

Microwave heating coupled with ionic liquids: Synthesis and properties of novel optically active polyamides, thermal degradation and electrochemical stability on multi-walled carbon nanotubes electrode

Shadpour Mallakpour*, Mehdi Taghavi

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

ARTICLE INFO

Article history:

Received 9 February 2008

Received in revised form 25 May 2008

Accepted 1 June 2008

Available online 4 June 2008

Keywords:

Room temperature ionic liquids

Carbon nanotube

Microwave irradiation

ABSTRACT

Rapid and efficient synthesis of novel optically active polyamides (**PA**s) was achieved under microwave irradiation. Thus, step-growth polymerization of a novel chiral diacid containing naphthalimide and flexible chiral groups with different diisocyanates in the presence of a small amount of ionic liquids that act as a primary microwave absorber as well as conventional heating was carried out. The **PA**s were characterized using FT-IR, ¹H NMR, UV–vis spectroscopy, fluorimetry and elemental analysis. Thermal properties of new **PA**s were evaluated by thermogravimetric analysis and differential scanning calorimetry. The interpretation of kinetic parameters (*E*, ΔH , ΔS and ΔG) of thermal decomposition stages has been evaluated using Coats–Redfern equations. Here also for the first time we report an electrochemical oxidation method based on the adsorptive stripping cyclic voltammetry technique on the multi-walled carbon nanotube-modified glassy carbon electrode for the investigation of electrochemical stability of the resulting polymers in aqueous solution at various pH values.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Ionic liquids (**IL**s) are organic salts that are generally liquid at ambient temperatures, preferably close to room temperature. Due to deterioration of the environment, green chemistry has been receiving increasingly more attention since 1990s [1,2]. Recently, water and **IL**s have been recognized and are attracting attentions as eco-friendly solvents for organic synthesis. The toxicological studies available show that **IL**s are relatively non-toxic substances (LD50 is 1400 mg/kg). The “green solvents” aspects of **IL**s are derived mainly from their negligible vapor pressure, volatility, and flammability, since this will decrease the risk of exposure and loss of solvent due to evaporation. However, these properties can be beneficial only to prevent air pollution but not water pollution especially water-miscible [3,4]. Their distinctive physico-chemical properties, such as a wide liquid range, a low melting point, good solubility characteristics, relatively low viscosity, high fluidity, a wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stabilities, provide their rapid appearance as alternative solvents and the concomitant rapid growing number of examples of uses [5–9].

The use of microwave ovens as tools for synthetic chemistry is a fast growing area of research. Their main advantages derive from the almost instantaneous “in core” heating of materials, in a homogeneous and selective manner [10–13]. This technique proves to be excellent in cases where traditional heating has a low efficiency because of poor heat transmission, and hence local overheating is a major inconvenience. To combine the advantages of microwave techniques and **IL**s recently several organic reactions such as acetylation, oligomerization, dimerization, polymerization and copolymerization reactions have been carried out in **IL** under microwave irradiation [14–16].

Chiral phenomena play important roles in nature. The synthesis and application of optically active polymers are topics currently attracting much attention. This may arise mainly from their chiral structure which is common to naturally occurring polymers. Most of the naturally occurring polymers for instance nucleic acids, proteins, and polysaccharides are chiral and optically active and some of them show characteristic functionalities such as molecular recognition ability and catalytic activity, due to their specific chiral structure as represented by genes and proteins. In the history of synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems and optically active synthetic polymers that will be as effective as those in living systems [17–21].

Polyamides (**PA**s) are high-molecular-weight materials containing amide units; the hydrocarbon segments between the amide

* Corresponding author. Tel.: +98 311 391 3267; fax: +98 311 391 2350.

E-mail addresses: mallak@cc.iut.ac.ir, mallak777@yahoo.com (S. Mallakpour).

groups can be aliphatic, partially aromatic, or wholly aromatic. The type of hydrocarbon segment used has an effect on the chain flexibility and structural regularity; this is important for the formation of the crystalline phase [22–25]. However, the applications are limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome these drawbacks, modifications of the **PA** structure have often been used, such as the introduction of flexible linkages, non-symmetrical structure, or bulky substituents into the polymer backbone. It is well known that **PAs** containing heterocyclic units in the main chain possess excellent thermal stabilities [26–28].

Carbon nanotubes (CNTs) continue to receive noteworthy attention in electrochemistry [29–33]. Since its discovery by Iijima [34] in 1991 by transmission electron microscopy, CNTs have been the topic of frequent explorations in materials, chemical and physical areas owing to their novel mechanical, electronic, structural and chemical properties [35]. The subtle electronic properties suggest that CNTs have the ability to promote charge-transfer reactions when used as an electrode. The modification of electrode substrates with multi-walled carbon nanotubes (MCNTs) for use in analytical sensing has been documented to result in high sensitivities, low detection limits, resistance to surface fouling and reduction of overpotentials. Electrochemical oxidation of polymers in various conditions can be a pattern of their stability. Whenever a compound was more stable, its potential of oxidation is the higher. By using electrochemical studies, the determinant bonds in the polymer structures, which are responsible for polymer oxidation, can be recognized and the ability of different monomer structures on polymer stability can be characterized [36–38].

Because of importance of optically active materials and polymers with amino acid and 1,8-naphthalimide moieties, in continuation of our study in developing high performance polymers containing pendent units under green conditions, herein we wish to demonstrate that combination of **IL** with microwave heating is an efficient method for the production of chiral extended **PAs** [39–42]. In another section of this research, we wish to report for the first time, electrochemical behavior and stability of the resulting **PAs** on MCNT-modified glassy carbon electrode (GCE). In this study mechanism of thermal decomposition behavior of these **PAs** is also reported.

2. Experimental

2.1. Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). *N,N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. 5-Aminoisophthalic acid (5AIPA) (**6**) was recrystallized from H₂O/DMF (*N,N*-dimethylformamide) (4/1) mixture. 1,8-Naphthalenedicarboxylic anhydride was recrystallized from hot acetic anhydride. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purchased from (Merck, Darmstadt, Germany) and was used without further purification. All room temperature ionic liquids (**RTIL**s) were prepared by reported procedure [3,7,8]. Universal buffer (boric acid, phosphoric acid, acetic acid and sodium hydroxide, 0.1 M) solutions with different pH values were used for the study of the pH influence. All aqueous solutions were prepared with deionized water of resistivity not less than 18.0 M Ω at 25 °C; 50 μ M solutions of compounds **4**, **6**, **7**, **9aIIB**–**9dIIB** were freshly prepared in ethanol and were used as the stock solution. Because of low solubility of the above compounds in aqueous solution, prior to the electrochemical experiments, sample solutions were stirred for 5 min by a magnet in open circuit potential and their adsorptive stripping cyclic voltammetric behavior was studied.

2.2. Techniques

Proton nuclear magnetic resonance ¹H NMR (500 MHz) spectra were recorded in DMSO-*d*₆ solution using a Bruker (Ettlingen, Germany) Avance 500 instrument. FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. All melting points were taken with a (Gallenkamp, England) melting point apparatus. The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz and 900 W). Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer (Cannon, Mainz, Germany). Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. Specific rotations were measured by a JASCO (P-1030) Polarimeter (Toyonaka, Osaka, Japan). Elemental analyses were performed by Research Institute of Polymer and Petrochemical of Iran (IPPI). Fluorescence and UV-vis spectra were recorded on a spectrofluorometer, JASCO, FP-750 and UV/Vis/NIR spectrophotometer, JASCO, V-570, respectively. Thermogravimetric analysis (TGA) data for polymers were taken on a TGA-Perkin Elmer (Pyris 1) at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument at a heating rate of 20 °C/min under nitrogen atmosphere by IPPI. All of the cyclic voltammetric measurements were performed using an Autolab PGSTAT 12, potentiostat/galvanostat connected to a three electrode cell, Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with Autolab software. The MCNT-modified GCE, a graphite electrode and a saturated Ag/AgCl reference electrode were employed as a working, auxiliary and reference electrodes, respectively. The MCNT was purchased from Iran's Research Institute of Petroleum Industry and was synthesized by chemical vapor deposition with a diameter of 8–15 nm, a length of 50 μ m and a purity of 95%. The modified electrodes with carbon nanotube layers were characterized by scanning electron microscopy.

