Direct Polycondensation of New Poly(amide-imide)s Containig N-(4-Carboxy phenyl) Trimellitimide By Using Triphenyl Phosphite

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Abstract

Introduction: Aromatic polyimides are heat resistant polymers that generally show excellent mechanical strength and stability. However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(sulfone-imide)s, poly (ether-imide)s, poly(ester-imide)s and other copolymers have been prepared.

Aim: In this article, we describe synthesis and characterization a series of novel PAIs (5a-f) containing trimethylene and hydantoin segments between imide rings in the main chain by the direct polycondensation reaction of N-(4- carboxyphenyl)-trimellitimide (3) with six hydantoin derivatives (4a-f) in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

Materials and Methods: All chemicals were purchased from Fluka and Merck Chemical Company. The ¹H-NMR spectrum (300 MHz) was recorded on a Bruker Avance 300 spectrometer (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England).

Results: Six new poly(amide-imide)s (**5a-f**) were prepared by direct polycondensation reaction of N-(4-carboxyphenyl)-trimellitimide (**3**) with six different of 5,5-disubstituted hydantoin derivatives (**4a-f**) using triphenyl phosphate (TPP) and pyridine as condensing agents in N-methyl-2-pyrolidone (NMP) solution containing dissolved calcium chloride. The polycondensation reaction produced a series of novel poly(amide-imide)s (**5a-f**) in high yields with inherent viscosities between 0.26-0.62 dL/g. The resulted polymers were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test and FT-IR spectroscopy.

Conclusion: This work involved the synthesis and characterization of several new PAIs (**5a-f**) by direct polycondensation reaction of N-(4-carboxyphenyl)trimellitimide (**3**) with different 5,5-disubstituted hydantoin derivatives (**4a-f**) using TPP and pyridine as condensing agents in NMP solution containing dissolved calcium chloride. These new PAIs are soluble in various organic solvents and have good thermal stability. These properties could make these PAIs attractive for practical applications, such as processable high-performance engineering plastics.

Keywords: Thermallystablepolymers, Poly(amide-imide), N-(4-Carboxyphenyl)-trimellitimide, Hydantoin derivatives.

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Introduction

Aromatic polyimides are heat resistant polymers that generally show excellent mechanical strength and stability. Due to the increased performance characteristics demanded on polymers in various fields including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers in growing steadily.^[1] However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures.^[2] Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors. Therefore, some significant synthetic efforts, in the area of high-temperature resistant polymers, have been focused on improving their processability and solubility through the design and synthesis of new monomers.^[3] Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(sulfone-imide)s, poly(ether-imide)s, poly(ester-imide)s and other copolymers have been prepared.^[4–13] The triphenyl phosphate activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides has been reported by Yamazaki et al.^[14]

In this article, we describe synthesis and characterization a series of novel PAIs (**5a-f**) containing trimethylene and hydantoin segments between imide rings in the main chain by the direct polycondensation reaction of N-(4-carboxyphenyl)-trimellitimide (**3**) with six hydantoin derivatives (**4a-f**) in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

Materials and Methods

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI, USA) and Merck Chemical Co. (Germany). **Techniques**

The ¹H-NMR spectrum (300 MHz) was recorded on a Bruker Avance 300 spectrometer (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies were reported in wave number (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were recorded on a Mettler TA 4000 System under N2 atmosphere at a rate of 10 °C/min. Elemental analyses were performed by Arak Petrochemical Company, Arak, Iran.

Monomer synthesis

N-(4-Carboxyphenyl)trimellitimide (3)

Trimellitic anhydride (1) (1.92 g, 10 mmol), 4-amino benzoic acid (2) (1.33 g, 10 mmol) and 32 ml of acetic acid were added into a 250 ml round-bottomed flask and a reflux system was set up. The mixture was stirred over night at room temperature and then refluxed for 8 hrs at 130 °C. The solvent was removed under reduced pressure until a white-cream precipitate formed. Then 100 ml of water and 5 ml of concentrated HCl were added into the flask. The mixture was stirred vigorously, filtered off and dried to give 2.84 g (91%) of compound (3). Mp: 375–377 °C. FT-IR (KBr): 2800-3100 (m, br), 1782 (w), 1724 (s), 1685 (s), 1601 (s), 1425 (s), 1377 (s), 1298 (s, sh), 1296 (m), 1091 (m), 925 (w), 854 (w), 769 (m), 723 (s), 507 (w) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.61-7.64 (d, 2H,); 8.08-8.12 (dd, 3H,); 8.33 (s, 1H); 8.42-8.45 (dd, 1H,) ppm. Analysis: Calculated for C₁₆H₉NO₆: C, 61.74; H, 2.91; N, 4.50; found: C, 61.40; H, 2.80; N, 4.30.

