldehyde, (21.02 g, 0.1 mol) benzil, (53.09 g, 0.70 mol) ammonium acetate and 300 mL glacial acetic acid was heated for 24 h. On cooling, the white precipitate was collected by filtration and washed with ethanol. The yield of the crude product was 27.42 g (87%). The crude product was recrystallized from ethanol to afford white solid with mp = 278–280°C. FTIR (KBr, cm^{-1}): 3423 (NH), 3031(OH), 1612 (C=C), and 1545 (C=N).

2-(4-(4-Nitrophenoxy) phenyl)-4,5-diphenyl-1H-imidazole (NPDI)

In a 100 mL round-bottomed, two-necked flask equipped with a reflux condenser and a magnetic stirrer bar, a mixture of (3.12 g, 0.01 mol) DIP, (1.37 g, 0.01 mol) p-fluoronitrobenzene, and (1.50 g, 0.01 mol) potassium carbonate was heated for 2 h in 40 mL DMAc. During this time, the progress of the reaction was followed by thin layer chromatography (TLC). Then the mixture was cooled and poured into 100 mL water. The precipitate was collected by filtration, washed with water and dried in a vacuum oven at 80°C for 12 h. The yield of the product was 96% and mp = 208–210°C. FTIR (KBr, cm^{-1}): 1522, 1346 (NO$_2$), 1254 (C—O—C stretching) and 1588 (C=N). Anal. Calcd. For C$_{27}$H$_{19}$N$_3$O$_3$: C, 74.82%; H, 4.38%; N, 9.69%. Found, C, 74.93%; H, 4.44%; N, 9.59%.

4-(4-(4, 5-Diphenyl-1H-imidazol-2-yl) phenoxy) aniline (DIPA)

In a 100 mL two-necked round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a dropping funnel, a mixture of (4 g, 9.20 mmol) NPDI, 0.5 g of 10% Pd/C and 20 mL ethanol was charged. A total of 3.50 mL hydrazine monohydrate was added drop-by-drop over a 30-min period through dropping funnel. The reaction mixture was heated for 1 h, and then filtered while hot to remove Pd/C and heated to reduce the volume of solvent. After cooling, the precipitate was isolated by filtration and recrystallized from ethanol and dried in a vacuum oven at 80°C. The yield of the product was 85% and mp = 198–200°C. FTIR (KBr, cm^{-1}): 3443–3464 (NH$_2$), 1267 (C—O—C), 1520 (C=N), and 1492 (C=C). Anal. Calcd. for C$_{27}$H$_{21}$N$_3$O: C, 80.39%; H, 5.21%; N, 10.42%. Found, C, 80.48%; H, 5.35%; N, 10.52%.

N-(4-(4-(4,5-Diphenyl-1H imidazol-2-yl) phenoxy) phenyl)-3,5 dinitrobenzamide (DIDN)

In a 100 mL two-necked round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a dropping funnel, (3 g, 7.40 mmol) DIPA was dissolved in 50 mL acetone. 4 mL triethylamine (Et$_3$N) was added to the solution and (4.30 g, 7.40 mmol) 3,5-dinitrobenzoylchloride in 5 mL of dry
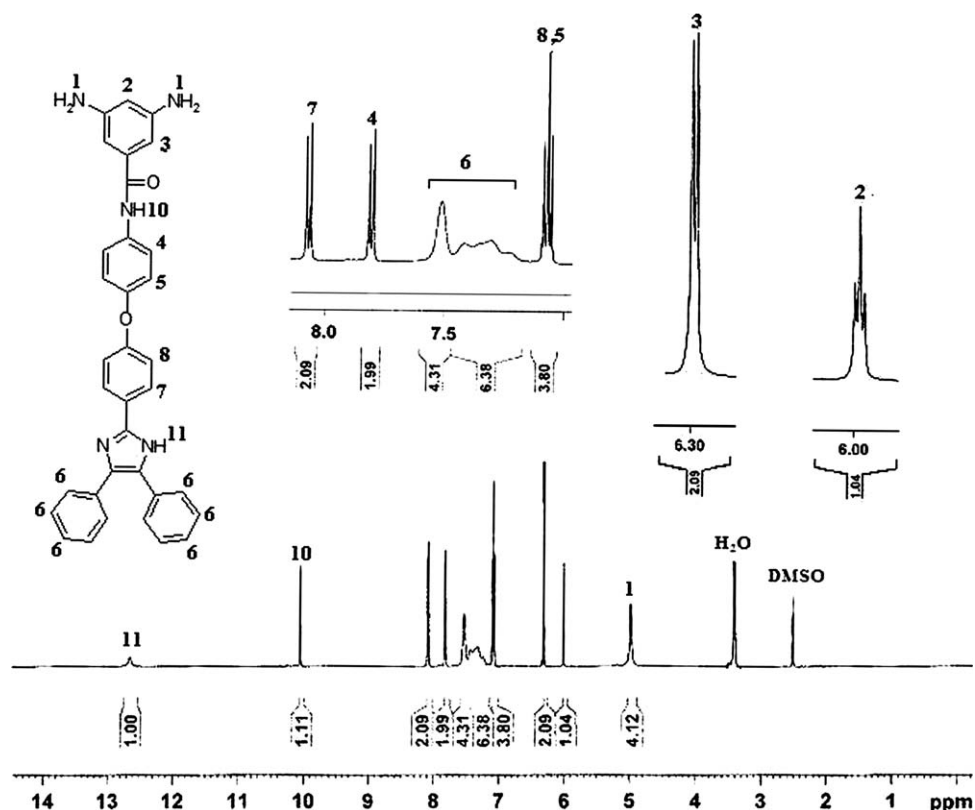
Figure 1 ^{1}H-NMR spectrum of diamine, DIDA.

