

A New Rigid Rodlike Colored Poly(amide hydrazide): Thermal, Optical Anisotropic, and Mechanical Behavior

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ABSTRACT: A new aromatic all-*para* oriented poly(amide hydrazide) containing an azo group in the main chain was prepared by reacting a symmetric diamine containing a preformed hydrazide group, viz., *N,N'*-bis(4-aminobenzoyl)hydrazine (BABH), with 4,4'-azobenzoyl chloride (ADBC). The thermal behavior of the polymer was studied by TGA and DSC in air and nitrogen. Films of the polymer were prepared by two processes, viz., wet and dry processes, by using its solution in DMAc containing LiCl. The optical anisotropy, surface morphology, and tensile properties of the films were studied. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1211–1215, 1997

Key words: rigid rodlike polymer; poly(amide hydrazide); optical anisotropy; surface morphology

INTRODUCTION

Wholly aromatic rigid rodlike poly(amide hydrazide)s are one of the most important classes of high-performance polymers.^{1–3} Poly(terephthaloyl-*p*-aminobenzoyl hydrazide), commercially known as X-500 (Monsanto Co., USA), can produce high-modulus and high-strength fibers when spun from its solutions in organic solvents.^{1,4} Although this polymer has been reported to form optically isotropic solutions in organic solvents in the quiescent state,^{5,6} during fiber spinning, the orientation and chain extension are pronounced due to a phase transition from isotropic to anisotropic under the imposed flow field.^{7,8} At high temperatures (~ 300–350°C), the hydrazide groups of this polymer undergo cyclodehydration to form thermally more stable 1,3,4-oxadiazole rings.^{3,9} An azo-*p*-phenylene moiety in a polymer main chain not only has a special effect on the photochromic and photocontractile behavior of the polymer,^{10,11} but also can impart rigidity of the polymer chain.¹²

We reported earlier the synthesis and charac-

terization of a new wholly aromatic all-*para* oriented poly(amide hydrazide) with azo linkage in the polymer backbone.¹³ In this communication, we report the thermal behavior of the polymer in detail along with the optical anisotropy, surface morphology, and tensile properties of the polymer films.

EXPERIMENTAL

Synthesis of Polymer

The method of the polymer synthesis from *N,N'*-bis(4-aminobenzoyl)hydrazine (BABH) and 4,4'-azobenzoyl chloride (ADBC) using DMAc containing 5% (w/v) dissolved LiCl as a solvent medium was described in our previous communication.¹³

In one batch (B_1), the polymer was prepared from 0.5062 g (1.875 mmol) BABH and 0.5756 g (1.875 mmol) ADBC in 40 mL solvent (monomer concentration 0.047 mol/L; polymer content 2.34% [w/w]), with yield = 97% and $\eta_{inh} = 2.32$ dL/g (measured at 30°C using the polymer solution of concentration 0.1 g/dL).

In another batch (B_2), the polymer was pre-

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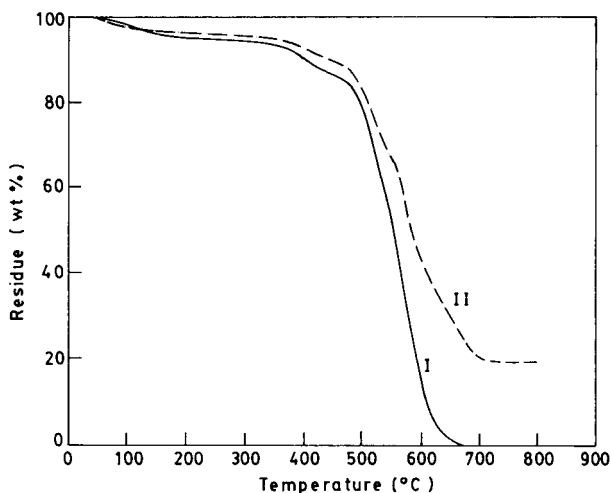


Figure 1 TGA curves of the polymer: (I) in air; (II) in nitrogen.

pared from 1.0800 g (4.000 mmol) BABH and 1.2280 g (4.000 mmol) ADBC in 40 mL solvent (monomer concentration 0.100 mol/L; polymer content 4.78% [w/w]; LiCl content 4.75% [w/w]), with yield = 98% and $\eta_{inh} = 4.26$ dL/g (measured at 30°C using the polymer solution of concentration 0.1 g/dL).

