NOTE

Synthesis of hyperbranched fluorinated polymers with controllable refractive indices

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INTRODUCTION

Polymers containing fluorine atoms (fluorinated polymers) exhibit increased thermal stability, hydrophobicity, improved chemical resistance and decreased intermolecular attractive forces in comparison with their hydrocarbon analogs. These properties are derived from the fundamental atomic properties of fluorine, such as high ionization potential, low polarizability and high electronegativity.¹ The high ionization potential, combined with the low polarizability, leads to weak intermolecular interactions, which in turn leads to low-surface energy and low refractive indices of fluorinated polymers. Recently, fluoropolymers have received considerable attention as high-performance materials for applications in optoelectronic fields. Specifically, the refractive index is a very important property of polymers for photonic applications, for which highly fluorinated polymers such as Teflon (DuPont, Wilmington, DE, USA) and CYTOP (ASAHI GLASS CO., LTD., Tokyo, Japan) are well known and widely used in optical communication networks. Current optical communication networks are based on silica optical fiber and devices. To integrate with these devices and materials, and to reduce the optical loss, polymer materials with refractive index values close to that of the silica materials (1.46) are desired.² Therefore, materials with a controllable refractive index are required for the successful design and fabrication of photonic devices. For example, the widely used fluorinated polyimides usually have relatively low refractive indices³ and this value can be easily manipulated by introducing polar groups and copolymerizing with comonomers containing heavier atoms, such as bromine to give high refractive indices. However, it appears difficult to lower the refractive index. We have modified fluoropolymers with the simple polyaddition of bis(epoxide)s with dicarboxylic acids and diols in the presence of quaternary onium salts and they exhibited a linear relationship between refractive indices and fluorine contents of the polymer.^{4,5} Similar investigations have been conducted with fluorinated aromatic–aliphatic copolyethers,⁶ fluorinated poly(phthalazinone ether)s⁷ and hyperbranched fluorinated polyimides.⁸ The relationship between the refractive index (n_D), density

(ρ g cm⁻³), molecular weight (M g mol⁻¹) and molecular refraction (R cm³ mol⁻¹) of a polymer is described by the Lorentz–Lorenz equation (Equation 1).⁹

$$n_D = \sqrt{\frac{M + 2\rho R}{M - \rho R}} \quad (1)$$

According to the Lorentz–Lorenz equation, the polymers with low ρ give low n_D . That is, hyperbranched polymers (HBPs) are good candidates for the production of low-density polymers because of their three dimensional globular architecture with higher branched structure.¹⁰ Recent study has indicated that hyperbranched structures have an increasingly important role in reducing crystallinity, to avoid significant optical loss. For example, we have observed and reported that the HBPs show no birefringence due to their highly branched globular structure, preventing their polymer orientation.¹¹ On the basis of this background information, we investigated a potentially novel approach for creating low n_D materials using HBPs consisting of bulky monomers.¹²

In this paper, we applied the simple polyaddition reaction to the preparation of a series of hyperbranched fluorinated polymers with different fluorine contents and comonomer structures. Furthermore, the HBPs obtained were chemically modified, and the effect of photoinitiated polymerization on refractive index was also examined.

EXPERIMENTAL PROCEDURE

Materials

The reaction solvent, *N*-methyl-2-pyrrolidone, and *o*-dichlorobenzene were dried with CaH₂ and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was crystallized from ethyl acetate. Bisphenol A and 4,4'-biphenol were purified by recrystallization from ethyl acetate/hexane and ethanol/hexane, respectively. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (BPAF), octafluoro-4,4'-biphenol, and 1,4-bis(hexafluorohydroxyisopropyl)-benzene (BFHPB) were purified by sublimation. 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-2-one (Irgacure 907, Ciba Japan K. K., Tokyo, Japan) and SP-150 (ADEKA Co., Tokyo, Japan) were used without further

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purification. 1,1',1''-Tris(4-glycidyoxyphenyl)methane (TGOPM) was prepared according to an established method.¹³ Unless otherwise stated, reagents were purchased from commercial suppliers and used without any further purification.

