

Synthesis and Characterization of New Adamantane-Based Cardo Polyamides

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ABSTRACT: A novel series of cardo polyamides bearing the 2,2-adamantylidene unit were directly prepared from a new adamantane-based dietheramine, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane, with various aromatic dicarboxylic acids using triphenyl phosphite (TPP) and pyridine as condensing agents. These polyamides had inherent viscosities ranging from 0.44 to 0.89 dL/g. All the polymers showed an amorphous nature by X-ray diffraction measurements, and most of them were easily soluble in polar aprotic solvents such as NMP and DMAc. The flexible and tough films cast from the polymer solutions possessed a tensile strength of 91–101 MPa and an elongation-at-break of 5–13%. The polyamides were thermally stable up to 450°C in air or in nitrogen. Most of them revealed distinct glass transition on the differential scanning calorimetry (DSC) traces, and their T_g s were recorded in the range of 230–269°C. Softening temperatures (T_s) of these polyamides were in the range of 272–308°C by thermomechanical analysis (TMA). © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 1435–1442, 1999

Keywords: 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane; cardo; polyamides; triphenyl phosphite

INTRODUCTION

Aromatic polyamides have been noted for their high thermal and chemical resistance as well as high strength and high modulus as fibers.^{1,2} However, these polymers are generally difficult to process due to their high glass transition or melting temperatures and limited solubility in organic solvents because of strong interchain forces, inherent macromolecular rigidity, or semicrystallinity. Therefore, many structural modifications^{3–14} have been carried out to improve their processing characteristics and solubility. Insertion of aryl ether linkages is a successful method for improving solubility without significant reduction in thermal properties. Incorporation of bulky pendant groups can impart a sig-

nificant increase in both glass transition temperature (T_g) and thermo-oxidative stability by restricting segmental mobility while providing good solubility due to decreasing packing density and crystallinity. Combining these two structural modifications minimizes the trade-off between processability and properties of wholly aromatic polymers. Aromatic polyamides with diamines containing backbone cardo groups, such as fluorene, phthalidimine, and phthalide,^{15–17} with diamines or dicarboxylic acids containing large spiro units,^{18–21} and with methyl-, *tert*-butyl-, and phenyl-substituted ether-linked dianilines or dibenzoic acids^{22–24} have been reported as processable polymers with good thermal stability.

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a highly symmetrical molecule composed of three cyclohexane rings into rigid, relatively strain-free chair conformations.²⁵ Adamantane has also been inserted into the backbone of many polymers in-

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cluding polysulfones, polyesters, polyamides, and polyimides.^{26–31} Insertion of this thermally and oxidatively stable, bulky, and rigid tetrahedral moiety into polymers modifies and improves physical properties such as decomposition and glass transition temperatures, chain stiffness, crystallinity, and solubility. Incorporation of pendant adamantyl groups into acrylates,^{32–34} phenolics,³⁵ poly(phenylene)s,³⁶ poly(ether ether ketone)s,³⁷ and poly(benzyl ether)s³⁸ also results in a large increase in T_g , thermal properties, and solubility when compared to the unsubstituted polymer analog. The rigidity and bulkiness of the adamantyl moiety greatly reduces chain mobility and inhibits chain packing. This increases T_g , lowers crystallinity, and enhances solubility. In addition, thermosetting polymers based on the acetylene or maleimide derivatives of adamantane have been reported as well.^{39–42}

Recently, much effort has been expended on synthesizing adamantane-based polyamides and polyimides by Chern and co-workers.^{43–47} Very recently, they successfully produced several organo-soluble, high-molar-mass polyimides and polyamides by using aromatic monomers with bulky adamantane-1,3-diyl and flexible ether units.^{45–47} The present work deals with the synthesis and basic characterization of a new series of cardo polyamides with adamantane-2,2-diyl units from 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane with various aromatic dicarboxylic acids. It was hoped that incorporation of the bulky 2,2-adamantylidene unit would be to decrease polymer interchain interactions such as hydrogen bonding and interfere with close chain packing. This should promote solubility while maintaining high T_g through controlled segmental mobility.

