

Synthesis of a Novel Epoxy Resin Containing Pyrene Moiety and Thermal Properties of Its Cured Polymer with Phenol Novolac

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ABSTRACT: A new epoxy resin containing the pyrene moiety in the backbone (**3**) was synthesized and confirmed by gel permeation chromatography and field-desorption mass spectroscopy and infrared spectroscopy. In addition, to evaluate the influence of the pyrene moiety on the structure, epoxy resins having an anthrylene moiety (**5**) and having a phenylene moiety (**7**) were synthesized. The cured polymer obtained through the curing reaction between **3** and phenol novolac was used for making a comparison of its thermal properties with those obtained from **5**, **7**, and bisphenol-A (4,4'-isopropylidenediphenyl)-type epoxy resin (Bis-EA). The cured polymer obtained from **3** showed a higher glass transition temperature, lower coefficient of linear thermal expansion, lower moisture absorption, and markedly higher anaerobic char yield at 700°C of 37.6 wt %, which might be attributed to the higher aromaticity of **3** containing the pyrene moiety. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 528–535, 2000

Key words: epoxy resin; pyrene derivative; anthracene derivative; phenol novolac; thermal properties

INTRODUCTION

Epoxy resins have been used in many industrial applications, such as in surface coatings, adhesives, structural composites, printed circuit boards, and insulating materials for electronic devices,^{1,2} because of their good heat and chemical resistance and superior mechanical and electrical properties, in addition to their excellent processabilities. However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials which require higher thermal and moisture resistance.^{3,4} For

example, it has been reported that a trade-off exists between the T_g and moisture absorption in the *o*-cresol novolac epoxy resin system.⁵

Modifications of the backbone of epoxy resins have been recently paid much attention in attempts to enhance the thermal and physical properties.⁶ We reported that the thermal properties of epoxy polymers can be improved by incorporation of a polynuclear aromatic structure, such as naphthalene, biphenyl, and anthracene.^{7–9} Especially, the polymer having an anthracene moiety in its backbone exhibited markedly higher thermal and moisture resistance, by the effect of the condensed polynuclear aromatic structure of anthracene.⁹

In this article, we report the incorporation of a pyrene moiety into the resin backbone in order to

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examine the effect of a four fused-ring aromatic structure. Although Otani reported a condensed polynuclear aromatic resin having the pyrene moiety in the resin backbone,¹⁰ few studies have been reported about pyrene-containing epoxy resin. A new type of epoxy resin having the pyrene moiety in the backbone was synthesized, and the thermal properties of the cured polymer obtained from the new epoxy resin and phenol novolac were compared with those from an epoxy resin having an anthrylene group, a phenylene group in place of the pyrene moiety, and a conventional bisphenol-A (4,4'-isopropylidenediphenyl)-type epoxy resin.

EXPERIMENTAL

Materials

Pyrene, anthracene, and 1,2,4,5-tetramethylbenzene were obtained from Aldrich (Milwaukee, WI) and were used without further purification. Phenol, chlorobenzene, and *p*-toluenesulfonic acid (PTS) were reagent grade from Kanto Chemical Co. (Tokyo, Japan) and used without further purification. Epichlorohydrin was reagent grade from Kanto Chemical Co. and was distilled before use. Commercially available *p*-xylylene glycol dimethylether (PXDM), bisphenol-A-type epoxy resin (Epikote 828), and phenol novolac (Tamanol 758) were obtained from the Ihara Nikkei Co. (Tokyo, Japan), the Yuka Shell Epoxy Co. (Tokyo, Japan), and the Arakawa Chemical Co. (Osaka, Japan), respectively. Triphenyl-phosphine (TPP), as a curing accelerator, was used as received from the Hokko Chemical Co. (Tokyo, Japan).

Synthesis of 2

A mixture of 50.5 g of pyrene, 166.0 g of PXDM, and 8.4 g of PTS was heated at 150°C with stirring under a nitrogen atmosphere for 2 h. During the reaction, generated methanol was removed from the solution. When 16.0 g of methanol was generated, 470.0 g of phenol was added to the mixture. The reaction was continued at 160°C for 4 h with removing the generated methanol from the mixture. The mixture was neutralized with sodium carbonate. From the mixture, unreacted phenol was removed by distillation under reduced pressure to give 237.5 g of **2** as a brown solid. The softening point (SP) was 78°C. The OH equivalent weight (OHEW) was 232 g/eq.

