

# High Refractive Coating Materials Using Hyperbranched Polymers

Naoya Nishimura<sup>†‡</sup>, Yuji Shibasaki<sup>‡</sup>, Masaaki Ozawa<sup>†</sup> and Yoshiyuki Oishi<sup>‡</sup>

<sup>†</sup>*Materials Research Department, Chemical Research Laboratories, Nissan Chemical Industries, Ltd.,  
2-10-1, Tsuboinishi, Funabashi-shi, Chiba, 274-8507, Japan*

<sup>‡</sup>*Department of Chemistry & Bioengineering, Faculty of Engineering, Iwate University,  
4-3-5, Ueda, Morioka, Iwate 020-8551, Japan*

**Keywords:** high refractive index, triazine ring, hyperbranched polymer

## 1. Introduction

Transparent resins, have been widely used as optical and electronic materials such as optical lenses, anti-reflective coating films, optical sensors, light-emitting diodes (OLED, LED), solid-state imaging devices, displays, touch panels, and solar cells. For such applications not only the excellent optical properties such as high transparency and high refractive index but also the high heat resistance are required. The general approach to improve refractive indices in polymers is the introduction of substituents with high molar refraction and low molar volume according to the Lorentz-Lorenz equation [1]. Thus, aromatic rings, heavy halogens (Cl, Br, and I) except for fluorine, sulfur, and metallic elements have been introduced in polymers to enhance their refractive index [2-4]. In particular, high-molecular episulfide compounds with sulfur atoms and high-molecular thiourethane compounds introduced therein have been put into practical use as spectacle lenses of high refractive index.

The use of an inorganic metal oxide such as ZrO<sub>2</sub> and TiO<sub>2</sub> makes a high refractive index possible [5], but the dispersion stability is the main issue to handle it. In addition, it is often that there is an issue in transparency in a case of using sulfur. Therefore, it can be said that the finest structure design and control of the aromatic polymers without the metal oxide additives and sulfur could be the most promising pathway to achieve a processable high refractive polymeric materials for industrial applications.

Hyper branched polymers (HBP)s have been receiving great attention for their unique properties such as intrinsic globular structure, low viscosity, high solubility, and large numbers of terminal functional groups. HBP is compared with a dendrimer, whose synthesis is

time-consuming and technically complicated. The HBPs consisting of triazine units have been recently reported, in which tedious synthetic pathways and the poor yield of the final polymers are the issue to be solved [6-8]. Linear polymers have also been reported using dichloro-triazine molecule, which have good heat resistance and high transparency.

In this report, novel HBPs are prepared by polycondensation with 2,4,6-trichloro-1,3,5-triazine (CYC) and diamine monomers in a one-step reaction, and investigated the thermal and optical properties for industrial applications.

## 2. Method

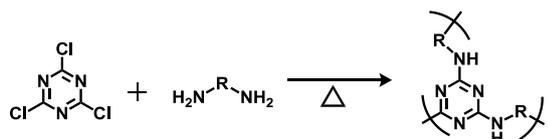
### 2.1 Materials

CYC was purchased from Evonik Degussa, and used as received. Bis(4-aminophenyl)fluorene (BAFL) and m-phenylene diamine (m-PDA) were purchased from Aldrich, and used as received. 4,4'-Diaminobisphenylamide (DABA) was obtained from Nippon Junryo Chemicals, and used as received. All the other chemical and solvents were used without further purification.

### 2.2 Synthesis of HBP having triazine units

As a typical example, a HBP based on CYC with BAFL was prepared according to the procedure described below (Table 1, Run 1). To a 200-mL three-necked round-bottom flask equipped with a high-power electromagnetic stirrer, a nitrogen inlet, and an oil bath were added BAFL (9.29 g, 0.0270 mol) and freshly-distilled DMAc (80 mL). The mixture was heated to 100 °C, and then CYC (3.69 g, 0.0200 mol) in DMAc (20 mL) was added in one-portion. After 5 min stirring, aniline (3.34 g, 0.0360 mol) was added into the solution to terminate the polymerization, and the mixture was cooled to room temperature. The <sup>355</sup> polymerization solution was poured into

water (1 L) containing potassium carbonate (15 g, 0.11 mol) to precipitate the polymer. The polymer was dissolved in tetrahydrofuran (THF) (50 mL), and reprecipitated with hexane-ethanol (540 mL / 60 mL) mixed solvent. By drying at 40 °C for 6 h, the white powdery polymer was obtained in 96% yield.



Scheme 1. Synthesis of ultra-high refractive index HBP

### 2.3 Characterization

Number and weight average molecular weights ( $M_n$  and  $M_w$ ) were measured by a gel permeation chromatography (GPC) on Tosoh HLC-8220 GPC equipped with a consecutive polystyrene gel column (SHODEX KF-804L+KF-805L), and with a RI (refractive index) and UV detectors at 40 °C eluted with THF at a flow rate of 1.0 mL / min calibrated by standard polystyrene samples. Nuclear magnetic resonance (NMR) was performed on a

JNM-ECX300 (JEOL) spectrometer at 300 MHz for  $^1\text{H}$  measurements. Deuterated dimethylsulfoxide ( $\text{DMSO-}d_6$ ) was used as a solvent with tetramethylsilane as an internal reference. Thermal analyses were performed on a Rigaku thermal analyzer (TG-8120 system) at a heating rate of 40 °C / min under air. UV-vis spectra were recorded on a SHIMADZU UV3600 spectrometer. Refractive index was measured with a J.A.Woollam JAPAN Co., Inc ellipsometer (VARIABLE ANGLE SPECTROSCOPIC ELLIPSOMETER VASE).