acetone was charged into the mixture through dropping funnel. Then the reaction mixture was refluxed for 24 h. The progress of the reaction was followed by thin layer chromatography. After cooling at room temperature, the reaction mixture was poured into large volume of water. The orange powder was collected by filtration, washed, and dried overnight in a vacuum oven at 70°C. The powder was then recrystallized from methanol, the yield was 95% and mp = 187–190°C. FTIR (KBr, cm^{-1}): 1542–1345 (NO$_2$), 1664 (C=O), 1244 (C—O—C), 1608 (C=N), and 1502 (C=C). Anal. Calcd. for C$_{34}$H$_{23}$N$_5$O$_6$:C, 68.34%,; H, 3.85%; N, 11.72%. Found, C, 68.22% H, 3.92%; N, 11.80%.

N-(4-(4-(4,5-Diphenyl-1H imidazol-2-yl) phenoxy) phenyl)-3,5 diaminobenzamide (DIDA)

In a 100 mL two-necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer bar, (1 g, 1.67 mmol) DIDN was refluxed in 20 mL of absolute ethanol in the presence of 0.5 g of 10% Pd/C catalyst. A total of 1.5 mL hydrazine monohydrate was added drop-by-drop over a 30-min period through dropping funnel. The reaction mixture was further refluxed for 1 h, and then filtered while hot to remove the catalyst and heated to reduce volume of the solvent. On cooling, a white powder was isolated by filtration

and then recrystallized from ethanol. The crystals were dried in a vacuum oven at 70°C overnight. The yield was 81% and mp = 176–178°C. FTIR (KBr, cm^{-1}): 3458, 3367 (NH$_2$), 3347 (NH, amide), 3408 (NH, imidazole), 1658 (C=O), 1259 (C—O—C), 1593 (C=N), 1512 (C=C). ^{1}H-NMR (500 MHz, DMSO-d_6, for peak assignments: see Fig. 1): δ 4.96 (s, 4H, NH$_2$), aromatic protons at δ: 6.0 (t, 1H, J = 2 Hz), 6.29 (d, 2H, J = 2 Hz), 7.06 (d, 2H, J = 8 Hz), 7.08 (d, 2H, J = 8 Hz), 7.31–7.51 (m, 10H), 7.82 (d, 2H, J = 7.5 Hz), 8.07 (d, 2H, J = 7.5 Hz), 10.03 (s, 1H, N—H amide), 12.63 ppm (s, 1H, N—H imidazole). ^{13}C-NMR (500 MHz, DMSO-d_6, for peak assignments: see Fig. 2): δ 167.2 (C, C=O), 157.7, 152.9, 151.1, 149.1, 145.2, 136.9, 136.8, 135.9, 135.2, 131.1, 128.6, 128.4, 128.2, 127.9, 127.7, 127.0, 126.9, 126.4, 125.1, 121.8, 121.6, 119.7, and 117.6 ppm (C, Ar). Anal. Calcd for C$_{34}$H$_{27}$N$_5$O$_2$: C, 75.97%; H, 5.02%; N, 13.03%. Found, C, 76.10%; H, 5.27%; N, 12.98%.

2,2′-(5-(4-(4-(4,5-Diphenyil-1H-imidazol-2-yl)phenoxy) phenylcarbamoyl)-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) (DADA)

A flask was charged with (1 g, 1.87 mmol) DIDA, (0.72 g, 3.70 mmol) trimellitic anhydride, and 40 mL of acetic acid. The mixture was heated to reflux at 120°C for about 12 h. The mixture was then cooled and poured into methanol. The white precipitate

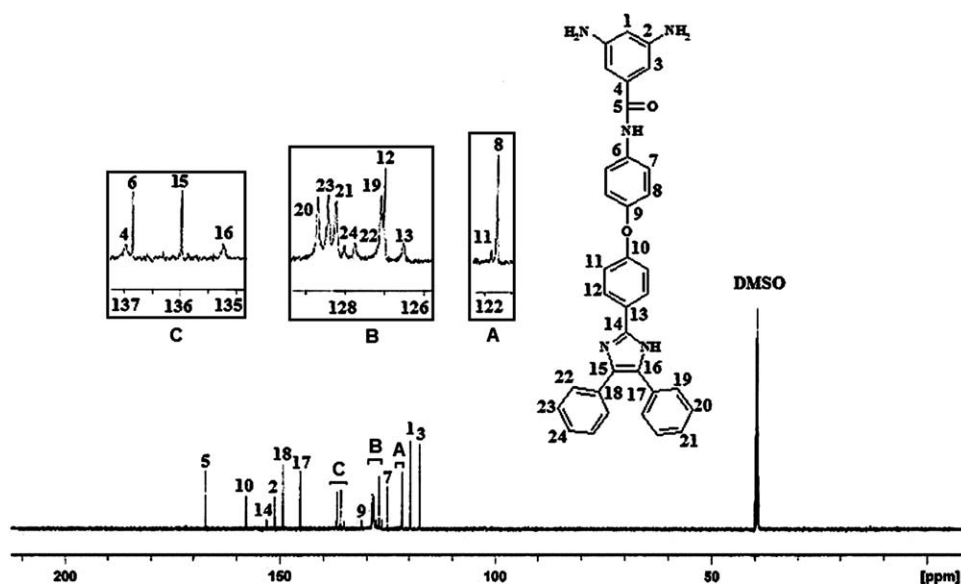**Figure 2** ^{13}C-NMR spectrum of diamine, DIDA.