IR(KBr): 3450, 2968, 1614, 1512, 1456, 1364, 1250, 1180, 1086, 1006, 824, 754, 566 cm⁻¹.

Synthesis of 3

Eighty grams of **2** was dissolved in 320.0 g of epichlorohydrin. The solution was heated at 65°C to obtain a homogeneous solution; then, to this solution was added, dropwise, 28.1 g of 48% aqueous sodium hydroxide with stirring under reduced pressure (~18 kPa) for 4 h. During the reaction, generated water was removed from the solution by azeotropic distillation with epichlorohydrin. The distilled epichlorohydrin was returned to the solution after separation with water. After the unreacted epichlorohydrin was distilled off from the solution, chlorobenzene was added to resolve the product. The solution was washed with water several times, and the chlorobenzene was distilled off to give 81.0 g of **3** as a dark brown solid. Yield 81.6%. SP 64°C. The epoxy equivalent weight (EEW) was 304 g/eq (calcd 288 g/eq).

IR(KBr): 3480, 3008, 2924, 1608, 1512, 1452, 1294, 1246, 1180, 1034, 916, 824, 752, 612, 526 cm⁻¹.

Synthesis of Anthracene-containing Phenolic Resin (4)

4 was prepared by using anthracene according to the same method as the preparation of **2**. Yield 93.5%. SP 74°C. The OHEW was 221 g/eq.

IR(KBr): 3548, 2978, 1622, 1512, 1472, 1326, 1264, 1190, 1110, 1022, 888, 828, 758 cm⁻¹.

Synthesis of 5

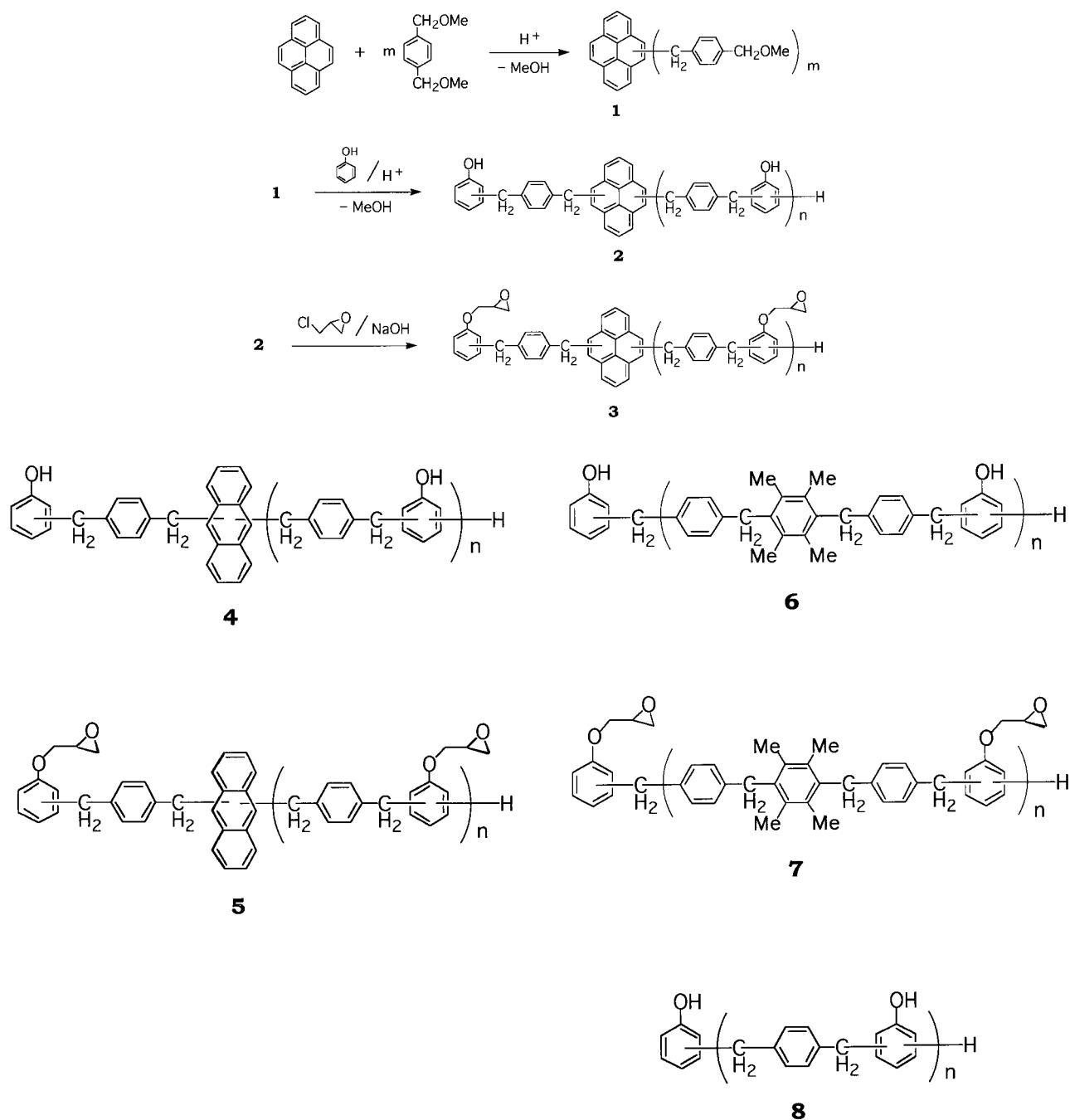
5 was prepared by using **4** according to the same method as in the preparation of **3**. Yield 82.3%. SP 61°C. The EEW was 297 g/eq.