EXPERIMENTAL

Materials

The adamantane-based dietheramine 2,2-bis[4-(4-aminophenoxy)-phenyl]adamantane (**3**) (mp 240°C) was prepared in two steps from chlorodisplacement of *p*-chloronitrobenzene with potassium phenolate of 2,2-bis(4-hydroxyphenyl)adamantane, followed by hydrazine catalytic reduction of the intermediate dinitro compound. Details of the synthesis and characterization data of the adamantane-based dietheramine **3** have been described in a separate paper.⁴⁸ The aromatic diacid monomers such as terephthalic acid (**4a**, Wako), isophthalic acid (**4b**, Wako), 4,4'-biphenyldicarboxylic acid (**4c**, TCI), 4,4'-oxydibenzoic acid (**4d**, TCI), 4,4'-sulfonyldibenzoic acid (**4e**, New Japan Chemical Co.), 4,4'-hexafluoroisopropylidenedibenzoic acid (**4f**, Chriskev), 2,6-naphthalenedicarboxylic acid (**4g**, TCI), 1,4-naphthalenedicarboxylic acid (**4h**, TCI) were used without further purification. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite was purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 8 h.

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Polymer Synthesis

A typical polymerization procedure for the preparation of polyamide **5a** is as follows. A mixture of 0.1661 g (1.00 mmol) of terephthalic acid (**4a**), 0.5026 g (1.00 mmol) of dietheramine **3**, 0.2 g of calcium chloride, 0.8 mL of triphenyl phosphite (TPP), 2.0 mL of NMP, and 0.5 mL of pyridine was heated with stirring at 110–120°C for 3 h. The resulting polymer solution was slowly poured into methanol with stirring to precipitate a fiber-like product which was washed thoroughly with methanol and hot water, collected by filtration and dried. The yield was 0.69 g (100%), the inherent viscosity of the polymer was 0.72 dL/g as measured in DMAc containing 5 wt % LiCl at a concentration of 0.5 g/dL at 30°C.

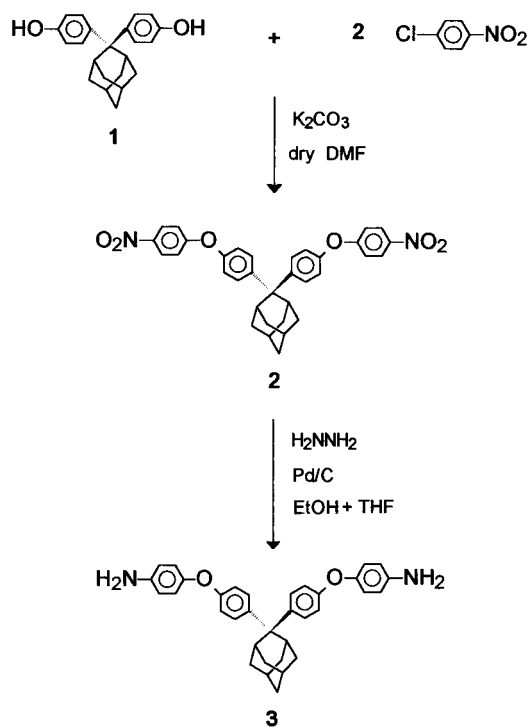
All other polyamides were synthesized by an analogous procedure.

Preparation of Polyamide Films

A polymer solution of approximately 10 wt % was made by dissolving polyamide in hot DMAc. The solution was poured into a glass culture dish 9 cm in diameter, which was placed in a 90°C oven for 12 h to remove the solvent. Then, the obtained semi-dried polymer film was lifted from the glass substrate and further dried *in vacuo* at 150°C for 8 h.

Characterization

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscometer at 30°C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a



Scheme 1.

