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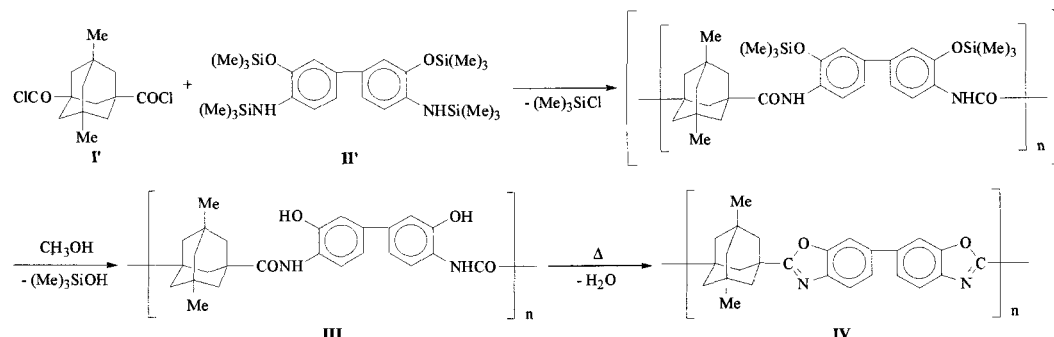
Synthesis and Characterization of Dimethyladamantane Unit-Containing Semi-Alicyclic Polybenzoxazole

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Heteroaromatic polymers, such as polyimides, polybenzoxazoles, and polybenzothiazoles, 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 greatly sacrificing their inherent superb properties; the first one is the introduction of fluorine atoms having low molecular polarizability into the polymers,^[1] the second approach is replacing the aromatic rings by bulky substituents like alicyclic rings in the polymers to lower the polymer packing density.^[2] We are interested in the preparation of semi-alicyclic heteroaromatic polymers with very bulky adamantane rings in the main chain.

In this study, dimethyladamantane unit-containing semi-alicyclic polybenzoxazole (**IV**) was synthesized from 5,7-dimethyladamantane-1,3-dicarbonyl chloride (**I'**) and 3,3'-bis(trimethylsiloxy)-4,4'-bis[(trimethylsilyl)amino]biphenyl (**II'**) by two-step procedure, and characterized with special interest in its mechanical, thermal, and dielectric properties.



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^[4] (PPA) or Eaton reagent^[5] (PPMA). However, no polymer was obtained both by the reactions first at 140°C for 24 h and then further at 200°C for 24 h in PPA and at 140°C for 48 h in PPMA. The low-temperature solution polycondensation of diacid chloride **I'** with **II** was tried in DMAc at 0°C-ambient temperature for 20 h, and this also yielded poly(*o*-hydroxy amide) (**III**) 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 from bis-*o*-aminophenol **II** by these two methods. Next, we applied the silylation method, which is useful for the activation of diamines.^[3] The low-temperature solution polycondensation of **I'** with 3,3'-bis(trimethylsiloxy)-4,4'-bis[(trimethylsilyl)amino]biphenyl **II'** was carried out in a polar aprotic solvent or chloroform at 0°C-room temperature for 20 h (**Table 1**). Poly(*o*-hydroxy amide) **III** 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 two absorptions at 3419 and 3188 cm^{-1} due to

respective amide N-H and hydroxyl O-H groups and a strong carbonyl absorption at 1651 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) **III** thus obtained was subjected to thermal

Table 1. Synthesis of Dimethyladamantane Unit-Containing Poly(*o*-hydroxy amide) **III**

Run	Monomers		Reaction Conditions ^{a)}		Polymer	
	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	0.08
4	I'	II'	DMAc	0-r.t./20	109	1.05
5	I'	II'	HMPA	0-r.t./20	102	0.67
6	I'	II'	NMP	0-r.t./20	99	0.80
7	I'	II'	Chloroform	0-r.t./20	66	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.

cyclodehydration. The TG curve of the poly(*o*-hydroxy amide) revealed that the weight loss started at around 200°C and came to an end at about 350°C. 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 wt-%) agreed 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°C, 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 12 h for its completion. The complete disappearance of the absorption bands at 3419, 3188, and 1651 cm⁻¹ indicated the completion of the cyclization process, together with the appearance of an absorption at 1599 cm⁻¹ characteristic of benzoxazole ring.

Poly(*o*-hydroxy amide) **III** was soluble in polar aprotic solvents such as DMAc, DMF, DMSO, and NMP, whereas polybenzoxazole **IV** dissolved only in strong acids like 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 semi-alicyclic polybenzoxazole did not lose weight up to around 400°C under nitrogen, and the temperature at which 5% weight loss was recorded was 420°C. The averaged refractive index of the polybenzoxazole was 1.618, and the dielectric constant that was estimated from the value according to the modified Maxwell equation^[6] was 2.880.

In conclusions, dimethyladamantane unit-containing polybenzoxazole was synthesized from 5,7-dimethyladamantane-1,3-dicarbonyl chloride and 3,3'-bis(trimethylsiloxy)-4,4'-bis[(trimethylsilyl)amino]biphenyl. The semi-alicyclic polybenzoxazole obtained had relatively high thermal stability, excellent mechanical properties, and low dielectric constant and is promising electric insulation material for the fields in microelectronics.

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