IR(KBr): 3444, 3004, 2924, 1608, 1510, 1456, 1346, 1252, 1184, 1130, 1022, 916, 836, 752, 566, 480 cm⁻¹.

Synthesis of Benzene-containing Phenolic Resin (6)

6 was prepared by using 1,2,4,5-tetramethylbenzene according to the same method as in the preparation of **2**. Yield 94.3%. SP 71°C. The OHEW was 211 g/eq.

IR(KBr): 3549, 2980, 1622, 1512, 1474, 1268, 1221, 1136, 1118, 1021, 872, 762 cm⁻¹.



Scheme 1 Synthesis of pyrene-containing epoxy resin.

Synthesis of 7

7 was prepared by using **6** according to the same method as in the preparation of **3**. Yield 89.8%. SP 60°C. The EEW was 263 g/eq.

IR(KBr): 3448, 3008, 2920, 1612, 1510, 1470, 1256, 1218, 1132, 1088, 1020, 914, 842, 758, 666 cm^{-1} .

Preparation of Cured Polymers: Typical Procedure

Epoxy resin and phenol novolac were mixed at 150°C with a 1:1 equivalent ratio. To the obtained homogeneous mixture, 1.3 wt % of TPP was added and the mixture was heated at 100°C by using a mixing-roll apparatus. The mixture was cured at 150°C for 3 min, followed by postcuring at 180°C for 12 h.

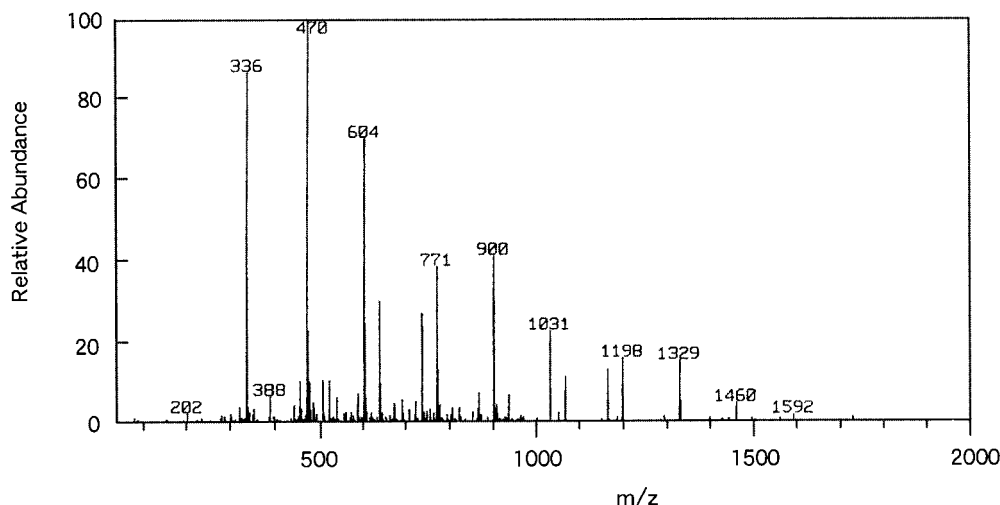


Figure 1 FD-MS spectrum of reaction product from pyrene and PXDM.