Measurements

¹H nuclear magnetic resonance (NMR) spectra (500 and 600 MHz) were obtained using JEOL JNM-ECA-600 and JEOL JNM-ECA-500 spectrometers (JEOL Ltd, Tokyo, Japan) using chloroform-*d* (CDCl₃) or dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) ((CD₃)₂SO) as the solvent. The chemical shift references were as follows: chloroform-*h*, 7.26 p.p.m.; DMSO-*d*₅, 2.50 p.p.m.

Infrared (IR) spectra were obtained using a Nicolet Avatar 380 FT-IR instrument (Thermo Scientific KK, Kanagawa, Japan). Real-time Infrared absorption spectra were recorded on a BIO-RAD Excalibur FTS-3000MX spectrometer (Bio-Rad Laboratories, K.K., Tokyo, Japan) equipped with a HOYA-SCHOTT EX250 UV light source (USHIO INC., Tokyo, Japan).

The number-average molecular weight (*M_n*) and molecular weight distribution (weight-average molecular weight/number-average molecular weight (*M_w*/*M_n*)) values of the polymers were estimated on a TOSOH size-exclusion chromatography system (HLC-8220; TOSOH Corp., Tokyo, Japan), which was equipped with four consecutive polystyrene gel columns (Shodex gels: GF-1G 7B, GF310-HQ×2 and GF510-HQ; TOSOH Corp.), a refractive-index detector (RI-8022; TOSOH Corp.) and an ultraviolet detector (UV-8020; TOSOH Corp.) at 40°C. The system was operated at a flow rate of 0.60 ml min⁻¹ using a *N,N*-dimethyl formamide solution (20 mM LiBr and

20 mM phosphoric acid) as an eluent. In this size-exclusion chromatography system, polystyrene standards were used for calibration.

The glass transition temperature (*T_g*) was measured with an EXSTAR 6000/DSC6200 (SEIKO Instruments Inc., Chiba, Japan) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere (monitoring range: -30 to 200 °C).

The thermal decomposition temperature (*T_d*) was measured with an EXSTAR 6000/TG/DTA6200 (SEIKO Instruments Inc.) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere (monitoring range: 50–600 °C).

The refractive index of the polymer film was determined by ellipsometry (DHA-OLX/S4, Mizojiri Optical Co. Ltd, Tokyo, Japan). The thin film (about 1000 Å in thickness) was prepared from the polymer solution (toluene or tetrahydrofuran), followed by spin coating on a silicon wafer and drying *in vacuo* at room temperature overnight (>12 h).

Synthesis of polymers

Synthesis of HBP_a-1 by polyaddition of TGOPM with bisphenol A. A typical procedure for the polyaddition of TGOPM and phenol derivatives was as follows: a mixture of TGOPM (92 mg, 0.2 mmol), bisphenol A (68 mg, 0.3 mmol) and TBAB (9.7 mg, 5 mol%) in *o*-dichlorobenzene (0.6 ml) was stirred at 100 °C for 2 h under inert atmosphere. The reaction mixture was poured into hexane to precipitate the polymer. The resulting polymer was precipitated twice from tetrahydrofuran to hexane and water. The precipitate was collected and dried under vacuum for 24 h. The yield of corresponding polymer was 0.12 g (76%). *M_n*=2.0×10³, *M_w*/*M_n*=2.2. IR (cm⁻¹): 3401 (ν_{OH}), 1608, 1508 (ν_{C=C} aromatic), 1299, 1041 (ν_{C-O-C} ether). ¹H NMR (600 MHz, DMSO-*d*₆, tetramethylsilane (TMS)): δ=1.54 (s, 6.0 H, CH₃), 2.65–2.70 (m, 0.9 H, epoxy-CH₂), 2.79–2.85 (m, 0.9 H, epoxy-CH₂), 3.27–3.32 (m, 1.0 H, epoxy-CH-), 3.75–3.81 (m, 1.0 H, -CH₂-epoxy), 3.92–4.04 (m, 5.2 H, -CH₂-CH-), 4.14–4.22 (m, 1.3 H, CH-OH), 4.22–4.30 (m, 0.9 H, -CH₂-epoxy), 5.31–5.37 (m, 1.3 H, CH-OH), 5.38–5.46 (m, 0.7 H, (Ph)₃CH), 6.62–7.12 (m, 16.8 H, aromatic H), 9.11–9.18 (m, 0.7 H, Ph-OH).