was filtered and dried in a vacuum oven at 70°C overnight. The yield of the product was 87% and mp = 183–185°C. FTIR (KBr, cm^{-1}): 2900–3500 (—OH, carboxylic acid), 3460 (NH, imidazole), 3400 (NH, amide), 1750 and 1732 (typical of imide carbonyl asymmetric and symmetric stretching), 1250 (C—O—C), 1355 (C=N) and 1510 (C=C). ^{1}H-NMR (500 MHz, DMSO-d_6, for peak assignments: see Fig. 3): δ 7.10–8.46 (27H, aromatic protons), 10.55 (s, 1H,

N—H amide), 12.14 (s, 1H, N—H imidazole) and 13.25 ppm (s, 1H, —OH, carboxylic acid). Anal. Calcd for $C_{52}H_{31}N_5O_{10}$: C, 70.50%; H, 3.50%; N, 7.09%. Found, C, 70.41%; H, 3.56%; N, 6.98%.

Poly(amide-imide)s synthesis

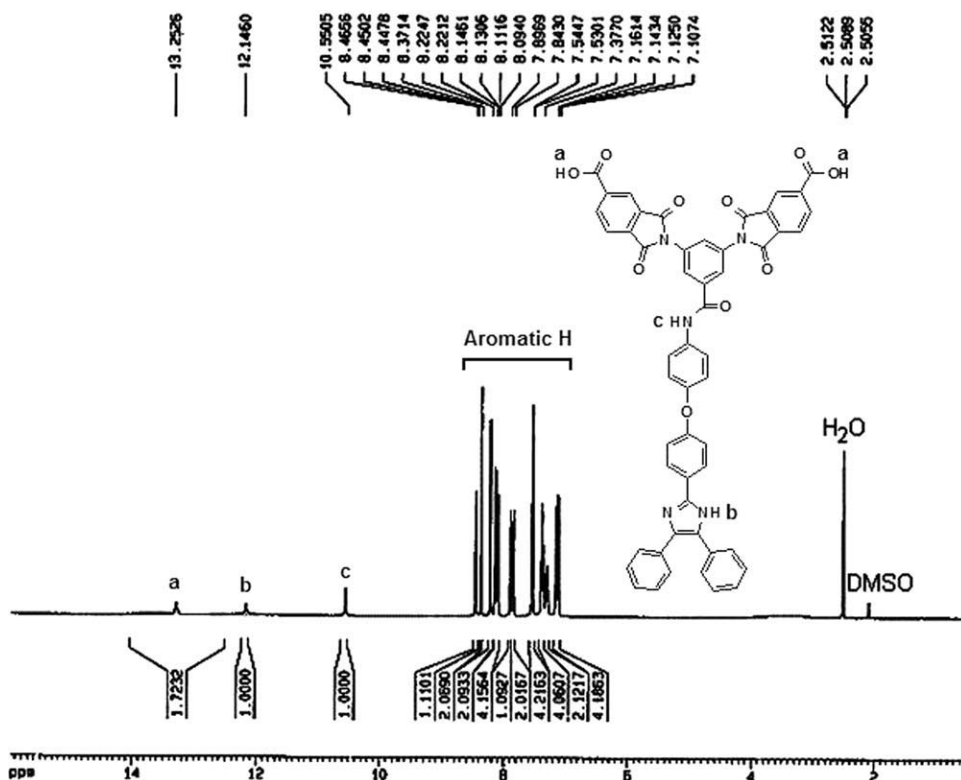The PAIs were prepared by the following general procedure: In a 50 mL two-necked round-bottomed

Figure 3 ^{1}H-NMR spectrum of diimide-diacid, DADA.

flask equipped with a reflux condenser, a magnetic stirrer bar, and a nitrogen gas inlet tube, a mixture of (0.50 g, 0.50 mmol) DADA, 0.50 mmol diamine, (1.20 mL, 5 mmol) TPP, (0.60 g, 14.15 mmol) LiCl, (0.60 g, 6.21 mmol) $CaCl_2$, 1 mL pyridine and 5.0 mL NMP was refluxed at 100°C for 12 h under a blanket of N_2. After cooling, the reaction mixture was poured into a large volume of methanol and the precipitate was collected and washed thoroughly with hot water, then dried in a vacuum oven at 80°C for 24 h. The inherent viscosities of the polymers were in the range of 0.35–0.47 dL/g. The yields of the polymerization reactions after extraction of polymers in hot methanol and removing low molecular weight oligomers were in the range of 80–87%.

PAI-1

FTIR (KBr, cm^{-1}): 3550 (N—H, imidazole), 3420 (NH, amide), 1779 and 1723 (typical of imide carbonyl asymmetric and symmetric stretching), 1374 (C—N stretching) and 1227 (C—O—C). ^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): 12.65 (1H, imidazole ring), 10.57–10.70 (3H, N—H amide), 6.62–8.59 (35H, aromatic protons).

PAI-2

FTIR (KBr, cm^{-1}): 3546 (N—H, imidazole), 3438 (NH, amide), 1782 and 1725 (typical of imide carbonyl asymmetric and symmetric stretching), 1378 (C—N stretching) and 1231 (C—O—C). ^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): 12.70 (1H, imidazole ring), 10.50–10.63 (3H, N—H amide), 3.83–3.93 (2H, aliphatic protons), 7.09–8.57 (35H, aromatic protons).