2.3. Monomer synthesis

2.3.1. Preparation of 3-methyl-2-(1,8-naphthalimidyl)butanoic acid

Into a 100 mL round-bottomed flask, 0.49 g (2.47×10^{-3} mol) of 1,8-naphthalenedicarboxylic anhydride (**1**), 0.32 g (2.72×10^{-3} mol) of *S*-valine (**2**), 5 mL of DMF and a stirring bar were placed. The solution was refluxed for 1 h. The solvent was removed under reduced pressure and to this residue a mixture of 50 mL of cold water and 1 mL of concentrated hydrochloric acid was added. The precipitate was collected by filtration and washed thoroughly with water and dried at 70 °C for 3 h to yield 0.45 g (94%) of imide acid **4**. The purity of this compound was checked with thin layer chromatography (TLC) in a mixture of 50/50 of ethyl acetate/cyclohexane. Recrystallization from methanol/water gave yellow crystals. Melting point: 210–212 °C, $[\alpha]_D^{25} = -181.3$ (0.05 g in 10 mL of DMF). FT-IR (KBr, cm⁻¹): 3109 (m), 2977 (w), 2932 (w), 1750 (s), 1695 (s), 1646 (s), 1621 (m), 1586 (s), 1438 (m), 1384 (s), 1335 (m), 1271 (w), 1241 (m), 1186 (m), 1105 (w), 1033 (w), 977 (w), 914 (w), 834 (w), 776 (s), 745 (w), 763 (w), 544 (w), 503 (w). ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.67 (d, 3H, CH₃, *J* = 6.83 Hz), 1.21 (d, 3H, CH₃, *J* = 6.38 Hz), 2.70 (m, 1H, CH), 5.18 (d, 1H, CH, *J* = 9.13 Hz), 7.82 (t, 2H, CH, Ar-H), 8.39 (d, 2H, Ar-H, *J* = 8.16 Hz), 8.48 (d, 2H, Ar-H, *J* = 7.19 Hz), 12.71 (s, 1H, COOH) ppm. ¹³C NMR (500 MHz, DMSO-*d*₆): δ 171.52 (C, COOH), 164.17 (C, C=O), 135.62 (CH, Ar), 132.22 (CH, Ar), 132.06 (C, Ar), 128.16 (CH, C, Ar), 122.07 (C, Ar), 58.82 (CH), 27.81 (CH), 23.00 (CH₃), 19.77 (CH₃) ppm. Elemental analysis calculated for C₁₇H₁₅NO₄ (297.31 g/mol): C, 68.68%; H, 5.09%; N, 4.71%. Found: C, 68.53%; H, 4.64%; N, 5.21%.

2.3.2. Preparation of 3-methyl-2-(1,8-naphthalimidyl)butanoyl chloride

Into a 50 mL round-bottomed flask, 0.40 g (1.34×10^{-3} mol) of imide acid **4**, 3 mL of thionyl chloride, and a stirring bar were placed. Stirring was started and the mixture was refluxed for 3 h. Then, the solvent was removed via distillation and 20 mL of *n*-hexane was added, and stirred for 30 min. *n*-Hexane was distilled off, and the product was collected and dried in vacuum to give 0.41 g (98%) of a white powder of acid chloride **5**. Melting point: 197–199 °C, $[\alpha]_D^{25} = -200.9$ (0.05 g in 10 mL of DMF). FT-IR (KBr, cm^{-1}): 3618 (w), 3074 (w), 2972 (w), 2933 (w), 1819 (m), 1779 (m), 1734 (s), 1701 (s), 1665 (s), 1587 (s), 1513 (w), 1437 (m), 1377 (s), 1360 (m), 1312 (w), 1239 (s), 1188 (m), 1103 (m), 1076 (w), 1006 (m), 911 (w), 890 (w), 845 (w), 827 (w), 779 (w), 747 (w), 726 (w), 704 (w). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 0.70 (d, 3H, CH_3 , $J = 6.93$ Hz), 1.21 (d, 3H, CH_3 , $J = 8.03$ Hz), 2.69 (m, 1H, CH), 5.17 (d, 2H, CH, $J = 9.21$ Hz), 7.92 (t, 2H, CH, Ar-H), 8.54 (dd, 2H, Ar-H, $J_1 = 8.22$ Hz, $J_2 = 8.35$ Hz) ppm.

2.3.3. Preparation of 5-[3-methyl-2-(1,8-naphthalimidyl)-butanoylamino]isophthalic acid

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 0.25 g (1.40×10^{-3} mol) of 5AIPA (**6**) in 3 mL of DMAc. The reaction mixture was cooled in an ice water bath. To this solution 0.40 g (1.27×10^{-3} mol) of acid chloride **5** in 2 mL of DMAc was added dropwise. The mixture was stirred for 3 h and then 0.17 mL (1.27×10^{-3} mol) of triethylamine (TEA) was added. The whole solution was stirred vigorously for 2 h at low temperature and for an overnight at room temperature (R.T.). Then, the solution was poured into a mixture of 100 mL/1 mL of cold water/concentrated HCl. The precipitate was collected by filtration and washed thoroughly with water and dried at 80 °C for 5 h to yield 1.39 g (91%) of diacid **7**. The purity of this compound **7** was checked with TLC in a mixture of 50/50 of ethyl acetate/cyclohexane which showed one spot. Recrystallization from acetone/water gave yellow crystals. Melting point: 312–314 °C, $[\alpha]_D^{25} = -7.6$ (0.05 g in 10 mL of DMF). FT-IR (KBr, cm^{-1}): 3344 (s), 2969 (m), 1711 (s), 1656 (s), 1705 (s), 1612 (s), 1588 (s), 1560 (s), 1443 (s), 1381 (s), 1343 (s), 1268 (s), 1240 (s), 1179 (m), 1132 (w), 1103 (w), 1029 (w), 905 (m), 844 (w), 777 (s), 758 (m), 687 (w), 625 (w), 540 (w), 498 (w). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 0.71 (d, 3H, CH_3 , $J = 6.35$ Hz), 1.23 (d, 3H, CH_3 , $J = 5.90$ Hz), 2.81 (m, 1H, CH), 5.30 (d, 2H, CH, $J = 8.45$ Hz), 7.91 (t, 2H, CH, Ar-H), 8.13 (s, 1H, CH, Ar-H), 8.40 (s, 2H, CH, Ar-H), 8.52 (d, 2H, Ar-H, $J = 8.06$ Hz), 8.56 (d, 2H, Ar-H, $J = 6.71$ Hz), 9.95 (s, 1H, NH), 13.25 (s, 1H, COOH) ppm. $^{13}\text{C NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 168.83 (C, C=O), 167.39 (C, COOH), 164.69 (C, C=O), 140.62 (C, Ar), 135.50 (CH, Ar), 132.29 (CH, Ar), 132.24 (C, Ar), 132.08 (C, Ar), 128.52 (CH, Ar), 128.22 (C, Ar), 125.39 (CH, Ar), 122.86 (CH, Ar), 59.54 (C, Ar), 27.58 (CH), 23.29 (CH_3), 19.47 (CH_3) ppm. Elemental analysis calculated for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_7$ (460.44 g/mol): C, 65.21%; H, 4.38%; N, 6.08%. Found: C, 65.59%; H, 4.39%; N, 5.99%. UV (DMF): λ_{max} (ϵ) 264 (11845.24), 335 nm ($17142.86 \text{ L mol}^{-1} \text{ cm}^{-1}$).

2.4. Polymer synthesis

2.4.1. Method I: polymerization of diacid **7** with diisocyanates in *RTIL* under conventional heating

Before each experiment, the *RTILs* were dried at 75 °C under reduced pressure. Several *RTILs* were used in this work, but 1,3-diisopropyl imidazolium bromide [(1,3-Isopr₂im)Br] was selected for all the polymerization reactions under optimum conditions. A 25 mL round-bottomed flask equipped with a mechanical stirrer was charged with a mixture of diacid **7** (0.10 g, 2.17×10^{-4} mol), 4,4'-methylenebis(phenyl isocyanate), MDI (**8a**) (0.05 g, 2.17×10^{-4} mol), dibutyltin dilaurate (DBTDL)

(0.02 g, 3.61×10^{-5} mol)/TEA (0.02 mL, 1.80×10^{-4} mol) (a ratio of 1/5), and [(1,3-Isopr₂im)Br] (0.300 g, 2.02×10^{-3} mol). The mixture, blanketed by nitrogen, was stirred and heated to 110 °C for 8 h. The viscous final solution was poured into 30 mL of methanol to precipitate the polymer. The white solid was washed thoroughly with water. The resulting polymer dried under vacuum at 80 °C yielded 0.13 g (89%) of **PA9aIG**. All other **PA**s were also synthesized with a similar procedure and using pyridine (Py), TEA, tributylamine (TBA), DABCO, DBTDL, DBTDL/TEA (1/10), (1/15) as catalysts and without any catalyst.

2.4.2. Method II: polymerization of diacid **7** with diisocyanates in *RTIL* under microwave irradiation

The **PA**s were prepared by the following general procedure (taking **PA9aIID** as an example): Into a porcelain dish, [(1,3-Isopr₂im)Br] (0.300 g, 2.02×10^{-3} mol) and monomer **7** (0.10 g, 2.17×10^{-4} mol) were added. After the mixture was completely ground, DBTDL (0.02 g, 3.61×10^{-5} mol) was added and the mixture was ground for 5 min, then MDI (**8a**) (0.05 g, 2.17×10^{-4} mol) was added and the mixture was ground again for additional 2 min. The reaction mixture was irradiated in the microwave oven for 1 min then it was cooled and irradiated for 1 more minute at 100% (900 W) of its power level. The resulting product was isolated by the addition of 30 mL of methanol. It was then filtered and dried at 80 °C for 7 h in vacuum, this yielded 0.13 g (91%) of white **PA9aIID**. The above polymerization was also repeated and the reaction mixture was irradiated in a microwave oven using Py, TEA, TBA and DABCO as catalysts, and without any catalyst. For each method, the optimized reaction conditions according to reaction time and reaction catalysts were selected for the polymerization of diacid monomer **7** with other diisocyanates such as toluylene-2,4-diisocyanate, TDI (**8b**), isophorone diisocyanate, IPDI (**8c**), hexamethylene diisocyanate, HDI (**8d**).