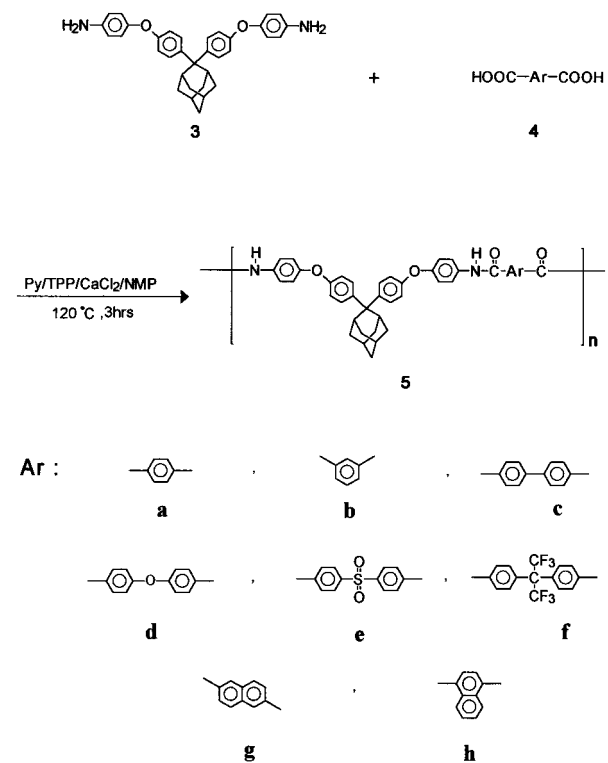
Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. The heating rate was 20°C/min. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling. Thermo-mechanical analysis (TMA) was conducted with a Rigaku TMA 8140 coupled to a Rigaku TAS-100 thermal analysis station with a penetration probe of 1.0 mm diameter and using an applied constant load of 5 g at a scan rate of 10°C/min. The TMA experiments were conducted in duplicate. Softening temperatures (T_s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of inflection from the second TMA traces. Thermogravimetry (TG) was conducted with a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 Thermal Analyst. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. An universal testing machine model HT-9102

(Hung Ta Instrument Co., Taiwan) with a load cell 10 kg was used to study the stress-strain behavior of the polymer films (6 cm long, 0.5 cm wide, and about 0.1 mm thick), using a gauge-length of 2 cm and 5 cm/min rate of extension. An average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

The adamantane-based dietheramine, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane (**3**), was prepared in two steps according to Scheme 1. The dinitro compound **2** was synthesized by nucleophilic aromatic substitution of 2,2-bis(4-hydroxyphenyl)adamantane (**1**) with *p*-chloronitrobenzene in the presence of potassium carbonate in DMF and then reduced to diamine **3** by using hydrazine hydrate and Pd-C catalyst in refluxing ethanol/THF. A series of aromatic polyamides **5a-h** were prepared by the Yamazaki-Higashi phosphorylation polyamidation technique⁴⁹ from diamine **3** and dicarboxylic acids **4a-h** using triphenyl phosphite (TPP) and pyridine as condens-



Scheme 2.

Table I. Inherent Viscosities and Film Quality of Polyamides^a

Polymer Code	η_{inh}^b (dL/g)	Film ^c Quality
5a	0.72	Flexible
5b	0.44	Flexible
5c	0.49	Flexible
5d	0.65	Flexible
5e	0.53	Flexible
5f	0.63	Flexible
5g	0.89	Flexible
5h	0.63	Brittle ^d

^a Amount of each diacid and diamine monomer = 1 mmol; NMP = 2.0 mL; pyridine = 0.5 mL; TPP = 0.8 mL (2 mmol); CaCl₂ = 0.2 g; reaction temperature = 110–120°C; reaction time = 3 h.

^b Measured in DMAc containing 5 wt % LiCl on 0.5 g/dL at 30°C by a Cannon-Fenske viscometer.

^c Films were cast by slow evaporation of polymer solutions in DMAc.

^d Cast from NMP.

ing agent in the NMP solution containing dissolved CaCl₂ (Scheme 2). All polyamidations proceeded in homogeneous and transparent solutions throughout the reaction, and the polyamides were isolated as fibers in quantitative yields. As shown in Table I, these polyamides had inherent viscosities in the range of 0.44–0.89 dL/g and afforded free-standing films by means of solution-casting. The film made from polyamide **5h** cracked upon creasing, probably due to the structural rigidity. Other polyamide films were transparent, flexible, and tough.

