

Synthesis and Properties of a High-Molecular-Weight Poly(amic acid) and Polyimide Based on 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane

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ABSTRACT: The feasibility of using the conventional two-step procedure involving the thermal imidization of a high-molecular-weight poly(amic acid) (PAA) for the preparation of self-supporting polyimide (PI) films was studied. Synthesized PAA and PI were analyzed with respect to their molecular weights, chemical structures, and mechanical and thermal properties. The results showed that a high-molecular-weight PAA was successfully synthesized from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane with 3,3',4,4'-benzophenone tetracarboxylic dianhydride. The high intrinsic viscosity of PAA was 1.5 dL/g. Self-supporting PI films were successfully prepared by the thermal imidization of PAA and reached maximum ten-

sile strength, tensile modulus, and elongation at break values of 103 MPa, 2.2 GPa, and 10.7%, respectively. The PI films were stable to 426–483°C (the 5% weight loss temperature) and had a glass transition at 271–283°C. All these results indicate that the conventional two-step procedure involving thermal imidization is a promising method for preparing self-supporting PI films with reasonable levels of mechanical and thermal properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 702–706, 2011

Key words: films; mechanical properties; polyimide; thermal properties

INTRODUCTION

Polyimides (PIs) are a class of polymers known for their high thermal stability, excellent mechanical properties, and chemical resistance. These properties make them highly desirable for high-performance applications. Recently, considerable efforts have been made to modify their chemical and molecular structures with respect to specific applications or particular properties.^{1–4}

Some hydroxyl PIs with one or two free OH groups per repeating unit have recently been synthesized from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF),^{5,6} trimethylsilylated 2,4-diaminophenol,⁷ and 4,6-diamino-resorcinol dichloride.⁸ They

have been reported to be potential materials for gas-separation membranes, photoresists, and nonlinear optic applications.^{5–11} However, in comparison with these monomers, Bis-AP-AF is stable under normal conditions, and conventional synthetic procedures can be applied to obtain a desired hydroxyl PI.⁵ PIs based on Bis-AP-AF diamine have been prepared by a routine two-step procedure involving the thermal imidization of poly(amic acid)s (PAAs). The synthesized PAAs have had moderate molecular weights and an inherent viscosity of 0.5 dL/g.^{12–14} These low-molecular-weight hydroxyl PIs have been used as thin films on substrates to produce photoresists. However, they are not suitable for self-supporting films with a reasonable level of mechanical properties.⁵ Likhatchev et al.⁵ explored the synthesis of high-molecular-weight PI from Bis-AP-AF and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA). Although BTDA/Bis-AP-AF PAA with a higher inherent viscosity (0.7 dL/g) was synthesized, the thermal imidization of PAA induced dramatic embrittlement of the PI film. Therefore, this brittle PI film was not suitable for producing self-supporting films or for tensile tests. Jung and Lee⁶ prepared a BTDA/Bis-AP-AF PI membrane by the conventional two-step procedure involving the

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thermal imidization of PAA for gas separation. Although the membrane showed high gas selectivity, it also showed low gas permeability. In addition, the molecular weight and mechanical properties of the PI membrane were not evaluated. Lozano et al.¹⁵ reported that PI membranes could show outstanding gas-separation properties when the molecular weight was very high. However, to the best of our knowledge, little information has been published about the synthesis of a high-molecular-weight PI based on Bis-AP-AF and BTDA.

In this study, our objective was to investigate the feasibility of using the conventional two-step procedure involving the thermal imidization of PAA for the production of a high-molecular-weight PI based on Bis-AP-AF and BTDA. Synthesized PAA and PI were analyzed with respect to their molecular weights, chemical structures, and mechanical and thermal properties. All the results show that this two-step procedure involving the thermal imidization of PAA for the synthesis of high-molecular-weight PI is a promising method for preparing self-supporting PI films with reasonable levels of mechanical and thermal properties. On the basis of previous reports,^{5,15,16} this self-supporting PI appears to be a promising candidate for a wide and diversified range of applications in gas separation, optoelectronic devices, and other advanced applications.

