

Synthesis and Characterization of Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages

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ABSTRACT: Four novel wholly para-oriented aromatic polyamide-hydrazides containing flexibilizing sulfone-ether linkages in their main chains have been synthesized from 4-amino-3-hydroxy benzhydrazide (4A3HBH) with either 4,4'-sulfonyldibenzoyl chloride (SDBC), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC), 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSODBC), or 4,4'-(1,4-phenylenedioxy)dibenzoyl chloride (ODBC) via a low-temperature solution polycondensation reaction. A polyamide-hydrazide without the flexibilizing linkages is also investigated for comparison. It was synthesized from 4A3HBH and terephthaloyl chloride (TCl) by the same synthetic route. The intrinsic viscosities of the polymer ranged from 2.85 to 4.83 dL g⁻¹ in *N,N*-dimethyl acetamide (DMAc) at 30°C and decreased with introducing the flexibilizing linkages into the polymer. All the polymers were soluble in DMAc, *N,N*-dimethyl form-

amide (DMF), and *N*-methyl-2-pyrrolidone (NMP), and their solutions could be cast into films with good mechanical strengths. Further, they exhibited a great affinity to water sorption. Their solubility and hydrophilicity increased remarkably by introducing the flexibilizing linkages. The polymers could be thermally cyclodehydrated into the corresponding poly(1,3,4-oxadiazolyl-benzoxazoles) approximately in the region of 295–470°C either in nitrogen or in air atmospheres. The flexibilizing linkages improve the solubility of the resulting poly(1,3,4-oxadiazolyl-benzoxazoles) when compared with poly(1,3,4-oxadiazolyl-benzoxazoles) free from these linkages. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 767–776, 2009

Key words: polyamide-hydrazides; sulfone-ether linkages; synthesis; viscosity; solubility; moisture regain; mechanical properties; thermal and thermo-oxidative stability

INTRODUCTION

Wholly aromatic polyamide-hydrazides 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 favorable rheo-

logical behavior that allowed for successful preparation of fibers and films from their solutions in DMAc^{16,17} and dimethyl sulfoxide.⁷ Their appropriately drawn fibers showed very high mechanical strength and moduli, which are superior to that of glass fiber and steel wire.^{7,18,19} These fibers 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 semipermeable 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 fibers^{39,40} and thermally stable membranes for gas separation.⁴¹ In addition, they have been

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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 Earlier reports from this laboratory were concerned with the synthesis and characterization of several wholly aromatic polyamide-hydrazides⁵ and azopolyamide-hydrazides,^{6,36} which contained different predetermined amounts of para- and meta-oriented phenylene moieties, while still retaining the 1 : 1 content of amide and hydrazide linking bonds. The polyamide-hydrazides⁵ were prepared from either 4-amino-3-hydroxybenzhydrazide or 3-amino-4-hydroxybenzhydrazide with either terephthaloyl chloride (TCl), isophthaloyl chloride, or mixtures of various molar ratios of TCl and isophthaloyl chloride in anhydrous DMAc at -10°C as a solvent. However, azopolyamide-hydrazides^{6,36} have been synthesized from para-aminosalicylic acid hydrazide and either 4,4'-azodibenzoyl chloride, 3,3'-azodibenzoyl chloride, or their appropriate combinations in anhydrous DMAc containing LiCl as a solvent at -10°C . In this study, a series of novel wholly aromatic polyamide-hydrazides with *o*-hydroxyl groups is synthesized. Basic characterization of these polymers and the thermal cyclodehydration to poly(1,3,4-oxadiazolyl-benzoxazole)s are also investigated. Further, we will present approaches to make poly(1,3,4-oxadiazolyl-benzoxazole)s soluble while maintaining their high thermal stability. For this, flexible groups are introduced into the polyamide-hydrazides backbone using four diacid dichlorides possessing sulfone, ether, or sulfone-ether linkages.

EXPERIMENTAL

Materials

Reagents

4-Amino-3-hydroxybenzoic acid (Fluka, Seelze, Germany), concentrated sulfuric acid and sodium carbonate (BDH, Leicestershire, England), phosphorous pentoxide and hydrazine hydrate (90%; Riedel-DeHaen, Seelze, Germany), calcium hydride, TCl (Acros, Renningen, Germany), 4,4'-sulfonyldiphenol, 4,4'-sulfonyl bis(2,6-dimethyl-phenol), hydroquinone, *p*-flouorobenzonitrile, potassium carbonate, potassium hydroxide, thionyl chloride, and dichloromethane (Aldrich, Seelze, Germany) were of analytical grade and were used as received.

Solvents

Methanol, 99.8%, and ethanol, 99.9% (Hayman, Eastways Withan, England), acetone and *N,N*-dimethyl formamide (DMF; BDH, Leicestershire, England), *N*-methyl-2-pyrrolidone (NMP), toluene, acetonitrile, hexane (Aldrich, Seelze, Germany) were extra pure solvents and were used as received. *N,N*-Dimethyl acetamide (DMAc) (Aldrich, Seelze) was a guaranteed reagent, dried over calcium hydride for 24 h, and followed by distillation under reduced pressure. The fractions, which boiled at $40\text{--}42^{\circ}\text{C}/2\text{ mmHg}$, were collected and stored over 4-Å molecular sieves before use.

