

Synthesis of Novel Thermally Stable Poly(Amide-Imide)s

Fereh Mamedaliyeva

fereh.m@rambler.ru

Institute of Polymer Materials of the Ministry of Science and Education of Republic of Azerbaijan

Research Article

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Abstract

High-performance polymers such as polyimides (PIs), polyamides (PAs) and poly(amide imide)s (PAI), have attracted great attention in recent times due to the unique combination of their toughness, low weight, dimensional stability at high temperatures and resistance to thermo-oxidative degradation. Poly(amide-imide)s containing preformed imide rings were synthesized through the direct polycondensation of aromatic diamines with an dicarboxylic acid derivative. The polymerization process produced high-molecular weight materials exhibiting good film-forming ability and excellent solubility in polar amidic solvents, including N-methylpyrrolidinone (NMP) and dimethylformamide (DMF). The resulting polymers were readily processed into uniform, flexible films and protective coatings. Thermal characterization demonstrated remarkable thermal resistance, with decomposition temperatures exceeding 270°C and glass transition temperatures ranging from 232–246°C. The incorporation of rigid aromatic segments together with imide and amide functionalities contributed significantly to the outstanding thermal performance and mechanical integrity of the synthesized materials. These results indicate that the developed poly(amide-imide)s are promising candidates for advanced engineering applications requiring a combination of thermal stability, solvent processability, and durable mechanical properties. The PAIs were soluble in polar aprotic solvents. They were able to form dense films with good mechanical properties and they present high thermal stability.

INTRODUCTION

Aromatic polyimides and polyamides are important classes of polymers that have found applications as high performance materials due to their excellent thermo-oxidative stability, electrical properties, high radiation and solvent resistance and high mechanical strength [1]. However, these polymers often suffer from high softening temperatures and insolubility that make their processing difficult and expensive. Among the copolyimides, poly(amideimide) (PAI) is the most successful material having good compromise between high temperature stability and processability [2], [3]. PAIs are generally synthesized by trimellitic anhydride route, from an amide containing monomer or from an imide containing monomer [4], [5].

Organic polymers containing imide groups in the main chain have excellent thermal stability and mechanical properties, good chemical resistance, high dimensional stability, and good electric properties [6, 7]. 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 [8].

High-performance polymeric materials are currently receiving considerable attention for their potential applications in advanced technologies demands. Aromatic polyimides are well known high-performance polymers that have excellent thermal and mechanical properties [9–11].

Wholly aromatic polyamides and polyimides are these polyamides have generally been reduced by widely used and belong to the class of high-performance polymers which occupy an important place

among the other polymers. Polyamides exhibit good mechanical strength and thermal resistance, and are suitable materials for composites. However, the versatile applications of these polyamides have generally been reduced by the high crystallinity and limited solubility in common solvents [12].

Polyimides are one of the most important classes of polymers used in the microelectronics and photoelectronics industries. Because of their high thermal stability, chemical resistance, and good mechanical and electric properties, polyimides are often applied in photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays [13]. Polyimides and polyamide-imides are of high interest for many engineering applications due to their excellent thermal and mechanical properties. The aerospace, automobile, and microelectronics industries have developed many important applications [14–16].

PAIs have been developed as an alternative material for PIs and PAs with a promising balance of thermal stability with processability. These polymers combine the superior mechanical properties associated with the amide group, and the high thermal stability of the imide ring in the same material, thus making the material even stronger. In addition, the synthetic route to PAIs offers the possibility of incorporating specific functionalities between the amide and imide groups. [17, 18]. In the present paper we synthesised and characterized the poly(amide-imide)s obtained by solution polycondensation of a dicarboxylic acid having preformed imide rings with certain aromatic diamines containing different groups between phenylene units. The properties of these polymers such as solubility, inherent viscosity, molecular weight, thermal stability, glass transition temperature and the quality of thin films made from these polymers have been investigated and compared with those of related compounds

EXPERIMENTAL PART

Synthesis of the monomers

Aromatic diamine 2,6-bis(p-aminophenoxy) benzonitrile was used in this paper to synthesized the poly(amide-imide)s. Melting point (M. p.) : 210–213°C; The diamine, 2,6-bis(p-aminophenoxy)benzonitril, was synthesized by the reaction of p-aminophenol with 2,6-dichlorobenzonitril, in dimethylacetamide (DMAc) with potassium carbonate, according to a published procedure [19]. It was recrystallized from a mixture of dimethylformamide with water. The structures of aromatic diamines are shown in Scheme 1.