PA9bIF: FT-IR (KBr, cm^{-1}): 3311 (s), 3118 (w), 2922 (s), 2853 (s), 1710 (s), 1665 (s), 1654 (s), 1587 (m), 1561 (s), 1436 (w), 1379 (m), 1345 (m), 1269 (w), 1239 (m), 1187 (w), 1130 (w), 1106 (w), 1024 (w), 905 (m), 842 (w), 778 (s), 746 (w), 685 (w), 624 (w), 597 (w), 539 (w), 497 (w), 473 (w). Elemental analysis calculated for $\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_5$ (546.57 g/mol): C, 70.32%; H, 4.79%; N, 10.25%. Found: C, 69.74%; H, 5.24%; N, 10.17%.

PA9cID: FT-IR (KBr, cm^{-1}): 3311 (m), 3075 (m), 2955 (m), 2924 (s), 2852 (s), 1706 (m), 1667 (s), 1587 (s), 1554 (s), 1432 (s), 1377 (m), 1343 (m), 1282 (w), 1239 (w), 1188 (w), 1153 (w), 1106 (m), 1072 (m), 1027 (w), 909 (s), 842 (s), 780 (m), 745 (s), 712 (s), 679 (w), 618 (w), 548 (w), 495 (w). Elemental analysis calculated for $\text{C}_{35}\text{H}_{37}\text{N}_4\text{O}_5$ (593.69 g/mol): C, 70.81%; H, 6.28%; N, 9.44%. Found: C, 70.64%; H, 6.31%; N, 9.37%.

PA9aIID: FT-IR (KBr, cm^{-1}): 3317 (w), 3109 (w), 2965 (w), 1702 (m), 1662 (s), 1590 (s), 1509 (s), 1436 (w), 1409 (m), 1379 (m), 1340 (m), 1312 (m), 1238 (m), 1200 (w), 1103 (w), 1018 (w), 909 (w), 845 (w), 781 (w), 754 (w). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 0.73 (d, 3H, CH_3 , $J = 5.05$ Hz), 1.24 (d, 3H, CH_3 , $J = 4.90$ Hz), 2.84 (m, 1H, CH), 3.87 (s, 2H, CH_2), 5.31 (d, 1H, CH, $J = 8.35$ Hz), 7.19 (d, 2H, CH, $J = 7.20$ Hz), 7.66 (d, 2H, CH, $J = 7.40$ Hz), 7.91 (s, 2H, CH), 8.14 (s, 1H, CH), 8.26 (s, 2H, CH), 8.54 (dd, 2H, CH, $J_1 = 16.05$ Hz, $J_2 = 6.60$ Hz), 9.95 (s, 1H, NH), 10.35 (s, 1H, NH). UV (DMF): λ_{max} (ϵ) 264 (57380.95), 335 nm ($29404.76 \text{ L mol}^{-1} \text{ cm}^{-1}$).

PA9bIID: FT-IR (KBr, cm^{-1}): 3306 (s), 3119 (w), 2924 (s), 2853 (s), 1711 (s), 1663 (s), 1657 (s), 1588 (m), 1560 (s), 1437 (w), 1379 (m), 1345 (m), 1267 (w), 1239 (m), 1186 (w), 1132 (w), 1104 (w), 1028 (w), 905 (m), 844 (w), 778 (s), 746 (w), 687 (w), 625 (w), 597 (w), 539 (w), 497 (w), 473 (w). UV (DMF): λ_{max} (ϵ) 264 (104670.36), 335 nm ($39349.76 \text{ L mol}^{-1} \text{ cm}^{-1}$).

PA9cIID: FT-IR (KBr, cm^{-1}): 3314 (m), 3073 (m), 2955 (m), 2925 (s), 2854 (s), 1706 (m), 1665 (s), 1588 (s), 1550 (s), 1436 (s), 1378 (m), 1341 (m), 1282 (w), 1239 (w), 1186 (w), 1154 (w), 1103 (m), 1074 (m),

1028 (w), 909 (s), 844 (s), 780 (m), 745 (s), 712 (s), 679 (w), 618 (w), 547 (w), 497 (w). UV (DMF): λ_{\max} (ϵ) 264 (28690.48), 335 nm (31488.09 L mol⁻¹ cm⁻¹).

PA9dIID: FT-IR (KBr, cm⁻¹): 3305 (s), 3070 (w), 2921 (s), 2851 (s), 1707 (s), 1665 (s), 1633 (s), 1588 (m), 1541 (s), 1466 (w), 1436 (w), 1378 (m), 1341 (m), 1273 (w), 1239 (m), 1185 (w), 1102 (w), 1028 (w), 938 (w), 909 (w), 844 (w), 779 (m), 744 (w), 687 (w), 587 (w), 541 (w), 497 (w), 476 (w). ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.71 (d, 3H, CH₃, *J* = 5.17 Hz), 1.23 (d, 3H, CH₃, *J* = 5.59 Hz), 1.22–1.31 (m, 12H, CH₂), 2.82 (m, 1H, CH, *J* = 6.40 Hz), 5.27 (d, 1H, CH, *J* = 8.06 Hz), 8.00 (s, 2H, CH), 8.11 (s, 1H, CH), 8.41 (s, 2H, CH), 8.57 (t, 4H, CH, *J* = 11.18, Hz), 9.77 (s, 2H, NH), 9.85 (s, 1H, NH). UV (DMF): λ_{\max} (ϵ) 264 (21607.14), 335 nm (31488.05 L mol⁻¹ cm⁻¹).

2.5. Preparation of MCNT suspension and modified GCE

To eliminate metal oxide catalysts within the nanotubes, multi-walled carbon nanotubes were refluxed in a 2.0 M HNO₃ for 15 h, and then was washed thoroughly with twice-distilled water and dried at R.T. The purified MCNTs were dispersed in acetonitrile (0.1 mg MCNTs/10 mL) by using ultrasonic agitation to obtain a relative stable suspension. The GCE was carefully polished with 0.05 μ m alumina slurry on a polishing cloth, and then washed ultrasonically in methanol and water. The cleaned GCE was coated by casting 300 μ L of the black suspension of MCNTs and dried in an oven at 60 °C. The microscopic areas of the MCNT-modified GCE and the bare GCE were obtained by CV using 1 mM of K₃Fe(CN)₆ as a probe at different scan rates. For a reversible process, the Randles–Sevcik formula has been used:

$$i_{pa} = 2.69 \times 10^5 n^{3/2} A C_0 D_R^{1/2} \nu^{1/2} \quad (1)$$

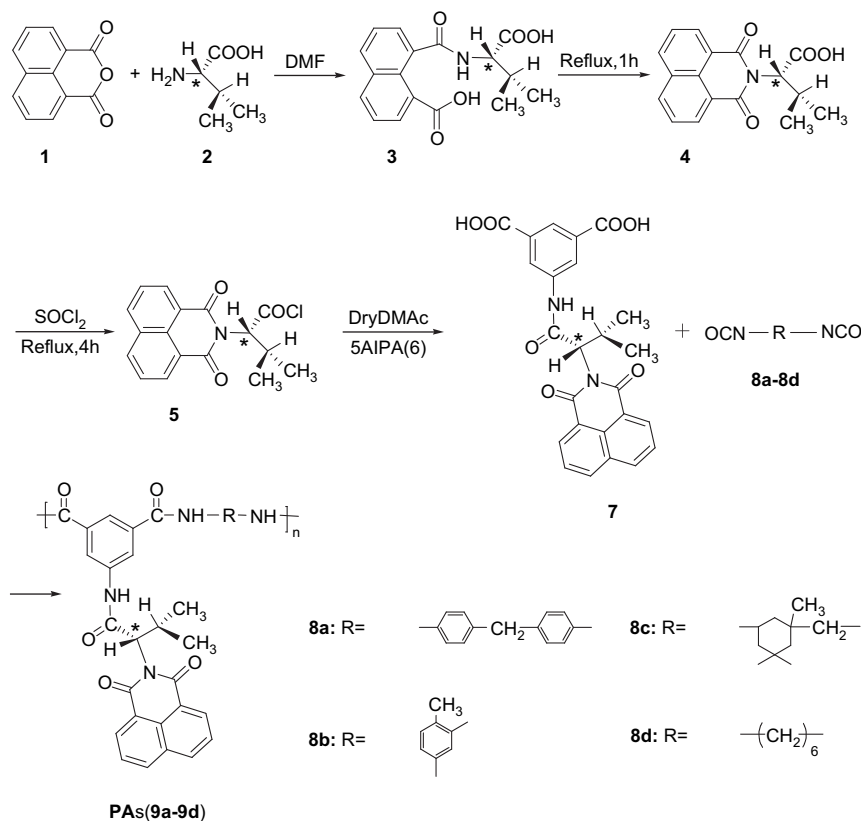
where i_{pa} refers to the anodic peak current, n is the electron transfer number, A is the surface area of the electrode, D_R is diffusion

coefficient, C_0 is the concentration of K₃Fe(CN)₆ and ν is the scan rate. For 1 mM of K₃Fe(CN)₆ in the 0.1 M KCl electrolyte, $n = 1$ and $D_R = 7.6 \times 10^{-6}$ cm² s⁻¹, then from the slope of the i_{pa} versus $\nu^{1/2}$ relation, the microscopic areas can be calculated. On bare GCE, the electrode surface was found to be 0.0314 cm² and for MCNT-modified GCE the surface was nearly 1.8–2 times greater [43].