PAI-3

FTIR (KBr, cm^{-1}): 3543 (N—H, imidazole), 3494 (NH, amide), 1786 and 1727 (typical of imide carbonyl asymmetric and symmetric stretching), 1398 (C—N stretching) and 1233 (C—O—C). ^{1}H-NMR (500 MHz, DMSO-d_6, for peak assignments: see Fig. 4): δ 12.65 (1H, imidazole ring), 10.94–11.05 (2H, N—H amide), 10.55 (1H, N—H amide), 7.10–8.57 ppm (35 H, aromatic protons).

PAI-4

FTIR (KBr, cm^{-1}): 3558 (N—H, imidazole), 3374 (NH, amide), 1780 and 1726 (typical of imide carbonyl asymmetric and symmetric stretching), 1373 (C—N stretching) and 1239 (C—O—C). ^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): 12.68 (1H, imidazole ring), 10.65–10.84 (3H, N—H amide), 7.07–8.39 (33H, aromatic protons).

PAI-5

FTIR (KBr, cm^{-1}): 3487 (N—H, imidazole), 3294 (NH, amide), 1780 and 1726 (typical of imide carbonyl
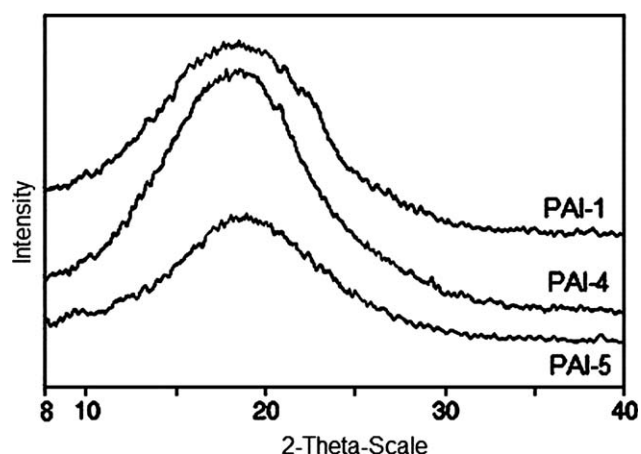


Figure 4 X-ray diffraction patterns of PAI-1, PAI-4, and PAI-5.

asymmetric and symmetric stretching), 1389 (C—N stretching), and 1229 (C—O—C). ^{1}H-NMR (500 MHz, DMSO-d_6, for peak assignments: see Fig. 4): δ 12.64 (1H, imidazole ring), 10.42–10.70 (3H, N—H amide), 7.09–8.78 (27H, aromatic protons), 1.36–1.55 ppm (12H, aliphatic protons).

RESULTS AND DISCUSSION

Monomer synthesis and characterization

A new aromatic diimide-diacid compound was synthesized according to the synthetic route depicted in Scheme 1. DIP was prepared according to the procedure reported in our previous publication.[30] The reaction of DIP with p-flouronitrobenzene in the presence of K_2CO_3 in DMAc afforded the NPDI, which was followed by reduction of the nitro into amine group by means of Pd/C-catalyzed hydrazine monohydrate in ethanol to afford DIPA. A nucleophilic substitution reaction of 3,5-dinitrobenzoyl chloride with DIPA in the presence of triethyl amine gave DIDN, which was followed by the catalytic hydrogenation of the nitro groups to afford DIDA. DADA was prepared by the condensation of DIDA with two mole equivalents of trimellitic anhydride in acetic acid. FTIR spectrum of DIDN showed absorption bands at 1542 cm^{-1} and 1345 cm^{-1} which are related to —NO_2 symmetric and asymmetric stretching. FT-IR spectrum of DIDA showed the characteristic absorption bands of the primary amine at 3458 and 3367 cm^{-1} due to N-H stretching. The ^{1}H-NMR spectrum of DIDA showed signals at 12.63 and 10.03 ppm related to the protons of NH group in imidazole ring and amide linkage, respectively. The ^{1}H-NMR spectrum also confirmed that the nitro groups have been completely transformed into the amino groups by the high field shift of the aromatic protons and by the signal at 4.96 ppm. The ^{1}H-NMR and ^{13}C-NMR spectra of DIDA are shown with
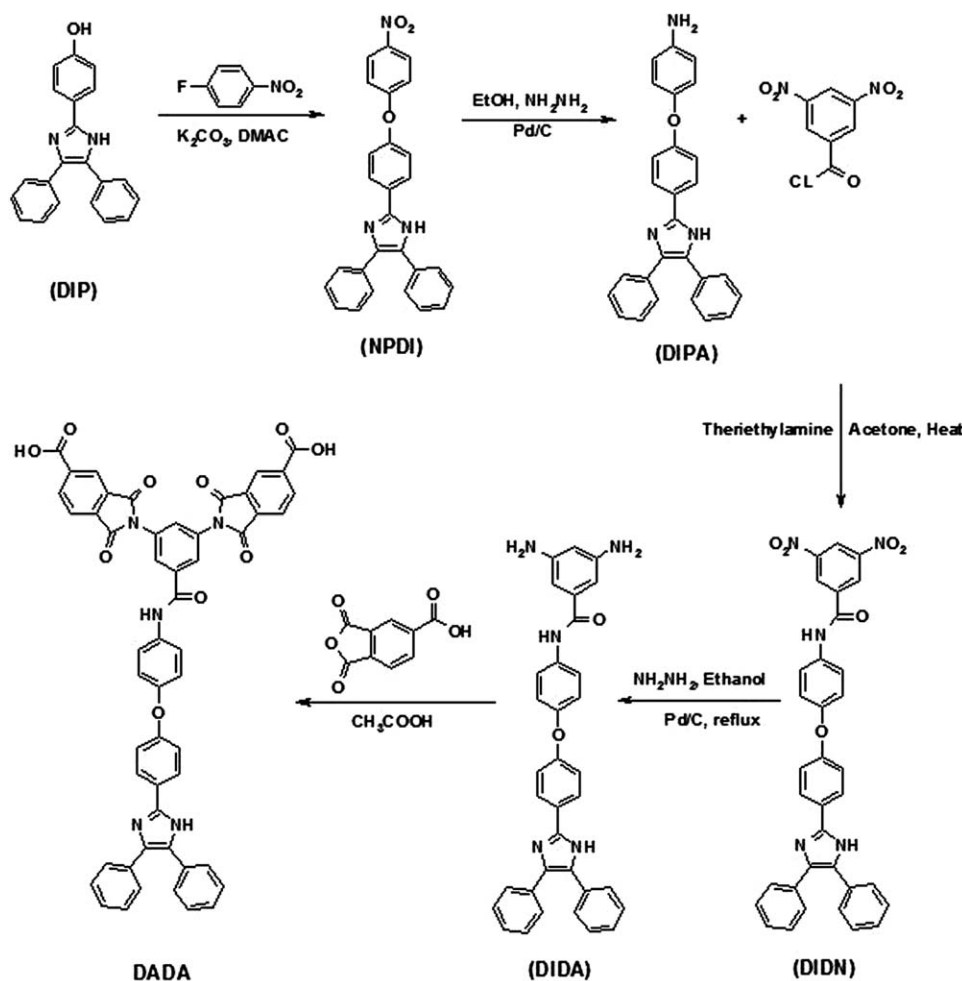
Scheme 1 Synthesis of diimide-diacid, DADA.