Investigation of photosensitive properties of the copolymer

The preparation of dicarboxylic acid bis[N-(3 carboxyphenyl)phthalimidy]benzophenone was carried out in a round-bottom flask equipped with a condenser, CaCl₂ drying tube, magnetic stirrer and heating source. The concentration of reactants used in this synthesis was 10% solids (w/v) which allowed efficient mixing. 150 mL of glacial acetic acid and 6.85 g (0.05 mol) of m-aminobenzoic acid were placed in the flask and 8.05 g (0.025 mol) of benzophenontetracarboxylic dianhydride was added with rapid

stirring. The reaction mixture was heated at reflux temperature for 16–20 h. The resulting white product dicarboxylic acid was filtered, washed with ethanol and dried (yield 90%) (Scheme 2).

Elemental analysis: calculated for $C_{31}H_{16}N_2O_9$: C, 66.42%; H, 2.88%; N, 5%. Found: C, 66.36%; H, 2.83%; N, 4.57%. IR spectrum (KBr, cm^{-1}): 3200 – 2800 (-OH stretching); 1780 (imide carbonyl symmetric stretching); 1730 (imide carbonyl asymmetric stretching and carboxylic C = O); 1375 (C-N stretching); 740 (imide ring) and 1640 due to the carbonyl group from benzophenone. Melting point: > 350°C.

Synthesis of the polymers

The direct polycondensation reaction of equimolar amounts of diamine and dicarboxylic acid at 105°C, in NMP as a solvent and in the presence of triphenylphosphite (TPP) and pyridine as condensating agents with $CaCl_2$ for maintaining the formed polymer in solution, was run for preparation of polymers. Scheme 3 shows the synthesis of the polymers.

A mixture of 0.834 g (0.0015 mol) of dicarboxylic diacid bis[N-(3 carboxyphenyl)phthalimidyl]benzophenone, 0.4755 g (0.0015 mol) diamine 2,6-bis(p-aminophenoxy) benzonitril, 0.5 g calcium chloride, 2 ml triphenyl phosphite, 4 ml of pyridine and 12 ml of N-methylpyrrolidinone was heated with stirring at 105°C for 5 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 105°C for two days. The inherent viscosity of the polymer in NMP was 0.72 dL/g, measured at a concentration of 0.5 g/dL at 20°C.

RESULTS AND DISCUSSION

The synthesis of the dicarboxylic acid containing carbonyl group and imide rings, namely bis[N-(3 carboxyphenyl)phthalimidyl]benzophenone, was performed in the same manner as described in the literature for similar compounds [20, 21]. Direct polycondensation of dicarboxylic acids with aromatic diamines by using triphenyl phosphite and pyridine as condensating agents has been known as a convenient preparative method for aromatic polyamides [22, 23]. This method, requires the use of an aprotic polar solvent and a basic co-solvent, such as pyridine, at a moderate temperature (100°C), generally in the presence of inorganic salts such as calcium chloride or lithium chloride or their mixture [24, 25].

The poly(amide-imide), was synthesized according to Scheme 3 (II). All the polycondensation reactions readily proceeded in homogenous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol. Yields over 96.5% were always achieved [26].

The structure of poly(amide-imide) was identified by FTIR spectra. Strong bands at 1780 cm^{-1} and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl

groups of imide. The absorption band at 1370 cm^{-1} is due to C-N stretching in imide ring and the absorption at 740 cm^{-1} is possibly due to imide ring deformation. The wide bands which appeared at 3420 cm^{-1} were attributed to N-H stretching vibration in the amide group. Characteristic absorptions appeared at $1670 - 1660\text{ cm}^{-1}$ due to carbonyl stretching vibration and at 1520 cm^{-1} due to N-H deformational vibration. The CN group from benzonitril appears in poly(amide-imide) at 2230 cm^{-1} . FTIR spectrum of the poly(amide-imide) is presented in Fig. 1.

Table 1
Characterization of the poly(amide-imide)s

Polymer	IDT ^a (°C)	T ₁₀ ^b (°C)	T ^c _{max} (°C)	T _g ^d (°C)	Inh. Viscosity ^e	Mn	Mw	Mw/Mn
IIa	270	420	560	246	0.68	70250	140500	2
IIb	290	435	565	ND	0.70	64000	154500	2.4
IIc	350	460	565	ND	0.65	62000	128000	2.05
IId	320	460	560	ND	0.72	64500	143000	2.22
Ile	400	468	562	240	0.52	51000	98000	1.93
II f	280	420	555	232	0.45	59500	119000	2.0
IIg	280	435	554	ND	0.47	57500	120000	2.09

^aInitial decomposition temperature = temperature of 5% weight loss.