3. Results and discussion

3.1. Monomer synthesis

Imide acid **4** was synthesized by the condensation reaction of phthalic anhydride (**1**) with 1.1 molar ratio of *S*-valine (**2**) in DMF solution. The chemical structure and purity of compound **4** were proven by using TLC, elemental analysis, FT-IR, ¹H NMR and ¹³C NMR spectroscopic techniques. The ¹H NMR spectrum of this compound shows the characteristic absorption of two diastrotopic CH₃ (doublet) at 0.70 and 1.21 ppm, C–H chiral center (doublet) and acidic O–H at 5.17 and 12.71 ppm, respectively. The ¹³C NMR spectrum shows four different carbons for the aliphatic chiral segment, five carbons for the aromatic segment, imide and acid carbon groups. Imide acid **4** was reacted with thionyl chloride and acid chloride **5** was obtained in high yield. FT-IR spectrum of this compound does not show a broad peak at 2400–3400 cm⁻¹, which confirms that the acidic hydroxyl group is completely converted to acid chloride. The ¹H NMR spectrum of this compound shows a pattern similar to that of compound **4**, but the peaks shifted downfield and the acidic proton is omitted in the ¹H NMR spectrum. The reaction of compound **5** with 5AIPA was performed in dry DMAc in the presence of TEA at 10 °C. The resulting novel optically active aromatic diacid **7** with pendent amide, imide and chiral groups was obtained in high yield (Scheme 1), and its chemical structure and purity were confirmed by TLC, elemental analysis,



Scheme 1. Synthesis and polycondensation reactions of monomer **7** with different diisocyanates.

FT-IR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The ^1H NMR spectrum of this monomer shows the characteristic absorption of the C–H chiral center (doublet), N–H amide group and acidic O–H at 5.30, 9.95 and 13.25 ppm, respectively. The ^{13}C NMR spectrum shows four different carbons for the aliphatic chiral segment, nine carbons for aromatic parts, imide, amide and acid carbon groups (Figs. 1 and 2). The elemental analysis results are also in good agreement with calculated percentages for carbon, hydrogen, and nitrogen contents.

3.2. Polymer synthesis

In this investigation, polycondensation reactions of novel monomer **7** with diisocyanates both via conventional heating (method I) and under microwave irradiation conditions (method II) in RTILs as reaction media are reported for the first time. RTILs, predominantly those based on substituted imidazolium cations, which can be prepared simply from the commercially available starting material, *N*-trimethylsilylimidazole and alkyl halides, were used in this investigation [3,7,8]. Thus, 1,3-dipropyl imidazolium bromide [(1,3-Pr₂im)Br], 1,3-diisopropyl imidazolium bromide [(1,3-Isopr₂im)Br], 1,3-dibutyl imidazolium bromide [(1,3-Bu₂im)Br], 1,3-dipentyl imidazolium bromide [(1,3-Pent₂im)Br], 1,3-dihexyl imidazolium bromide [(1,3-Hex₂im)Br], 1,3-diheptyl imidazolium bromide [(1,3-Hep₂im)Br], 1,3-diallyl imidazolium bromide [(1,3-Al₂im)Br], 1,3-diallyl imidazolium chloride [(1,3-Al₂im)Cl], 1,3-dibenzyl imidazolium bromide [(1,3-Bz₂im)Br], 1,3-dibenzyl imidazolium chloride [(1,3-Bz₂im)Cl] as ILs were selected. It is important to mention that all aforementioned ILs made in this work are liquid at room temperature and are thermally stable [3]. Initially, we examined the formation of PAs via polycondensation of compound **7** with the MDI (**8a**) in RTILs under conventional heating (method I). The optimization of the procedure by varying different types of ILs, the time of heating and using different types of catalysts was carried out to achieve polymers with high yields and

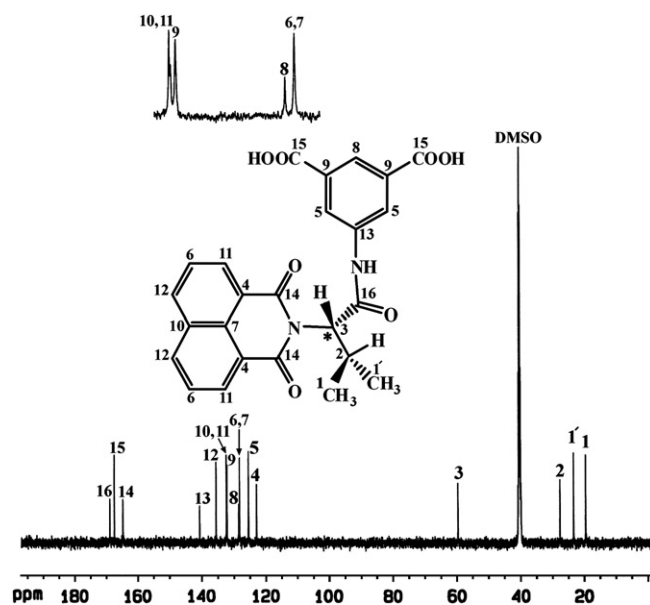


Fig. 2. ^{13}C NMR (500 MHz) spectrum of monomer **7** in $\text{DMSO-}d_6$ at R.T.

moderate inherent viscosities. As it is shown in Tables 1 and 2 all of these parameters have significant effect on the polymer chain growth. In order to optimize the reaction conditions, initially, the effect of ILs' nature was studied. According to Table 1, [(1,3-Isopr₂im)Br] gave satisfactory results, therefore it was selected for the synthesis of other PAs. As alkyl chain in ILs was increased, yields and inherent viscosities decreased. This may be explained by the decrease of polarity and as a result, the lower solubility power of longer alkyl chain of ILs. We also studied the effect of microwave power on the reaction of monomer **7** with MDI (**8a**) using [(1,3-Isopr₂im)Br] as the reaction medium (Table 2). A collection of experiments performed with different reaction times and power levels under microwave irradiation revealed that the optimal result was obtained after 60 s at 100% of power level (900 W). At this step, a clear polymeric film was formed. At higher reaction time, overheating of the reaction mixture took place with evolution of vapor, leading to decomposition of the reaction mixture probably due to the localized heating of the IL, which ultimately results in lower yields. The microwave-assisted polycondensation method with conventional heating technique was compared. When the same experiment was conducted by conventional heating in the presence of [(1,3-Isopr₂im)Br] as a solvent, it took very long time (8 h) for completion of the reaction. Thus, notable rate of acceleration was observed under microwave conditions. This demonstrated the beneficial effect of microwave as the energy source. The optimum conditions which were obtained under microwave and conventional heating conditions have been applied for the preparation of other PAs by the reaction of monomer **7** with TDI (**8b**), IPDI (**8c**) and HDI (**8d**) (Scheme 1), and the results are shown in Tables 3 and 4. The unsymmetric diisocyanates such as TDI and IPDI gave polymers with lower inherent viscosities compared to the symmetric MDI and HDI. This could pertain to the better possibility of chain arrangement and chain growth, when a step-growth polymerization reaction mechanism is performed during a defined reaction time. The inherent viscosities of the resulting polymers under microwave irradiation were in the range of 0.26–0.54 dL/g and the yields were 75–91%. The comparative results are summarized in Tables 3 and 4. Because of, microwave to heat molecules directly through the interaction between microwave energy and molecular dipole moments of the monomers containing polar groups that favor the absorption of microwaves, the yields and inherent viscosities of the

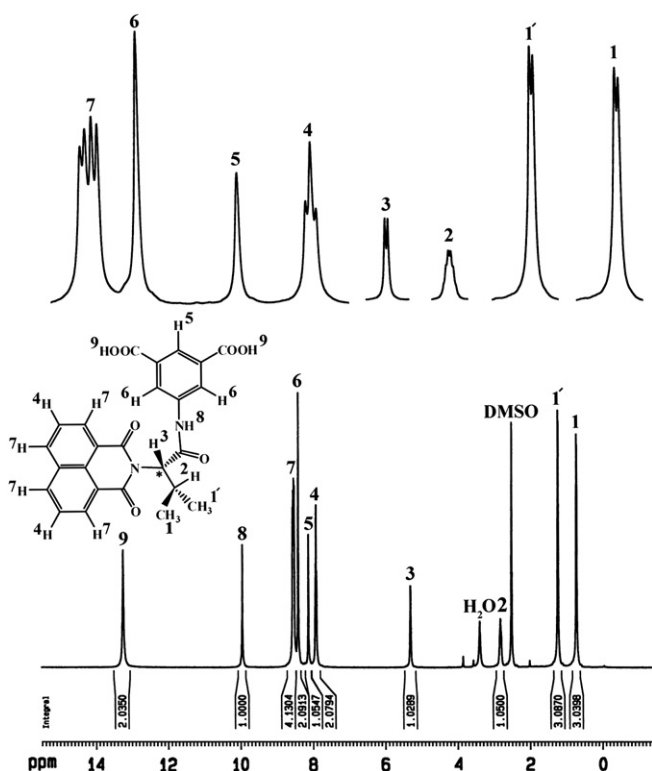


Fig. 1. ^1H NMR (500 MHz) spectrum of monomer **7** in $\text{DMSO-}d_6$ at R.T.