Methods

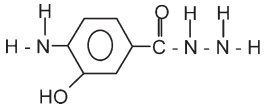
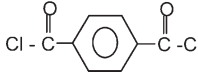
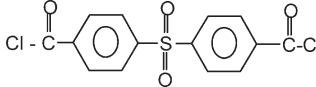
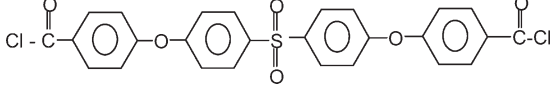
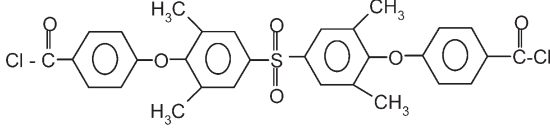
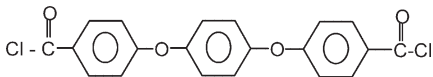
Monomers synthesis

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 recrystallized twice from aqueous ethanol. A detailed description of this procedure has been given elsewhere.⁵ The diacyl chloride monomers such as 4,4'-sulfonyldibenzoyl chloride (SDBC), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC), and 4,4'-[sulfonylbis(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 DMF and were purified by crystallization from toluene/*n*-hexane according to the method described by Hsiao and Chiou.⁴⁴ 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 the melting points and elemental analyses. All the results agreed well and confirmed the representative structures of these compounds as shown in Table I.

Polymerization procedure

All polymers were prepared by essentially the same experimental procedure, which will be given here for the preparation of polymer E. A dry 250 mL four-necked round bottom flask equipped with a Teflon-coated half-moon mechanical stirring bar, a thermometer, and a drying tube was placed in a dry box. 4A3HBH (3.34 g; 0.02 mol) was charged into the reaction flask followed by 80 mL of dry DMAc. Stirring was started until complete dissolution. The reaction flask was placed in a crushed ice-salt water bath and cooled at -10°C for 15 min. When this was completed, 7.74 g (0.02 mol) solid ODBC was added slowly under constant stirring over a period of 1 h

TABLE I
Some Characteristics of the Monomers

Monomer name	Monomer code	Monomer structure	Melting point (°C)
4-Amino-3-hydroxy-benzhydrazide	4A3HBH		223–224
Terephthaloyl chloride	TCl		82–83
4,4'-Sulfonyl dibenzoyl chloride	SDBC		162–163
4,4'-[Sulfonyl bis(1,4-phenylene)dioxy] dibenzoyl chloride	SODBC		184–185
4,4'-[Sulfonyl bis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride	4Me SODBC		190–191
4,4'-(1,4-Phenylene dioxy)dibenzoyl chloride	ODBC		208–209

by means of a funnel with weighing paper that was positioned just slightly above the surface of the stirred polycondensation reaction solution. After this period, stirring was continued for another 2 h at the aforementioned temperature. Then, the cooling bath was removed and the temperature of the polymerization reaction was allowed to rise gradually to room temperature and maintained for 24 h with stirring. Afterward, a clear, slightly yellow, highly viscous solution was obtained. Finally, the polymer solution was slowly poured into 600 mL of rapidly stirred methanol upon which a fibrous white precipitate of polymer E immediately formed. The polymer was isolated by filtration, washed successively with methanol and acetone, and dried in a vacuum oven at 75°C to constant weight. Polymer samples were purified by repeated precipitation from their solutions in DMAc using methanol as a nonsolvent. The precipitated polymers were isolated, washed, and dried to constant weights.

Film preparation

Films were prepared by casting 5% (w/v) polymer solutions (in DMAc) onto dry clean Pyrex glass plates to a uniform thickness. Solvent evaporation was performed at a constant temperature of 100°C in an electrically heated oven with forced air circulation. The resulting films were kept in the oven until

no change in weight could be observed. The films were then immersed in deionized water overnight to remove any residual solvent. Finally, the films were dried in a vacuum oven at 75°C to constant weight. The thickness of the films was 0.1 mm ± 0.02 mm.

Polymer identification

Infrared spectra of the prepared polymers were measured on a Perkin-Elmer infrared spectrophotometer (FTIR 1650). The samples were thin films of similar thickness of 3 μm. All spectra were recorded within the wave number range of 4000–400 cm⁻¹ at 25°C. Elemental analyses of the prepared polymers were performed at the Micro Analytical Unit, Cairo University, Egypt.

Polymer characterization

Viscosity

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. Flow times were measured at five different concentrations of the polymer sample. All the plots obtained were linear. Intrinsic viscosity was determined by usual extrapolation of η_{sp}/c to zero concentration and expressed in deciliter per gram (dL g⁻¹).