The homogeneous polymer solution obtained at the end of the reaction was directly used for film casting and properly diluted with a DMAc/5% LiCl solution to prepare a 0.1% (w/v) polymer solution for measurement of the inherent viscosity.

Preparation of Polymer Films

As the polymer solution of higher viscosity resulted from batch B₂, the solution was used for film casting. The films were cast on clean and dry glass plates with a Doctor's blade. The solvent was removed from the cast films by a (i) wet process and (ii) a dry process.

- (i) Wet process: After the polymer films were cast onto glass plates, these were immersed in water; the coagulated films were detached from the plates within 5–10 s. The films were kept in water at room temperature for 4 h to leach out the solvent and LiCl. The films were dried first in air and then in a vacuum at 60°C for 2 h. Finally, dry transparent free-standing films were obtained.
- (ii) Dry process: After film casting, the glass plates were kept horizontally in a vacuum oven and dried at 90°C under a vacuum for 4 h. Then, the glass plates were immersed in water and the films were separated from the plates within 10–15 s. The films were kept in water at room temperature for 4 h, air-dried, and finally oven-dried at 60°C for 2 h under vacuum. Relatively fewer transparent films were obtained by this process.

Characterization

Inherent Viscosity

Inherent viscosities of the polymer solutions in DMAc/5% LiCl at a concentration of 0.1 g/dL were measured at 30°C using an Ubbelohde suspended level viscometer.

Film Test Specimens

Strips of length 80 mm and width 10 mm were cut from the free-standing polymer films along the draw direction and used as test specimens. The thickness of the film specimens was measured using a digital micrometer (Digimatic Mitutoyo, Japan). For a particular specimen, measurements were done at five different points and the average value was taken. The average thickness of the films prepared by both the wet and dry processes was the same (18 μm).

Table I Thermal Behavior of the Polymer

Atmosphere	Cyclodehydration			First-step Degradation			Overall Degradation, Ends at °C	Char Residue at 800°C (Wt %)
	Starts at (°C)	Ends at (°C)	Residue at 475°C (Wt %)	Starts at (°C)	Ends at (°C)	Residue at 575°C (Wt %)		
Air	345	445	84	450	535	33	675	0
N ₂	365	470	88	475	560	60	715	19

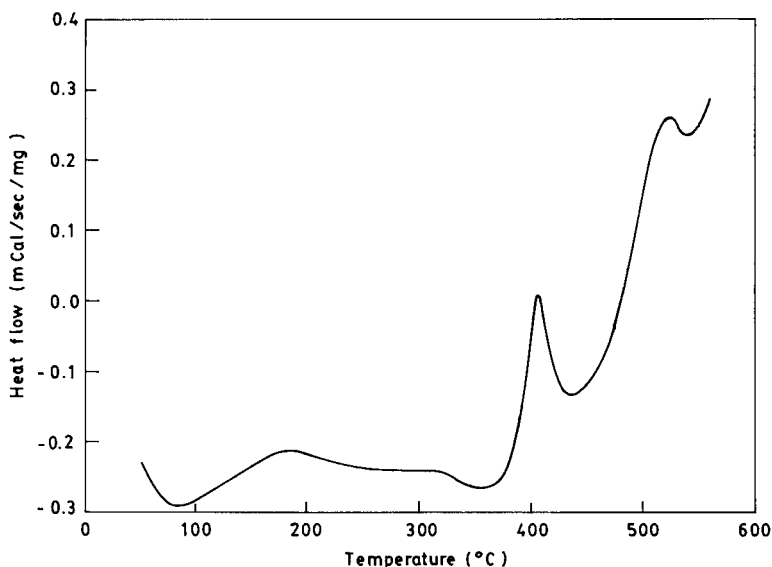


Figure 2 DSC curve of the polymer in nitrogen.

