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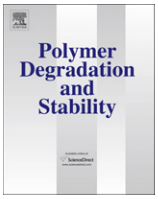

Thermal degradation behaviour of novel wholly para-oriented aromatic polyamide–hydrazides containing sulfone–ether linkages

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ABSTRACT

Thermal stability and degradation behaviour of a series of novel wholly para-oriented aromatic polyamide–hydrazides containing flexibilising sulfone–ether linkages in their main chains have been investigated in nitrogen and in air using differential scanning calorimetry (DSC), thermogravimetry (TG), infrared spectroscopy (IR) and elemental analysis. All of these polymers have similar structural formula except for the presence of sulfone, ether, or sulfone–ether linking groups between appropriate aromatic nuclei in their main chains. The influence of incorporation of these linkages on the thermal stability and degradation behaviour of these polymers has also been studied. The polymers were prepared by a low temperature solution polycondensation reaction of 4-amino-3-hydroxybenzhydrazide (4A3HBH) and an equimolar amount of either 4,4′-sulfonyl dibenzoyl chloride (SDBC), 4,4′-[sulfonyl bis (1,4-phenylene)dioxy] dibenzoyl chloride (SODBC), 4,4′-[sulfonyl bis (2,6-dimethyl- 1,4-phenylene)dioxy] dibenzoyl chloride (4MeSODBC), or 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (ODBC) in anhydrous *N*,*N*-dimethyl acetamide (DMAc) as a solvent at −10 °C. A related polyamide–hydrazide without the flexibilising linkages is also investigated for comparison. It was synthesized from 4A3HBH and terephthaloyl chloride (TCl) by the same synthetic route. The results clearly reveal that these polymers are characterized by high thermal stability. Their weight loss occurred in three distinctive steps. The first was small and was assigned to the evaporation of absorbed moisture. The second was appreciable and was attributed to the cyclodehydration reaction of the o-hydroxy polyamide–hydrazides into the corresponding poly (1,3,4-oxadiazolyl-benzoxazoles) by losing water. This is not a true degradation, but rather a thermo-chemical transformation reaction. The third was relatively severe and sharp, particularly in air, and corresponded to the decomposition of the resulting poly(1,3,4-oxadiazolyl-benzoxazoles). There is a slight shift of the decomposition temperature of these polymers to a lower temperature as the sulfone–ether linkages were introduced into the polymer chains. The decomposition seems to start by breaking the sulfonyl groups as confirmed from DSC measurements. The results also indicate that the incorporation of the flexibilising linkages into the polymer main chains did not seem to significantly influence the thermal stability of these polymers in comparison with that of the polymer free from these linkages.

1. Introduction

Wholly aromatic polyamide–hydrazides are a unique class of materials which combine the properties of both the aromatic polyamides and the aromatic polyhydrazides. The general structural formula of these polymers could be represented as follows: –[–CO–NH Ar–CO–NH–NH–CO–Ar′–]–, where Ar and Ar′ are para- and/or meta- substituted phenylene units. They are generally synthesized by a low temperature solution polycondensation reaction of aromatic aminohydrazides with aromatic dicarboxylic acid dichlorides in an amide solvent [1–6]. Completely ordered polyamide–hydrazides are prepared from diamines containing preformed hydrazides with diacid dichlorides [7–10]. A few polyamide–hydrazides that were obtained from dihydrazides having preformed amide linkages with diacid dichlorides have been reported [11]. The polyamide–hydrazides could also be synthesized via a phosphorylation method through the direct polycondensation reaction using an aromatic aminohydrazide and an aromatic dicarboxylic acid by means of di- or triphenyl phosphite [12–15]. These polymers could be classified among the high performance materials because they possess some interesting and potentially useful properties. They exhibit favourable rheological behaviour

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that allowed for successful preparation of fibres and films from their solutions in dimethyl acetamide [16,17] and dimethyl sulfoxide [7]. Their appropriately drawn fibres showed very high mechanical strength and moduli, which are superior to that of glass fibre and steel wire [7,18,19]. These fibres can be successfully applied in fabrics, rigid composites, tire-cords, impact-absorbing devices, and for ballistic protection [20]. polyamide–hydrazide films are useful as reverse osmosis membranes in water-pollution control, and for concentration fruit juices [21], and as semi-permeable membranes for desalination of artificial and natural seawater [16,22–28]. Further, their modified transition metal chelates have shown good electrical conductivity [29–32]. Moreover, these polymers are characterized by high thermal and thermo-oxidative stability [2,33–36]. Aromatic polyamide–hydrazides are well known as precursors to polyamide-1,3,4-oxadiazoles, which are one of the most important classes of chemically and thermally stable heterocyclic polymers [37,38]. Polyamide-1,3,4-oxadiazoles are considered to be interesting alternative for the development of high-temperature and flame-resistance fibres [39,40] and thermally stable membranes for gas separation [41]. In addition, they have been widely investigated in the field of polymer light-emitting diodes as well as other fields of polymer electronics [42,43]. Unfortunately, these polymers are difficult to process because of low solubility in organic solvents and high melting or softening temperatures. Many efforts have been made to improve the solubility and lower the glass transition temperature to make such polymers more processable by the introduction of flexible linkages in the backbone [13,14] or bulky pendant group on the aromatic rings [15]. It is well established that all aromatic polymers containing only benzoxazole [44,45] or 1,3,4-oxadiazole [46,47] moieties as the main structural feature of the polymer chains exhibit excellent thermal stability and other attractive physical properties.