descriptions in Figures 1 and 2, respectively. The FTIR spectrum of DADA showed absorption bands around 2900–3500 (COOH), 1750 and 1732 (typical of imide carbonyl asymmetric and symmetric stretching), 1250 (C—O—C), 1355 (C=N), and 1510 (C=C) confirming the presence of imide ring and carboxylic acid groups in the structure. In the ^{1}H-NMR spectrum of DADA (Fig. 3), the resonance signal at 7.10–8.46 ppm is ascribed to the aromatic protons. The signals at 13.25, 12.14, and 10.55 ppm are related to the protons of carboxylic acid, NH group in imidazole ring and amide linkage, respectively. These results clearly confirmed that DADA prepared herein is consistent with the proposed structure.

Polymer synthesis and characterization

A series of PAIs (1–5) containing triaryl imidazole pendent group was prepared according to the direct polycondensation reaction between diimide-diacid DADA and five commercial available aromatic and aliphatic diamines, as shown in Scheme 2. The polymerization was carried out via solution polyconden-

sation using triphenyl phosphite and pyridine as condensing agents. The reaction readily proceeded within a homogeneous solution in NMP and in the presence of LiCl and CaCl$_2$. The PAIs were obtained in the range of 80–87% and their inherent viscosities were between 0.35 and 0.47 dL/g, indicative of the formation of moderate molecular weights polymers. The structures of these PAIs were confirmed by means of FTIR and ^{1}H-NMR spectroscopy. In general, FTIR spectra of the PAIs showed the two bands appearing around 1775 cm^{-1} and 1725 cm^{-1} were attributed to symmetrical and asymmetrical stretching vibration of carbonyl groups of imide rings, absorption bands around 1375 cm^{-1} is due to C—N stretching of imide rings and around 1225 cm^{-1} for the C—O bond. The ^{1}H-NMR spectra of all PAIs showed a signal at 12.64–12.70 ppm related to a proton of imidazole ring and in the range of 10.50–11.05 related to the proton of amide groups. In addition to the signals in the region of 7.10–8.78 ppm related to the aromatic protons, PAI-2 and PAI-5 also showed signals at 3.83–3.93 and at 1.36–1.55 ppm, respectively, related to the aliphatic protons. Assignment
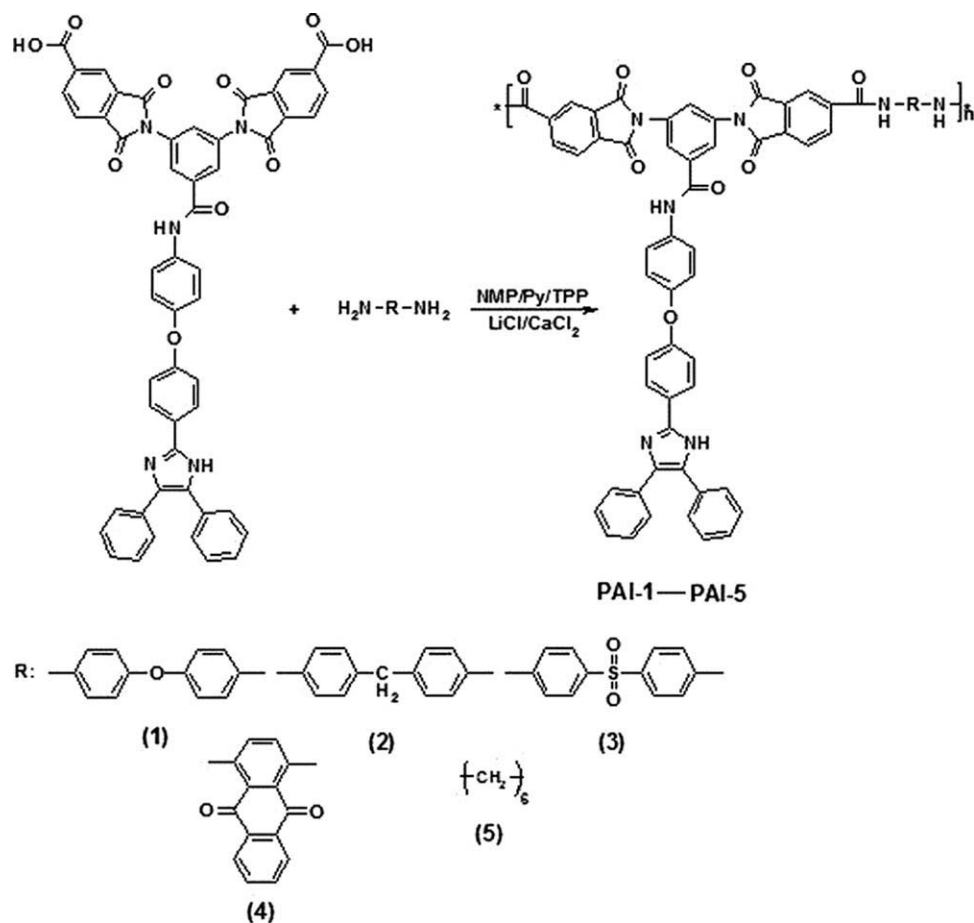
Scheme 2 Synthesis of poly(amide-imide)s, PAIs.