Solubility

The solubility of polymers in various amide solvents such as DMF, DMAc, and NMP was determined at room temperature (25°C). It was performed by gradual addition of the polymer to the solvent and stirred well till saturation. The maximum solubilities of the polymers were calculated as percent weight of the polymer per hundred milliliter of solvent (% w/v).

Percent moisture regain

A perfectly dried polymer sample was allowed to absorb moisture until constant weight in a humidity chamber maintained at 85% relative humidity at 23°C. Then, a weighed amount of the moisture-absorbed sample was dried in a vacuum oven at 75°C to a constant weight. The percent moisture regained by the polymer sample was calculated on the basis of weight loss.

X-ray measurements

A RAD-B (Rigaku Denki) system diffractometer with a Ni monochromator was used to record the X-ray diffractograms of the prepared polymer films. X-ray source was Cu K α (40 kV/15 mA). The samples were maintained at stationary while scattering angles from 3° to 90° were scanned in the reflection mode at a scanning rate of 1° min⁻¹.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) curves were recorded on a Shimadzu TGA-50 H in air and nitrogen atmospheres at a heating rate of 10°C min⁻¹ and a heating range from room temperature to 800°C. The sample weights ranged from 3 to 5 mg, and the gas flow rate was 30 mL min⁻¹.

Mechanical properties

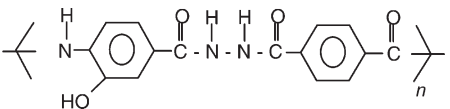
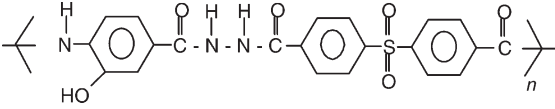
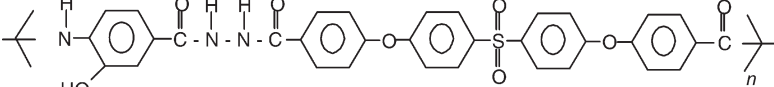
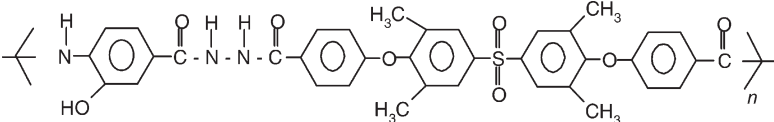
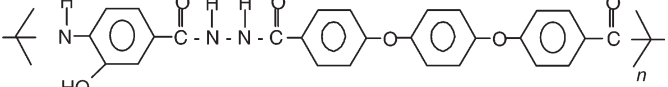
Tensile strength (*T*), elastic modulus (*M*), and elongation-to-break (%) (*E*) of the polymers films were measured on Shimadzu Autograph in air at room temperature.

RESULTS AND DISCUSSION

Polymer synthesis

Four novel wholly para-oriented aromatic polyamide-hydrazides containing sulfone, ether, or sulfone-ether linkages (Table II) have been synthesized by a low-temperature (-10°C) solution (in anhydrous DMAc) polycondensation reaction of 4A3HBH with stoichiometric amount of SDBC, SODBC, 4MeSODBC, or ODBC. All the polymers were produced in a quantitative yield that ranged between 99.85 and 98.95% (Table II). The basic reaction employed here is the Schotten-Bumann condensation of an aromatic acid chloride and an aminohydrazide, which is generally

TABLE II
Some Characteristics of the Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages

Polymer code	Repeat unit	Intrinsic viscosity ^a (dL g ⁻¹)	Yield (%)
A		4.83	99.66
B		4.39	99.53
C		3.72	99.41
D		3.41	98.95
E		2.85	99.85

^a Determined in DMAc at 30°C; polymer concentration was 0.5 g dL⁻¹.

known to be fast and quantitative. It is established that the rate by which hydrazide groups of aminobenzhydrazide reacted with acid chloride is about seven times greater than that of the amino groups with the same acid chloride.^{45,46} These properties indicate that when this polymerization is performed by the gradual addition of solid acid chloride in a solution of aminobenzhydrazide monomer, the hydrazide groups of the latter react first, and the so-called wholly ordered polymer with alternating amide and hydrazide linkages is formed. The eliminated HCl, as a byproduct, may be expected to show a twofold effect on the polycondensation reaction. First, HCl acts as a reaction catalyst, and second, it reacts with the solvent (DMAc) to form a salt (DMAc-HCl).⁴⁷ This salt is useful in making and keeping in solution polyamide-hydrazides through enhancing the solubility of the growing polymer,^{23,47} thereby assisting in molecular weight buildup and should direct the polycondensation equilibrium toward completion and be an additional driving force for the process. Consequently, since the basic reaction is rapid even at low temperatures and one of the polymerization products is continuously being withdrawn from the equilibrium, this condensation polymerization is expected to proceed to acceptably high conversions and thus satisfy one of the mentioned requirements for preparation of high-molecular-weight products imposed by the nature of this step-growth process.