Thus, our goal will be the evaluation of the thermal and thermo-oxidative stability of several novel wholly para-oriented aromatic polyamide–hydrazides with o-hydroxy groups which would be expected to undergo thermo-chemical transformation into linear aromatic polymers with alternating 1,3,4-oxadiazole and benzoxazole structural units within the same polymer backbone in order to classify these materials as a category of heat resistance polymers. The second phase of this work will be extended to study the effect of introducing sulfone, ether or sulfone-ether flexibilising linkages into the polymer backbone chains on their degradation behaviour. The effect of introducing methyl substituents in the aromatic rings of the polymers was also investigated. For a comparison, a related polymer without these linkages was also studied.

2. Experimental

2.1. Materials

2.1.1. Reagents

4-Amino-3-hydroxybenzoic acid (Fluka, Germany), concentrated sulfuric acid and sodium carbonate (BDH, England), phosphorous pentoxide and hydrazine hydrate (90%; Riedal-De-Haen, Germany), calcium hydride, terephthaloyl chloride (Acros, Germany), 4,4′-sulfonyl diphenol, 4,4′-sulfonyl bis(2,6-dimethylphenol), hydroquinone, p-fluorobenzonitrile, potassium carbonate, potassium hydroxide, thionyl chloride, and dichloromethane (Aldrich, Germany) were of analytical grade and were used as received.

2.1.2. Solvents

Methanol, 99.8%, and ethanol, 99.9% (Hayman, England), acetone (BDH, England), toluene, acetonitrile, hexane (Aldrich, Germany) were extra pure solvents and were used as received. *N,N*-Dimethyl acetamide (DMAc) (Aldrich, Germany) was a guaranteed solvent, dried over calcium hydride for 24 h, and followed by distillation under reduced pressure. The fractions, which boiled at 40–42 °C/2 mmHg, were collected and stored over 4 Å molecular sieves before use.

2.2. Methods

2.2.1. Monomers synthesis

4-Amino-3-hydroxybenzhydrazide (4A3HBH) was synthesized from the corresponding acid by a two-step procedure in which the acid was esterified to its methyl ester followed by reaction of the produced ester with hydrazine hydrate. The crude material was recrystallised twice from aqueous ethanol. A detailed description of this procedure has given elsewhere [5]. The diacyl chloride monomers such as 4,4′-sulfonyl dibenzoyl chloride (SDBC); 4,4′-[sulfonyl bis (1,4-phenylene)dioxy] dibenzoyl chloride (SODBC); and 4,4′-[sulfonyl bis (2,6-dimethyl- 1,4-phenylene)dioxy] dibenzoyl chloride (4MeSODBC) were prepared by the reaction of their corresponding acids with thionyl chloride in the presence of a catalytic amount of *N,N*-dimethyl formamide and were purified by crystallization from toluene/n-hexane according to the method described by Hsiao and Chiou [48]. 4, 4′-(1,4-phenylenedioxy)-dibenzoyl chloride (ODBC) was prepared following the method of Hsiao et al. [15]. The purity of the prepared monomers was checked by melting points and elemental analyses. All the results agreed well and confirmed the representative structures of these compounds as shown in Table 1.

2.2.2. Polymers synthesis

The polymers evaluated in this work were synthesized by a low temperature (at −10 °C) solution (in anhydrous DMAc) polycondensation reaction of 4A3HBH with an equimolar amount of either TCl, SDBC, SODBC, 4MeSODBC or ODBC. The polycondensation reaction was preceded through the gradual addition of the solid acid chloride into the cooling DMAc solution of aminohydroxybenzhydrazide. The resulting polycondensation reaction mixtures were precipitated into methanol, filtered and dried in vacuum at 75 °C to constant weight. Polymer samples were purified by repeated precipitation from their solutions in DMAc using methanol as a non-solvent. A detailed description of this polymerization technique was given elsewhere [49]. A series of five wholly para-oriented aromatic polyamide–hydrazides containing sulfone–ether linkages was obtained as shown in Table 2. All of these polymers are novel and prepared for the first time in our laboratory [49] except poly[4-(terephthaloylamino)-3-hydroxy benzoic acid hydrazide], or polymer A in this work, which had already been reported previously [1,5]. The resulting samples were characterized by elemental analysis and IR spectrophotometry. The results obtained agreed well with data reported previously [49] and they confirmed the expected polymers structures, which are illustrated in Table 2. All the polymers were produced in a quantitative yield which ranged between 98.95 and 99.85%. The intrinsic viscosity values reflected the high molecular weights of these polymers (Table 2). Regardless to the appreciable difference in viscosities, it would be expected that the molecular weights of these polymers are generally comparable since the purity level of the different acid chlorides used is similar [49].

2.2.3. Polymer characterization

Intrinsic viscosity measurements were carried out on 0.5% solutions of the polymers in DMAc at 30 °C using a suspended-level Ubbelohde viscometer with negligible kinetic energy correction and which allowed dilution in the viscometer. Flow times were