of protons in the spectra is consistent with the proposed chemical structure of polymers.

Properties of polymers

X-ray diffraction

The results from XRD test for the representative polymers of PAI-1, PAI-4, and PAI-5, X-ray diffraction patterns are shown in Figure 4, reveal the amorphous nature of these polymers. The amorphous behavior of these poly(amide-imide)s can be attrib-

uted to the long and bulky pendent triphenyl imidazole moiety which hindered significantly the regular macromolecular packing in chains and therefore caused less chain packing. In addition, the pendent group also decreases the intermolecular force between the polymer chains, subsequently causing a decrease in crystallinity.[31]

Solubility and viscosity

Solubility of the PAIs in several organic solvents at 5% (w/v) is summarized in Table I. All the prepared

TABLE I
Solubility Behavior and Inherent Viscosities of PAIs

Polymer code	η_{inh} (dL/g)[a]	DMAc	DMF	NMP	DMSO	Py	THF	Methanol	HMPA
PAI-1	0.40	++	++	++	++	++	−	−	++
PAI-2	0.39	++	++	++	++	++	−	−	++
PAI-3	0.42	++	++	++	++	++	−	−	++
PAI-4	0.47	++	++	++	++	++	−	−	++
PAI-5	0.35	++	++	++	++	++	+	−	++

The solubility was determined by using 5 g sample in 100 mL of solvent.
Abbreviations: DMAc, *N,N*-dimethyl acetamide; DMF, *N,N*-dimethyl formamide; NMP, *N*-methyl pyrrolidone; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; Py, pyridine; HMPA, hexamethylphosphoramide; ++, soluble at room temperature; +, soluble on heating at 60°C; −, insoluble on heating at 60°C.
[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 25°C.
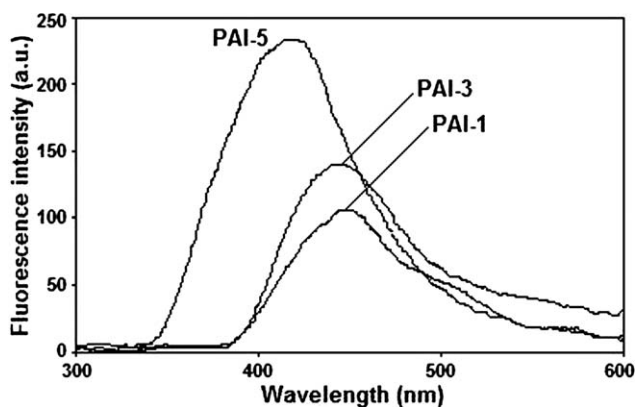
Figure 5 Photoluminescence emission spectra of the PAI-1, PAI-3, and PAI-5.

PAIs exhibited excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, HMPA and even in less polar solvents like pyridine at room temperature. The good solubility should be the result of the introduction of the bulky pendent triphenyl imidazole group in polymer backbone. Dense packing of the polymer chains was probably disturbed by the bulky pendent which led to the increased chain distances and decreased chain interactions; consequently, the solvent molecules were able to penetrate more easily to solubilize the polymer chains. We believe, however, that the presence of polar amide and ether groups in the pendent can also contribute effectively in the solubility of these PAIs by interacting with the polar molecules of solvents. The polymers can be processed by casting from their solutions.

Photophysical properties

Photoluminescence (PL) spectra of the PAI-1, PAI-3, and PAI-5 in dilute (0.2 g/dL) NMP solution are shown in Figure 5. The PAIs exhibited shape-similar absorption bands having their $\lambda_{max,ab}$ at 320 nm, which can be attributed to the $\pi-\pi^*$ transitions derived from the polymer backbones. An excitation wavelength of 315 nm was used in all cases. The fluorescence spectra of three PAIs in NMP solutions exhibited broad emission from 400 nm to 600 nm with the maxima at 425–450 nm. The PAI-5 containing the remained aliphatic unit of the diamine in the backbone exhibited higher intensity emission at lower wavelength of 425 nm as compared with the emission of aromatic PAIs. The aliphatic poly(amide-imide) in solution, PAI-5, exhibited high intensity emission at $\lambda e.max = 425$ nm and the aromatic poly(amide-imide)s, PAI-1 and PAI-3, exhibited emission at $\lambda e.max = 450$ nm. The blue shift and higher intensity of the photoluminescence peak of the aliphatic poly(amide-imide), PAI-5, compared

with the aromatic PAIs could be attributed to the effectively reduced conjugation and capability of charge-transfer complex formation by aliphatic diamines in comparison with the electron-donating diimide-diacid moiety and the strongly electron-accepting aromatic diamine unit.[32]

