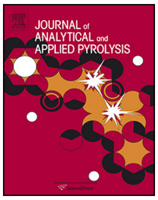
Journal of Analytical and Applied Pyrolysis xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



On the thermal stability of some aromatic-aliphatic polyimides

Cristian-Dragos Varganici [a], Dan Rosu [a,*], Cristian Barbu-Mic [c,d], Liliana Rosu [a],
Dumitru Popovici [b], Camelia Hulubei [b], Bogdan C. Simionescu [a,d]

[a] *Centre of Advanced Research in Bionanoconjugates and Biopolymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania*
[b] *Laboratory of Polycondensation and Thermostable Polymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania*
[c] *"Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania*
[d] *Department of Natural and Synthetic Polymers,"Gh. Asachi" Technical University of Iasi, 73 Dimitrie Mangeron Boulevard, 700050 Iasi, Romania*

ARTICLE INFO

Article history:
Received 8 August 2014
Received in revised form 20 January 2015
Accepted 14 February 2015
Available online xxx

Keywords:
Polyimides
Thermogravimetric analysis
Thermal degradation kinetics
Evolved gas analysis

ABSTRACT

Aromatic-aliphatic polyimides were synthesized and their thermal decomposition process was investigated. Thermal degradation processes had been undertaken by dynamic thermogravimetry in nitrogen atmosphere, up to 700 °C. Comparative thermal stability studies of the samples were also undertaken. Evolved gases analyses were conducted by using a coupling to a quadrupole mass spectrometer and a Fourier transform infrared spectrophotometer equipped with external modulus for gas analysis. Kinetic study was conducted by applying Flynn–Wall–Ozawa, Friedman and non-linear regression methods. Kinetic parameters values decreased with the increase in conversion degree values, suggesting the occurrence of a change in rate determining step.

1. Introduction

Properties such as high glass transition temperature, excellent electrical, thermal and mechanical stability and chemical resistance make polyimides valuable candidates for widespread applicability [1,2]. Depending on their structural characteristics, polyimides and their copolymers may be successfully used in different industrial segments. For example, aromatic polyimides have found a wide range of applications in the microelectronics and photoelectronics industries as alignment films in displays, circuit boards, photoresists and dielectric films [2–4]. Other applications include membranes for gas separation [5] and matrices for high temperature applications [6]. In order to surpass a series of impediments concerning aromatic polyimides, such as low transparency, processability, solubility and high dielectric constants, greatly limiting some of their applications, the need for aliphatic and alicyclic polyimides has emerged [7]. These compounds may be divided in the following classes: (1) aliphatic dianhydrides and aromatic diamines, (2) aromatic dianhydrides and aliphatic diamines and (3) aliphatic dianhydrides and aliphatic diamines (fully aliphatic) [8]. Aromatic-aliphatic polyimides have gained much attention as interlayer dielectric materials and in optoelectronics [9]. By introducing alicyclic entities as bridges between aromatic units, in both main and side chains of aromatic polyimides, the aromatic-aliphatic polyimides will possess lower dielectric constants, due to lowering of molecular density, and higher transparency due to a reduction in inter- and intramolecular charge-transfer complexes formation [2]. Introduction of aliphatic entities improve polyimide ionomers hydrolytic stability without affecting properties such as mechanical and oxidative stability or proton conductivity [7,10]. Also, by incorporating aliphatic moieties in the aromatic polyimides structures greatly reduces water nucleophilic attack of the imide linkage, thus leading to formation of excellent proton conducting membranes [7,11]. Aromatic-aliphatic polyimides with heterocyclic rings in the main chain also possess a superior heat resistance than aromatic polyimides [12].

The aim of this paper consists in the obtaining of some aromatic-aliphatic polyimides and the comparative study of the structural influence on their thermal stability. This aspect is for further predicting material life-time based on thermal analysis data in order to correctly establish both application domains and conditions. Another major interest consists in the evaluation of environmental impact of the released gaseous products for the possibility of material recovery from polymeric waste.

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* Corresponding author. Tel.: +40 232 217 454; fax: +40 232 211 299.
E-mail addresses: drosu@icmpp.ro, dan_rosu50@yahoo.com (D. Rosu).