Table 1
The influence of IL cation and anion upon yield and molecular weight (η_{inh}) of **PA9aIB**

Polymer	IL structure	IL	Yield (%)	η_{inh}^a	$[\alpha]_D^{25b}$
9aIB		[(1,3-Isopr ₂ im)Br]	81	0.37	-53.2
9aIB		[(1,3-Pr ₂ im)Br]	80	0.32	-39.4
9aIB		[(1,3-Bu ₂ im)Br]	79	0.32	-46.6
9aIB		[(1,3-Pent ₂ im)Br]	71	0.31	-46.2
9aIB		[(1,3-Hex ₂ im)Br]	76	0.29	-38.3
9aIB		[(1,3-Hep ₂ im)Br]	77	0.29	-37.1
9aIB		[(1,3-Bz ₂ im)Br]	76	0.31	-35.2
9aIB		[(1,3-All ₂ im)Br]	78	0.32	-44.9
9aIB		[(1,3-Bz ₂ im)Cl]	74	0.30	-34.4
9aIB		[(1,3-All ₂ im)Cl]	72	0.30	-42.0

Using conventional heating (MDI = diacid = 2.17×10^{-4} mol, **RTILs** = 0.30 g, $T = 110$ °C, 8 h).

^a Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

^b Measured under the conditions the same as inherent viscosity.

products obtained by microwave irradiation versus thermal heating are higher. It is interesting to mention that all of the resulting polymers show optical rotation and therefore are optically active. Polymers made by different methods (Tables 3 and 4) show different optical rotation and this is consistent for all types of polymers made from different diisocyanates. These could be explained in terms of that optical rotation is highly dependent to the overall structure and regularity of the resulting polymer chains.

3.3. Polymer characterization

3.3.1. FT-IR and ¹H NMR study

The structure of polymers was implemented by means of elemental analysis, FT-IR and ¹H NMR (500 MHz) spectroscopic techniques. The elemental analysis results were in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in **PA** repeating unit. The FT-IR spectra of polymers show peak at around 3300 cm^{-1} for the N–H bond. Main absorption bands at $1770\text{--}1650\text{ cm}^{-1}$ range were attributed to the carbonyl groups. The two absorption bands at 2900 and 2850 cm^{-1} are related to the corresponding C–H stretching vibration. The ¹H NMR

spectrum of **PA9aIB** (Fig. 3) shows the N–H protons of amide groups at 9.95 and 10.35 ppm as two singlet peaks, which indicates the presence of amide groups in the polymer's side chain as well as main chain. The absorption of aromatic protons appeared in the range of 7.19–8.54 ppm. The proton of the chiral center appeared as quartet at 5.31 ppm. The ¹H NMR spectrum of **PA9dIB** based on HDI showed all peaks for aliphatic and aromatic protons which are consistent with the expected structure of corresponding polymer. The elemental analysis results are also in good agreement with the calculated percentages of carbon, hydrogen and nitrogen contents in the polymer repeating units.

3.3.2. Solubility of **PAs**

The solubility properties of **PAs** were studied in different solvents. Polymers are soluble in organic polar solvents such as DMAc, DMF, NMP, and in sulfuric acid at R.T. and are insoluble in solvents such as chloroform, methylene chloride, acetone, cyclohexane, tetrahydrofuran and water. Some polymers were partially soluble in methanol and ethanol and precipitated in MeOH/H₂O mixture. Because of the presence of bulky side chain, these polymers show good solubility.

Table 2

Optimization of reaction conditions for the preparation of **PAs** using conventional heating (method I) and microwave irradiation (method II)

Polymer	Microwave power	Reaction temperature	Reaction time	Yield (%)	η_{inh}^a (dL/g)	$[\alpha]_D^{25b}$
9aIB	100	–	30 s	–	–	–
9aIB	100	–	60 s	53	0.18	–32.3
9aIB	100	–	90 s	65	0.23	–37.2
9aIB	100	–	120 s	78	0.26	–47.1
9aIB	100	–	150 s	35	0.26	–30.5
9aIB	100	–	180 s ^c	–	–	–
9aIB	100	–	30 + 90 s	71	0.24	–32.9
9aIB	100	–	60 + 60 s	75	0.28	–30.0
9aIB	100	–	90 + 30 s	63	0.26	–27.4
9aIB	80	–	30 s	–	–	–
9aIB	80	–	60 s	47	0.12	–37.8
9aIB	80	–	90 s	56	0.16	–43.3
9aIB	80	–	120 s	63	0.18	–41.5
9aIB	80	–	150 s	52	0.19	–44.7
9aIB	70	–	30 s	–	–	–
9aIB	70	–	60 s	–	–	–
9aIB	70	–	90 s	66	0.19	–39.8
9aIB	70	–	120 s	66	0.20	–37.2
9aIB	70	–	150 s	54	0.20	–41.0
9aIB	–	120	6 h	69	0.32	–45.2
9aIB	–	110	6 h	74	0.35	–59.3
9aIB	–	100	6 h	79	0.32	–51.5
9aIB	–	120	8 h	73	0.36	–51.1
9aIB	–	110	8 h	81	0.37	–53.2
9aIB	–	100	8 h	84	0.34	–57.7
9aIB	–	120	10 h	65	0.33	–60.0
9aIB	–	110	10 h	76	0.33	–53.1
9aIB	–	100	10 h	80	0.31	–51.4
9aIB	–	120	12 h	42	0.35	–64.1
9aIB	–	110	12 h	57	0.35	–62.0
9aIB	–	100	12 h	71	0.35	–58.1

IL, [(1,3-Isopr₂im)Br]; MDI = monomer = 2.17×10^{-4} mol (methods I and II).

^a Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

^b Measured under the same conditions as inherent viscosity.

^c Decomposition occurred at higher power or extended irradiation time.

3.3.3. UV–vis absorption and fluorescence characteristics

Monomer **7** exhibited maximum UV–vis absorption at 264 and 335 nm in DMF solution because of the π – π^* transitions of the aromatic chromophore (naphthalene). Comparison of UV–vis absorption of the resulting polymers with a series of segmented **PAs** containing naphthalene shows that the latter polymers gave absorption at 264 and 335 nm in DMF solution [7,44]. The absorption and fluorescence spectra of the monomer **7**, **PA9aIB**, **PA9bIB**, **PA9cIB** and **PA9dIB** are shown in Figs. 4 and 5, respectively. For example, in the case of **PA9dIB**;

Table 3

Reaction conditions for the polymerization of diacid **7** with different diisocyanates and some physical properties of **PAs**, **9aIA–9dIB** prepared by method I^a

Polymer	Diisocyanate	Catalyst	Non-solvent	Yield (%)	η_{inh}^b (dL/g)	$[\alpha]_D^{25c}$
9aIA	8a	TEA	MeOH/water	82	0.52	–61.0
9aIB	8a	No cat	MeOH/water	81	0.37	–53.2
9aIC	8a	Py	MeOH/water	78	0.51	–73.1
9aID	8a	DBTDL	MeOH/water	90	0.40	–62.5
9aIE	8a	TBA	MeOH/water	80	0.46	–58.2
9aIF	8a	DABCO	MeOH/water	78	0.51	–58.3
9aIG	8a	DBTDL/5TEA	MeOH/water	89	0.52	–57.1
9aIH	8a	DBTDL/10TEA	MeOH/water	86	0.52	–51.2
9aIJ	8a	DBTDL/15TEA	MeOH/water	86	0.52	–57.0
9bIF	8b	DBTDL/5TEA	Water	81	0.33	–53.1
9bIB	8b	No cat	Water	80	0.30	–37.0
9cIF	8c	DBTDL/5TEA	Water	87	0.26	–44.1
9cIB	8c	No cat	Water	84	0.21	–41.1
9dIF	8d	DBTDL/5TEA	MeOH/water	75	0.38	–53.1
9dIB	8d	No cat	MeOH/water	77	0.33	–33.1

^a Method I: polymerization under conventional heating, 8 h at 110 °C.