EXPERIMENTAL

Materials

N,N-Dimethylacetamide (DMAc; Tianjin Bodi Chemical Holding Co., Ltd., Tianjin, China) and 1-methyl-2-pyrrolidinone (NMP; Tianjin Bodi Chemical Holding) were both distilled over P₂O₅ under reduced pressure. BTDA (Zigong Tianlong Chemical Co., Ltd., Sichuan, China) was purified by vacuum sublimation before use. Bis-AP-AF (99.9% pure; Chriskev Co., Inc., Lenexa, KS) was used without purification.

Synthesis of the PAA and PI films

PI films were obtained through a reaction between Bis-AP-AF and BTDA in a two-step procedure. In the first step, the PI precursor, PAA, was synthesized by low-temperature (0°C) solution polycondensation of Bis-AP-AF and BTDA in DMAc under a nitrogen atmosphere. The concentration of the synthesized PAA in DMAc was 25 wt %. In the second step, PI films were obtained by the thermal imidization of PAA. First, the cast PAA was dried at 60°C for 8 h under a nitrogen flow to volatilize the DMAc solvent and thus produce PAA films. Then, the temperature was raised at a rate of 15°C/min to 250–325°C and was kept there for 1 h so that the thermal imidization

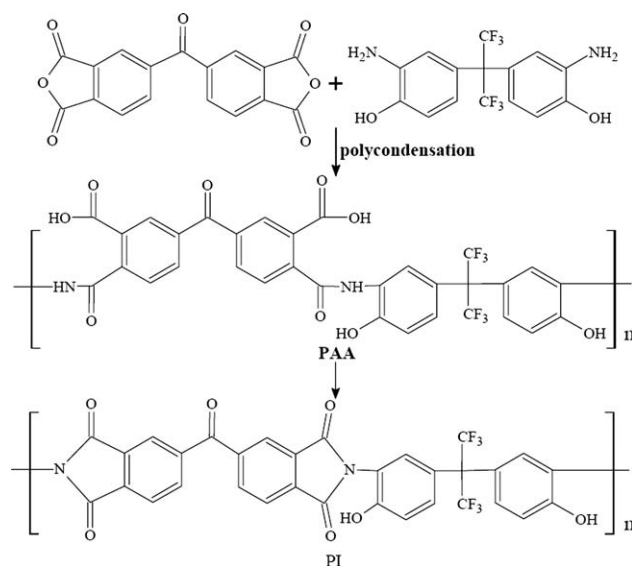


Figure 1 General scheme for the synthesis of PI.

of PAA could produce PI films. The thickness of the PI films was approximately 40 μm . The general scheme for the synthesis of PI is shown in Figure 1.

Measurements

The intrinsic viscosity of PAA was measured with an Ostwald viscometer (Westingarea Technology Co., Ltd., Shanghai, China); the solvent was NMP, and the temperature was 25°C. The chemical structures of PAA and PI were studied with Fourier transform infrared (FTIR) spectroscopy (IR Prestige-21, Shimadzu Corp., Kyoto, Japan) in the range of 400–4000 cm^{-1} . The tensile properties of the PI films were measured on an electronic universal testing machine (GT-TS-2000, Gotech Testing Machines, Inc., Taiwan, China) at room temperature (23°C) with a crosshead speed of 10 mm/min according to ISO Standard 527-3:1995. Thermogravimetric analysis (TGA) of the PI films was performed with a TGA-60 apparatus (Shimadzu) in the temperature range of 23–600°C at a heating rate of 10°C/min in air and nitrogen atmospheres. The initial decomposition temperature was characterized as the temperature at which a 5% weight loss was achieved ($T_{5\%}$). The glass-transition temperature (T_g) of the PI films was measured with a DSC-60 apparatus (Shimadzu) in the temperature range of 23–400°C at a heating rate of 10°C/min under an atmosphere of flowing nitrogen.