The structure of the polyamides was confirmed by IR spectroscopy. The characteristic absorp-

tions can be observed in the IR spectra, such as N—H stretching at 3300 cm⁻¹, carbonyl stretching at 1650 cm⁻¹, and aryl ether stretching at 1230 cm⁻¹.

Properties of Polymers

The solubility of polyamides in various organic solvents was tested qualitatively and the results are given in Table II. All the polyamides were soluble in *m*-cresol, and most of them were soluble in polar aprotic solvents such as NMP, DMAc, and DMF at room temperature or on heating. The enhanced solubility of these polyamides is believed to be related to the presence of bulky 2,2-adamantylidene which inhibits close packing of polymer chains and leads to less intermolecular interactions.

X-ray diffractograms of some representative polyamides are illustrated in Figure 1. Polyamide **5h** was measured in a powder form, and the other polyamides were determined with film specimens. Generally, these polyamides displayed amorphous nature due to the presence of the packing-disruptive adamantylidene unit. When polyamides **5c**, **5g**, and **5h** are compared with the other polyamides, it seems that the former displayed a strong reflection hump approximately between $2\theta = 10\text{--}30^\circ$, indicating a higher packing density. The flexible films were subjected to tensile testing, and their tensile properties are given in Table III. They possessed a tensile strength of 91–101 MPa and elongation-at-break of 5–13%.

Thermal properties of all the polyamides were evaluated by thermogravimetry (TG), differential scanning calorimetry (DSC), and thermomechanical

Table II. Solubility Behavior of Polyamides^a

Polymer Code	Solvents ^b					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
5a	+	+	+h	s	+	–
5b	+	+	+h	s	+	s
5c	+	+h	–	–	+	–
5d	+	+	+–	+h	+	s
5e	+	+	+	+h	+	s
5f	+	+	+	+h	+	+
5g	+	+h	+h	s	+	–
5h	+h	–	+h	+h	+	s

^a Solubility: +, soluble at room temperature; +h, soluble on heating, and –, insoluble even on heating; s, swollen.

^b NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. All the polymers were soluble in DMAc +5% LiCl.

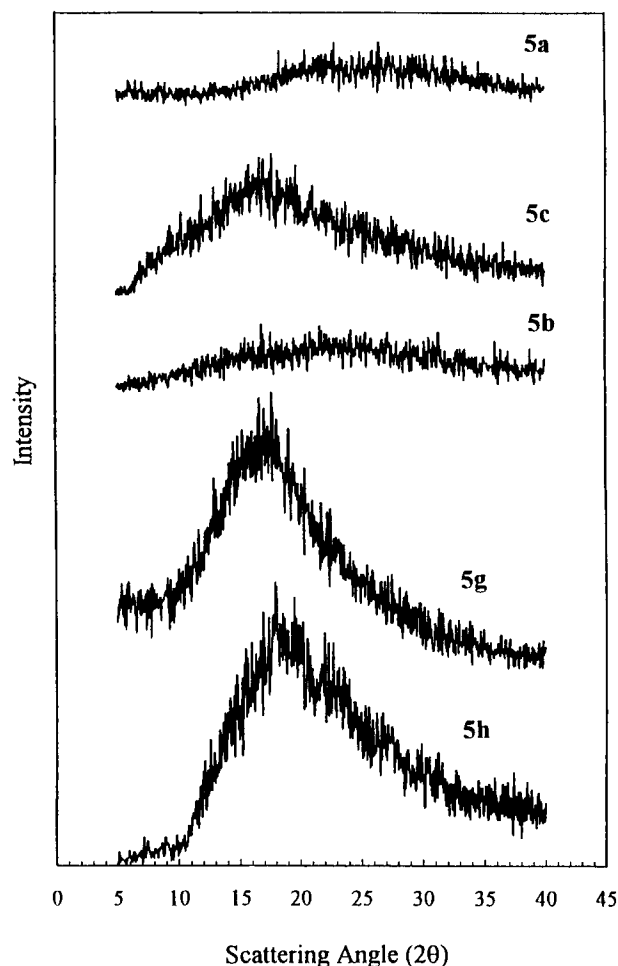


Figure 1. Wide-angle X-ray diffractograms of polyamides.

cal analysis (TMA). The thermal behavior data of all the polyamides are also summarized in Table III. The representative TG diagrams of polyamide **5d** measured in air and in nitrogen are reproduced in Figure 2. All the other polyamides showed similar patterns of decomposition with no significant weight loss below 450°C in air or nitrogen, with more than 51 wt % residue remaining when heated to 800°C in nitrogen. The 10% weight loss temperatures of these polyamides were recorded in the range of 471–516°C in air and 455–515°C in nitrogen.