^b Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

^c Measured under the conditions the same as inherent viscosity.

Table 4

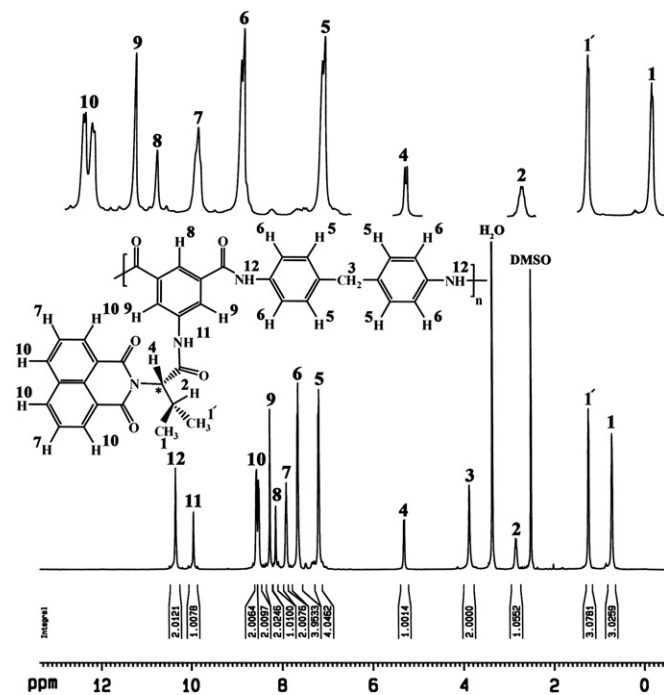
Reaction conditions for the polymerization of diacid **7** with different diisocyanates and some physical properties of **PAs**, **9aIA–9dIB** prepared by method II^a

Polymer	Diisocyanate	Catalyst	Non-solvent	Yield (%)	η_{inh}^b (dL/g)	$[\alpha]_D^{25c}$
9aIIA	8a	TEA	MeOH/water	85	0.54	–37.2
9aIIB	8a	No cat	MeOH/water	75	0.28	–30.0
9aIIC	8a	Py	MeOH/water	84	0.51	–25.1
9aIID	8a	DBTDL	MeOH/water	91	0.56	–22.5
9aIIE	8a	TBA	MeOH/water	83	0.36	–47.0
9aIIF	8a	DABCO	MeOH/water	81	0.48	–39.2
9bIID	8b	DBTDL	Water	80	0.34	–59.1
9bIIB	8b	No cat	Water	80	0.34	–53.6
9cIID	8c	DBTDL	Water	89	0.28	–37.1
9cIIB	8c	No cat	Water	87	0.26	–32.6
9dIID	8d	DBTDL	MeOH/water	83	0.42	–48.8
9dIIB	8d	No cat	MeOH/water	75	0.33	–39.2

^a Method II: the reaction mixture was irradiated in the microwave oven for 1 min then cooled and irradiated for 1 min again at 100% of its power.

^b Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

^c Measured under the conditions the same as inherent viscosity.



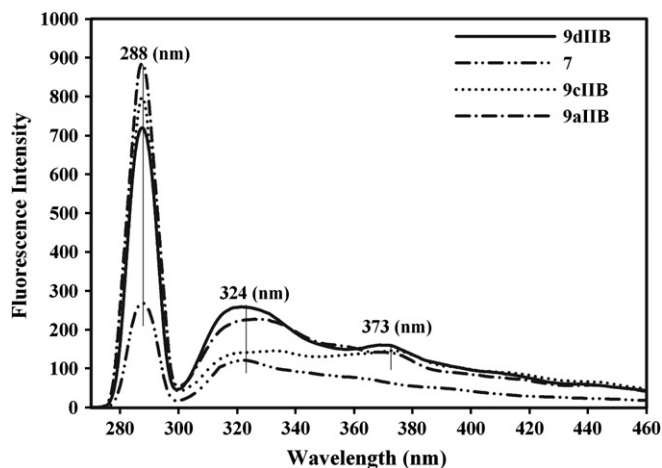


Fig. 5. Fluorescence spectrum of monomer 7, PA9aIIB, PA9cIIB and PA9dIIB.

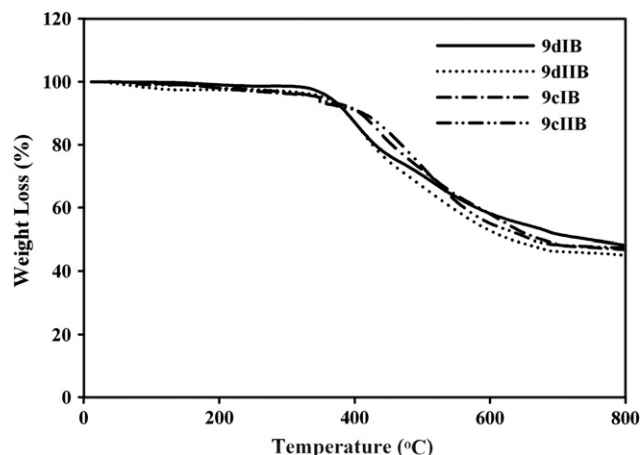


Fig. 6. TGA thermograms of PA9cIB, PA9cIIB, PA9dIB and PA9dIIB under a nitrogen atmosphere at a heating rate of 10 °C/min.

when it was excited at 264 nm, emission fluorescence wavelengths were observed at 288, 324 and 373 nm. The emission fluorescence pattern of these polymers was also compared with the PAs and poly(urea-urethane) which gave similar pattern [7,44,45]. All of these compounds show almost similar UV-vis and fluorescence spectral pattern.

3.3.4. Thermal properties

The thermal stability of some PAs was investigated by TGA/DTG and DSC techniques under a nitrogen atmosphere. Fig. 6 shows the TGA curves for some PA9cIB, PA9cIIB, PA9dIB and PA9dIIB. Samples were heated up to 300 °C at the rate of 20 °C min⁻¹ in N₂, quenched to -50 °C and return to obtain T_g. Thermal stability of the polymers was studied based on 5 and 10% weight loss (T₅, T₁₀) of the polymers and residue at 800 °C (char yield). Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftzyer equation [46]. $LOI = 17.5 + 0.4CR$ where CR = char yield. For all the polymers LOI values calculated based on their char yield at 800 °C was higher than 28. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers. T₁₀ (°C), char yield and LOI of these polymers are in the range of 388–448, 45–63 and 35–43, respectively. According to Table 5 it is clear that polymers based on TDI and MDI have better thermal stability and higher LOI as compared to other PAs. It could be pertained to aromatic, rigid structure of diisocyanates compared to aliphatic, flexible structure

Table 5
Thermal properties of novel PAs

Polymer	T ₅ ^a (°C)	T ₁₀ ^b (°C)	Char yield ^c	T _g ^d (°C)	DTG	LOI ^e
9aIB	391	428	52	180	417	38
9aIIB	394	428	50	–	419	37
9bIB	407	448	63	155	430	43
9bIIB	402	446	58	–	429	41
9cIB	363	388	45	120	400	35
9cIIB	363	392	49	–	410	37
9dIB	355	410	47	135	388	36
9dIIB	355	415	47	–	375	36

^a Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

^c Percentage weight of material left undecomposed after TGA analysis at a temperature of 800 °C in a nitrogen atmosphere.

^d Glass transition temperature was recorded at a heating rate of 20 °C/min in a nitrogen atmosphere.

^e Limiting oxygen index (LOI) evaluating at char yield at 800 °C.

of diisocyanates. The T_gs of the PAs were determined by DSC and the results are given in Table 5. The DSC analyses for PAs show T_g at around 120–180 °C. Fig. 7 shows the DSC curve for PA9bIIB.

3.4. Electrochemical behavior of compounds on MCNT-modified electrode

Modification of glassy carbon electrodes with a MCNT layer leads to a strong interfacial accumulation of materials and provides highly sensitive adsorptive stripping measurements. Such an ability of the surface-confined MCNT to promote the accumulation of polymer 9cIIB which is illustrated in Fig. 8 displays that electro-oxidation potential of this polymer in acidic solutions is more than basic solutions, as shown in cycle 1 of voltammograms (Fig. 8). Polymer 9cIIB is oxidized at pH = 2 in the region of a potential of 1.2 V (peak 1) and at pH = 9 at around 0.8 V (peak 6). Electro-oxidized products of this polymer can be reduced (peaks 2, 3 at pH = 2 or peak 7 at pH = 9 in Fig. 8). Fouling effects on the electrode prevent more oxidation of this polymer, thus in the next cycle of voltammograms the oxidation current of polymers reduces (peak 1 at pH = 2 and peak 6 at pH = 9 in Fig. 8).