RESULTS AND DISCUSSION

Synthesis of the PAA

The preparation of PI by the conventional two-step procedure is known to be very sensitive to the stoichiometry of the reactants. It requires monomers

and solvents of very high purity. In this study, the purity of all monomers and solvents was high. A small excess of a dianhydride has often been used to increase the molecular weight of PAA.⁵ Therefore, the diamine/dianhydride molar ratio in the polycondensation reaction was 1:1.015. Meanwhile, BTDA is a highly active dianhydride. As a result, polycondensation between a dianhydride and a diamine is rapid in the aprotic solvent DMAc. However, higher reactivity for polymerization often means a lower molecular weight. To form PAA with a high molecular weight, the polycondensation of BTDA and Bis-AP-AF was performed at a lower temperature (0°C) for 4 h under a nitrogen atmosphere. In addition, to enhance the reaction of BTDA and Bis-AP-AF, intense mechanical stirring was used because of the high viscosity of the reaction mixture. The inherent viscosity was taken as a measure of the molecular weight.

The inherent viscosity, usually used to express the molecular weight of a polycondensation product, was used to characterize the molecular weight of the BTDA/Bis-AP-AF PAA. Although this relationship can be rigorously established only when the viscosimetric equation is known, it can be used to compare the results for the same polymer.^{15,17} The intrinsic viscosity of PAA was 1.5 dL/g in NMP. This result represents a great advance because a BTDA/Bis-AP-AF PAA with an inherent viscosity higher than 0.7 dL/g has never been reported to the best of our knowledge. The thermal imidization of PAA with a moderate molecular weight (inherent viscosity = 0.7 dL/g) induced a dramatic embrittlement of the resulting PI film. Therefore, the brittle PI film was not suitable for producing self-supporting films or for tensile tests.⁵ However, in this study, the high molecular weight (intrinsic viscosity = 1.5 dL/g) of the obtained PAA was enough to produce flexible PI films. This is discussed later along with the mechanical properties of the PI films.

FTIR analysis of PAA and PI

The PI film was prepared by the thermal imidization of the PI precursor PAA. If PAA was successfully imidized, the expected imide peaks could appear without the characteristic peak of PAA in the FTIR spectrum. Therefore, the chemical structures of PAA and PI were confirmed with FTIR. Figure 2 shows the FTIR spectra of the PAA and PI films by thermal imidization at 300°C. In the spectrum of PAA, stretching vibration peaks of N—H at 3071 cm⁻¹ and O—H (—COOH) at 2932 cm⁻¹ appear. In addition, stretching vibration peaks of C=O (—COOH), C=O (—CONH), and C—N appear at 1709, 1651, and 1389 cm⁻¹, respectively. In the spectrum of PI, the absorption peak attributed to N—H and O—H (—COOH)

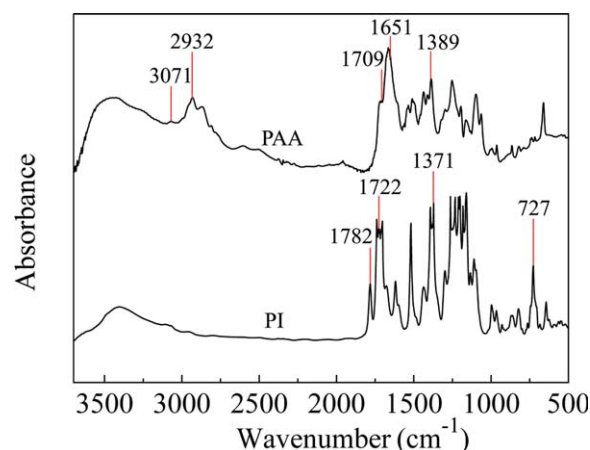


Figure 2 FTIR spectra of PAA and PI (imidization temperature = 300°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bonds does not appear. A higher frequency of imides appears at 1782 (C=O, asymmetric stretching) and 1722 cm⁻¹ (C=O, symmetric stretching). Also, the C—N—C absorption at 1371 (stretching vibration) and 727 cm⁻¹ (bending vibration) confirms the formation of imides.