Characterization and Measurements

The softening point was determined according to JIS K-6911. The viscosity was measured by a Contraves Rheomat 115 viscometer. The gel permeation chromatography (GPC) measurement was carried out in tetrahydrofuran on a Tosoh HLC-82A equipped with four consecutive linear polystyrene gel columns (Tosoh TSK gels G2000HXL \times 3, and G4000HXL) at 38°C at a flow rate of 1.0 mL/min. The infrared (IR) spectrum was examined using a Hitachi 270-50 infrared spectrometer. The spectrum of field-desorption mass spectroscopy (FD-MS) was obtained from a JEOL DX-303 mass spectrometer. Thermomechanical analysis (TMA) was carried out by a Seiko TMA 120C at a heating rate of 10°C/min under a nitrogen atmosphere. The coeffi-

cient of linear thermal expansion (CTE) was obtained from the thermal-expansion quantity. Thermogravimetric analysis (TGA) was done on a Seiko TG/DTA 220 in a nitrogen atmosphere at a heating rate of 10°C/min. Moisture absorption was performed using a Tabai Espec TPC-410 pressure-cooker tester. The quantity of absorbed water was determined by the weight difference before and after moisture absorption.

RESULTS AND DISCUSSION

Synthesis of Pyrene-containing Epoxy Resin

The new pyrene-containing epoxy resin (**3**) was prepared by the following three steps: Syntheses

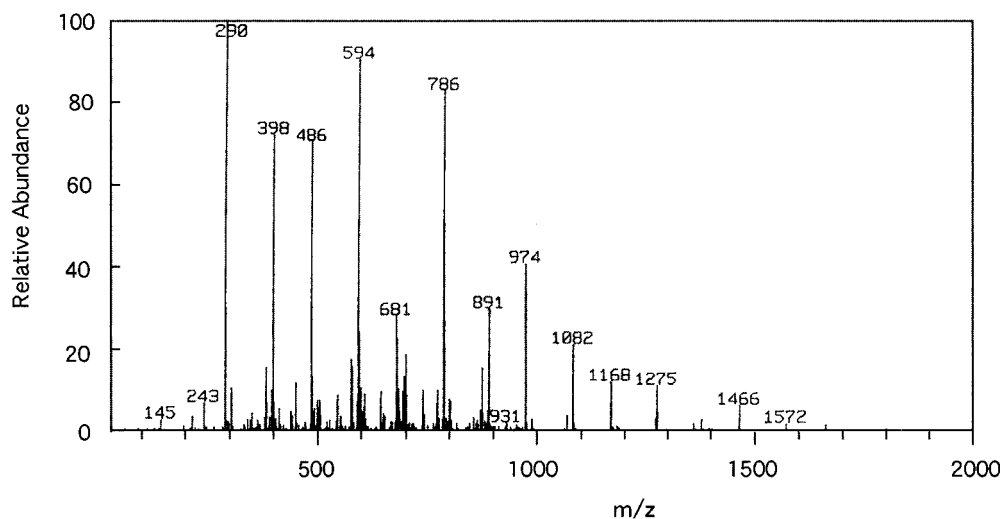


Figure 2 FD-MS spectrum of reaction product from **1** and phenol.