DSC measurements were carried out at a heating rate of 20°C/min in nitrogen. Rapid cooling from an elevated temperature of approximately 350°C to room temperature yielded predominantly amorphous samples so that in all cases distinct baseline shifts could be observed in the subsequent second heating traces of DSC. Except for the polyamide **5c**, all the other polymers showed distinct baseline shifts on their DSC heating traces. Glass transition temperatures (T_g s), defined by the midpoint of baseline shift, of the polyamides stayed in the range of 230–269°C. The softening temperatures (T_s , which may be considered as apparent T_g) as determined by TMA were recorded between 272–308°C, which are generally 13 to 46°C higher than the T_g values obtained by DSC. Polyamides **5b** and **5d** revealed lower T_g s in this polymer series, possibly due to their more flexible diacid moieties. The relatively

Table III. Tensile and Thermal Properties of Polyamides based on 2,2-Bis[4-(4-aminophenoxy)phenyl]adamantane

Polymer Code	Tensile Properties		T_g^b (°C)	T_s^c (°C)	Decomposition ^d Temperature (°C)		Char Yield ^e (%)
	Strength at Break (MPa)	Elongation at Break (%)			in N ₂	in Air	
5a	92	13	264	277	462	472	51
5b	91	5	231	277	470	479	52
5c	101	9	—	308	515	516	59
5d	97	9	230	272	480	488	55
5e	92	11	252	275	463	480	53
5f	92	12	241	278	476	497	52
5g	97	8	266	295	472	487	58
5h	— ^a	—	269	—	455	471	53

^a The film was too brittle to test.

^b Base line shifts in the second heating DSC traces, with a heating rate of 20°C/min.

^c Softening temperatures measured by the TMA (penetration method) with a load of 5 g at a heating rate of 10°C/min.

^d Temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min.

^e Residual wt % when heated to 800°C in nitrogen.

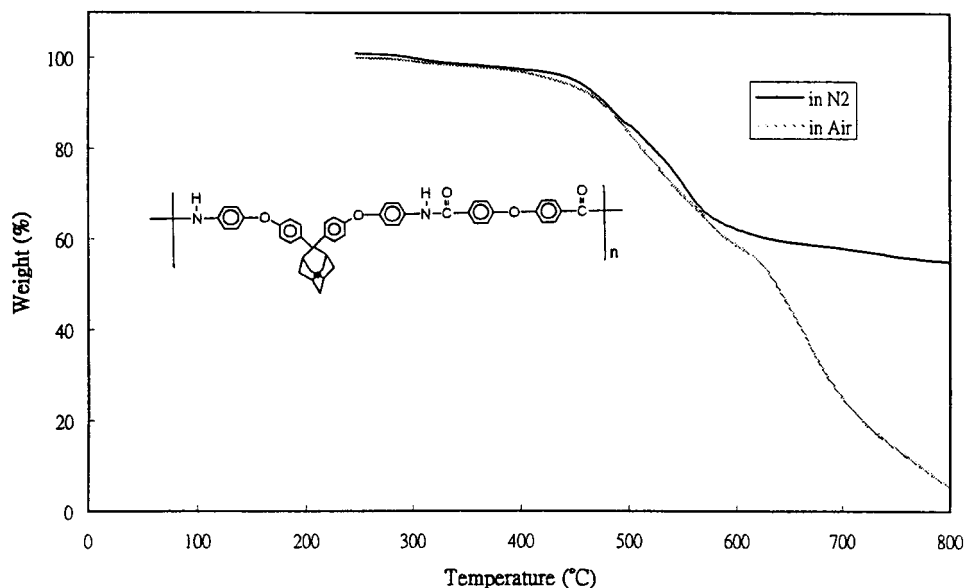


Figure 2. TG curves of polyamide **5d** at a heating rate of 20°C/min.