Mechanical properties of the PI films

Figure 3 shows the values of the tensile strength, tensile modulus, and elongation at break of the PI films at various thermal imidization temperatures (250–325°C). The thermal imidization temperature could affect the tensile properties of the PI films. When the thermal imidization temperature was 250°C, the tensile strength, tensile modulus, and elongation at break of the PI films were 84 MPa, 1.7 GPa, and 6.1%, respectively. When the thermal imidization temperature was increased to 275°C, the tensile strength, tensile modulus, and elongation at break of the PI films increased to 98 MPa, 2.0 GPa, and 8.3%, respectively. When the thermal imidization temperature was further increased to 300°C, the tensile strength, tensile modulus, and elongation at break of the PI films increased and reached maximum values of 103 MPa, 2.2 GPa, and 10.7%, respectively. This occurred mainly because the higher temperature was more beneficial for the thermally induced orientation of the molecule.

The tensile property analysis of these films indicated that thermal imidization at 250–300°C could prepare self-supporting PI films with reasonable tensile properties and elongation at break values. The better mechanical properties of the PI films could be attributed to both the high molecular weight of the obtained PAA and the appropriate thermal imidization process technology. The higher thermal imidization temperature could be beneficial for the

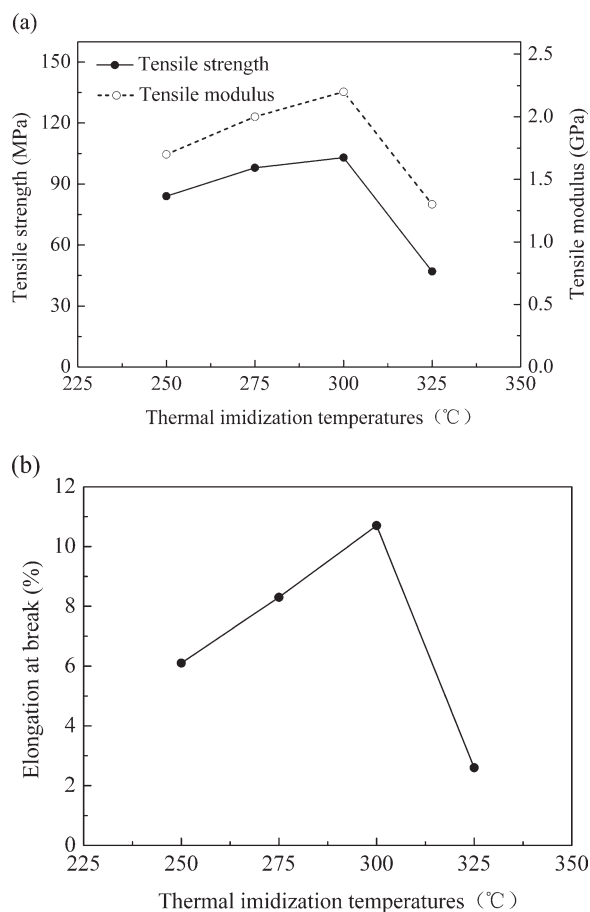


Figure 3 Tensile properties of the PI films.

tensile properties of PI films, but an exorbitant thermal imidization temperature could reduce the tensile properties. When the thermal imidization temperature was increased to 325°C, the tensile strength, tensile modulus, and elongation at break of the PI films decreased rapidly. The maximum reductions of the tensile strength, tensile modulus, and elongation at break of the PI films were 54.4, 40.9, and 75.7%, respectively, in comparison with the PI films produced with a thermal imidization temperature of 300°C. This occurred mainly because the exorbitant thermal imidization temperature could induce degradation of the polymer and thus cause a reduction of the tensile properties of the PI films.

