

New Film-Forming Aromatic Poly(amide-imide)s Containing Isoindoloquinazolinedione Unit in the Backbone. 2. Physical Properties of the Film Cast from Poly(biphenylphthalic dianhydride-oxydianiline-4,4'-diamino-3'-carbamoyl-benzanilide) [Poly(BPDA-ODA-DACB)]

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Received 16 July 1999; accepted 15 January 2000

ABSTRACT: New aromatic poly(amide-imide) films containing isoindoloquinazolinedione unit in the backbone chain were directly obtained by thermal cyclization of the prepolymer of poly(amic acid-carbonamide) type, i.e., poly(biphenylphthalic dianhydride-oxydianiline-4,4'-diamino-3'-carbamoyl-benzanilide) [poly(BPDA-ODA-DACB)]. The films, before heat treatment, exhibited the tensile strength of $30 \approx 40$ MPa and the tensile modulus of $1.3 \approx 1.9$ GPa. After heat treatment, the strength and modulus increased to $135 \approx 150$ MPa and $2.6 \approx 2.7$ GPa, respectively. The films remained transparent throughout the thermal treatment. The cyclized films were much more chemically resistant to alkali than the commercial products such as "Kapton" film and "P84" film, while thermal properties were comparable. The isoindoloquinazolinedione unit induced in the chain backbone on the heat treatment of the films was considered to be a major factor responsible for the superior physical properties of the films. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 118–123, 2000

Key words: new poly(amide-imide-IQ) film; isoindoloquinazolinedione (IQ); solvent castable film; high alkaline resistance; improved mechanical performance