### 2.4 HBP-acrylate blend film

The obtained HBP sample and multifunctional acrylate were dissolved in cyclohexanone (10 wt%). This solution was dropped on a glass plate, spin-coated at 1,500 rpm for 35 s, baked at 150 °C for 1min, then 250 °C for 5min under air. The film thickness was around 500 nm to 1,000 nm.

### 2.5 Characterization of photo-curable coating materials

The 15 wt% polymer varnish was prepared to

Table 1. Polymerization of CYC with aromatic diamines

Run	Diamine	Monomer in feed [mol/mol]			Yield <sup>a</sup> [%]	$M_w^b$ [ $10^3$ ]	$M_w/M_n^b$
		CYC	diamine	Aniline			
1	BAFL	1	1.35	1.8	95.5	9.2	2.3
2	m-PDA	1	1.35	3	30.2	4.6	2.4
3	DABA	1	1.31	3	91.9	3.2	2.4

<sup>a</sup>: Yield [%] = [Polymer] / ([CYC] + [BAFL]), <sup>b</sup>: Determined by GPC with polystyrene standard.

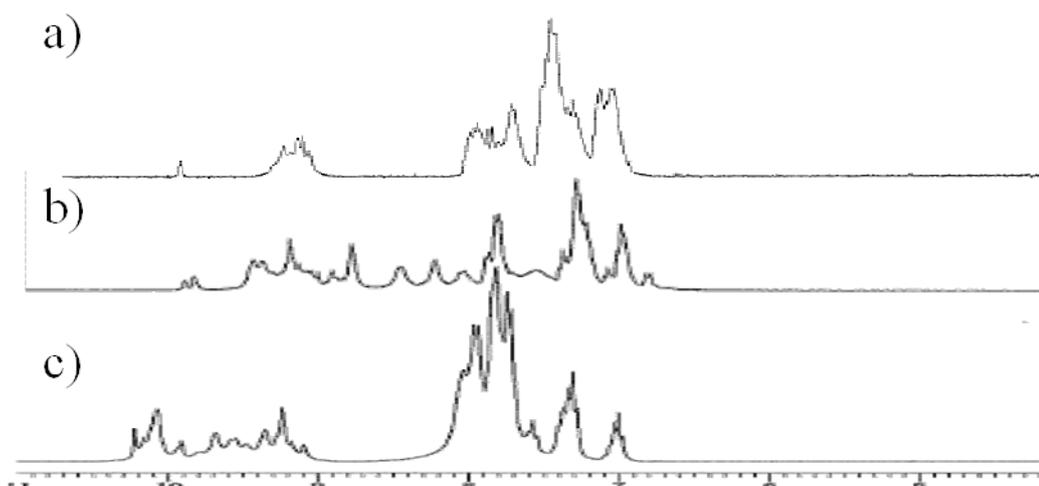


Figure 1  $^1\text{H}$  NMR spectra of HBP a) Run 1, b) Run 2, c) Run 3

make thin film, which was obtained in the similar manner described in 2.3. Then, the film was irradiated with the high-pressure mercury lamp 20mW/cm<sup>2</sup> for 40sec.

### 3. Results and discussion

#### 3.1 Synthesis of HBPs having triazine units

Polymers having a large number of aromatic rings tend to be insoluble. However, it is possible to maintain the high solubility by introducing a branching structure. Thus, we designed and prepared HBPs having triazine units as shown in Scheme 1. Table 1 shows the polymerization results. The corresponding HBPs were obtained with the molecular weights of 3,000 to 9,600. Since this polymerization is based on the A<sub>3</sub>-B<sub>2</sub> system, we quenched the polymerization by the addition of aniline. Thus, the molecular weights of the resulting polymers were not very high. Figure 1 shows the <sup>1</sup>H NMR spectra of the resulting HBPs. In addition to the polymer main unit assignable to aromatic ring part were observed around 7-9 ppm. The typical guanamine proton between triazine and aromatic ring units were observed at 9 ppm, and the protons from terminal anilino amine were observed at 9-10 ppm[8].

Table2. Characterizations of HBPs

Entry	RI <sup>a</sup>			Abbe's Number	Transmittance <sup>b</sup> (@400nm)	Td(5%) <sup>c</sup> [°C]
	550nm	589nm	633nm			
1	1.74	1.73	1.721	15.3	>90%	498
2	1.803	1.791	1.781	14.1	>90%	453
3	1.957	1.936	1.919	9.9	>90%	417

a); measured with Variable angle spectroscopic ellipsometer. b) recorded on UV-vis spectrometer. c) determined by TG-DTA.