Polymer identification

The structure of the prepared polymers is proposed on the basis of their elemental analyses and IR spectra. The elemental analyses values are in good agreement with the theoretical ones calculated for their expected repeating units as shown in Table III. On the other hand, all the IR spectra of these polymers showed common absorption stretching vibration bands at the following wave numbers: (I) 3600–3100 cm⁻¹ (intensive and broad) assigned the overlapped NH, –OH (phenolic) and the possible interchain hydrogen bonding; (II) 2360–2340 cm⁻¹ (weak) is attributed to possible enol-type configuration of hydrazide and amide groups; (III) 1670–1650 cm⁻¹ (strong) corresponded to the amide carbonyl groups; (IV) 1600 cm⁻¹ indicated the aromatic carbon–carbon double bonds; (V) 1540–1520 cm⁻¹ is due to =NH of amide II; (VI) 1500 cm⁻¹ indicated carbon–carbon single bond in ring; (VII) 1420 cm⁻¹ is attributed to carbon–oxygen (phenolic); (VIII) 1330–1320, 1290–1280, 1260 cm⁻¹ corresponded to carbon–hydrogen combined with =NH of amide III. Moreover, it would be expected that 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. This expectation was evidenced experi-

TABLE III
Elemental Analyses of the Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages

Polymer code ^a	Elemental analyses ^b				
	%C	%H	%N	%S	%O ^c
A	60.55 (60.61)	3.76 (3.70)	14.07 (14.14)	– –	21.62 (21.55)
B	57.56 (57.67)	3.44 (3.43)	9.56 (9.61)	7.29 (7.32)	22.10 (21.97)
C	63.67 (63.77)	3.76 (3.71)	6.73 (6.76)	5.13 (5.15)	20.71 (20.61)
D	65.47 (65.58)	4.63 (4.58)	6.17 (6.20)	4.70 (4.73)	19.03 (18.91)
E	67.21 (67.36)	4.01 (3.95)	8.69 (8.73)	– –	20.09 (19.96)

^a Polymer samples were thermally treated at 150°C for 30 min, in nitrogen atmosphere to get rid of their adsorbed surface moisture.

^b Data given in parantheses correspond to the calculated values.

^c Calculated as %O = 100–(%C + %H + %N + %S).

mentally by comparing the IR spectra of these polymers in the region of 1300–1110 cm⁻¹, which is characteristic for stretching vibration bands of these groups as shown in Figure 1. It can be seen from this figure that polymers B, C, and D showed bands at 1275 and 1150 cm⁻¹, which corresponded to the asymmetric and symmetric stretching of the sulfonyl groups, respectively. The ether linkages stretching at 1225 cm⁻¹ for polymers C, D, and E have also been shown. Thus, the results of elemental analyses coupled with the results of IR spectra seemed to be in good agreement with the expected structures of the prepared polymers, which are illustrated in Table II.

Polymer characterization

Viscosity

The intrinsic viscosity values for the prepared polymers are represented in Table II. These values reflect the high molecular weight of the polymers. The difference in viscosities observed among the polymers may be explained in terms of the relative rigidity and the different concentrations of the polar linkages resulted from the various lengths of the polymers segment. The highest viscosity of 4.83 dL g⁻¹ observed for polymer A may be attributed to the increase in rigidity, much interchain hydrogen bonding associated with increased packing efficiency. On the other hand, the introduction of sulfone (polymer B) or sulfone-ether (polymers C and D) linkages resulted in a decreased intrinsic viscosity. This may be attributed to the presence of the packing disruptive sulfone or sulfone-ether groups, which decrease the intermolecular hydrogen bonding. Further,

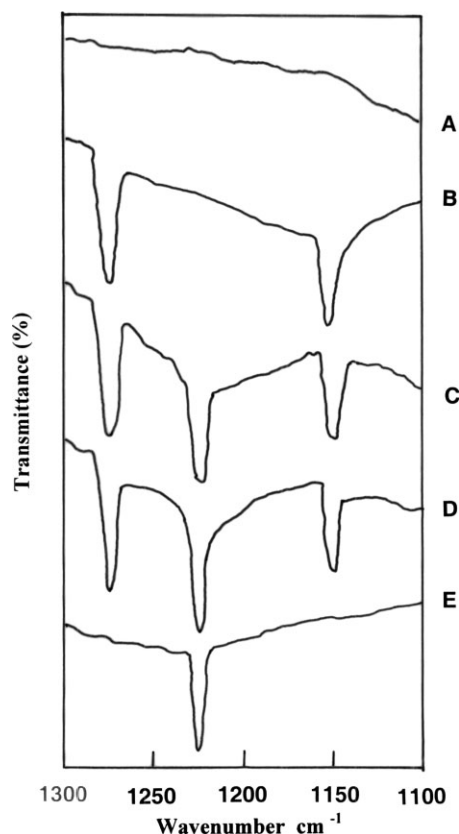


Figure 1 Variations of the FTIR spectra of novel wholly para-oriented aromatic polyamide-hydrazides containing sulfone-ether linkages.