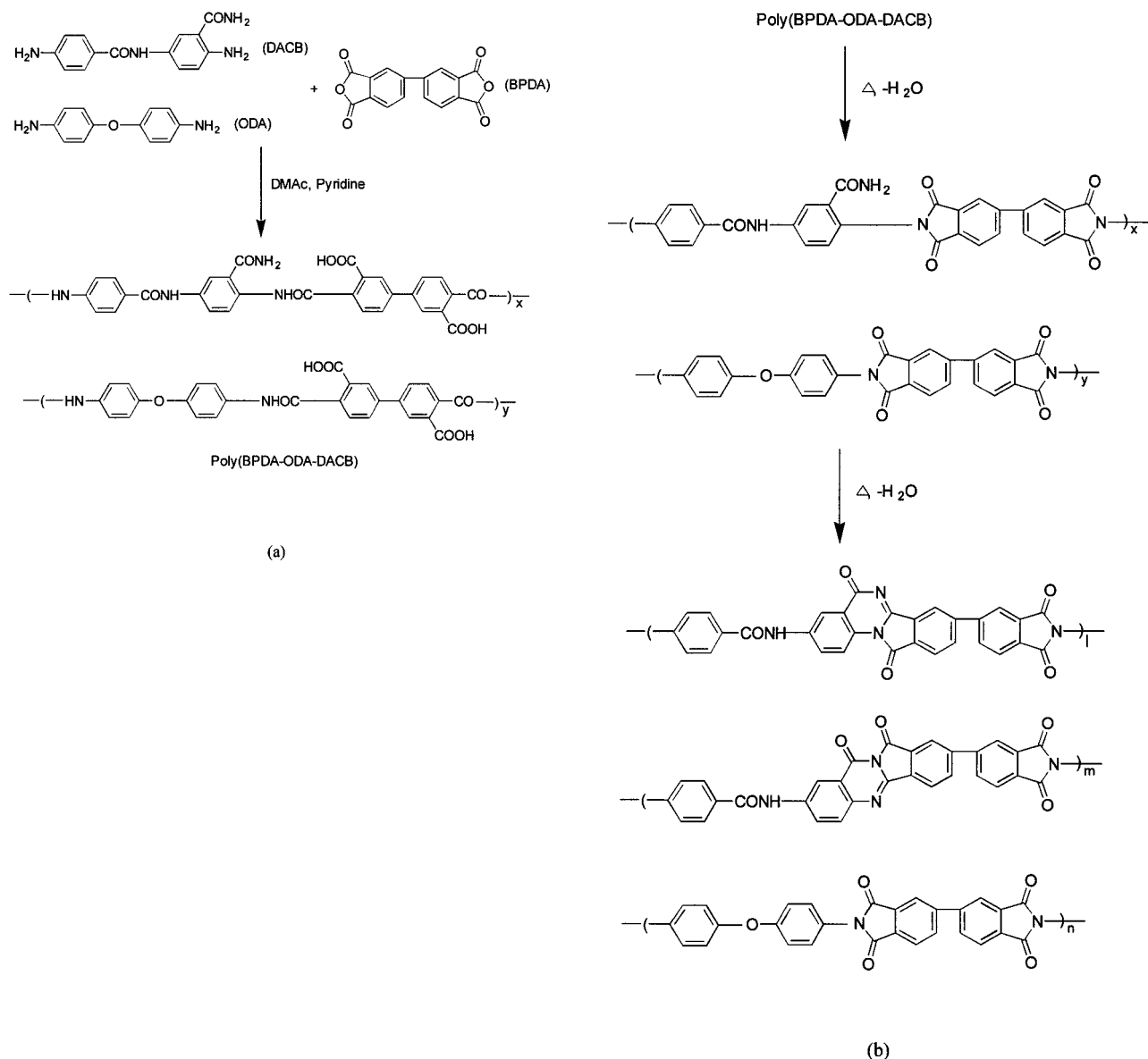
INTRODUCTION

In recent years, some liquid crystalline polymers such as poly(*p*-phenylene terephthalamide) (PPTA) and polyimides have been studied as promising materials for the formation of high performance films of better mechanical and thermal properties than those of polyester films.^{1,2} However, it has been indicated that these polymers have some draw-

backs in processibility because of their poor solubility. Despite various patented processes which include the extrusion of an aromatic polyamide solution through a short air gap into a coagulation bath,^{3,4} the inflation of a para-oriented aromatic polyamide solution having optical anisotropy through a ring die,⁵ and the extrusion of anisotropic or isotropic PPTA dope through a ring die while giving a mechanical shear force in both extrusion and transverse directions,⁶ there is little commercial production of films of economic significance. Flood et al.⁷ have proposed a method to obtain a biaxially oriented film by extrusion of PPTA dope in

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Journal of Applied Polymer Science, Vol. 78, 118–123 (2000)
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Scheme 1 Synthetic route of (a) poly(BPDA-ODA-DACB), and (b) poly(amide-imide-IQ).

sulfuric acid through annular die, running over an oil coated conical mandrel, and finally into the coagulation bath. They have obtained a film of 96 MPa in tensile strength and 2.3 GPa in tensile modulus. A better film of 450 MPa in tensile strength and 14 GPa in tensile modulus has been obtained by the Asahi Kasei Co.^{8–13} by heat treating at 350°C for 20 min, the film prepared by phase separation technique just before the coagulation bath. However, this process also has some drawbacks in that it is quite difficult to control the process due to sulfuric acid used as a solvent.^{14,15} Nu-

merous efforts have also been expended to prepare solvent soluble polyimides with which tough films may be prepared.^{16–23} Despite all efforts, novel polymers are still required with which strong films can be manufactured without sacrificing the mechanical performance and thermal resistance.

In an earlier article,²⁴ we reported the synthetic route for new aromatic polyamides, poly(biphenylphthalic dianhydride-oxydianiline-4,4'-diamino-3'-carbamoyl-benzanilide) [poly(BPDA-ODA-DACB)s], which are soluble in organic solvents such as dimethylacetamide and *N*-methyl-2-pyrrolidone,

from which it is thus expected to obtain a film. We have tested, in the meantime, various physico-chemical properties of the films prepared by casting the solution of poly(BPDA-ODA-DACB)s in the above-mentioned solvents, and report herein the promising results of thermal, chemical, and mechanical properties of the films.