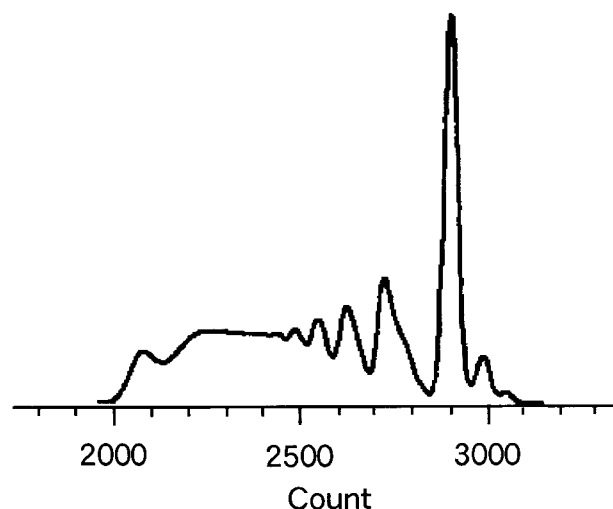


Figure 3 GPC chromatogram of reaction product from **1** and phenol.

of a reaction product (**1**) from pyrene with PXDM, a pyrene-containing phenolic resin (**2**), and epoxidation of **2** were carried out as shown in Scheme 1. Generation of **3** was confirmed by FD-MS and IR spectroscopy.

1 was obtained by the reaction of pyrene with PXDM in an acidic condition at 150°C. The reaction was continued until twice the mol of methanol to PXDM was generated in order to avoid crosslinking. Otani reported a pyrene-containing resin using *p*-xylylene glycol, which has a higher reactivity than has PXDM.¹⁰ In this study, PXDM was used for ease of controlling the reaction rate. As shown in Figure 1 (FD-MS spectrum of the

reaction product of pyrene and PXDM), $m/z = 336, 470, 604,$ and 738 were observed corresponding to $m = 1, 2, 3,$ and 4 in the structure of **1**, respectively.

2 was obtained by a condensation reaction of **1** with an excess amount of phenol in an acidic condition, followed by elimination of unreacted phenol. Figures 2 and 3 show the FD-MS spectrum and GPC chromatogram of the reaction product of phenol with **1**, respectively. In the FD-MS spectrum, $m/z = 290, 486,$ and 682 were observed corresponding to $n = 1, 2,$ and 3 in the structure of **8** which might be produced by the reaction of phenol and unreacted PXDM, in addition to $m/z = 398, 594,$ and 786 corresponding to $n = 0, 1,$ and 2 in the structure of **2**.

As shown in Figure 4 (IR spectrum of the reaction product of **2** with epichlorohydrin), the characteristic band of the oxirane ring was observed at 916 cm^{-1} . The GPC chromatogram is shown in Figure 5. The same peak pattern as in **2** was observed. The epoxy equivalent weight (EEW) of **2** was found to be 304 g/eq (calculated 288 g/eq). To examine the influence of the pyrene moiety in the main chain, epoxy resins **5** and **7**, which have anthracene and benzene moieties in place of the pyrene moiety, were synthesized in the same manner.

Table I summarizes the results of syntheses of the phenolic resins and the epoxy resins. **3** and **5** gave a lower yield of 81.6–82.3% compared to **7** of 89.8%, which might depend on the poor solubilities in epichlorohydrin of **3** and **5** which have a condensed polynuclear aromatic structure.

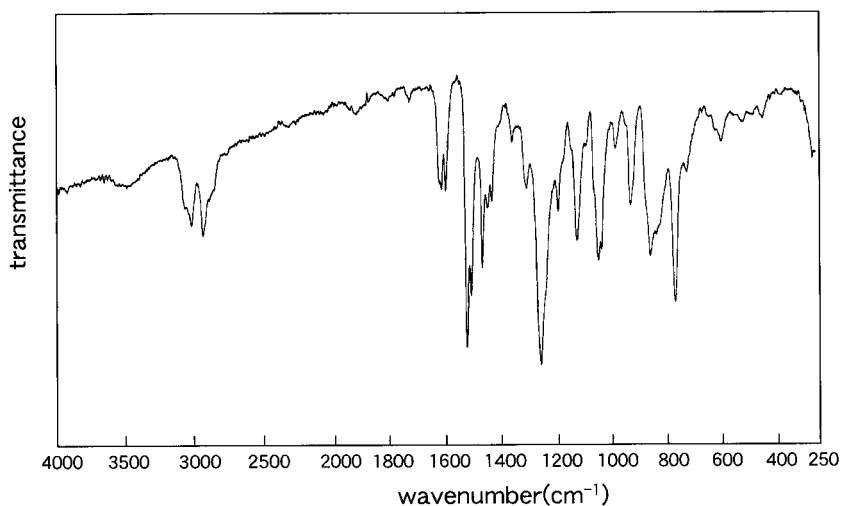


Figure 4 IR spectrum of reaction product from **2** and epichlorohydrin.