Thermal properties

DSC and TGA methods applied to evaluate the thermal properties of the PAI-3, PAI-4, and PAI-5, and the thermal analysis data are summarized in Table II. The T_g values of these PAIs were taken as the midpoint of the change in slope of the baseline in DSC curve obtained from second scan, Figure 6. Quenching from temperature of 350°C to room temperature yielded amorphous samples so that in most cases the T_gs could easily be observed in the second heating traces of DSC. The DSC curves did not exhibit endothermic peak up to 350°C which can be associated to the amorphous nature of the PAIs. The T_g values of the PAIs were in the range of 207–271°C, depending on the stiffness of the residue of diamines in the polymer backbone. The lowest T_g value of PAI-5 in these series polymers can be explained in terms of the flexible methylene linkages in its diamine component. Among these PAIs, PAI-4 based on 1,4-diaminoanthraquinone showed the highest T_g value because of the highest rigidity, which inhibited the molecular motion. The lower T_g of PAI-3 in comparison with the PAI-4 can be correlated with that of chain flexibility because of the sulfone linkage between the phenyl rings. It is evident that the bridging sulfone group between two phenyl rings in 4,4′-diaminodiphenyl sulfone, facilitated bond rotation and reduced T_g.

The thermal stability of PAIs was evaluated by TGA at 10°C/min in nitrogen atmosphere. The TGA curves for three PAIs are shown in Figure 7. The thermal stability data determined from original TGA

TABLE II
Thermal Characteristic Data of PAI (3–5)

Polymer code	T_g (°C)[a]	T_i (°C)	T_{10} (°C)	Char yield at 600°C (%)[b]
PAI-3	262	310	450	68
PAI-4	271	330	520	71
PAI-5	207	260	325	58

T_g, glass transition temperature.

Decomposition temperature, recorded via TGA at a heating rate of 10°C/min under N_2 (20 cm³/min). T_i, temperature for 0% weight loss. T_{10}, temperature for 10% weight loss.

[a] Midpoint temperature of baseline shift on the second DSC heating trace (10°C/min, under N_2, 20 cm³/min) of the sample after quenching from 350°C.

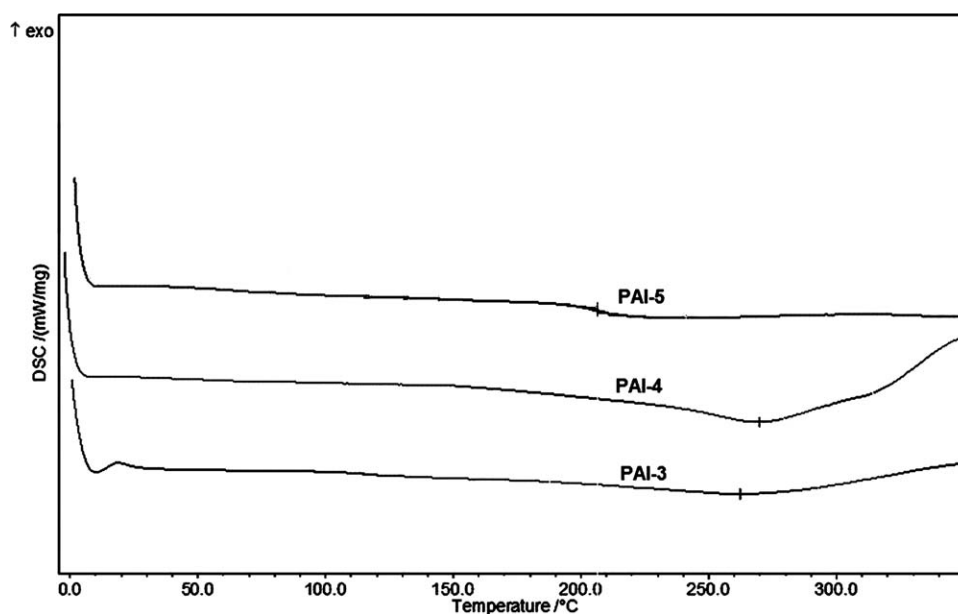[b] (Char yield): Residual weight percentage at 600°C in N_2.

Figure 6 DSC curves of PAIs (3–5).

curves are tabulated in Table II. The initial decomposition temperatures (T_i) for these PAIs were in the range of 260–330°C, and the temperature at 10% weight loss were in the range of 325–520°C. The char yield at 600°C in nitrogen was about 58% for PAI-5, whereas for the aromatic poly(amide-imide)s of PAI-3 and PAI-4 were more than 68%. To compare thermal behavior of poly(amide-imide)s, the PAI-5 has lower thermal stability in comparison with the aromatic PAIs such as PAI-3 and PAI-4 which can be related to introduction of methylene units in PAI-5 backbone. The PAI-4 has shown the highest thermal stability, which can be due to absence of flexible linkage such as ether, methylene, or sulfone group in the polymer backbone and also due to bulky rigid side group of anthraquinone unit.