^bTemperature of 10% weight loss.

^cTemperature of maximum rate of decomposition.

^dGlass transition temperature.

^eMeasured in NMP at 0.5 g/dL

Thermal properties

The thermal stability was evaluated by thermogravimetric analysis (TGA). These polymers do not show significant weight loss below 250°C (Fig. 2). They begin to decompose in the range of $270 - 400^{\circ}\text{C}$; they show 10% weight loss in the range of $420 - 470^{\circ}\text{C}$ (Table 1). The maximum rate of decomposition is around 560°C for all the investigated polymers.

CONCLUSION

These polymers maintain high thermal stability, with decomposition temperature being above 300°C and a glass transition in the range of 232–246°C. The poly(amide-imide)s have a fairly high molecular weight with Mn being in the range of 51000–70000 and polydispersity of 1.93–2.4. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics.

Declarations

CONFLICT OF INTEREST

The author declare that she has no conflicts of interest.

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Scheme

Scheme 1 to 3 are available in the Supplementary Files section.

Figures

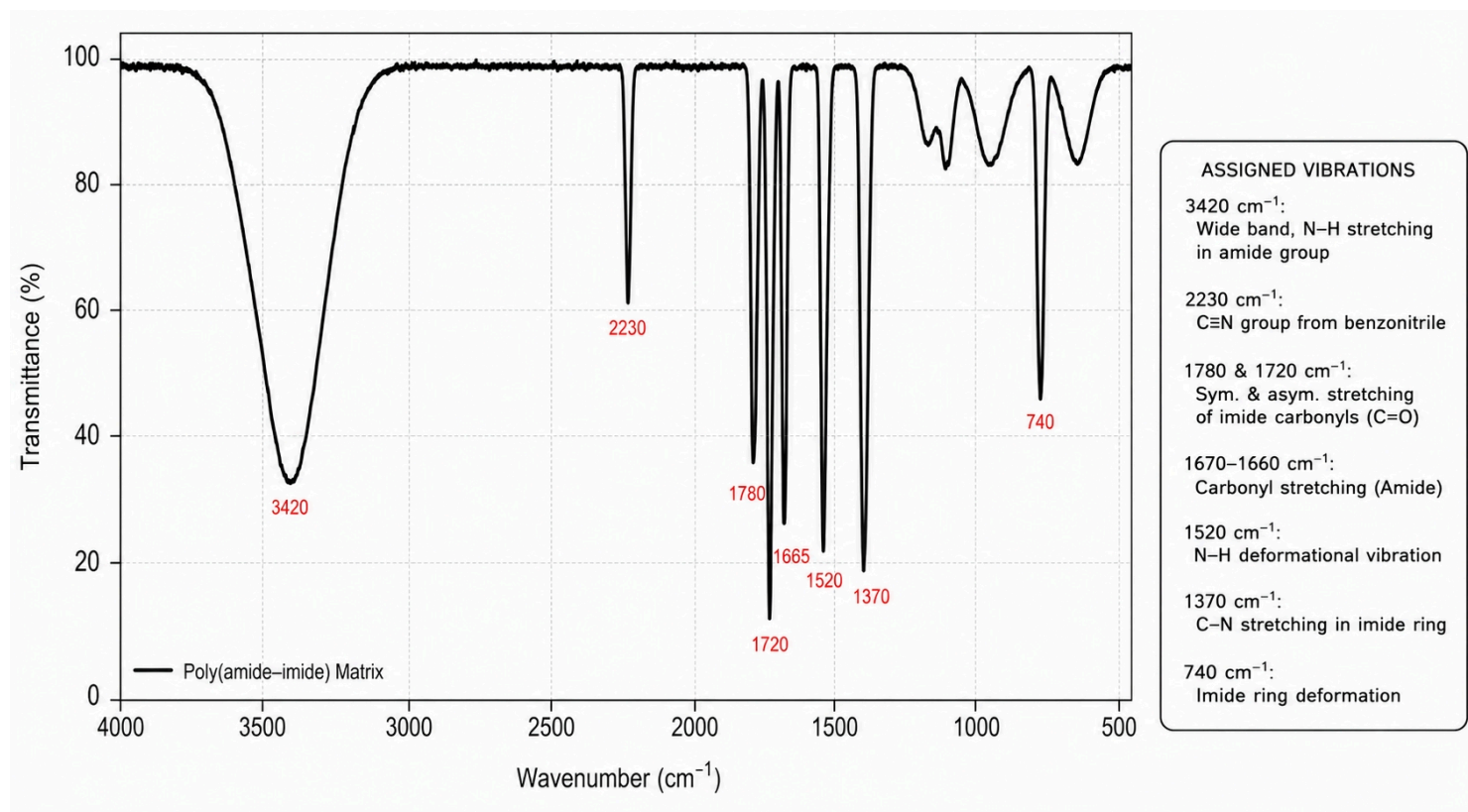


Figure 1

FTIR spectrum of poly(amide-imide)s.

