Synthesis and Photochemical Properties of Novel Hyperbranched Polymers

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ABSTRACT

Dendritic polymers have been of great interest in the field of polymer chemistry, because these polymers have excellent physical and chemical properties such as low viscosity, good solubility, and many terminal functional groups. Among them, hyperbranched polymers have been of great interest as new high performance photo-curable materials. In this article, we examine the synthesis and photochemical reaction of certain hyperbranched polymers such as hyperbranched epoxy-methacrylates, hyperbranched oxetane-methacrylates, and hyperbranched polyurethane-methacrylates, and some physical properties of the resulting cured films, and it was found that these polymers have some new characteristic properties.

Keywords: Hyperbranched polymers. Epoxy-methacrylates. Oxetane-methacrylates. Polyuretane-metharylates. Synthesis. Photo-chemical reaction. New characteristic properties.

1. INTRODUCTION

Ultraviolet light (UV) processing technologies have been widely used in following industries[1,2] as from surface processing of paper, plastics and metal to imaging formation, fabrication and molding, printing inks, and adhesives. Recently, this curing system has also been applied to electronics and information technology fields[3] such as liquid crystal displays and plasma panels, printed circuit boards, adhesives or surface processing for CD and DVD production, surface processing for optical-fibers, processing of optical-devices, processing of nano-imprints, processing of micro-machines, and holographic memory. In these UV curing systems, methacrylate- or acrylate-polymers such as methacrylated epoxy resins [epoxy-methacrylate]s, poly(urethane)-methacrylates, and poly(ester)-methacrylates are mainly used due to their high photochemical reactivities and excellent physical properties. However, these methacrylate polymers have relatively high viscosity, because these polymers were composed from linear long chains.

Dendritic polymers have been of great interest due to their unique properties such as low viscosity[4,5], good solubility[6], and many terminal reactive groups. Dendritic polymers can be categorized two types such as dendrimers with the uniformed structures[7,8] and hyperbranched polymers with randomly branched structure[9]. The former compounds are synthesized by multi-step reactions with purification procedures, and the latter materials are synthesized by one-pot process in general.

More than 10 years ago, Shi and Ranby[10] reported the first synthesis of dendritic polyesters with many terminal methacryloyl groups by multi-step reactions and purification procedures, and they found that the synthesized photo-curable dendrimers have high glass transition temperatures and other interesting physical properties.

Recently, hyperbranched polymers (HBPs) have been of great interest due to their convenient synthetic process. That is, there are many synthetic methods of HBPs such chain growth polymerizations as vinyl polymerization[11] and ring-opening polymerization[12] accompanying suitable chain transfer reaction. HBPs can be also prepared by step-growth polymerizations such as polycondensations and polyadditions, in which there are two differential methods; one is the self-polycondensation or -polyaddition reactions of AB_2 monomers[13,14]. However, these AB_2 monomers are not always commercially available. The other is the polycondensation or polyaddition reactions[15,16] of A_2-type monomers with B_3-type monomers. This method is practically advantageous in industrial applications, because numerous numbers of monomers are commercially available for the synthesis of HBPs.

From these backgrounds, we designed[17-19] new high-performance photo-curable hyperbranched polymers such as epoxy-methacrylates (HBPEMA)s with many terminal methacryloyl groups by the polyaddition of bisphenol A di(glycidyl)ether (BPAGE) with 1,3,5-benzenetricarboxylic acid (TMA) and methacrylic acid (MAA). We also performed the synthesis of the hyperbranched oxetane-methacrylates (HBPOMA)s with pendant primary hydroxyl groups and terminal methacryloyl groups by the polyaddition of bis(oxetane)s such as 1,4-bis[(3-ethyl-3-oxetanyl)methoxymethyl]benzene (BEOB) and 4,4'-bis[(3-ethyl-3-oxetanyl)-methoxy]biphenyl (4,4'-BEOBP) with TMA and MAA, and the synthesis of the hyperbranched polyurethane-methacrylates (HBPUMA)s with terminal methacryloyl groups by the polyaddition of dicyclohexylmethane 4,4'-diisocyanate (CMDI) with trimethylol propane (TMP) and 2-(methacryloyloxy)ethyl isocyanate (MOI), respectively. Furthermore, we examined the photochemical reaction of the synthesized HBPs and some physical properties of the resulting cured materials.