Table 2 shows the results of the optical and thermal properties of HBPs. These HBPs have high transparency and high refractive index  $n_D > 1.70$ . In addition, 5% weight-loss temperature is more than 400 °C. HBP of Entry 1 makes a heat resistance of about 500 °C possible. We think that one of factors having a high refractive is hydrogen bonding. In particular, the HBP based on the diamine monomer having an amide unit show the  $n_D > 1.90$ , which is considered to be the best value in organic materials.

Successively, Figure 2 shows the compatibility of HBPs with multifunctional acrylate.

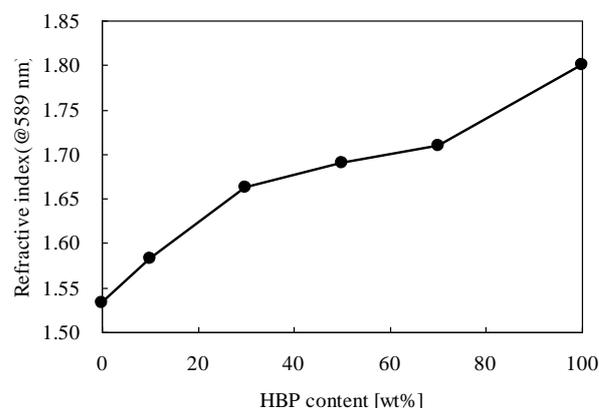


Figure 2. Refractive index as a function of weight percent of HBP in transparent HBP-acrylate.

The HBP of any concentration were able to mix in a general acrylate monomer to obtain transparent thin films. Terminal functional groups of the HBP can be readily reacted with the acrylate monomer. Therefore, we can say that the transparency of the thermosetting material is enough high even after curing. By blending with in a general acrylate in a wide range, it has become possible to control the refractive index. This blending can be expected to use for various functional optical films.

#### 3.2 UV-curing coating material using HBP

UV-curable composition was prepared with combination of HBP and cross-linking agent having reacted by UV. The film properties were shown in Table 3.

In the same way as the characteristics of the HBP, UV cured film had high transparency and high refractive index. UV-vis spectra of cured film were shown in Figure 3. The cured film has high heat resistance, because there is no transparency change in the visible region even after heating treatment at 300 °C.

Table3. Optical properties of light curing film.

$n_D$	1.76
Film thickness	1000nm
Transmittance@400nm	>90%

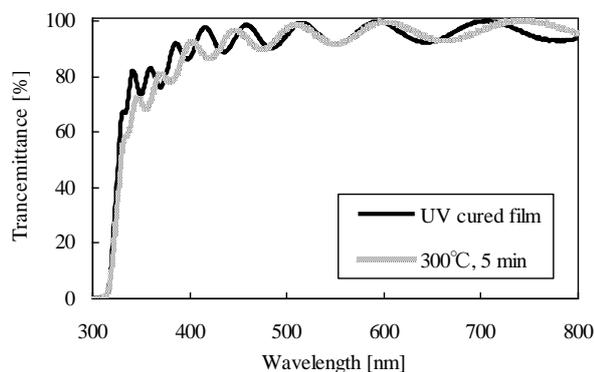


Figure 3. UV-vis spectra for UV cured film and after heating treatment.

#### 4. Conclusion

We performed synthesis of HBPs having triazine rings and the optical characteristic evaluations. And we confirmed that it is characteristic materials having high refractive index, high transparency, and high heat resistance. Applications to optical materials are expected in the future because of addition to acrylic polymer and control of the refractive index. In addition, combination with any photoreactive cross-linking agent and HBPs were able to light-curing coating materials. The

resulting film has retained the characteristics of the HBP that is excellent in heat resistance. These materials are expected to apply the field of electronic materials in the future.

#### 5. Reference

- 1) Ando, S.; Fujigaya and T.; Ueda, M. *Jpn. J. Appl. Phys.* **41** (2002) L105.
- 2) J. G. Liu, Y. Nakamura, C. A. Terraza, Y. Suzuki, Y. Shibasaki, S. Ando and M. Ueda, *Macromol. Chem. Phys.* **209** (2008) 195.
- 3) J. G. Liu, Y. Nakamura, T. Ogura, Y. Shibasaki and S. Ando, M. Ueda, *M. Chem. Mater.* **20** (2008) 273.
- 4) M.-C. Choi, J. Wakita, C. S. Ha and S. Ando, *Macromolecules.* **42** (2009) 5112.
- 5) H. Nio, N. Arai and A. Suwa, *Jpn. Kokai Tokkyo Koho* (2007), JP 2007246877
- 6) S. S. Mahapatra and N. Karak. *Polym. J.*, **41** (2009) 20.
- 7) K. Takagi, T. Hattori, H. Kunisada and Y. Yuki, *J. Polym. Sci., PartA: Polym. Chem.*, **38**, (2000) 4385.
- 8) Y. Shibasaki, T. Koizumi, N. Nishimura and Y. Oishi, *Chem. Let.*, **40** (2011) 1132.