Synthesis of HBP_b-1 by polyaddition of TGOPM with 4,4'-biphenol. Yield=91%. *M_n*=1.6. × 10³, *M_w*/*M_n*=1.7. IR (cm⁻¹): 3378 (ν_{OH}), 1608, 1501 (ν_{C=C} aromatic), 1290, 1045 (ν_{C-O-C} ether). ¹H NMR (600 MHz, DMSO-*d*₆, TMS): δ=2.57–2.65 (m, 1.2 H, epoxy-CH₂), 2.71–2.77 (m, 1.1 H, epoxy-CH₂), 3.18–3.25 (m, 1.2 H, epoxy-CH-), 3.64–3.75 (m, 1.5 H, -CH₂-epoxy), 3.79–4.12 (m, 10.2 H, -CH₂-CH-CH₂-), 4.15–4.26 (m, 1.3 H, -CH₂-epoxy), 5.34 (br, 3.0 H, (Ph)₃CH, OH), 6.71–7.50 (m, 23.0 H, aromatic H), 8.53–9.82 (br, 0.5 H, Ph-OH).

Synthesis of HBP_c (HBP_c-EPOX) by polyaddition of TGOPM with BFHPB. In the case of TGOPM/BFHPB=2:3 (mmol/mmol) (run 3 in Table 3): Yield=60%. *M_n*=5.3×10³, *M_w*/*M_n*=2.4. IR (cm⁻¹): 3393 (ν_{OH}), 1609, 1584,

Table 1 Polyaddition of TGOPM (B₃) with BPA (M₁) or BPAF (M₂)^a

Polymer	Feed ratio M ₁ /M ₂ /B ₃	Yield ^b (%)	<i>M_n</i> ^c (×10 ³)	<i>M_w</i> / <i>M_n</i> ^c	<i>T_g</i> ^d (°C)	<i>n_D</i> ^e
HBP _a -1	3/0/2	76	2.0	2.2	67	1.608
HBP _a -2	2/1/2	83	2.4	4.2	78	1.592
HBP _a -3	1/2/2	73	3.2	4.0	94	1.572
HBP _a -4	0/3/2	88	3.8	4.8	100	1.567

Abbreviations: BPA, bisphenol A; BPAF, bisphenol AF; TBAB, tetrabutylammonium bromide; TGOPM, 1,1',1''-tris(4-glycidyoxyphenyl)methane.

^aConditions: tris(epoxide) (B₃, 0.2 mmol), diol (M₁, M₂, 0.3 mmol), TBAB (5.0 mol%) and *o*-dichlorobenzene (0.6 ml) at 100 °C for 2 h.

^b*n*-Hexane insoluble parts.

^cEstimated by size-exclusion chromatography (eluent: *N,N*-dimethyl formamide) based on polystyrene standards.

^dDetermined by differential scanning calorimeter at heating rate 10 °C–min⁻¹ under N₂.

^eAverage value of refractive index determined by ellipsometer with 632.8 nm laser ray.

Scheme 1 Synthesis of hyperbranched polymers (HBPs). BFHPB, 1,4-bis(hexafluoroisopropyl)benzene; BP, 4,4'-biphenol; BPA, bisphenol A; OFBP, octafluoro-4,4'-biphenol; TBAB, tetrabutylammonium bromide; TGOPM, 1,1',1''-tris(4-glycidyoxyphenyl)methane.

