

[研究論文]

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

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Abstract

3,5-Dimethyladamantyl unit-containing semi-alicyclic poly(*o*-hydroxy amide), precursor polymer of the polybenzoxazole, of high molecular weight was synthesized by the low-temperature solution polycondensation of 5,7-dimethyladamantane-1,3-dicarbonyl chloride with *N,N',O,O'*-tetrakis(trimethylsilyl)-substituted 4,4'-diamino-3,3'-dihydroxybiphenyl. Subsequent thermal cyclodehydration of the precursor polymer at 300°C successfully 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 medium tested. The polybenzoxazole was stable up to around 400°C under nitrogen and had a low dielectric constant of 2.866. 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.

Keywords: Dimethyladamantyl unit, semi-alicyclic polybenzoxazole, silylation method, high thermal stability, low dielectric constant

INTRODUCTION

In microelectric industry, much attention has been paid to rigid-rod polymers, such as polyimides and polybenzoxazoles, with high thermal and dimensional stabilities and low dielectric constant to minimize the stresses between films and substrates and to increase circuit speeds. Many aromatic rigid-rod polymers with high thermal and dimensional stabilities were developed in the last few decades. Most of them, however, have high dielectric constants over 3.0.

Aliphatic structures display a lower dielectric constant because of a low molecular density and polarity. Aliphatic polymers, however, generally have serious disadvantages of low thermal and dimensional stabilities, caused by the high flexibility and low bonding strength of aliphatic compounds as compared to aromatic ones. In 1996, Chern and Chung¹⁾ reported on the synthesis of semi-alicyclic polyimides from 1,3-diaminoadamantane and aromatic dianhydrides. Seino *et al.*²⁾ synthesized fully aliphatic polyimides from adamantyl unit-containing diamines, 1,3-diaminoadamantane and 3,3'-diamino-1,1'-biadamantyl, and alicyclic dianhydride, bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride. However, no detailed properties of these polymers, except solubility in some solvents and thermal ones, has been disclosed. Recently, Fukukawa *et al.*³⁾ synthesized and characterized adamantyl unit-containing semi-alicyclic polybenzoxazole from 1,3-adamantanedicarbonyl chloride and 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol). This polymer had high thermal and dimensional stabilities, a low dielectric constant, and high transparency in UV-Vis region. Thus, the incorporation of adamantyl units is advantageous to this type of rigid-rod polymer because it provides a low dielectric constant and high transparency as well as high thermal and dimensional stabilities.

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

EXPERIMENTAL

Materials

5,7-Dimethyladamantane-1,3-dicarboxylic acid **I**, kindly provided by Nippon Steel Chemical Co., Ltd. (Japan), was used after two recrystallizations from aqueous methanol; it had a melting point of 272-275°C. 5,7-Dimethyladamantane-1,3-dicarbonyl chloride (**II**) was prepared by the conventional chlorination of **I** with thionyl chloride in the presence of a few drops of *N,N*-dimethylformamide (DMF) as a catalyst and purified by distillation *in vacuo*; it had a boiling point of 151.5-152°C at 4 mmHg and a melting point of 56.5-58.5°C. Reagent grade 4,4'-diamino-3,3'-dihydroxybiphenyl (**III**) was used as purchased. 3,3'-Bis(trimethylsiloxy)-4,4'-bis[(trimethylsilyl)amino]biphenyl (**IV**) was synthesized as previously reported⁴⁾ by the reaction of **III** with trimethylsilyl chloride in the presence of triethylamine as a hydrogen chloride acceptor; it had a boiling point of 205-207°C at 2 mmHg (Lit.⁴⁾ 200-230°C/0.5 Torr). Phosphorus pentoxide/methanesulfonic acid (PPMA) was prepared according to the reported procedure.⁵⁾ Solvents such as *N,N*-dimethylacetamide (DMAc), hexamethylphosphoramide (HMPA), and *N*-methyl-2-pyrrolidinone (NMP) were vacuum distilled under nitrogen. Other reagents, including polyphosphoric acid (PPA), were used as received.