Hydantoin derivatives (4a-f)

Hydantoin derivatives were prepared according to a typical procedure.¹² Chemical reactions involved, are shown in scheme 1.



Scheme 1- Synthesis route for Hydantoin derivatives (4a-f)

Polymer synthesis

An equimolar mixture of diacid (3) (0.15 g, 0.482 mmol) and 5-spiro cyclopenthyl hydantoin (4f) (0.0742 g, 0.482 mmol) were placed in a 50 ml round-bottomed flask containing of 0.15 g CaCl₂, 1.26 ml triphenyl phosphite, 0.26 ml pyridine and 1.2 ml N-methyl-2-pyrolydone (NMP). The mixture was heated for 1 hr at 60 °C, 1 hr at 90 °C and then refluxed at 130 °C for 8 hrs until a viscose solution was formed. Then it was cooled to room temperature and 20 ml of methanol was added to reaction mixture. The precipitate was formed, filtered off and washed with methanol. The resulting polymer (5f) was dried under vacuum to yield 0.16 g (78%) of a white solid. All of the other PAIs (5a-f) were synthesized via the above method.

Polymer (5a)

FT-IR(KBr): 3067(w), 2943(w), 1780(w), 1742(s), 1720(s), 1591(m), 1510(m), 1489(s), 1390(s), 1275(s), 1197(s, sh), 1095(m), 949(m, sh), 748(m), 719(m), 688(m) cm⁻¹.

Polymer (5b)

Polymer (5c)

FT-IR(KBr): 3067(w), 2897(w), 1778(w), 1734(s), 1709(s), 1591(m), 1491(m), 1392(s), 1268(s, br), 1221(s), 1191(s), 1078(m), 933(m), 759(s), 732(m), 701(m) cm⁻¹.

Polymer (5d)

FT-IR(KBr): 3016(w), 1782(w), 1743(s), 1718(s), 1591(m), 1489(m), 1390(m), 1275(s), 1197(s, sh), 1122(w), 1022(w), 719(m) cm⁻¹.

Polymer (5e)

FT-IR(KBr): 3049(w), 2922(w), 1782(w), 1741(s), 1716(s), 1591(w), 1516(w), 1489(m), 1390(s), 1273(s, br), 1221(s), 1195(s), 1122(m), 1078(m), 1020(m), 748(m), 719(m), cm⁻¹. **Polymer (5f)**

FT-IR(KBr): 3063(w), 2943(w), 1782(s), 1745(s), 1716(s), 1591(m), 1489(m), 1390(m), 1282(s, br), 1197(s, sh), 1093(m), 1022(w), 933(m), 746(m, sh), 719(m), 688(m), 545(w) cm⁻¹

Results and Discussion Monomer synthesis

N-(4-Carboxyphenyl)trimellitimide (3) was prepared by one-step reaction as shown in Scheme 2. Diacid (3) was synthesized by condensation of one equimolar amount of anhydride (1) with one equimolar amount of 4-amino benzoic acid (2) in acetic acid which gives a white solid after extracting of solvent and adding HCl and water to the reaction mixture. The chemical structure and purity of this monomer were determined by using elemental analysis, FT-IR and ¹H-NMR spectroscopic techniques. The ¹H-NMR spectrum of compound (3) showed peaks between 7.61 and 7.64 ppm as a "doublet" which was assigned to H(b), peaks between 8.08 and 8.12 ppm as "doublet of doublet" was assigned to H(a) and H(c), peak at 8.33 ppm as "singlet" is assigned to H(e), and peaks between 8.42 and 8.45 ppm as "doublet of doublet" was assigned to H(d) (Fig.1). FT-IR spectrum of compound (3) showed a broad peak between 2800 and 3100 cm⁻¹ which was related to COOH groups. Two absorption bands at 1782, 1724, 1377 and 723 cm⁻¹ were characteristic peaks for imide ring. The absorption band of carbonyl of acidic groups was appeared at 1685 cm⁻¹ (Fig. 2).



Scheme 2- Synthesis route for diacid 3





Polymer Synthesis

The poly (amide-imide)s (PAIs) (**5a-f**) were synthesized by solution polycondensation reaction of an equimolar mixture of monomer (**3**) with six different derivatives of 5,5- disubstituted hydantoin compounds (**4a-f**) using NMP as solvent. TPP and pyridine are used as condensing agents to speed up the reaction and to achieve polymers whit higher molecular weights, scheme 3 shows the typical reaction.