1509, ($\nu_{\text{C}=\text{C}}$ aromatic), 1298, 1049 ($\nu_{\text{C}-\text{O}-\text{C}}$ ether), 1222, 1198 ($\nu_{\text{C}-\text{F}}$). ^1H NMR (600 MHz, CDCl_3 , TMS): δ =2.67–2.76 (m, 0.8 H, epoxy- CH_2), 2.81–2.92 (m, 0.7 H, epoxy- CH_2), 3.28–3.36 (m, 0.8 H, epoxy- CH_2), 3.48–4.37 (m, 12.8 H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2$ -epoxy), 5.39 (m, 2.1 H, $(\text{Ph})_3\text{CH}$, OH), 6.61–7.08 (m, 12.0 H, aromatic H), 7.54–7.81 (m, 5.3 H, aromatic H). T_g =92 °C. $T_d^{5\%}$ =377 °C.

Introduction of photo-functional group

Synthesis of HBP_c-OX. A typical procedure for the introduction of photo-functional group was as follows: a mixture of HBP_c-EPOX (terminal epoxy content >99%; 200 mg), 3-carboxy-3-ethyloxethane (260 mg, 2.0 mmol) and TBAB (15 mg, 46 μmol , 2.25 mol%) in *N*-methyl-2-pyrrolidone (2.0 ml) was stirred at 60 °C for 36 h under inert atmosphere. The reaction mixture was poured into water/methanol (1:1) to precipitate the polymer. The resulting polymer was re-precipitated from tetrahydrofuran to hexane. The precipitate was collected and dried under vacuum for 24 h. The yield of HBP_c-OX was 0.14 g with degree of introduction=91%. IR (cm^{-1}): 3417 (ν_{OH}), 1734 ($\nu_{\text{C}=\text{O}}$ ester), 1608, 1584, 1509, ($\nu_{\text{C}=\text{C}}$ aromatic), 1222, 1198 ($\nu_{\text{C}-\text{F}}$), 977 ($\nu_{\text{C}-\text{O}-\text{C}}$ cyclic ether). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, TMS): δ =0.70–0.80 (m, 3.0 H, oxetane- CH_2CH_3), 1.85–1.96 (m, 1.8 H, CH_2CH_3), 3.50–4.45 (m, 15.8 H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 4.65–4.73 (m, 1.9 H, oxetane- CH_2), 5.35–5.42 (m, 1.8 H, OH), 5.50–5.60 (m, 1.8 H, oxetane- CH_2), 6.75–7.00 (m, 12.7 H, aromatic H), 7.75–7.78 (m, 3.3 H, aromatic H).

Synthesis of HBP_c-MA. HBP_c-methacrylic acid (MA) was also prepared by the reaction of HBP_c-EPOX with MA. The yield of HBP_c-MA was 0.22 g with D I=91%. IR (cm^{-1}): 3432 (ν_{OH}), 1719 ($\nu_{\text{C}=\text{O}}$ ester), 1638 ($\nu_{\text{C}=\text{C}}$ allyl), 1609, 1586, 1509, ($\nu_{\text{C}=\text{C}}$ aromatic), 1222, 1198 ($\nu_{\text{C}-\text{F}}$). ^1H NMR (600 MHz, $\text{DMSO}-d_6$, TMS): δ =1.79–2.02 (m, 3.0 H, CH_3), 3.55–4.38 (m, 10.5 H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 5.33–5.52 (m, 1.6 H, $(\text{Ph})_3\text{CH}$, OH), 5.63–5.72 (m, 1.0 H, OH), 5.52–5.61 (m, 0.9 H, $-\text{C}=\text{CH}_2$), 6.00–6.13 (m, 0.9 H, $-\text{C}=\text{CH}_2$), 6.71–7.21 (m, 8.6 H, aromatic H), 7.74–7.96 (m, 1.5 H, aromatic H).