Polymerization

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

As a typical example of polymerization, 0.504 g (1 mmol) of **IV** was dissolved in 4 mL of NMP under nitrogen. To this was added 0.289 g (1 mmol) of **II** in one portion at 0°C. The mixture was stirred at that temperature for 15 min and then at ambient temperature for 20 h. The viscous solution obtained was poured dropwise into 300 mL of methanol. The precipitated fibrous polymer was collected, washed thoroughly with methanol, and vacuum dried at 60°C. 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°C. IR (film): 3420 (N-H and OH); 1655 cm⁻¹ (C=O). ANAL. Calcd. for (C₂₆H₂₈N₂O₄)_n (432.5)_n: C, 72.20%; H, 6.53%; N, 6.48%. Found: C, 71.97%; H, 6.23%; N, 6.17%.

Polybenzoxazole **VII** from **VI**

The thermal cyclodehydration of polymer **VI** film was carried out by heating at 300°C for 20 h under nitrogen. IR (film): 1620 cm⁻¹ (C=N). ANAL. Calcd. for (C₂₆H₂₄N₂O₂)_n (396.5)_n: C, 78.76%; H, 6.10%; N, 7.07%. Found: C, 77.81%; H, 5.81%; N, 6.72%.

Measurements

IR spectra were recorded on a Jasco FT/IR-460 spectrophotometer as films. Thermogravimetry (TG) was performed on film specimens with Seiko TG/DTA 6200 under nitrogen at a heating rate of 10K/min. Tensile properties were determined from stress-strain curves obtained with an Orientec STA-1150 at an elongation rate of 10%/min with film specimens (3 mm wide, 20 mm long, *ca.* 0.1 mm thick). Refractive indices of the polymer films were measured by an Atago Abbe refractometer 4T at ambient temperature in air. The measurements were made by using monobromonaphthalene (*n*=1.661) as binder at a wavelength of 590 nm.

RESULTS AND DISCUSSION

Polymer Synthesis

Aromatic polybenzoxazoles are generally synthesized by four methods: The first synthesis was described by Kubota and Nakanishi,⁶⁾ who obtained organic-insoluble polybenzoxazoles in two steps by the prior formation of soluble poly(*o*-hydroxy amides) having high molecular weights through the low-temperature solution polycondensation of bis(*o*-aminophenols) with aromatic diacid chlorides, followed by thermal cyclodehydration. A different approach, the one-step synthesis of aromatic polybenzoxazoles, was investigated by Moyer *et al.*,⁷⁾ which involved the high-temperature melt or solid-state polycondensation of bis(*o*-aminophenols) with aromatic diacid diphenyl esters. Imai *et al.*⁸⁾ demonstrated a more facile method for the preparation of aromatic polybenzoxazoles by the direct polycondensation of bis(*o*-aminophenols) with aromatic diacids using polyphosphoric acid PPA that acts as both reaction medium and condensing agent. Ueda *et al.*⁹⁾ developed a modified method for the synthesis of

polybenzoxazoles with the use of a mixture PPMA of phosphorous pentoxide and methanesulfonic acid in place of PPA. In this study, the direct solution polycondensation of 5,7-dimethyladamantane-1,3-dicarboxylic acid **I** with 4,4'-diamino-3,3'-dihydroxybiphenyl **III** was first attempted in PPA or PPMA. However, no polymer was obtained both by the reaction first at 140°C for 24 h and then further at 200°C for 24 h in PPA and the reaction at 140°C for 48 h in PPMA (Table I).