attachment of methyl substituents on the benzene ring (polymer D) leads to increased packing distance, introduces lateral disorder, and decreases polar forces; thus polymer D exhibit a lower viscosity. The lowest viscosity of 2.85 dL g^{-1} observed for polymer E may be due to the insertion of flexible ether linkages in the polymer backbone that reduce the rigidity and hence the effective volume. 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. This observation seems to support the results previously reported.^{5,16,18,23}

Solubility

All the prepared polymers were found to be readily soluble in several polar solvents such as DMAc, DMF, and NMP at room temperature. In general, high solubility is a desired requirement for polymer processing. Polyamide-hydrazides showed a higher solubility than that of Kevlar (polyterephthalamide), which can be attributed to their weaker intermolecular forces relative to interaction with the solvent.⁴⁸ The maximum solubility (% w/v) of the prepared polymers are listed in Table IV. Regardless of the

nature of the solvent used, it can be noted that polymer A appears to be less soluble relative to the other polymers containing sulfone, ether, or sulfone-ether linkages and forms very high viscous solutions even at lower concentrations; however, at high concentrations, these solutions appear as gel. Generally, the solubility characteristic of these polymers is in the order: $E > D > C > B > A$. The introduction of ether linkages provides increased chain flexibility, and the attachment of methyl substituents on the benzene rings introduces lateral disorder by forcing the chains apart and interferes with the intermolecular cohesion of the existing polar linkages, leading to increased chain packing distance and decreased interchain interactions such as hydrogen bonding; thus the polymers D and E were more soluble than the other polymers. It is well established that the intermolecular hydrogen bonding is significantly influenced by the distance between the polar linkages in the repeating unit and it decreases by increasing their spacing (i.e., as the concentration of the polar linkages decreases, by increasing their spacing, the solubility of the polymer increases). The lower solubility of A can be attributed to the higher stiffness and much interchain hydrogen bonding associated with higher packing efficiency.

Percent moisture regain

All the prepared polymers showed strong hydrophilicity, which can be proved by their high moisture regain values that lie between 17.90% and 24.34% (at 23°C , relative humidity 85%) as listed in Table IV. The hydrophilicity of these polymers can be attributed to their polar structures that possess both amide, hydroxyl, and hydrazide, in addition to ether, sulfone, or ether-sulfone groups in their repeating units. These polar groups form hydrogen bonds with water readily promoting its adsorption by these polymers. The enhancements of the moisture regain of these polymers relative to that of the Nomex (12% MR at 25°C , relative humidity 85%)⁴⁹ is attributable

TABLE IV
Maximum Solubility and Moisture Regain of the Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages

Polymer code	Maximum solubility (% w/v)			Moisture regain ^a (%)
	DMAc	DMF	NMP	
A	22	20	10	17.90
B	24	21	13	19.46
C	29	25	18	21.12
D	33	29	24	22.25
E	38	34	29	24.34

^a Determined at 23°C and relative humidity 85%.

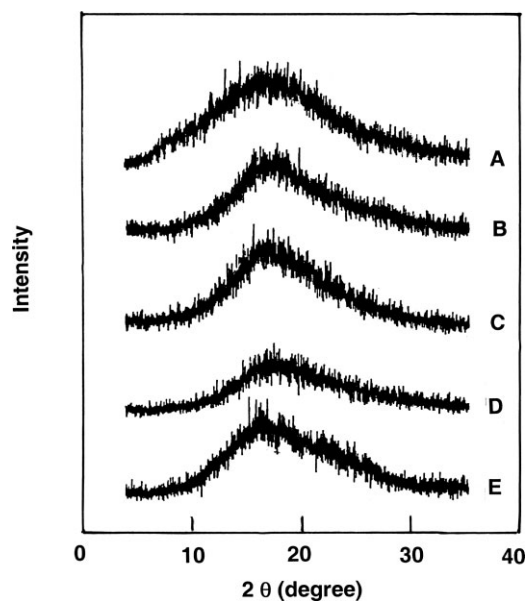


Figure 2 Wide-angle X-ray diffraction patterns of novel wholly para-oriented aromatic polyamide-hydrazides containing sulfone-ether linkages.

to the presence of the aforementioned functional groups against only one amide group in the Nomex repeating unit. The hydrophilicity of these polymers can be correlated with their structures. It is increased with the insertion of both ether and sulfone linkages in the investigated polymers. It can be explained by the combined favorable effects of ether and sulfone linkages present in the polymer chain. The kink introduced into the polymer chain by the angle sustained by these linkages leads to the separation between the macromolecular segments of these polymers, particularly in the presence of water, and consequently the inter or intrahydrogen bonds would be partially sterically prevented. Thus, they are free to interact with water. The insertion of methyl groups introduces lateral disorder by forcing the chains apart and interferes with the intermolecular cohesion of the existing polar groups; thus, the

