Synthesis and Characterization of Adamantane-Containing Semi-Alicyclic Polybenzoxazole

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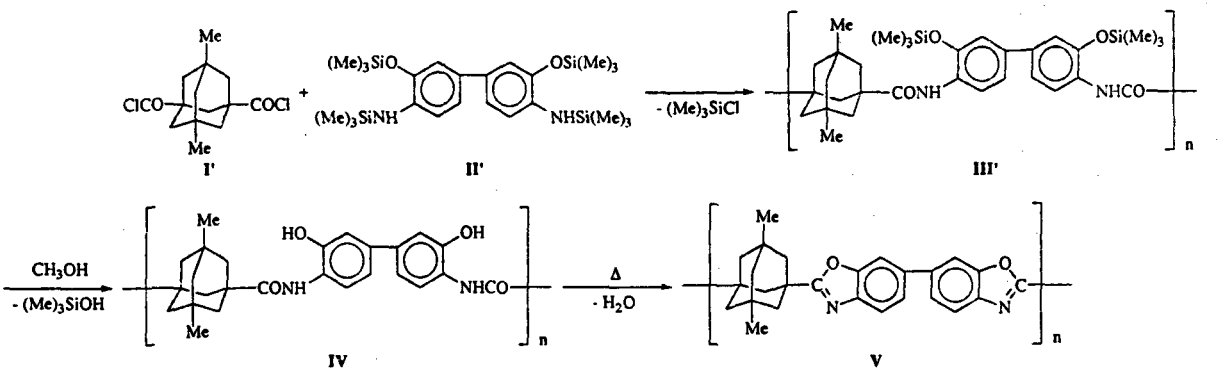
Summary

Adamantane-containing semi-alicyclic poly(*o*-hydroxy amide) of high molecular weight was synthesized by the low-temperature solution polycondensation of 5,7-dimethyladamantane-1,3-dicarbonyl chloride with 3,3'-bis(trimethylsiloxy)-4,4'-bis((trimethylsilyl)amino)biphenyl. Subsequent thermal cyclodehydration of the poly(*o*-hydroxy amide) at 300℃ afforded the polybenzoxazole with high molecular weight. The poly(*o*-hydroxy amide) dissolved in polar aprotic solvents, whereas the polybenzoxazole was insoluble in any organic solvent tested. The polybenzoxazole was stable up to around 500℃ under nitrogen and had a low dielectric constant of 2.880. The mechanical properties of the polybenzoxazole film were excellent, its tensile strength, elongation at break, and tensile modulus were 110 MPa, 6%, and 3.3 GPa, respectively.

Introduction

Heteroaromatic polymers, such as polyimides and polybenzoxazoles, have high thermal stability and excellent mechanical properties. However, most of them have relatively higher dielectric constants over 3.0. Two approaches in molecular design have been developed in order to lower dielectric constants of the polymers without sacrificing their inherent superb properties; the first one is the introduction of fluorine atoms having low molecular polarizability into the polymers, the second approach is replacing the aromatic rings by bulky substituents like alicyclic rings in the polymers to lower the polymer packing density. We are interested in the preparation of semi-alicyclic polymers with very bulky adamantane rings in the main chain.

In this article, adamantane-containing semi-alicyclic polybenzoxazole derived from 5,7-dimethyladamantane-1,3-dicarboxylic acid (**I**) was synthesized, and characterized with special interest in its mechanical, thermal, and dielectric properties.



Experimental

Materials

5,7-Dimethyladamantane-1,3-dicarboxylic acid **I**, supplied by Nippon Steel Chemical Co., Ltd. (Japan), was used after two recrystallizations from aqueous methanol; mp 272-275℃. 5,7-Dimethyladamantane-1,3-dicarbonyl chloride (**I'**) was prepared by the conventional chlorination of **I** with thionyl chloride and purified by distillation *in vacuo*; bp 151.5-152℃/4 mmHg; mp 56.5-58.5℃. Reagent grade 4,4'-diamino-3,3'-dihydroxybiphenyl (**II**) was used as purchased. 3,3'-Bis(trimethylsiloxy)-4,4'-bis((trimethylsilyl)amino)biphenyl (**II'**) was synthesized as previously reported by the reaction of **II** with trimethylsilyl chloride;[1] bp 205-207℃/2 mmHg (Lit.[1] bp 200-230℃/0.5 torr).

Polymerization

Poly(*o*-hydroxy amide) (IV) from I' and II'

In a flask, 0.504 g (1 mmol) of **II'** was dissolved in 4 mL of NMP under nitrogen. To this was added 0.289 g (1 mmol) of **I'** in one portion at 0℃. The mixture was stirred at 0℃ for 15 min and then at ambient temperature for 20 h. The viscous solution obtained was poured into 300 mL of methanol. The precipitated fibrous polymer was collected, washed thoroughly with methanol, and vacuum dried at 60℃. The yield was 0.429 g (99%). The reduced viscosity of the polymer was 0.80 dL/g, measured at a polymer concentration of 0.5 g/dL in NMP at 30℃. IR (film): 3420 (N-H and OH); 1655 cm^{-1} (C=O). ANAL. Calcd. for $(C_{26}H_{28}N_2O_4)_n$ $(432.5)_n$: C, 72.20%; H, 6.53%; N, 6.48%. Found: C, 71.97%; H, 6.23%; N, 6.17%.