EXPERIMENTAL

Preparation of Poly(BPDA-ODA-DACB)

To prepare poly[BPDA-ODA(75)/DACB(25)], 1.320 g (6.59 mmol) of ODA and 0.594 g (2.20 mmol) of DACB were dissolved in 30 mL of dimethylacetamide containing 1.5 mL of pyridine in a stream of nitrogen at room temperature. With vigorous stirring, 2.586 g (8.79 mmol) of biphenylphthalic anhydride was added at once at room temperature to obtain a viscous solution after 3 h. Similarly, poly[BPDA-ODA(50)/DACB(50)] was obtained from the reaction between 0.589 g (2.94 mmol) of ODA, 0.795 g (2.94 mmol) of DACB, and 1.731 g (5.88 mmol) of BPDA in 30 mL of *N*-methyl-2-pyrrolidone containing 0.15 mL of pyridine under a nitrogen stream at room temperature. The synthetic route is presented in Scheme 1(a).

Film Preparation

The viscous prepolymer solution of poly(amic acid-carbonamide) type was directly cast onto an aluminum frame. After the evaporation of the solvent by vacuum drying at 80°C, the thin film was heat treated under nitrogen atmosphere at a specified temperature to obtain finally transparent thin film of poly[(amide-imide-isoindoloquinazolidione (IQ)] type, of which structural change of the film is shown in Scheme 1(b).

Measurement of Thermal Resistance

A Perkin-Elmer thermogravimetric analyzer (TGA), model TGA7 (USA), was used for the measurement of thermal resistance of the film with a scan rate of 10°C/min under nitrogen atmosphere. Perkin-Elmer differential scanning calorimeter (DSC; USA) was also used with a scan rate of 20°C/min under nitrogen gas purging.

Measurement of Tensile Properties

Tensile properties of the films such as Young's modulus and tensile strength were measured by

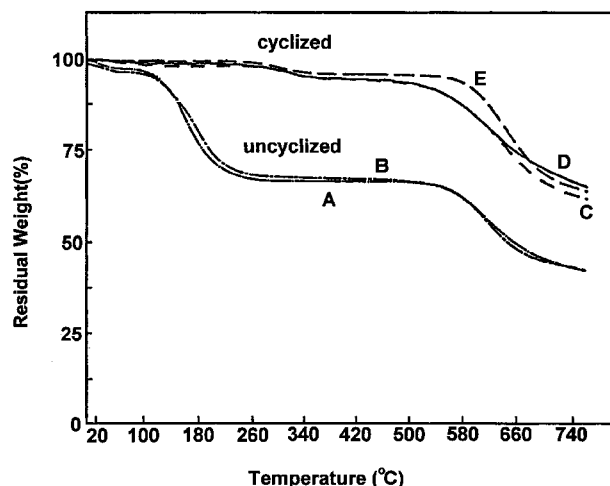


Figure 1 TGA thermograms of the various films based on (A) uncyclized poly(BPDA-ODA), (B) uncyclized poly[BPDA-ODA(75)-DACB(25)], (C) poly[BPDA-ODA(75)-DACB(50)] cyclized at 270°C, (D) poly[BPDA-ODA(75)-DACB(25)] cyclized at 270°C, and (E) poly(BPDA-ODA) cyclized at 270°C.

Instron Model 4202 (USA) with a crosshead speed of 20 mm/min and a specimen length of 30 mm. The film samples have the dimension of 10 mm in width and $10 \approx 20 \mu\text{m}$ in thickness.

Measurement of Chemical Resistance

The chemical resistance of the films to an alkaline condition was tested at intervals during several months' time by examining whether the immersed films in 10% NaOH solution are dissolved or fractured.

Wide Angle X-ray Diffractometry (WAXD)

WAX diffractograms of the films were obtained using Mac Science X-ray diffractometer MXP-18 (Japan) operated at 40 kV and 200 mA. X-ray of nickel filtered $\text{CuK}\alpha$ was used to scan the sample from 10 to 50° with the scan speed of 4°/min and the step angle of 0.05°.