Table I Synthesis of Dimethyladamantyl Unit-Containing Semi-Alicyclic Poly(*o*-hydroxy amide) **VI**

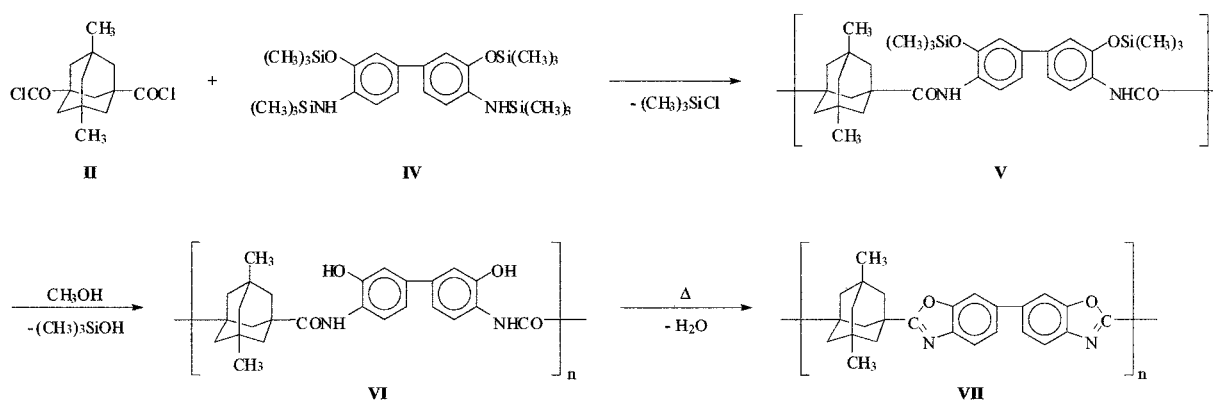
Run	Monomers		Reaction Conditions ^{a)}		Polymer	
	Diacid	Bis(<i>o</i> -amino-phenol)	Solvent	Temp. / Time °C/h	Yield %	$\eta_{\text{red}}^{\text{b)}}$ dL/g
1	I	III	PPA	140/24 → 200/24	- ^{c)}	-
2	I	III	PPMA	140/48	- ^{c)}	-
3	II	III	DMAc	0-r.t./20	67	0.08
4	II	IV	DMAc	0-r.t./20	109	1.05
5	II	IV	HMPA	0-r.t./20	102	0.67
6	II	IV	NMP	0-r.t./20	99	0.80
7	II	IV	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.

The low-temperature solution polycondensation of 5,7-dimethyladamantane-1,3-dicarbonyl chloride **II** with bis(*o*-aminophenol) **III** was next tried in DMAc at 0°C-ambient temperature for 20 h, and this also yielded poly(*o*-hydroxy amide) **VI** with a low reduced viscosity of 0.08 dL/g in a low yield of 67% (Table I). The prolonged reaction time had no remarkable effect on the reduced viscosity of the resulting polymer. Thus, attempts to prepare polybenzoxazole or poly(*o*-hydroxy amide) of sufficient high molecular weight were unsuccessful both from **I** and **II** by these two methods.



Scheme 1. Synthesis of Dimethyladamantyl Unit-Containing Semi-Alicyclic Polybenzoxazole **VII**.

In the syntheses of fluorine-containing aromatic polybenzoxazoles, Maruyama *et al.*⁴⁾ found that *N,N',O,O'*-tetrakis(trimethylsilyl)-substituted bis(*o*-aminophenol) was more reactive than the parent bis(*o*-aminophenol) toward diacid chlorides, giving high-molecular-weight polybenzoxazoles. The silylation method brings about another advantage of undergoing a selective reaction. For example, *N,O*-bis(trimethylsilyl)-*o*-aminophenol should be attacked by an acid chloride at the *N*-silylated amine site selectively, forming exclusively the corresponding amide product, a precursor of the benzoxazole compound. The reason is that the

amino group of *o*-aminophenol is activated through silylation, whereas the hydroxy group is deactivated, as it is well demonstrated that the silylation of the hydroxy group is normally a protection against electrophilic attack.^{10,11)} We applied the silylation method, which might be useful for the activation of amino group of bis(*o*-aminophenol) **III**. The low-temperature solution polycondensation of diacid chloride **II** with 3,3'-bis(trimethylsiloxy)-4,4'-bis[(trimethylsilyl)amino]biphenyl **IV** was carried out in polar aprotic solvents like DMAc, HMPA, and NMP or chloroform at 0°C-room temperature for 20 h. Poly(*o*-hydroxy amide) **VI** with high reduced viscosities of above 0.6 dL/g was quite readily obtained in high yields (Table I), and the versatility of the silylation method was demonstrated.