Thermal Analyses

Thermogravimetric analyses (TGA) of the powdered polymer samples were carried out with a DuPont 951 thermal analyzer at a heating rate of 10°C/min in static air and nitrogen. Differential scanning calorimetry (DSC) was done with a Stanton Redcroft STA 625 thermal analyzer in nitrogen at a heating rate of 10°C/min. The polymer samples were heated at 150°C under a vacuum for 2 h before the analyses were done.

Optical Anisotropy

Optical anisotropic textures of the transparent film specimens placed on glass slides were observed on a Leitz Laborlux 12 Pols optical microscope with crossed polars. A λ -plate was inserted below the analyzer as a fixed compensator to observe the interference patterns more distinctly.

Surface Morphology

Surface morphology of the films (sample size 5 × 5 mm) was studied by a Cam Scan-Series 2 scanning electron microscope. The films were coated with gold using an E 5200 Polaron automatic sputter coater.

Tensile Measurement

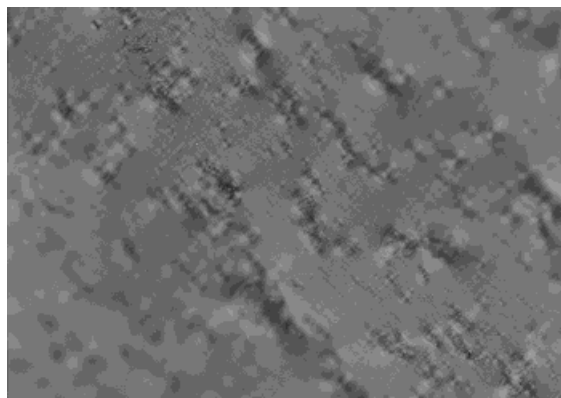
Tensile properties of the film specimens (gauge length 40 mm, width 10 mm) were measured with four different specimens.

RESULTS AND DISCUSSION

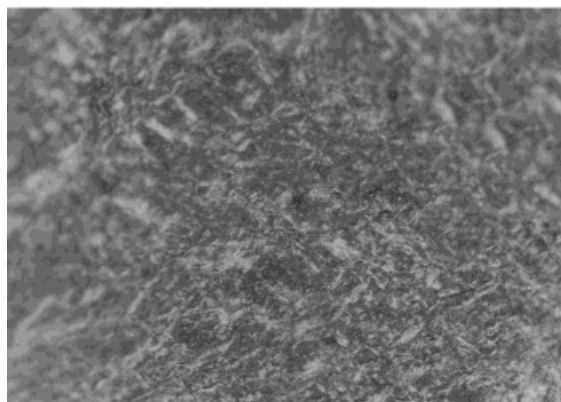
Thermal Analyses

The decomposition behavior of the polymer in air and in nitrogen are shown by the TGA curves (Fig. 1) and detailed thermal characteristics are presented in Table I. The polymer undergoes major weight losses in three steps in both atmospheres. The initial weight loss of about 4–5% occurs between 80 and 150°C due to loss of absorbed moisture. Between 350 and 470°C, the polymer undergoes a weight loss of about 7–9% due to loss of water associated with the cyclodehydration of the hydrazide groups to form 1,3,4-oxadiazole rings.^{9,14,15} Along with cyclodehydration, the polymer may lose molecular nitrogen.^{16,17} The third-step weight loss is associated with polymer degradation. The rate of polymer degradation is much faster in air than in nitrogen, probably due to the slower rate of elimination of molecular nitrogen in a nitrogen atmosphere as well as a faster rate of thermooxidative degradation.

The DSC study was carried out in a nitrogen atmosphere from room temperature to 560°C (Fig. 2). The endotherm centered at about 85°C is due to loss of absorbed moisture¹⁸ at about 355°C due to cyclodehydration^{18,19} and at about 535°C due to polymer degradation. The exotherm centered at about 405°C appears probably due to the elimination of molecular nitrogen^{16,17} combined with *trans* to *cis* conversion of the azo group accompanied by volume contraction.^{20,21}



(a)



(b)

Figure 3 Polarizing optical micrographs of the polymer films prepared by (a) a wet process (PW) and (b) a dry process (PD) (magnification 100 \times).