Table 2 Polyaddition of TGOPM (B_3) with BP (M_3) or OFBP (M_4)^a

Polymer	Feed ratio		M_n^c ($\times 10^3$)	M_w/M_n^c	T_g^d (°C)	n_D^e
	$\text{M}_3/\text{M}_4/\text{B}_3$	Yield ^b (%)				
HBP _b -1	3/0/2	91	1.6	1.7	71	1.634
HBP _b -2	2/1/2	84	2.4	3.9	85	1.609
HBP _b -3	1/2/2	85	3.9	5.8	92	1.585
HBP _b -4	0/3/2	81	3.0	2.8	93	1.572

Abbreviations: BP, 4,4-biphenol; OFBP, octafluoro-4,4'-biphenol; TBAB, tetrabutylammonium bromide; TGOPM, 1,1',1''-tris(4-glycidyloxyphenyl)methane.

^aConditions: tris(epoxide) (B_3 , 0.2 mmol), diol (M_3 , M_4 , 0.3 mmol), TBAB (5.0 mol%) and *o*-dichlorobenzene (0.6 ml) at 100 °C for 2 h.

^b*n*-Hexane insoluble parts.

^cEstimated by size-exclusion chromatography (eluent: *N,N*-dimethyl formamide) based on polystyrene standards.

^dDetermined by differential scanning calorimeter at heating rate 10 °C min⁻¹ under N_2 .

^eAverage value of refractive index determined by ellipsometer with 632.8 nm laser ray.

Photoinitiated polymerization

The photoinitiated polymerization of HBP_c-EPOX, HBP_c-OX and HBP_c-MA was performed in the film states, which were prepared with SP-150 (10 wt%) for HBP_c-EPOX and HBP_c-OX and with Irgacure907 (3 wt%) for HBP_c-MA. The reaction was followed by real-time IR spectroscopy under UV irradiation with a 250 W high-pressure mercury lamp (6 mW cm⁻² at 254 nm) for 15 min.

RESULTS AND DISCUSSION

Synthesis and chemical modification of HBPs

Polyadditions of TGOPM (0.2 mmol) and bisphenol derivatives (0.3 mmol) were conducted at 100 °C in the presence of quaternary onium salts (TBAB) as a catalyst. Using the bisphenol A and bisphenol AF (BPAF) with different feed ratios, the corresponding HBPs (HBP_a-1 ~ HBP_a-4) were obtained with M_n =2.0–3.8 $\times 10^3$ and M_w/M_n =2.2–4.8 in 70–80% yield (Table 1 and Scheme 1).

The structure of the synthesized polymers (HBP_a-1 ~ HBP_a-4) was confirmed by ^1H NMR and IR spectroscopy. The ^1H NMR spectrum showed new signals around 3.92–4.04, 4.14–4.22 and 5.31–5.37 p.p.m., which were assignable to the methylene, methane and hydroxy groups of the obtained polymers by the ring opening of oxirane moieties. Regarding the IR spectrum, the signal intensity of cyclic ether ($\nu_{\text{C}-\text{O}-\text{C}}$ =914 cm⁻¹) decreased, and characteristic new absorption was present that could be assigned to alcohol ($\nu_{\text{O}-\text{H}}$ ~ 3400 cm⁻¹).