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 represents TGA thermograms of poly(BPDA-ODA-DACB) and poly(BPDA-ODA). It is apparent that the uncyclized polymers exhibit the first weight loss from 150 to 250°C due to cyclization and the second one at 580°C due to degrada-

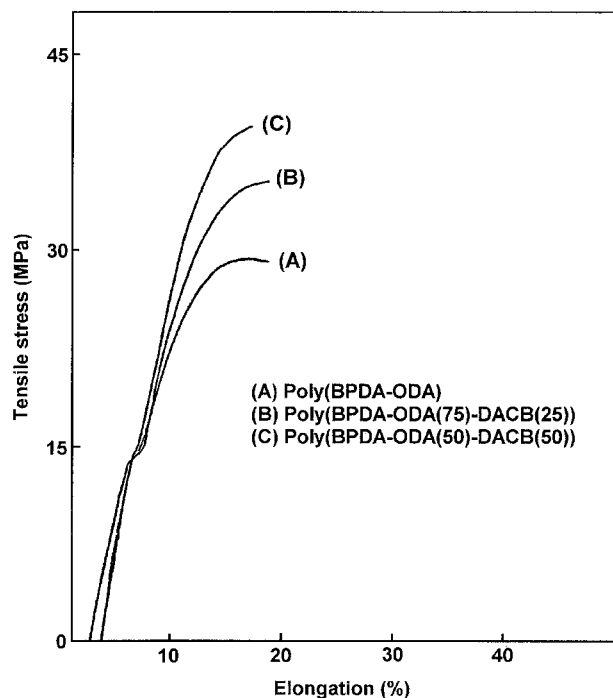


Figure 2 Stress-strain curves of the cyclized poly(amide-imide) films.

tion. The decomposition onset temperature of the heat-treated poly(BPDA-ODA) at 270°C for 3 h is 584°C and that of poly(BPDA-ODA-DACB) is 566°C. This result implies that the introduction of imide and IQ units in the structure does not improve conceivably the decomposition onset temperature because the thermal degradation is governed mainly by thermal cleavage of amide bond. The degradation rate, however, is somewhat slow to give similar char yield to that of polyimide. Another thing to note is that the increase of the

amount of DACB from 25 to 50% little improves the thermal resistance of the film.

Tensile Property

Figure 2 and Table I illustrate the effect of imide and IQ unit introduced in the backbone of polymer chain for the purpose of improving chemical and thermal stability on tensile property. It is clear that the tensile strength and modulus increase as the moiety of amide increases in the polymer structure. The uncyclized poly(BPDA-ODA) gives the tensile strength of 20 MPa and the modulus of 1.1 GPa. However, when 50% of DACB is copolymerized, i.e., poly[BPDA-ODA(50)-DACB(50)], the tensile strength and the modulus increase to 41 MPa and 1.9 GPa, respectively. Similar behavior has been observed for the cyclized polyimide and poly(amide-imide-IQ) films. This is considered because the number of hydrogen bonds increases due to the amide bonds as the amount of DACB increases. The increased number of hydrogen bonds is indeed expected to increase the chain rigidity that is consequently related to the tensile strength and modulus of the films. Although it has not been attempted, the drawing the film may improve the tensile properties of the films.

Chemical Resistance in NaOH Solution

It is generally known that aromatic polyamides have good chemical resistance; however, they have comparatively poor resistance in alkaline conditions. It is thus tempting to evaluate the alkaline resistance of new aromatic polyamides, poly(BPDA-ODA-DACB)s.

Table II clearly shows that the “Kapton” film based on polyimide of DuPont Co. has been dis-

Table I Tensile Properties of Uncyclized and Cyclized Poly(amide-imide)s

Films ^a	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)
Uncyclized			
BPDA-ODA	20	30	1.1
BPDA-ODA(75)-DACB(25)	30	20	1.3
BPDA-ODA(50)-DACB(50)	41	18	1.9
Cyclized			
BPDA-ODA	120	17	2.3
BPDA-ODA(75)-DACB(25)	134	13	2.6
BPDA-ODA(50)-DACB(50)	149	11	2.7

^aAll were prepared from the polymers synthesized in this study.