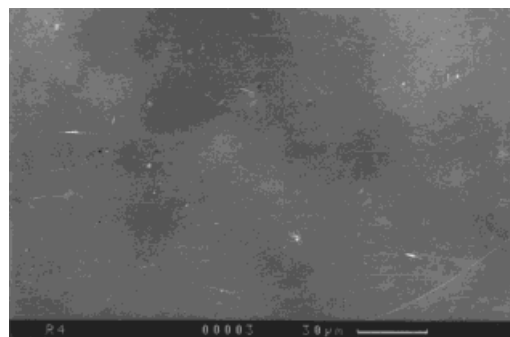
Optical Anisotropy

The polarizing optical micrographs of the polymer films prepared by wet (designated as PW) and dry (designated as PD) processes are shown in Figure 3(a) and (b), respectively. Although, in both the cases, birefringent nematic texture is observed, the order is relatively more pronounced in the PD film. In the PW film, the texture is thread-like (green-colored regions), whereas in the PD film, threadlike lines resembling oil streaks are present in the whole region, which are more or less oriented in a particular direction. The relatively more ordered texture in the PD film may be due to two reasons: (i) The polymer concentration in the film cast onto the glass plate is gradu-

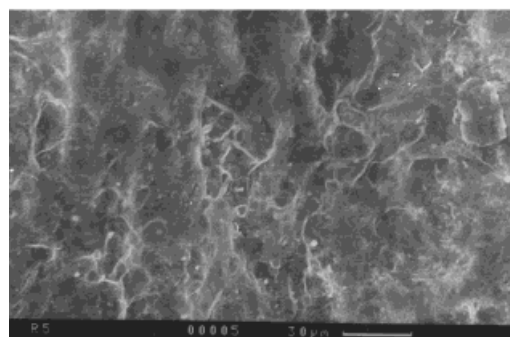
ally increased due to slow evaporation of the solvent during vacuum drying in the dry process, and (ii) the polymer chains are relatively more oriented in the film prepared by the dry process. In the wet process, the films are detached from the glass surface during coagulation and, thereby, the orientation of the polymer chains attained during casting is somewhat disturbed. But in the dry process, the films are in contact with the glass surface for a long time and the orientation attained during casting is maintained until the drying of the films.

Surface Morphology

The surface morphology of the polymer films was studied to observe the effect of the process used for solvent removal from the cast films. The scanning electron micrographs of PW and PD films are shown in Figure 4. Although the surface of the PW film is smooth, that of the PD film is fractured. The observation may be explained by the fact that, in the wet process, when the cast film is immersed in water, both DMAc and LiCl are likely to be



(a)



(b)

Figure 4 Scanning electron micrographs of the polymer films prepared by (a) a wet process (PW) and (b) a dry process (PD).

Table II Tensile Properties of the Polymer Films

Film Specimen	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
PW	228–240	2.6–3.0	10.8–11.2
PD	138–164	0.8–1.6	11.6–12.4

dissolved in water. So, after drying, there is little possibility of the presence of LiCl either in the bulk or at the surface of the film and, therefore, a smooth surface results. In the dry process, due to evaporation of solvent during vacuum drying of the cast film, LiCl remains trapped in the dry film, and as the LiCl content is very high (4.75%, w/w), which is almost the same as the polymer content (4.79%, w/w), in the polymer solution used for film casting, the fractured surface results. During washing of the film, LiCl present on the surface may dissolve into water, resulting in the increase of the size and amount of fractures.

Tensile Properties

The tensile data of the polymer films are presented in Table II. The PD film has a higher modulus but lower strength and elongation at break than those of PW film. The variation in the tensile values is wider in the PW film specimens. The observation may be explained in the following way: As discussed earlier, there may not be any LiCl either in the bulk or at the surface of the PW film. But LiCl is present in the bulk, although it may not be at the surface of the PD film. Although optical anisotropy of the films reveals that there are relatively more polymer chain orientations in the PD film, the presence of LiCl in this film lowers its tensile properties. As the polymer content (4.79%, w/w) is almost the same as the LiCl content (4.75%, w/w) in the polymer solution used for film casting, the PD film exhibits a more brittle nature than the homogeneous PW film. There is a wider variation in the tensile values of the PD specimens due to nonuniform distribution and the size of solid LiCl deposited in the film.

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