CONCLUSIONS

A new diimide-dicarboxylic acid monomer containing bulky pendent group was successfully prepared and used to synthesize a series of poly(amide-imide)s via phosphorylation polycondensation method using triphenyl phosphite and pyridine. Because of the presence of long and bulky pendent bearing triaryl imidazole group, these polymers were essentially amorphous and showed excellent solubility in many polar aprotic solvents. These PAIs exhibited a desired combination of properties (T_g, T_i, and T_{10} up to 270°C, 330°C, and 520°C, respectively, with the remained residue of 71% at 600°C in N_2) requiring high-performance materials with excellent solubility in organic solvents for fabrication.
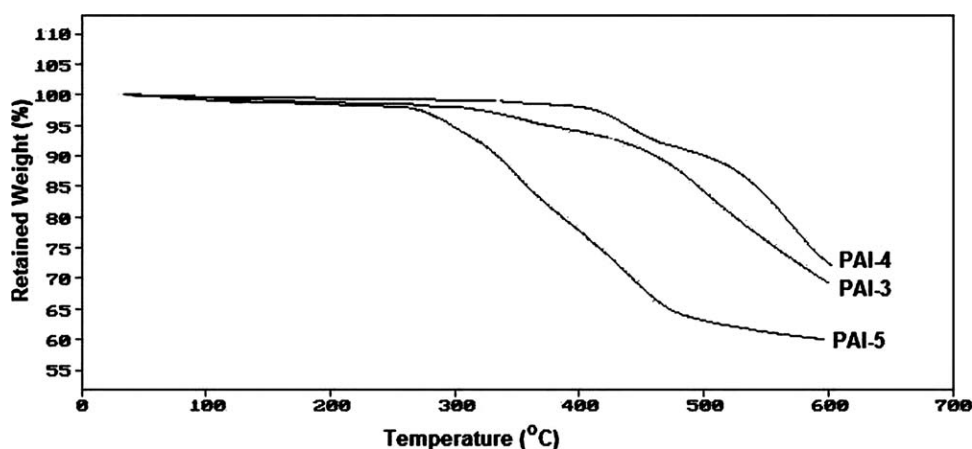

Figure 7 TGA thermograms of PAIs (3–5).

References

1. Ghosh, M. K.; Mittal, K. L. Polyimide: Fundamentals and Applications; Marcel Dekker: New York, 1996.
2. Abadie, M. J.; Sillion, B. Polyimides and Other High-Temperature Polymers; Elsevier: Amsterdam, 1991.
3. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. Polyimide; Blackie: Glasgow, UK, 1991.
4. Liaw, D. J.; Liaw, B. Y.; Li, L. J.; Sillion, B.; Mercier, R.; Thiria, R.; Sekiguchi, H. Chem Mater 1998, 10, 734.
5. Ghaemy, M.; Alizadeh, R.; Behmadi, H. Eur Polym J 2009, 45, 3108.
6. Ghaemy, M.; Barghamadi, M. J Appl Polym Sci 2009, 112, 815.
7. Liaw, D. J.; Liaw, B. Y. Polymer 2001, 42, 839.
8. Shockravi, A.; Abouzari-Lotf, E.; Javadi, A.; Atabaki, F. Eur Polym J 2009, 45, 1599.
9. Liaw, D. J.; Huang, C. C.; Chen, W. H. Polymer 2006, 47, 2337.
10. Faghihi, K.; Gholizadeh, M. Macromol Res 2010, 18, 2.
11. Liaw, D. J.; Liaw, B. Y.; Chen, Y. S. Polymer 1999, 40, 4041.
12. Liaw, D. J.; Hsu, P. N.; Chen, W. H.; Lin, S. L. Macromolecules 2002, 35, 4669.
13. Song, C. E. J Polym Sci D 1979, 11, 161.
14. Cassidy, P. E. Thermally Stable Polymers; Marcel Dekker: New York, 1980.
15. Mullen, K. Organic Light Emitting Devices: Synthesis, Properties and Applications; Wiley-VCH: Weinheim, Germany, 2006.
16. Mikroyannidis, J. A.; Panayiotis, D.; Panayiotis, V. I.; Spiliopoulos, K. Syn Met 2004, 145, 87.
17. Zhou, X. H.; Yan, J. C.; Pei, J. Macromolecules 2004, 37, 7078.
18. Pan, Y.; Tang, X.; Zhu, L.; Huang, Y. Eur Polym J 2007, 43, 1091.
19. Feng, K.; Hsub, F. L.; Van DerVeer, D.; Bota, K.; Xiu, R. J Photochem Photobiol A: Chem 2004, 165, 223.
20. Hadjikallis, G.; Hadjiyannakou, S. C.; Vamvakaki, M.; Patrickios, C. S. Polymer 2002, 43, 7269.
21. Pan, Y.; Tang, X. Eur Polym J 2008, 44, 408.
22. Ghaemy, M.; Amini Nasab, S. M. React Funct Polym 2010, 70, 306.
23. Fridman, N.; Kaftory, M.; Speiser, S. Sens Actuators B 2007, 126, 107.
24. Yamazaki, N.; Matsumato M.; Higashi, F. J Polym Sci Polym Chem Ed 1975, 13, 1373.
25. Yamazaki, N.; Higashi, F. Tetrahedron 1974, 30, 1323.
26. Higashi, F.; Takakura, T.; Sumi, Y. J Polym Sci Part A: Polym Chem 2004, 42, 2321.
27. Wrasidlo, W.; Augl, A. M. J Polym Sci Polym Chem Ed 1969, 7, 321.
28. Nieto, J. L.; de la Campa, J. G.; de Abajo, J. Makromol Chem 1982, 183, 557.
29. de la Campa, J. G.; de Abajo, J.; Nieto, J. L. Makromol Chem 1982, 183, 571.
30. Ghaemy, M.; Alizadeh, R. Eur polym J 2009, 45, 1681.
31. Liaw, D. J.; Liaw, B. Y.; Yang, C. M. Macromolecules 1999, 32, 7248.
32. Liou, G. S.; Chang, C. W. Macromolecules 2008, 41, 1667.