The other HBPs such as HBP_b-1 ~ HBP_b-4 and HBP_c were prepared by the polyaddition of TGOPM and biphenyl derivatives (4,4-biphenol and octafluoro-4,4'-biphenol) or BFHPB. The results are summarized in Tables 2 and 3. In the case of HBP_c, the polymer with the different amount of terminal epoxy was prepared by changing the feed ratio of BFHPB/TGOPM. As the feed ratio of BFHPB/TGOPM was 1.5 (run 3 in Table 3), HBP_c with relatively high M_n (5.3 $\times 10^3$) and 63% terminal epoxy contents was obtained. When the feed ratio of BFHPB/TGOPM decreased to 0.5 (run 1 in Table 3), the corresponding HBP_c had a significant amount of glycidyl groups (>99%) on the terminal that was calculated from ^1H NMR. The terminal functional glycidyl ether and phenol groups were controllable by changing the feed ratio of BFHPB/TGOPM. The thermal properties of these polymers were analyzed by DSC and TGA; the results are summarized in tables. Glass-transition temperatures (T_g) of the polymers were in the range of 60–100 °C. In all cases, higher T_g was observed for increasing fluorine contents and for the corresponding linear polymers. It was also found that HBPs showed lower T_g than the corresponding linear polymers.

Chemical modification of HBP_c-EPOX (run 1 in Table 3) for the synthesis of the photo-curable and refractive index change material

Table 3 Effect of feed ratio on polyaddition of TGOPM (B_3) with BFHPB (M_5)^a

Run	BFHPB (mmol)	Time (min)	Yield ^b (%)	M_n^c ($\times 10^3$)	M_w/M_n^c	Terminal epoxy content (%) ^d	F content ^d	n_D^e
1	0.2	300	69	1.9	4.3	>99	19	1.531
2	0.4	180	82	3.9	4.8	74	27	—
3	0.6	130	63	5.3	2.4	63	30	1.511
4	0.9	200	55	7.7	3.0	31	34	—
5	1.2	300	85	6.7	2.2	11	36	1.500
6	1.5	300	41	5.2	1.7	7	37	—

Abbreviations: BFHPB, 1,4-bis(hexafluorohydroxyisopropyl)benzene; TBAB, tetrabutylammonium bromide; TGOPM, 1,1',1''-tris(4-glycidyloxyphenyl)methane.

^aConditions: tris(epoxide) (B_3 , 0.4 mmol), diol (M_5 , 0.2, 0.4, 0.6, 0.9, 1.2, 1.5), TBAB (5.0 mol%), and *o*-dichlorobenzene (1.2 ml) at 100 °C.

^b*n*-hexane insoluble parts.

^cEstimated by size-exclusion chromatography (eluent: *N,N*-dimethyl formamide) based on polystyrene standards.

^dCalculated by ^1H nuclear magnetic resonance.

^eAverage value of refractive index determined by ellipsometer with 632.8 nm laser ray.

Scheme 2 Chemical modification and photoinitiated polymerization. CEO, 3-carboxy-3-ethyloxethane; HBP, hyperbranched polymer; MA, methacrylic acid; NMP, *N*-methyl-2-pyrrolidone; TBAB, tetrabutylammonium bromide.

Figure 1 Relationship between the refractive index and fluorine content of hyperbranched polymers.

was examined. Addition reactions of HBP_c-EPOX with 3-carboxy-3-ethyloxethane and methacrylic acid (MA) were carried out in the presence of TBAB in *N*-methyl-2-pyrrolidone at 60 °C for 24–48 h. The reaction progressed efficiently, and in the IR spectra of these polymers, a new characteristic absorption peak appeared at 1734 ($\nu_{\text{C=O}}$) for carbonyl groups, and at 1719 ($\nu_{\text{C=O}}$) and 1638 ($\nu_{\text{C=C}}$, allyl) for methacryloyl groups. The degrees of introduction of oxetanyl and methacryloyl groups estimated from ¹H NMR for both were 91% (Scheme 2).