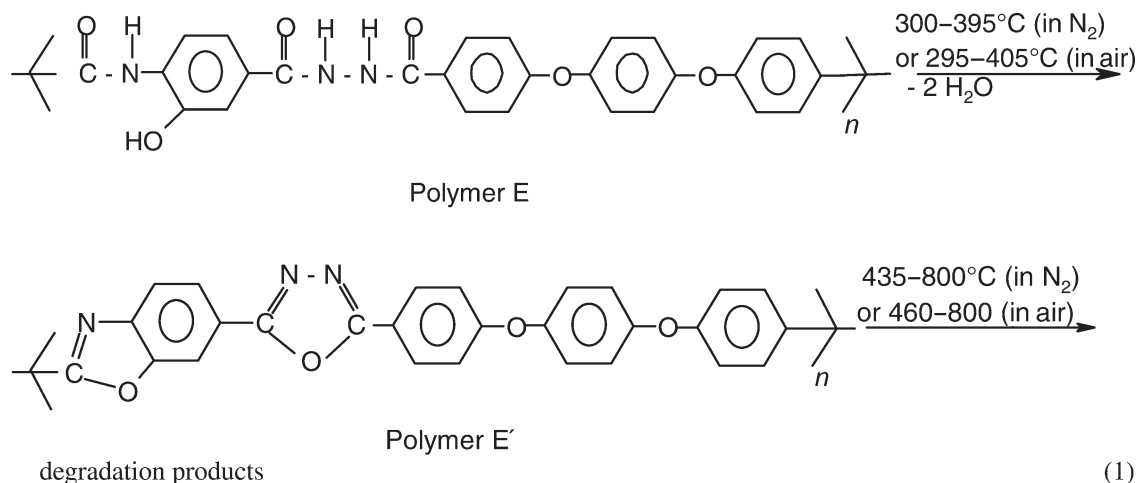
water absorption increases. On the other hand, polymer A being more strongly hydrogen bonded than those containing sulfone-ether linkages as a result of its shorter interchain distance; thus, the water absorption reduces.

X-ray measurements

The typical wide-angle X-ray diffraction patterns of the investigated polymers are shown in Figure 2. These diffractograms indicated that all these polymers are amorphous and showed a broad reflection hump in the range of 10°–30°.

Thermogravimetric analysis

TG measurements were performed on the evaluated polymers to examine the influence of their structural differences on their degradation behavior under the purely thermal and thermo-oxidative conditions. These experiments were carried out in nitrogen and in air, and the thermograms thus obtained are shown in Figures 3 and 4, respectively. Important parameter characteristics of these degradation processes are summarized in Table V. It can be noted from these results that in both degradation atmospheres, all the polymers showed a similar characteristic thermal behavior, and their weight losses could be observed in three distinctive stages. First, a small weight loss (1–3 wt % based on the original polymer weight) occurred at 90–130°C and assigned to evaporation of adsorbed water from the surface of the polymers. Second, a significant weight loss (5–12 wt % based on the perfectly dried polymers) was obtained at different temperature ranges for various polymers in nitrogen and air atmospheres as listed in Table V. This weight loss can be attributed to the thermally induced cyclodehydration reaction^{1,5} of the polymers into the corresponding poly(1,3,4-oxadiazolyl-benzoxazoles) [eq. (1)] and corresponded well to the calculated amount of water released from cyclization.



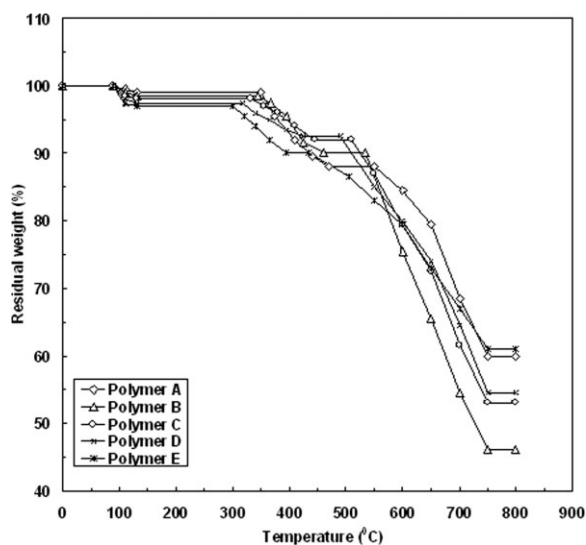


Figure 3 Thermogravimetric curves of novel wholly para-oriented aromatic polyamide-hydrazides containing sulfone-ether linkages in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$ and a gas flow rate of 30 mL min^{-1} .