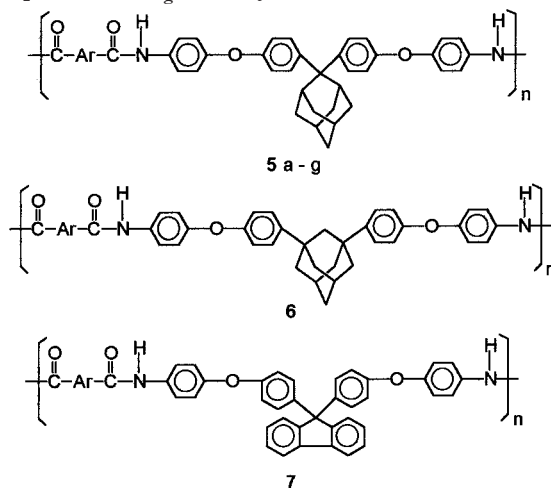
higher T_g s of polyamides **5g** and **5h** indicated that the introduction of naphthalene ring resulted in an increased stiffness of the macromolecular chain.

Table IV compares the T_g values of some related polyamides. A comparison with some adamantane-1,3-diyl polyamides (**6**)⁴⁷ reveals that the differences between the T_g values of polyamides **5a/6a** and **5d/6d** are not significant; however, polyamide **5b**, from isophthalic acid, shows a slightly lower value than **6b** by 14°C. These results are different from those observed by Pixton and Paul.³¹ They observed that the T_g of polysulfone with adamantane-2,2-diyl units was 55°C higher than that of polysulfone with adamantane-1,3-diyl units. They demonstrated that adamantane-2,2-diyl cardo unit has greater stiffening effect on the polymer backbone than its counterpart, adamantane-1,3-diyl, due to the fact that the bisphenol phenyl rings of the 1,3-isomer are relatively free to rotate around the bond axes, while those of the 2,2-isomer are constrained in their relative position and rotational freedom by steric interactions. The reason why the polyamides based on the 2,2-isomer did not show an obviously higher T_g s than those of 1,3-isomer is not very clear. However, it may be attributed to the fact that the polyamides (**5**) from the 2,2-isomer suffer stronger steric interference between the pendant 2,2-adamantylidene group, which forces the polymer chains apart from one another

and so disrupts the hydrogen bonds. As compared with the polyamides with 9,9-fluorenylidene unit,¹⁵ a more common cardo structure, the corresponding polyamides with 2,2-adamantylidene unit showed lower T_g values by approximately 35–59°C. This is reasonable as the fluorenylidene connector group is quite rigid and has a higher molar mass than the 2,2-adamantylidene connector group.

CONCLUSIONS

A series of novel polyamides containing 2,2-adamantylidene as a cardo group have been prepared from direct polycondensation of 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane with various aromatic dicarboxylic acids by means of triphenyl phosphite and pyridine. Except for the polyamide derived from 1,4-naphthalenedicarboxylic acid, all other polyamides could be solution cast into flexible and tough films. All the polyamides were noncrystalline and revealed excellent solubility in a variety of organic solvents. These polyamides showed moderately high thermal stability and glass transition temperatures. Thus, the incorporation of 2,2-adamantylidene into the polyamide main chain is a successful method for improving processability with retention of high T_g s.

Table IV. Glass Transition Temperatures (T_g) of Polyamides^a

Polymer 5	T_g ^a (°C)	Polymer 6	T_g ^b (°C)	Polymer 7	T_g ^c (°C)
a	264	a	269	a	300
b	231	b	245	b	290
c	—	—	—	c	309
d	230	d	228	—	—
e	252	—	—	e	302
f	241	—	—	f	284
g	266	—	—	g	301

^a The structure of —Ar— used here is the same as in Scheme 2.

^b Data from Ref. 47.

^c Data from Ref. 15.

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