http://dx.doi.org/10.1016/j.jaap.2015.02.031
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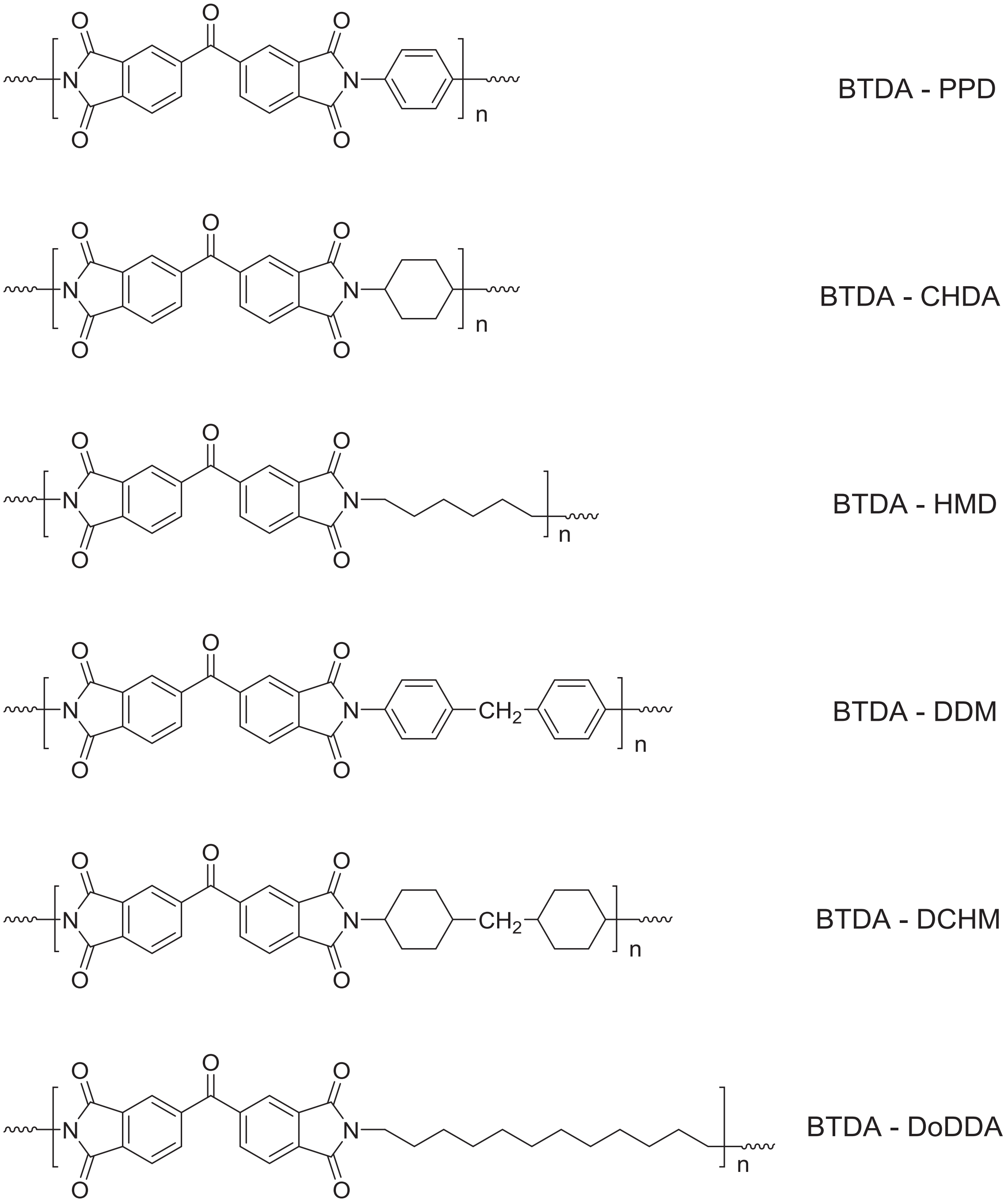
2. Materials and methods

2.1. Materials

Monomers 1,6-hexamethylenediamine (HMD), *trans*-1,4-diaminocyclohexane (CHDA), *para*-phenylenediamine (PPD), 1,12-dodecanediamine (DoDDA) were purchased from Aldrich and used as received. Benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) (Fluka) was recrystallized from acetic anhydride, washed with ethyl ether and dried under vacuum before use. 4,4′-diaminodicyclohexylmethane (DCHM) (Aldrich) was purified by recrystallization from n hexane, dried under vacuum and stored under inert atmosphere (N_2) in a dark and cold place. 4,4′-diaminodiphenylmethane (DDM) (Aldrich) was purified by recrystallization from ethanol. *N*-methyl-2-pyrrolidone (NMP) (Aldrich) was purified by distillation under reduced pressure and stored under 4 Å molecular sieves. Triethylamine (TEA) was purchased from Aldrich.

2.2. Synthesis

The structures of the synthesized polymers are given in Scheme 1. To prevent formation of charge transfer complex between highly reactive aliphatic diamine and carboxylic groups [13–16], synthesis was carried out using the esterification method [17,18]. All polymers were obtained using the same synthesis protocol. For example, the synthesis of BTDA–DCHM was carried out as follows. In a round bottom flask with three necks



Scheme 1. Structures of the studied compounds.

Please cite this article in press as: C.-D. Varganici, et al., On the thermal stability of some aromatic-aliphatic polyimides, J. Anal. Appl. Pyrol. (2015), http://dx.doi.org/10.1016/j.jaap.2015.02.031