The cyclodehydration reaction was proved experimentally by following the FTIR spectra of Sample B (as a representative study), which had been thermally treated at 460°C in nitrogen for 10–30 min (Fig. 5). The gradual reduction of the intensity of the absorption peak at 3320 cm^{-1} , which corresponds to NH and OH groups, indicating almost complete cleavage of the hydrogen bonds and deprotonation of these groups. The gradual disappearance of the carbonyl vibration bond (at 1650 cm^{-1}) suggested loss of the carbonyl double bond character. Moreover, IR spectra showed the appearance of a new characteristic absorption band at 1620 cm^{-1} , corre-

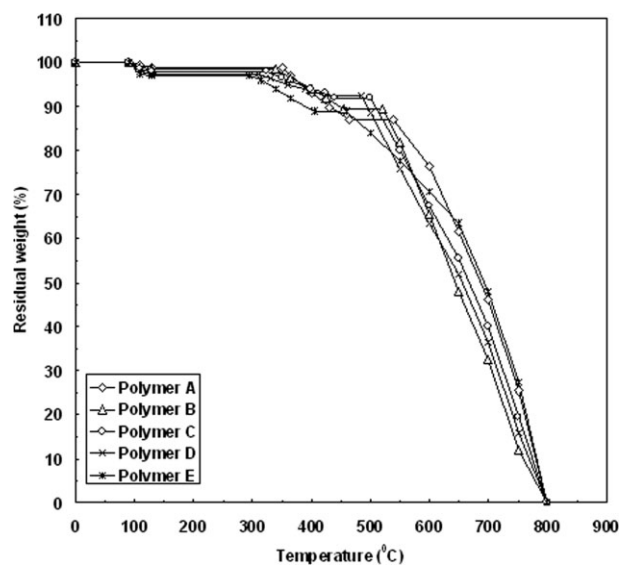


Figure 4 Thermogravimetric curves of novel wholly para-oriented aromatic polyamide-hydrazides containing sulfone-ether linkages in air at a heating rate of $10^{\circ}\text{C min}^{-1}$.

sponding to the C=N stretching vibration of benzoxazole and 1,3,4-oxadiazole rings, in addition to the appearance of two reasonably bands at 1020 and 970 cm^{-1} , which are assigned to the $=\text{C}-\text{O}-\text{C}=\text{O}$ groups.^{1,2} The third weight loss step is steep and assigned to the decomposition of the poly(1,3,4-oxadiazolyl-benzoxazole)s, which were formed *in situ*. Moreover, the resulting poly(1,3,4-oxadiazolyl-benzoxazole)s start to degrade in the temperature range above $435\text{--}550^{\circ}\text{C}$ in nitrogen and above $460\text{--}540^{\circ}\text{C}$ in air without weight loss at a lower temperature. The percentage residue of poly(1,3,4-oxadiazolyl-benzoxazole)s at 800°C in nitrogen was 72–56% of their original weights (Table V). On the other hand,

TABLE V
TG Analyses of the Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages at a Heating Rate of $10^{\circ}\text{C min}^{-1}$ and Gas Flow Rate of 30 mL min^{-1}

Polymer code	Degradation atmosphere	Onset of cyclodehydration reaction ($^{\circ}\text{C}$)	End of cyclodehydration reaction ($^{\circ}\text{C}$)	Weight loss during cyclodehydration reaction (%) ^a	Onset of decomposition ($^{\circ}\text{C}$)	Percentage residue at ($^{\circ}\text{C}$) ^b		
						600	700	750–800
A	Nitrogen	350	470	11 (12.12)	550	96.5	80.5	72.0
B	Nitrogen	345	460	8.5 (8.24)	535	85.5	64.5	56.0
C	Nitrogen	333	445	6 (5.80)	510	87.5	69.5	61.0
D	Nitrogen	318	425	5 (5.32)	490	87.5	72.0	62.0
E	Nitrogen	300	395	7 (7.48)	435	89.5	77.0	71.0
A	Air	350	465	12 (12.12)	540	89.5	59.0	38.5–13
B	Air	340	455	9 (8.24)	520	76.0	43.0	22.5–10.5
C	Air	325	440	6 (5.80)	500	75.5	48.0	27.5–8.0
D	Air	310	425	5 (5.32)	485	71.0	44.0	23.5–7.5
E	Air	295	405	8 (7.48)	460	81.5	59.0	38.5–11

^a All the weight losses were determined relative to the samples weights at the beginning of the cyclodehydration step. The data given in parantheses correspond to the calculated values.

^b All the weight residues were determined relative to the samples weights at the beginning of the decomposition step.

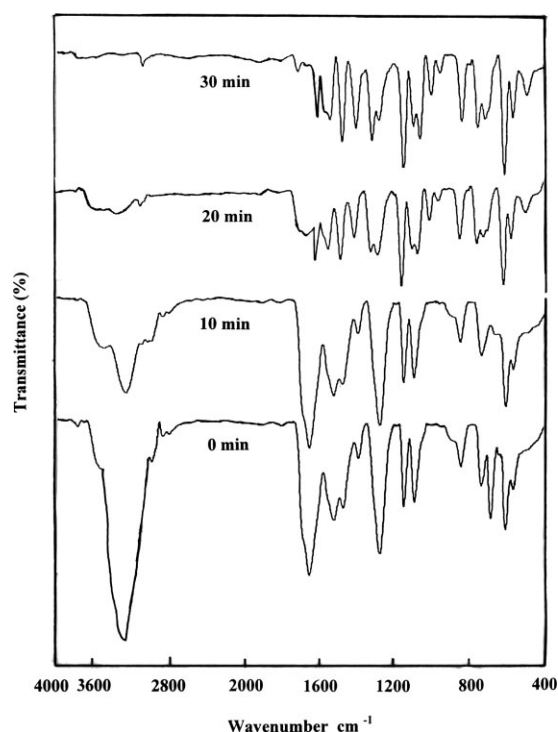


Figure 5 Changes of the FTIR spectra of polymer B, which had been thermally treated at 470°C in nitrogen for various time intervals.