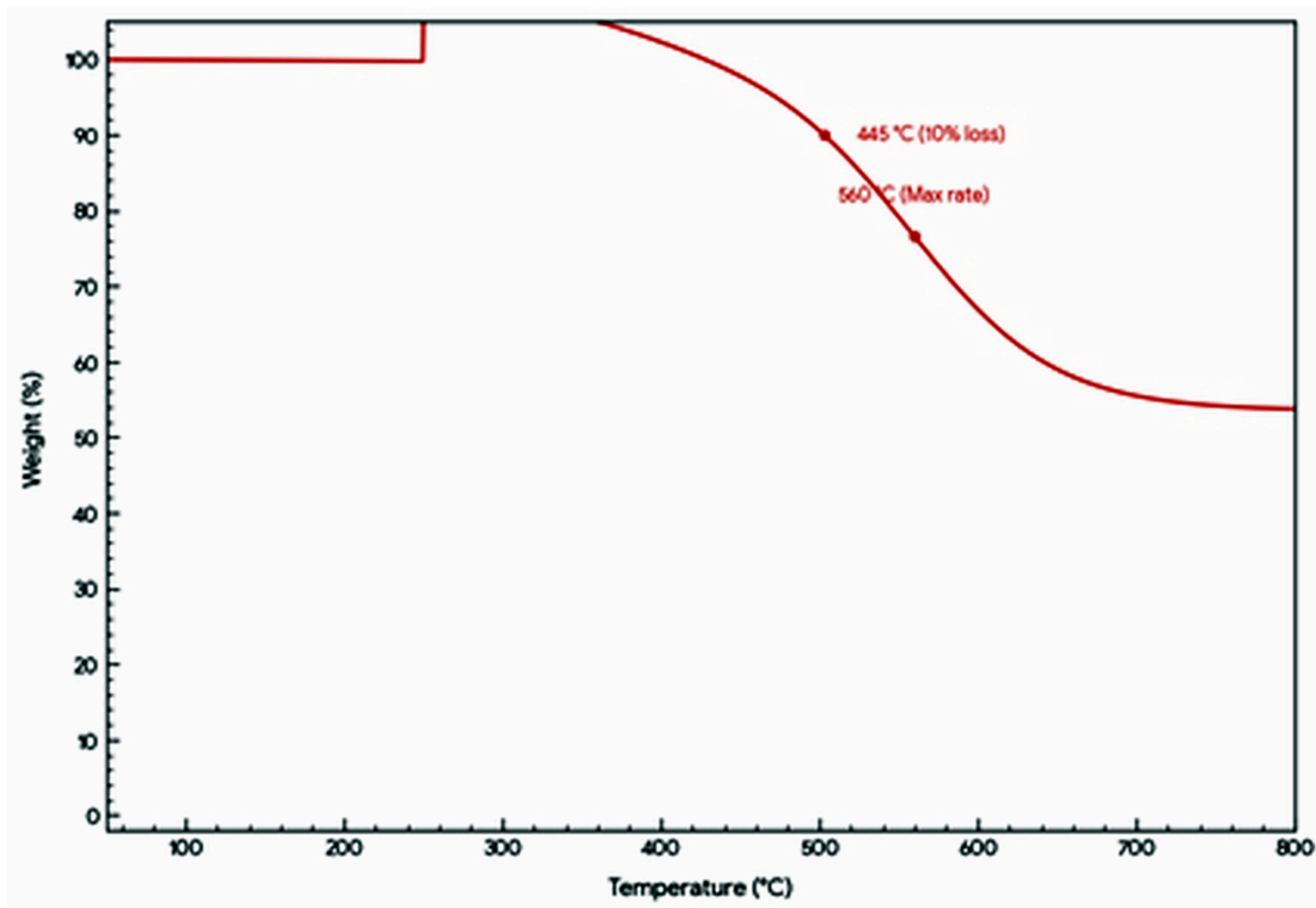


Figure 2

Thermogravimetric analysis (TGA) of poly(amide-imide)s

Supplementary Files

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- [Scheme123.docx](#)