The formation of poly(*o*-hydroxy amide) **VI** 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 ones of the proposed structure of the polymer.

In the second stage, poly(*o*-hydroxy amide) **VI** 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°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%) agreed quite well with that of the calculated value of 8.3%. Therefore, the conversion to polybenzoxazole **VII** 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 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. The elemental analysis values of the converted polymer agreed well with the values calculated for the polymer with benzoxazole structure.

Polymer Characterization

Poly(*o*-hydroxy amide) **VI** was amorphous and readily soluble in polar aprotic solvents such as DMAc, DMF, dimethylsulfoxide, and NMP, whereas polybenzoxazole **VII** dissolved only in protic strong acids like concentrated sulfuric acid and methanesulfonic acid. Despite the fact that polybenzoxazole **VII** was also amorphous, the polymer was quite insoluble in organic solvents tried. Transparent, flexible, and tough film of the poly(*o*-hydroxy amide) could be cast from the DMAc solution.

The polybenzoxazole did not loss weight up to 400°C under nitrogen, and the temperatures at which a 5% weight loss and a 10% weight loss recorded were 420 and 439°C, respectively (Table II). The excellent thermal stability is almost comparable to those of adamantyl unit-containing fully aliphatic polyimides,²⁾ but evidently inferior to that of adamantyl unit-containing semi-alicyclic polybenzoxazole.³⁾ Neither glass transition temperature nor melting temperature was detectable for polybenzoxazole **VII**.

Table II Thermal, Mechanical, Optical, and Dielectric Properties of Dimethyladamantyl Unit-Containing Semi-Alicyclic Polybenzoxazole **VII**

Thermal Properties			Mechanical Properties			Optical Property	Dielectric Property
DT ₅ ^{a)} °C	DT ₁₀ ^{b)} °C	RW ₅₀₀ ^{c)} %	Tensile Strength MPa	Elongation at Break %	Tensile Modulus GPa	Refractive Index <i>n</i>	Dielectric Constant ^{d)} <i>ε</i> (<i>opt.</i>)
420	439	62	110	6	3.3	1.614	2.866

a) A 5%-weight-loss temperature was measured by TG at a heating rate of 10K/min under nitrogen.

b) A 10%-weight-loss temperature.

c) Residual weight at 500°C.

d) Dielectric constant was calculated from the refractive index value, $\epsilon=1.1n^2$.

The mechanical properties of the polybenzoxazole film were excellent, *i.e.*, its tensile strength, elongation at break, and tensile modulus were 110 MPa, 6%, and 3.3 GPa, respectively (**Table II**).

The averaged refractive indices of the polybenzoxazole was 1.614, and the dielectric constant that was estimated from the value according to the modified Maxwell equation¹²⁾ was 2.866 (**Table II**). This value is fairly lower than those of conventional aromatic polybenzoxazoles. One of the purpose of this study was to lower the dielectric constants of rigid-rod polymers by incorporating alicyclic adamantyl unit. Thus, the incorporation of dimethyladamantyl unit is effective for decreasing dielectric constant of polybenzoxazoles. The decreased dielectric constant of polybenzoxazole **VII** might be ascribed to reduced molecular density and polarity due to the existence of bulky and non-polar dimethyladamantyl units in the polymer backbone.

CONCLUSIONS

Dimethyladamantyl unit-containing semi-alicyclic polybenzoxazole was synthesized from 5,7-dimethyladamantane-1,3-dicarbonyl chloride and *N,N',O,O'*-tetrakis(trimethylsilyl)-substituted 4,4'-diamino-3,3'-dihydroxybiphenyl by the two-step procedure that included low-temperature solution polycondensation in a polar aprotic amide-type solvent and subsequent thermal cyclodehydration. The polybenzoxazole obtained had high thermal stability, excellent mechanical properties, and a low dielectric constant and is promising electric insulation material for the fields in microelectronics.

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