smaller residues were observed at 800°C in air. These results confirm the expectation that the degradation rate of poly(1,3,4-oxadiazolyl-benzoxazole)s in air is faster than that obtained in nitrogen, supported by the residual weight of the samples at 800°C as well as at particular temperature (Table V). These observations indicate that poly(*o*-hydroxyamide-hydrazide)s can be used as precursor polymers for the synthesis of thermally stable poly(1,3,4-oxadiazolyl-benzoxazole)s. The incorporation of the evaluated flexibilizing linkages did not seem to

significantly influence the thermal stability of the oxadiazole-benzoxazole polymers. Although all poly(1,3,4-oxadiazolyl-benzoxazole)s showed significantly decreased solubility in DMF, DMAc, and NMP in comparison with the corresponding poly(*o*-hydroxyamide-hydrazide)s precursors, those containing the investigated flexibilizing linkages exhibit enhanced solubility in the same solvents with respect to that of the polymer free from these linkages. The latter dissolved only in concentrated sulfuric acid with degradation. The detailed thermal and thermo-oxidative characterization of these polymers will be reported in the forthcoming paper.

Mechanical properties

Flexible and tough films were obtained in all cases by the evaporation of solvent (DMAc) from the cast polymers solutions. Table VI demonstrates the mechanical properties of the investigated polymers before and after being drawn at various temperatures. The unoriented films showed good mechanical properties. Their elastic moduli, tensile strengths, and elongation to break were in the range of 6.45–3.54 GPa, 319.51–182.53 MPa, and 52.50–115.66%, respectively. Several attempts were made to improve the mechanical properties of these films by heat drawn as shown in Table VI, but their success was limited. Further improvements of the mechanical properties of these films and spinning of fibers are in progress.

CONCLUSION

High molecular weight easily processed new wholly para-oriented aromatic poly(amide-hydrazide)s containing flexibilizing groups such as sulfone, ether, or sulfone-ether groups have successfully been synthesized as highly viscous film-forming solutions. These

TABLE VI
Mechanical Properties of the Novel Wholly Para-Oriented Aromatic Polyamide-Hydrazides Containing Sulfone-Ether Linkages

Polymer code	Mechanical properties ^a											
	As cast			Heat drawn ^b								
				At 150°C			At 180°C			At 200°C		
	<i>M</i>	<i>E</i>	<i>T</i>	<i>M</i>	<i>E</i>	<i>T</i>	<i>M</i>	<i>E</i>	<i>T</i>	<i>M</i>	<i>E</i>	<i>T</i>
A	6.45	52.50	319.51	10.35	29.25	420.10	16.65	18.15	531.03	34.35	6.91	984.01
B	5.92	64.32	298.42	9.58	33.63	391.71	15.44	20.07	492.57	31.62	8.61	902.65
C	4.87	89.11	257.17	8.11	42.41	332.41	12.97	24.19	413.81	25.64	11.98	741.38
D	4.13	106.63	219.26	6.60	51.72	273.37	10.91	29.36	306.42	20.93	14.31	639.34
E	3.54	115.66	182.53	5.32	61.68	216.38	9.26	35.43	226.16	18.08	15.55	595.29

^a Measured at room temperature, *M* is the elastic modulus (GPa), *T* is the tensile strength (MPa), and *E* is the elongation at break (%).

^b Achieved by hand at a preselected temperature till break (maximum stretching).

polymers exhibited some desirable properties that mark them as promising candidates for corresponding engineering applications and perhaps also for some new ones. Polymers properties were strongly affected by their structural differences. In general, the introduction of the flexibilizing linkages leads to polymer of a higher solubility in DMF, DMA, and NMP and of higher affinity to water sorption relative to the polymer free from these linkages. On the other hand, the polymers containing the flexibilizing linkages showed relatively reduced mechanical and intrinsic viscosity with respect to the polymer free from these linkages. All the prepared polymers are highly thermally stable and could be thermally cyclodehydrated into the corresponding poly(1,3,4-oxadiazolyl-benzoxazole)s at elevated temperature ranges. Although the incorporation of the flexibilizing linkages into the polymer main chains did not seem to significantly influence the thermal stability of the poly(1,3,4-oxadiazolyl-benzoxazole)s, they remarkably enhanced the solubility of oxadiazolyl-benzoxazole polymers in comparison with that of polymer free from these linkages. Further, oxadiazolyl-benzoxazole polymers showed significantly decreased solubility with respect to the corresponding *o*-hydroxyamide-hydrazide precursors.

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