Optical properties

A tetrahydrofuran solution of the polymer was spin-coated onto a silicon wafer and dried *in vacuo* at room temperature over 12 h to prepare a thin film with a thickness of about 0.1 μm . The refractive indices of polymer films were measured by ellipsometry. A linear relationship was observed between the refractive indices (n_D) and fluorine contents of the polymers HBP_a-1~HBP_a-4 and HBP_b-1~HBP_b-4 (Tables 1 and 2, and Figure 1). The slopes of the refractive index against fluorine content were similar in both HBPs and corresponding LPs; however, the slope of HBP_b (biphenyl structure, -2.64×10^{-3}) was larger than HBP_a (bisphenol structure,

Table 4 Refractive-index change of photo-functional HBPs before and after photoirradiation

Polymer	Conversion ^a (%)	Refractive index ^b		Δn_D^b
		Before	After	
HBP _c -EPOX	64	1.558	1.575	+0.017
HBP _c -OX	24	1.549	1.553	+0.004
HBP _c -MA	92	1.555	1.558	+0.003

^aCalculated from infrared spectrum after 15 min irradiation.

^bAverage value of refractive-index by the ellipsometer using 632.8 nm ray.

-2.40×10^{-3}). This result might be due to the fluorine atom that is attached directly to the aromatic ring. The n_D of HBP_a-1 and HBP_b-1, which have no fluorine in their polymer structures, was 1.608 and 1.634, respectively. Furthermore, the n_D values of corresponding LP_a and LP_b were 1.611 and 1.645, respectively. HBPs displayed a lower n_D value than did LPs. This behavior supports the fact that HBPs have low density because of their three dimensional globular structure with a many branched arm. Notably, the difference of HBP_a-1 (LP_a-1) and HBP_b-1 (LP_b-1) could explain an A₂ monomer structure because the bended bisphenol skeleton produced by sp³-hybridized carbon produces lower n_D as compared with the relatively flat biphenyl structure.

Photoinitiated polymerization of HBP_c-EPOX, HBP_c-OX and HBP_c-MA and its optical properties

The photoinitiated polymerization of HBP_c-EPOX, HBP_c-OX and HBP_c-MA was performed in the film states. The conversion of glycidyl, oxetanyl and methacryloyl groups was calculated from the decrease in the absorbance at 913 ($\nu_{\text{C-O-C}}$), 977 ($\nu_{\text{C-O-C}}$) and 1638 cm^{-1} ($\nu_{\text{C=C}}$), respectively (Table 4). The conversion of HBP_c-MA that was reached was quite high (92 %) because the photoinitiated radical polymerization proceeded smoothly. In contrast, in the case of photoinitiated cationic polymerization, the conversion of HBP_c-EPOX and HBP_c-OX was 64 and 24%, respectively. The higher conversion of glycidyl versus oxetanyl could be explained by the high reactivity of the three-member ring glycidyl due to its highly strained structure. Furthermore, the reactivity of cationic polymerization of terminal oxetanyl groups was lowered by both hydroxyl and ester groups. A comparison of the refractive index change (Δn) of the photo-functional HBPs is summarized in Table 4.

After the photoinitiated cationic polymerization of HBP_c-EPOX and HBP_c-OX, increased refractive index changes (Δn_D 's) were observed because of the formation of crosslinked film with ca. 3% shrinkage of the film thickness. The Δn_D 's are dependent on the change of molar refraction (R) and density (ρ) before and after photoirradiation.¹³ The difference of Δn_D of HBP_c-EPOX and HBP_c-OX could be explained by the size of cyclic ether and the efficiency of photo-curing. The high reactivity and compact structure of glycidyl lead to higher crosslinking density, and as a consequence, HBP_c-EPOX shows larger Δn_D than HBP_c-OX. Notably, in the case of HBP_c-MA, higher conversion of methacryloyl was observed, but Δn_D was not significantly increased.

CONCLUSIONS

In this study, we synthesized hyperbranched fluorinated polymers using a simple polyaddition reaction of phenol derivatives and TGOPM as A₂ and B₃ monomers, respectively. The fluorine content of the HBPs could be controlled by changing the feed ratio and the refractive index values of the HBPs, and it tended to decrease with increasing fluorine content. The n_D was also affected by the monomer and polymer structures. Cured materials tended to increase n_D because of the increase in the crosslinking density of the film.

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