Polybenzoxazole (V) from IV

The thermal cyclodehydration of polymer film **IV** was carried out by heating at 300℃ for 20 h

under nitrogen. IR (film): 1620 cm^{-1} (C=N). ANAL. Calcd. for $(C_{26}H_{24}N_2O_2)_n$ $(396.5)_n$: C, 78.76%; H, 6.10%; N, 7.07%. Found: C, 77.81%; H, 5.81%; N, 6.72%.

Results and Discussion

Polymer Synthesis

The direct solution polycondensation of 5,7-dimethyladamantane-1,3-dicarboxylic acid **I** with 4,4'-diamino-3,3'-dihydroxybiphenyl **II** was first attempted in polyphosphoric acid (PPA) or Eaton reagent (PPMA). However, no polymer was obtained by the reactions first at 140℃ for 20 h and then further at 200℃ for 24 h in PPA and at 140℃ for 48 h in PPMA. The low-temperature solution polycondensation of diacid chloride **I'** with **II** was tried in DMAc at 0℃-ambient temperature for 20 h, and this also yielded poly(*o*-hydroxy amide) **IV** with a low reduced viscosity of 0.08 dL/g. Thus, attempts to prepare polybenzoxazole or poly(*o*-hydroxy amide) of sufficient high molecular weight were unsuccessful both from **I** and **I'** by these two methods. Next, we applied the silylation method, which is useful for the activation of diamines.[1] The low-temperature solution polycondensation of **I'** with 3,3'-bis(trimethylsiloxy)-4,4'-bis((trimethylsilyl)amino)biphenyl **II'** was carried out in polar aprotic solvents or chloroform at 0℃-room temperature for 20 h (**Table I**).

Table I Synthesis of Adamantane-Containing Semi-Alicyclic Polybenzoxazole **V**

	Monomers		Reaction Conditions[a]		Polymer	
Run	Acid	Aminophenol	Solvent	Temp. / Time °C/h	Yield %	η_{red}[b] dL/g
1	**I**	**II**	PPA	140/24→200/24	-[c]	-
2	**I**	**II**	PPMA	140/48	-[c]	-
3	**I'**	**II**	DMAc	0-r.t./20	67[d]	0.08
4	**I'**	**II'**	DMAc	0-r.t./20	109[d]	1.05
5	**I'**	**II'**	HMPA	0-r.t./20	102[d]	0.67
6	**I'**	**II'**	NMP	0-r.t./20	99[d]	0.80
7	**I'**	**II'**	Chloroform	0-r.t./20	66[d]	0.24

[a] Polymerization was carried out with each monomer (1 mmol) in the solvent (5 g or 4 mL) under nitrogen.
[b] Reduced viscosity was measured at a polymer concentration of 0.5 g/dL in NMP at 30°C.
[c] No polymer was obtained.
[d] The yield of poly(*o*-hydroxy amide) **IV**.

Poly(*o*-hydroxy amide) **IV** with high reduced viscosities of above 0.6 dL/g was readily

obtained in high yields, and the versatility of the silylation method was demonstrated.

The formation of poly(*o*-hydroxy amide) was confirmed by means of IR spectroscopy and elemental analysis. The polymer exhibited a broad absorption at 3420 cm^{-1} due to amide N-H and hydroxyl O-H groups and a strong carbonyl absorption at 1655 cm^{-1}. The elemental analysis values were in good agreement with the calculated values of the proposed structure of the polymer.

In the second stage, poly(*o*-hydroxy amide) **IV** thus obtained was subjected to thermal cyclodehydration. The TG curve of the poly(*o*-hydroxy amide) revealed that the weight loss started at around 200℃ and came to an end at about 350℃. The weight loss was due to the thermal cyclodehydration of the poly(*o*-hydroxy amide), which was also evidenced from the DTA curve, and the amount of weight loss (7.4%) agreed quite well with that of the calculated value of 8.3%. Therefore, the conversion to polybenzoxazole was carried out in the form of film at 300℃, and the conversion process was monitored as a function of time from the change in the IR spectra of the film. The conversion was found to require 20 h for its completion. The complete disappearance of the absorption bands at 3420 and 1655 cm^{-1} indicated the completion of the cyclization process, together with the appearance of an absorption at 1620 cm^{-1} characteristic of benzoxazole ring.

Polymer Characterization

Poly(*o*-hydroxy amide) **IV** was soluble in polar aprotic solvents such as DMAc, DMF, DMSO, and NMP, whereas polybenzoxazole **V** dissolved only in concentrated sulfuric acid and methanesulfonic acid. Transparent, flexible, and tough film of the poly(*o*-hydroxy amide) could be cast from the DMAc solution. The mechanical properties of the polybenzoxazole film were excellent, its tensile strength, elongation at break, and tensile modulus were 110 MPa, 6%, and 3.3 GPa, respectively. The polybenzoxazole did not loss weight up to 500℃ under nitrogen, and the temperature at which 10% weight loss was recorded was 531℃. The averaged refractive index of the polybenzoxazole was 1.618, and the dielectric constant estimated from the value was 2.880.

The adamantane-containing semi-alicyclic polybenzoxazole obtained had high thermal stability, excellent mechanical properties, and low dielectric constant and is promising electric insulation material for the fields in microelectronics.

References

[1] Y. Maruyama, Y. Oishi, M. Kakimoto, and Y. Imai, *Macromolecules*, **21**, 2305 (1988).