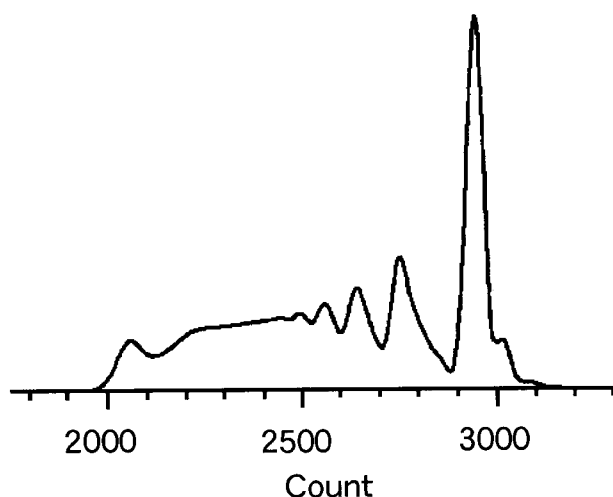


Figure 5 GPC chromatogram of reaction product from **2** and epichlorohydrin.

Properties of Cured Polymers

To examine the influence of the pyrene moiety in the backbone on the thermal and physical properties, the cured polymers were prepared from the new pyrene-containing epoxy resin (**3**), anthracene-containing epoxy resin (**5**), benzene-contain-

ing epoxy resin (**7**), and bisphenol-A-type epoxy resin (Bis-EA) using phenol novolac (PN) as a curing agent, that is, **3**/PN (polymer **3**), **5**/PN (polymer **5**), **7**/PN (polymer **7**), and Bis-EA/PN (Bis-EA polymer).

The results of TMA are summarized in Table II. The inflection point of thermal expansion was defined as the T_g . Although the crosslinking densities of polymer **3**, polymer **5**, polymer **7**, and the Bis-EA polymer might be considered to decrease in this order, judging from their functionalities, polymer **3** showed the highest T_g , followed by polymer **5**, the Bis-EA polymer, and polymer **7**, in this order. In polymer **3**, the bulkiness of the pyrene skeleton in the main chain may restrict the rotation of the polymer main chain. Also, the condensed polynuclear aromatic structure of pyrene can force the thermal movement of the polymer backbone compared to the other polymers. Incorporation of the pyrene moiety into the main chain may enhance the T_g of the cured polymer obtained from **3**.

Furthermore, the TMA results may show that polymer **3** and polymer **5** have the smaller CTE in the glassy region and the rubbery region, compared with polymer **7** and the Bis-EA polymer.

Table I Syntheses of Phenolic Resins and Epoxy Resins

Resin Type	Measurement	No.		
		1	2	3
		X ^a		
Phenolic resin	Softening point (°C)	78	74	71
	Viscosity (Pa s, 150°C)	0.42	0.40	0.38
	OHEW (g/eq.)	232	221	211
Epoxy resin	Softening point (°C)	64	61	60
	Viscosity (Pa s, 150°C)	0.16	0.15	0.17
	EEW (g/eq.)	304	297	263
	Yield (%)	81.6	82.3	89.8

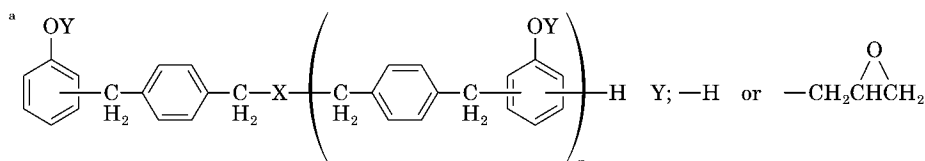


Table II Thermal Mechanical Properties of Cured Polymers

Epoxy Resin	T_g (°C)	CTE ^a ($\times 10^{-5}$, °C ⁻¹)	
		$< T_g$	$> T_g$
3	137	5.6	15.4
5	134	5.8	15.5
7	129	6.2	16.6
Bis-EA	132	6.2	17.8

^a Coefficient of linear thermal expansion.