In order to be able to interpret the voltammograms of resulting PAs, it was necessary to study the electrochemical behavior of monomer 7, imide acid 4 as well as starting material 5AIPA. The results showed that monomer 7 has the electrochemical behavior similar to polymers 9aIIB, 9bIIB, 9cIIB and 9dIIB. Imide acid 4 doesn't show any peak in this potential region in acidic as well as basic solution, but 5AIPA by scanning cyclic potential from +0.2 to

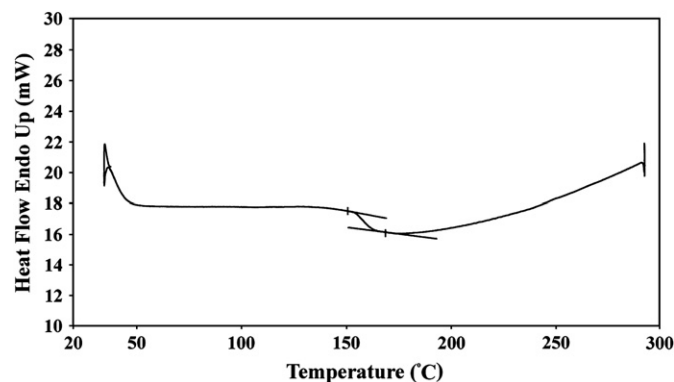


Fig. 7. DSC thermogram of PA9bIIB under a nitrogen atmosphere at a heating rate of 20 °C/min.

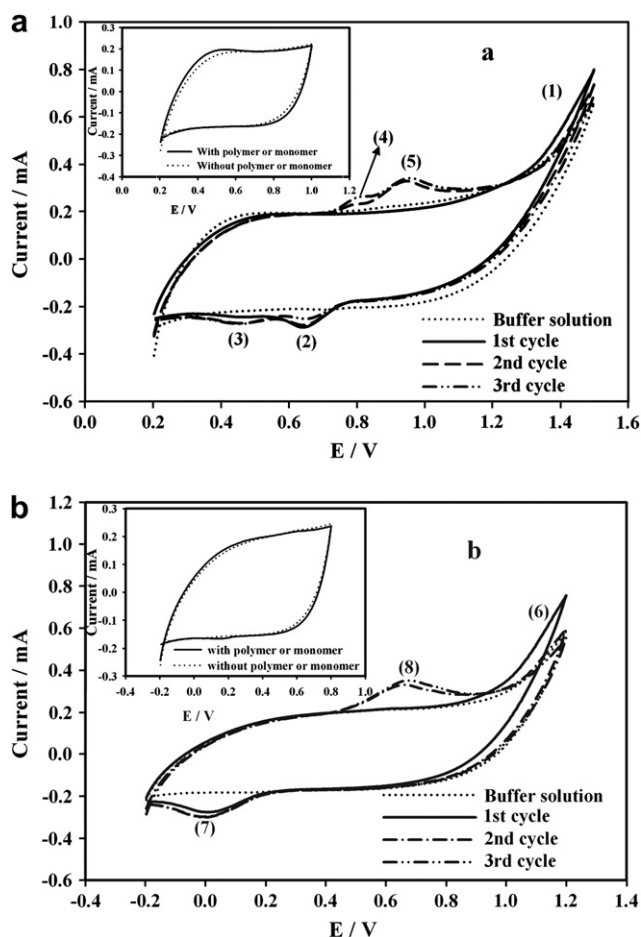


Fig. 8. Adsorptive stripping voltammograms at the MCNT-modified glassy carbon electrode for 50 μM of **PA9cIB** at (a) pH = 2; (b) pH = 9. Other conditions are scan rate of 100 mV s^{-1} and accumulation time of 5 min at open circuit potential. Insets show the voltammograms prior to oxidation of **PA9cIB**.

+1.5 V in acidic solution shows two oxidation and two reduction transition similar to peaks 4 and 5 (Fig. 8a in forward scanning) and peaks 2 and 3 (Fig. 8a in backward scanning). Also this compound shows one oxidation and one reduction peak in basic solution similar to peaks 7 and 8 shown in Fig. 8b. It is very interesting to mention that the overall electrochemical behavior of 5AIPA on MCNTs is very similar to electropolymerization of aniline since their cyclic voltammetric patterns are closely related. Since polyaniline made via electropolymerization technique has many applications for constructing electrochemical sensors, thus, 5AIPA moieties in the resulting **PA** backbone as well as in monomer **7**, which can in situ decompose by electro-oxidation process to aniline derivatives, are electroactive compounds and can be further electropolymerized on the electrode surface. Therefore, these kinds of

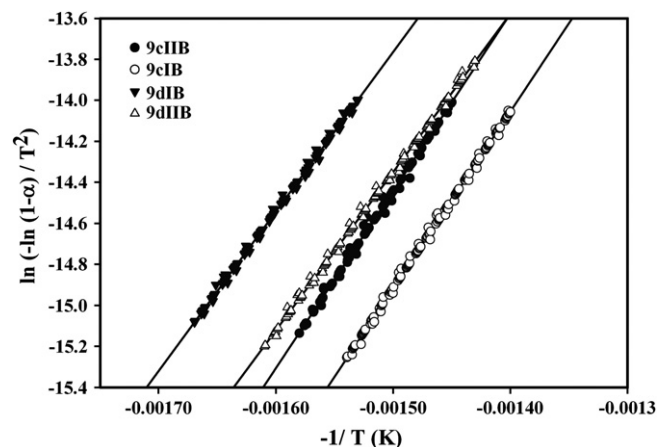


Fig. 9. Plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1/T$ for **PA9cIB**, **PA9cIIB**, **PA9dID** and **PA9dIID**.

monomers and polymers are very valuable to be used in electrochemical sensors [47–49].

3.5. Kinetic study of thermal decomposition of synthesized **PAs**

In order to study the effect of different existing functional groups in the resulted **PAs** on their thermal stability, the thermal kinetic investigation was carried out using the Coats–Redfern method, Eq. (2) [50–54]. The results are listed in Table 6. The calculating of thermodynamic data applied on the first decomposition peak in each of eight **PAs**.

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dT \quad (2)$$

For convenience of integration the lower limit T_1 is usually taken as zero. This equation upon integration gives Eq. (3):

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \quad (3)$$

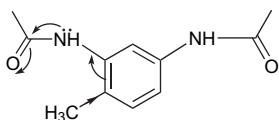
The correlation coefficient, r , computed using least square method for n value which gave the best fit ($r \cong 1$) was chosen as the order parameter for the decomposition stage in all cases by plotting the left-hand side of Eq. (3) versus $-1/T$ (Fig. 9). α and φ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$ and E is the activation energy in kJ mol^{-1} . A plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $-1/T$ was found to be linear; from the slope of this line, E was calculated and A (Arrhenius constant) can be deduced from the intercept. The entropy of activation ΔS in $\text{J mol}^{-1} \text{K}^{-1}$ was calculated by using Eq. (4).

$$\Delta S = R \ln\left(\frac{Ah}{K_B T_S}\right) \quad (4)$$

Table 6
Kinetic parameters for the degradation of **PAs** determined using the Coats–Redfern method

Polymer	Parameter					r
	E (kJ mol^{-1})	A (s^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
9aIB (380–488)	131.8	395.3	–0.20	126.1	264.1	0.996
9aIIB (375–487)	128.1	384.2	–0.20	122.4	260.8	0.994
9bIB (380–500)	223.6	45.1	–0.22	217.8	372.5	0.999
9bIIB (380–510)	237.2	43.2	–0.22	231.3	385.8	0.996
9cIB (350–465)	71.8	326.9	–0.20	66.2	200.8	0.996
9cIIB (365–480)	71.6	195.1	–0.20	65.9	202.6	0.998
9dIB (310–430)	64.6	158.3	–0.20	59.1	191.4	0.998
9dIIB (300–428)	64.2	80.3	–0.20	58.8	188.4	0.997

where K_B is the Boltzmann constant, h is the Plank's constant and T_S is the DTG peak temperature [52]. The other kinetic parameters such as enthalpy of activation (ΔH), and Gibbs free energy (ΔG) can be calculated via the equations; $\Delta H = E - RT_m$ and $\Delta G = \Delta H - T_m \Delta S$ accordingly, and are shown in Table 6. The positive values of ΔH indicate that the dissociation processes are endothermic in nature and enhanced with the rise of temperature. ΔG values for the dissociation constants are positive, thus dissociation processes are non-spontaneous. The negative ΔS values for the decomposition step indicate that the all studied **PAs** have a more ordered structure after the transition than the reactants in their activated states [53]. The overall activation energy for thermal decomposition of **PAs** based on TDI is 237.17 kJ mol⁻¹ which is much higher than other **PAs**. This reveals the more thermal stability for this **PA**. One way to explain this behavior would be from the initial homolytic cleavage of ph-CH₃ bond which produces radical intermediate and therefore, provides a more stable cross-linked structure [54]. The other way to explain this performance would be due to electron releasing (+I effect) property of methyl group which activates the amide linkages and makes them highly activated for hydrogen bonding formation as shown below:



4. Conclusions

In this study, we have successfully synthesized a novel chiral dicarboxylic acid (**7**), containing a rigid naphthalimide and flexible *S*-valine pendent group. A series of novel optically active **PAs** were prepared by direct polycondensation from compound **7** with various diisocyanates. Flexible pendent groups of these polymers disturbed the strong interchain forces and inherent macromolecular rigidity. The choice of 1,8-naphthalenedicarboxylic anhydride was due to the many derivatives of 1,8-naphthalic anhydride exhibit strong fluorescence emission and serve for this reason as fluorescent dyes and fluorescent whitening agents. The resulting polymers have many applications as photoactive materials which can be used in solar energy collectors as electro-optically sensitive materials and for laser activity [39–42]. The results presented herein also clearly demonstrate that incorporation of the naphthalimide group into the polymer side chain as well as combination of the aromatic backbone and aliphatic pendent group in the presence of several functional groups remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. Because of the existence of amino acids in the polymer pendent group these polymers are expected to be biodegradable and are therefore classified under environmentally friendly polymers. Here also we have developed an efficient, convenient and practical approach for the synthesis of thermally stable and photoactive **PAs** using microwave irradiation in conjunction with the potential of ILs as an eco-friendly solvent. In this study, advantages of both of the IL and microwave irradiation have been utilized. This methodology offers significant improvements with regard to yield of products, inherent viscosities, thermal stability, simplicity in operation, cost efficiency, green aspects avoiding toxic solvents and has much promise for further applications. Furthermore, the above results demonstrate that microwave heating is a convenient and facile method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. Moreover, electrochemical studies by adsorptive stripping cyclic voltammetry technique on the MCNT-modified glassy carbon electrode showed that electrochemical decomposition and stability of monomer **7** and polymers **9aIIb**,

9bIIb, **9cIIb**, **9dIIb** in acidic solution are more difficult than in basic solution and electrochemical behavior of polymers is very similar to monomer **7**. Also, 5AIPA moiety, one of the decomposing products of electro-oxidized polymers or monomer **7**, is only electroactive compound and can be electropolymerized on electrode surface. Studies on thermal degradation of polymers are a matter of major interest for determining the thermal stability of the polymers. Thermogravimetry has been extensively used for such studies. To perform the kinetic study of the integral curve directly obtained from thermogravimetric analysis, it is necessary to use an integral analysis method. In this paper we performed a study of the temperature integral for the determination of the activation energy. Although, the E values obtained by different methods show more than 2% error, but by using the Coats and Redfern method less than 2% error was achieved [55].

Acknowledgements

We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged. We also extend our thanks to Miss. Marziyeh Khani, Zahra Rafiee, Mr. Mehdi Moradi, Sajad Damiri and Majid Kolehdoozan.

References

- [1] Biedroń T, Kubisa P. *Polym Int* 2003;52:1584–8.
- [2] Poliakkoff M, Fitzpatrick JM, Farren TR, Anastas PT. *Science* 2002;297:807–10.
- [3] Vygodskii YS, Lozinskaya EI, Shaplov AS, Lyssenko KA, Antipin MY, Urman YG. *Polymer* 2004;45:5031–45.
- [4] Cho C, Thuy Pham TP, Jeon YC, Vijayaraghavan K, Choe WS, Yun YS. *Chemosphere* 2007;69:1003–7.
- [5] Welton T. *Chem Rev* 1999;99:2071–83.
- [6] Davis JH, Fox PA. *Chem Commun* 2003:1209–12.
- [7] Mallakpour S, Rafiee Z. *Polymer* 2007;48:5530–40.
- [8] Mallakpour S, Kowsari E. *J Polym Sci Part A Polym Chem* 2003;41:3974–88.
- [9] Liao L, Liu L, Zhang C, Gong S. *Macromol Rapid Commun* 2006;27:2060–4.
- [10] Kappe CO. *Angew Chem Int Ed* 2004;43:6250–84.
- [11] Mallakpour S, Rafiemanzelat F. *J Appl Polym Sci* 2005;98:1781–92.
- [12] Wiesbrock F, Hoogenboom R, Schubert US. *Macromol Rapid Commun* 2004;25:1739–64.
- [13] Kretschmann O, Schmitz S, Ritter H. *Macromol Rapid Commun* 2007;28:1265–9.
- [14] Hakala U, Wähälä K. *J Org Chem* 2007;72:5817–9.
- [15] Borriello A, Nicolais L, Fang X, Huang SJ, Scola DA. *J Appl Polym Sci* 2007;103:1952–8.
- [16] Zhu YJ, Wang WW, Qi RJ, Hu XL. *Angew Chem* 2004;116:1434–8.
- [17] Wulff G. *Angew Chem Int Ed Engl* 1989;28:21–37.
- [18] Okamoto Y. *Prog Polym Sci* 2000;25:159–62.
- [19] Liaw DJ, Liaw BY, Kang ET. *Macromol Chem Phys* 1999;200:2402–6.
- [20] Feng L, Hu J, Liu Z, Zhao F, Liu G. *Polymer* 2007;48:3616–23.
- [21] Sanda F, Yukawa Y, Masuda T. *Polymer* 2004;45:849–54.
- [22] Hsiao SH, Chen CW, Liou GS. *J Polym Sci Part A Polym Chem* 2004;42:3302–13.
- [23] Mallakpour S, Kolehdoozan M. *J Appl Polym Sci* 2007;104:1248–54.
- [24] Liaw DJ, Liaw BY, Yang CM, Hsu PN, Hwang CY. *J Polym Sci Part A Polym Chem* 2001;39:1156–61.
- [25] Liaw DJ, Hsu PN, Chen JJ, Liaw BY, Hwang CY. *J Polym Sci Part A Polym Chem* 2001;39:1557–63.
- [26] Onciu M. *J Appl Polym Sci* 2007;103:2013–20.
- [27] Mallakpour S, Rafiee Z. *J Appl Polym Sci* 2007;103:947–54.
- [28] Ferrero E, Espeso JF, Campa JG, Abajo JD, Lozano AE. *J Polym Sci Part A Polym Chem* 2002;40:3711–24.
- [29] Zhao Q, Gan Z, Zhuang Q. *Electroanalysis* 2002;14:1609–13.
- [30] Merkoçi A, Pumera M, Llopis X, Pérez B, del Valle M, Alegret S. *Trends Anal Chem* 2005;24:826–38.
- [31] Gooding JJ. *Electrochim Acta* 2005;50:3049–60.
- [32] Merkoçi A. *Electroanalysis* 2007;19:739–41.
- [33] Trojanowicz M. *Trends Anal Chem* 2006;25:480–9.
- [34] Iijima S. *Nature* 1991;354:56–8.
- [35] Ajayan PM. *Chem Rev* 1999;99:1787–99.
- [36] Nugent JM, Santhanam KS, Rubio A, Ajayan PM. *Nano Lett* 2001;1:87–91.
- [37] Gong K, Yan Y, Zhang M, Su L, Xiong S, Mao L. *Anal Sci* 2005;21:1383–93.
- [38] Wang J. *Electroanalysis* 2005;17:7–14.

- [39] Xuhong Q, Zhenghua Z, Kongchang C. *Dyes Pigments* 1989;11:13–20.
- [40] Wolarz E, Moryson H, Bauman D. *Displays* 1992;13:171–8.
- [41] Xuhong Q, Jun T, Jiandong Z, Yulan Z. *Dyes Pigments* 1994;25:109–14.
- [42] Adam W, Qian X, Saha-Moeller CR. *Tetrahedron* 1993;49:417–22.
- [43] Xu Q, Wang SF. *Mikrochim Acta* 2005;151:47–52.
- [44] Simas ER, Akcelrud L. *J Lumin* 2003;105:69–79.
- [45] Mallakpour S, Rafiee Z. *Eur Polym J* 2007;43:5017–25.
- [46] Van Krevelen DW, Hoftyzer PJ. *Properties of polymers*. 3rd ed. Elsevier Scientific Publishing; 1976.
- [47] Qu Fengli, Yang M, Jiang J, Shen G, Yu R. *Anal Biochem* 2005;344:108–14.
- [48] Nyffenegger RM, Penner RM. *J Phys Chem* 1996;100:17041–9.
- [49] Muñoz E, Colina A, Heras A, Ruiz V, Palmero S, López-Palacios J. *Anal Chim Acta* 2006;573–574:20–5.
- [50] Coats AW, Redfern JP. *Nature* 1954;201:68–9.
- [51] Chen Y, Wang Q. *Polym Degrad Stab* 2007;92:280–91.
- [52] Radhakrishnan Nair MN, Thomas GV, Gopinathan Nair MR. *Polym Degrad Stab* 2007;92:189–96.
- [53] Abu-Eittah RH, ZaKi NG, Mohamed MM, Kamel LT. *J Anal Appl Pyrolysis* 2006;77:1–11.
- [54] Rao VL, Sabeena PU, Saxena A, Gopalakrishnan C, Krishnan K, Ravindran PV, et al. *Eur Polym J* 2004;40:2645–51.
- [55] Pérez-Maqueda LA, Sánchez-Jiménez PE, Criado JM. *Polymer* 2005;46:2950–4.