Table II Chemical Resistance of the Cyclized Poly(amide-imide) Films

Polymer	Trade Name	Manufacturer	Chemical Resistance
Poly(PMDA-ODA)	Kapton	DuPont Co.	Soluble in 7 days
Polyimide	P84	Lenzing Co.	Soluble in 2 days
Poly(BPDA-ODA)	Upilex	Ube Co.	Slightly soluble in 7 months
Poly[BPDA-ODA(75)-DACB(25)]	—	This study	Slightly soluble in 7 months
Poly[BPDA-ODA(50)-DACB(50)]	—	This study	Slightly soluble in 4 months

solved completely over 7 days and “P84” film of Lenzing Co.(Austria) over only 2 days. The newly synthesized heterocyclic poly(amide-imide) containing quinazolone unit withstands for 15 days.²⁵ However, poly(BPDA-ODA) and poly[BPDA-ODA(75)-DACB(25)] which have the similar chemical structure to the “Upilex” of Ube Co. (Japan) retain their shape even after 7 months, although a little dissolution of surface is apparent. It may be worth mentioning that poly[BPDA-ODA(50)-DACB(50)] partly dissolves after 4 months and is fragmented after 7 months.

From the above results, it is clear that the newly synthesized aromatic poly(amide-imide) films in which amide bonds still remain together with the introduced imide bonds and IQ unit exhibit much more improved chemical resistance than does the Kapton film which is known to have mainly the imide bonds in the polymer chain structure. This fact is seemingly contradictory to the conventional knowledge that the amide bonds are somewhat labile to the attack by alkalis. In this sense, a further study on the chemical degradation by alkalis of the polymer synthesized newly in this work is underway. The behavior and

effect of moisture uptake on the degradation of dielectric properties also will be studied.

Structures of New Films

Figure 3 represents the wide angle X-ray diffractograms of Poly(BPDA-ODA) and Poly[BPDA-ODA(50)-DACB(50)]. Both polymers give rather broad diffraction peaks indicative of poor crystal structure. This result implies again that the high mechanical and chemical properties of the films are not due to high crystallinity or perfect crystal structures but due to the IQ unit and the increased number of hydrogen bonds given by DACB unit.

CONCLUSIONS

New aromatic polyamide films based on poly(BPDA-ODA-DACB) have been prepared by a casting method and subsequently heat treated to introduce IQ unit into the poly(amide-imide) backbone chain. The films exhibit, before heat treatment, the tensile strength of $30 \approx 40$ MPa and the tensile modulus of $1.3 \approx 1.9$ GPa. On heat treatment, the strength and modulus has increased to $135 \approx 150$ MPa and $2.6 \approx 2.7$ GPa, respectively. The thermal and chemical resistance of the films are comparable to those of “Upilex” polyimide films based on poly(BPDA-ODA). The films, however, are much more chemically resistant to alkaline than are the commercial products such as “Kapton” film and “P84” film.

This report is dedicated to the late Prof. W. S. Ha of the Department of Fiber and Polymer Science, Seoul National University.

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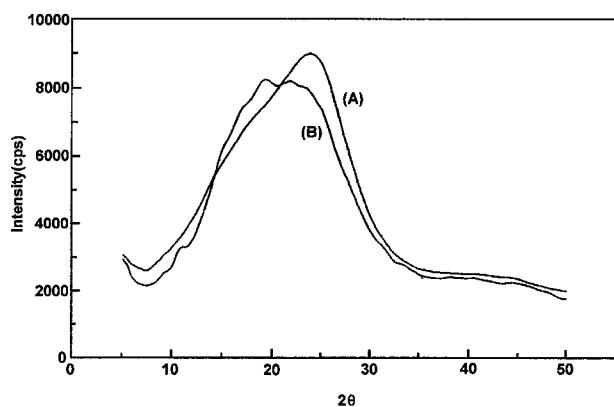


Figure 3 Wide angle X-ray diffraction patterns: (A) poly(BPDA-ODA) and (B) poly[BPDA-ODA(50)-DACB(50)]

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