We have reported the thermal behaviors in the cured polymers from the naphthalene-based epoxy resins, in which it was showed that the CTEs of the naphthalene-based epoxy polymers were in the range of 14.5×10^{-5} – 17.5×10^{-5} °C⁻¹ in the rubbery regions.¹¹ We also reported that the epoxy-cured polymer containing the anthracene moiety gave a characteristic smaller CTE in the rubbery region.⁹ The smaller CTEs of these epoxy polymers have been explained in terms of their condensed polynuclear aromatic structures. As a CTE is thought to correspond to molecular movement of the polymer main chain, it seemed that the characteristic small CTEs in polymer **3** and polymer **5** depended on the restricted molecular mobility arising from the condensed polynuclear

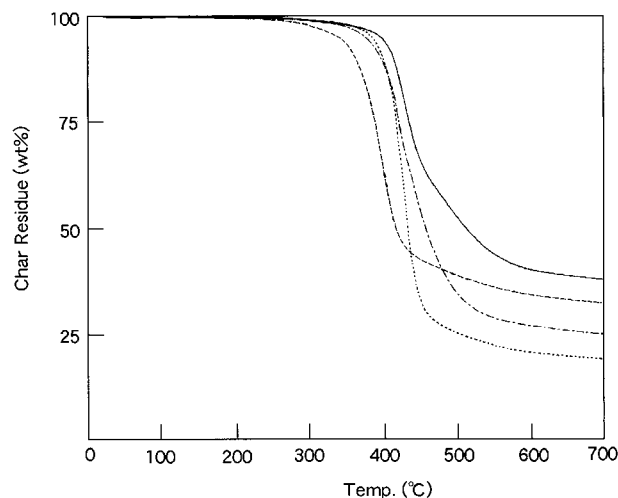


Figure 6 Results of thermogravimetric analysis of cured polymers: (—) cured polymer from **3**; (-----) cured polymer from **5**; (- - - - -) cured polymer from **7**; (· · · · ·) cured polymer from Bis-EA.

Table III Thermal Properties of Cured Polymers

Epoxy Resin	$T_{10\%}$ ^a (°C)	Anaerobic Char Yield (wt %, at 700°C)
3	412	37.6
5	368	31.0
7	398	24.4
Bis-EA	403	18.5

^a Temperature of 10% weight loss.

aromatic structures of pyrene and anthracene in the main chains.

The thermal stability of the cured polymers were compared by the temperature of 10% weight loss ($T_{10\%}$) and the percentage of char yield at 700°C in the TGA measurement. The TGA curves are shown in Figure 6, and the results are summarized in Table III. Polymer **3** gave the highest anaerobic char yield of 37.6 wt % at 700°C, followed in descending order by polymer **5**, polymer **7**, and the Bis-EA polymer. These results might be attributed to the highest aromaticity of polymer **3** containing the pyrene moiety.

The moisture absorption of the cured polymers is shown in Table IV. Polymer **3** gave the lowest moisture absorption among the cured polymers. This result seems to depend on the hydrophobic nature of the pyrene moiety. Ogata reported that the moisture absorption increases as the T_g increases in the cured polymers from *o*-cresol novolac-type epoxy resin and phenol novolac.⁵ This information may mean that it is difficult to decrease the moisture absorption by keeping a higher T_g in the conventional resin systems. However, incorporation of the pyrene structure into the epoxy-cured polymer was effective for improving the moisture resistance and the thermal stability.

Table IV Moisture Absorption of Cured Polymers

Epoxy Resin	Moisture Absorption ^a (wt %)
3	1.28
5	1.44
7	1.63
Bis-EA	2.15

^a 133°C, 3 atm, 96 h.

CONCLUSIONS

A new pyrene-containing epoxy resin **3** was synthesized and confirmed by the EEW, GPC, FD-MS, and IR analyses. A cured polymer obtained from **3** and phenol novolac showed a higher T_g , lower CTE, lower moisture absorption, and markedly higher anaerobic char yield at 700°C. The pronounced good properties of the cured polymer from **3** should originate from the condensed polynuclear aromatic structure of the pyrene unit.

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