In a word, self-supporting PI films could be successfully prepared by the conventional two-step procedure involving the thermal imidization of PAA and reach maximum tensile strength, tensile modulus, and elongation at break values of 103 MPa, 2.2 GPa, and 10.7%, respectively. In other words, the conventional two-step procedure involving the thermal imidization of PAA based on Bis-AP-AF and BTDA is a promising method for preparing self-supporting PI films for gas-separation applications with a reasonable level of mechanical properties. For the transformation of this material into a product for

potential practical applications in gas separation, the use of PI films will be discussed in the future.

Thermal properties of the PI films

Differential scanning calorimetry (DSC) and TGA were performed to verify the thermal stability of the PI films. These methods offer a convenient way of studying the reaction rates and mechanisms under controlled conditions. These values are particularly important for the conversion of materials into products for potential practical applications. The thermal properties of PI films with various thermal imidization temperatures (250–325°C) are summarized in Table I.

The thermal imidization temperatures could affect the T_g values of the PI films. When the thermal imidization temperature was 250°C, T_g of PI was 271°C. When the thermal imidization temperature was increased to 300°C, T_g of the PI films increased and reached a maximum value of 283°C. When the thermal imidization temperature was increased to 325°C, T_g of the PI films decreased to its value at 250 or 275°C. Similarly to T_g , the thermal imidization temperature could also affect the decomposition temperature of the PI films, as indicated by $T_{5\%}$. When the thermal imidization temperature was increased to 300°C, $T_{5\%}$ of the PI films increased and reached a maximum value of 463°C in an air atmosphere. This occurred mainly because the higher temperature was more beneficial for thermally induced orientation of the molecule, but the exorbitant temperature could induce degradation of the polymer. In addition, the nitrogen atmosphere also could affect the decomposition temperature of the PI films. The decomposition of all the PI films in nitrogen started at temperatures higher than those in an air atmosphere. In other words, T_g and $T_{5\%}$ of the PI films were higher than 271 and 426°C, respectively, and this indicated good thermal stability.

The changes in these properties meant that T_g and $T_{5\%}$ of the PI films did not increase linearly with the thermal imidization temperature, and there was an optimum thermal imidization temperature for the best thermal properties. According to a comprehensive evaluation of the mechanical and thermal

TABLE I
Thermal Properties of the PI Films

PI sample	Imidization temperature (°C)	T_g by DSC (°C)	$T_{5\%}$ in air (°C)	$T_{5\%}$ in N_2 (°C)
PI-a	250	271	426	432
PI-b	275	275	459	483
PI-c	300	283	463	481
PI-d	325	273	450	474

properties, the optimum thermal imidization temperature was 300°C.

CONCLUSIONS

A high-molecular-weight PAA was successfully synthesized from Bis-AP-AF with BTDA. The high intrinsic viscosity of PAA was 1.5 dL/g. This high-molecular-weight PAA was sufficient to produce flexible PI films.

Self-supporting PI films were successfully prepared and reached maximum tensile strength, tensile modulus, and elongation at break values of 103 MPa, 2.2 GPa, and 10.7%, respectively. TGA and DSC testing showed that the PI films were stable to 426–483°C ($T_{5\%}$) with a glass transition of 271–283°C. According to a comprehensive consideration of the mechanical and thermal properties, the optimum thermal imidization temperature was 300°C.

This study shows that the conventional two-step procedure involving the thermal imidization of PAA for the synthesis of high-molecular-weight PI is a promising method for preparing self-supporting PI films with a reasonable level of mechanical properties. This high-molecular-weight PI appears to be a promising candidate for a wide and diversified range of applications in gas separation, optoelectronic devices, and other advanced applications.

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