Scheme 3- Synthesis route for poly (amide-imide)s (5a-f)

Polymer characterization

Synthesis data and some physical properties of the PAIs (**5a-f**) are summarized in Table 1. These polymers have inherent viscosities in the range of $0.26-0.62 \text{ dLg}^{-1}$. The structure of these polymers was confirmed as PAIs by means of FT-IR spectroscopy and

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elemental analysis. A representative FT-IR spectrum of the PAI (**5e**) is shown in Figure 3. The broad absorption band at 2800-3100 cm⁻¹ due to the COOH groups of monomer (**3**) and also absorption bands related to N–H groups of hydantoin derivatives (**4a-f**) which were obvious in their FT-IR spectrum, here in this spectrum are faded out that confirms the conversion. Absorption bands at around 1720–1780 cm⁻¹ are due to amide and imide carbonyl linkages. Two absorption peaks in 1741 and 1716 cm⁻¹ were characteristic peaks for stretching vibration of two carbonyl groups in hydantoin ring in the main chain (Fig. 3). Other spectra show a similar pattern.

Table 1- Synthesis data and some physical properties of PAIs (5a-f)

Hydantoins	Polymer	Yield %	$\eta_{inh} \left(dl/g \right)^a$
4a	5a	81	0.40
4b	5b	72	0.28
4c	5c	70	0.26
4d	5d	70	0.31
4e	5e	71	0.62
4f	5f	78	0.48

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



Figure 3. FT-IR spectrum of poly (amide-imide) 5e

The elemental analysis values of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 2).

Polymer	Formula		С%	Н%	N%
5a	$C_{19}H_9N_3O_6 \ (375.2)_n$	Calc. Found.	60.80 60.00	2.40 2.00	11.20 10.30
5b	$\begin{array}{c} C_{21}H_{13}N_{3}O_{6}\\ (403.3)_{n} \end{array}$	Calc. Found.	62.50 61.70	3.22 2.80	10.42 9.40
5c	$\begin{array}{c} C_{22}H_{15}N_{3}O_{6}\\ (417.3)_{n}\end{array}$	Calc. Found.	63.30 63.50	3.60 3.10	10.00 9.30
5d	$\begin{array}{c} C_{31}H_{19}N_{3}O_{6}\\ (529.4)_{n}\end{array}$	Calc. Found.	70.60 69.40	3.20 2.80	7.90 7.00
5e	$\begin{array}{c} C_{24}H_{17}N_{3}O_{6}\\ (443.3)_{n}\end{array}$	Calc. Found.	65.00 64.20	3.80 3.00	9.50 8.80
5f	$\begin{array}{c} C_{23}H_{15}N_{3}O_{6}\\ (429.3)_{n}\end{array}$	Calc. Found.	64.30 65.00	3.50 3.00	9.80 8.30

Table 2- Elemental analysis of poly (amide-imide)s (5a-f)

The solubilities of the poly (amide-imide)s (**5a-f**) were investigated. All of the polymers are soluble in organic solvents such as DMF, DMAc, DMSO and NMP at room temperature and are insoluble in solvents such as methanol, ethanol, chloroform and water.

Thermal properties

The thermal properties of two samples of resulting polymer (**5a** & **f**) were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10° C/min⁻¹ and the thermal data are summarized in Table 3 (Fig. 4). The initial decomposition temperatures of 5, 10% weight losses (T₅ and T₁₀) and the char yield at 600°C for (**5a** & **f**) are summarized in Table 3. These polymers exhibited good resistance to thermal decomposition up to 245-265 °C in nitrogen and began to decompose gradually above that temperature. T₅ for polymers (**5a** & **f**) ranged from 245 to 265 °C and T₁₀ for all polymers ranged from 290 to 310 °C, and the residual weight for these polymers at 600 °C ranged from 16 to 20 % in nitrogen (Table 3). Results show that PAIs (**5f**) containing 5,5-spirocyclohexyl hydantoin moiety in the main chain has higher thermal stability in compare with other polymers because it has a rigid structure in position of 5 of hydantoin ring.



Fig. 4 TGA Thermograms of PAIs 5a & f

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Polymer	$T_5 (^{\circ}C)^{a}$	$T_{10} (^{\circ}C)^{b}$	Char yield ^c
5a	245-250	290-295	16 %
5f	265-270	310-315	20 %

Table 3- Thermal behaviour of poly(amide-imide) (5a & f)

^a and ^b: Temperature at which 5% and 10% weight loss respectively was recorded by TGA at a heating rate of 10 °C/min in N₂. ^c weight percentage of material left after TGA analysis at maximum temperature 600 °C in N₂.

Conclusion

This work involved the synthesis and characterization of several new PAIs (**5a-f**) by direct polycondensation reaction of N-(4-carboxyphenyl)trimellitimide (**3**) with different 5,5-disubstituted hydantoin derivatives (**4a-f**) using TPP and pyridine as condensing agents in NMP solution containing dissolved calcium chloride. These new PAIs are soluble in various organic solvents and have good thermal stability. These properties could make these PAIs attractive for practical applications, such as processable high-performance engineering plastics.

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