2. EXPERIMENTAL

Typical Procedure for the Synthesis of Hyperbranched Epoxy-methacrylate (HBPEMA)

The mixture of BPAGE (1.021 g, 6 mmol as epoxy group), TMA (0.210 g, 3 mmol as carboxyl group), MAA (0.258 g, 3 mmol as carboxyl group), tetrabutylammonium chloride (TBAC) (0.042 g) as a catalyst, and small amount of hydroquinone (HQ) as an inhibitor in dimethyl form amide (DMF) (4 mL) was stirred at 80 ^{o}C for 18 h. The resulting product was poured into a large amount of water to precipitate the polymer. The resulting polymer was reprecipitated twice from tetrahedrofuran (THF) into diethyl ether, and dried *in vacuo* at room temperature for 24 h. The yield of HBPEMA was 1.07 g (72 %). The M_n of HBPEMA estimated by size exclusion chromatography (SEC) was 5900 (M_w/M_n = 3.62). The ratio of methacryloyl groups in the end of polymer chain (RM) was

98 %, which was calculated by the intensity ratio of ^{1}H NMR. IR (film, cm^{-1}): 3406 (νO-H), 1725 (νC=O, ester), 1637 (νC=C, methacryloyl). ^{1}H NMR (500 MHz, DMSO-d_6) : 1.24 - 1.68 (m, 6.0 H, $-CH_3$), 1.80 - 1.90 (m, 1.2 H, $C(C\underline{H}_3)=CH_2$), 3.14 - 4.79 (m, 10.0 H, $-C\underline{H}_2-C\underline{H}(OH)-C\underline{H}_2-O-$), 5.63 - 6.20 (m, 2.8 H, $C(CH_3)=C\underline{H}_2$ and $-O\underline{H}$), 6.51 - 7.30 (m, 8.0 H, aromatic H in BPAGE unit), 8.16 - 8.90 (m, 1.6 H, aromatic H in TMA unit)

Typical Procedure for the Synthesis of HBPEMA-COOH

The mixture of HBPEMA (12.0 g, 50 mmol of hydroxyl group, M_n = 5900, M_w/M_n = 3.62), *cis*-1,2,3,6-tetrahydrophtalic anhydride (THPA) (3.81 g, 25 mmol), triphenylphosphine (TPP) (0.20 g, 1.5 mol%) as a catalyst, and small amount of HQ in 1,4-dioxane (16 mL) was stirred at 80 °C for 5 h. The resulting mixture was poured into a large amount of water to precipitate the polymer. The resulting polymer (HBPEMA-COOH) was reprecipitated twice from THF into diethyl ether, and dried *in vacuo* at room temperature for 24 h. The yield of HBPEMA-COOH was 14.2 g (90 %). IR (film, cm^{-1}): 3402 (νO-H), 2500 - 3500 (νO-H carboxylic acid) 1732 (νC=O of ester), 1637 (νC=C of methacryloyl). ^{1}H NMR (500 MHz, DMSO-d_6) : 1.30 - 1.68 (m, 6.0 H, $-CH_3$), 1.77 - 1.92 (m, 1.2 H, $C(C\underline{H}_3)=CH_2$), 2.00 - 2.46 (m, 4.0 H, $CH-C\underline{H}_2-CH=$), 2.70 - 3.06 (m, 2.0 H, $O-C-O-C\underline{H}-CH_2$), 3.50 - 4.77 (m, 10.0 H, $-C\underline{H}_2-C\underline{H}(OH)-C\underline{H}_2-O-$), 4.98 - 6.27 (m, 3.8 H, $-CH_2-C\underline{H}=$, $C(CH_3)=C\underline{H}_2$, $-O\underline{H}$), 6.50 - 7.31 (m, 8.0 H, aromatic H in BPAGE unit), 8.51 - 8.92 (m, 1.6 H, aromatic H in TMA unit).

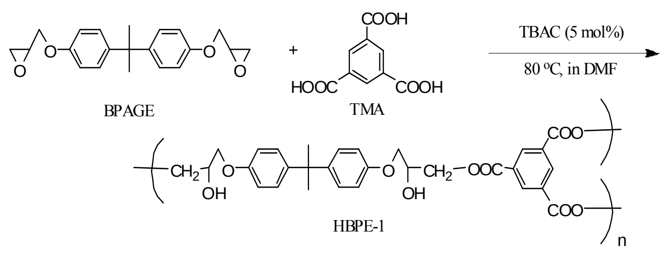
Typical Procedure for the Photo-initiated Radical Polymerization

HBPEMA (0.20 g) and Irgacure 907® (0.006 g) were dissolved in THF. The resulting solution was cast on a KBr plate and dried to make film on the plate. The film, containing a photo-initiator on the plate, was irradiated with a 250-W high-pressure mercury lamp (HOYA-SCHOTT Co.) without a filter under air. The intensity of the light was kept at 8 mW/cm^2 (at 254 nm). The rate of decrease in the C=C stretching near 1637 cm^{-1} due to methacryloyl group in HBPEMA was measured by RT-IR.

3. RESULTS AND DISCUSSION

Synthesis of the Hyperbranched Epoxy-methacrylate (HBPEMA)

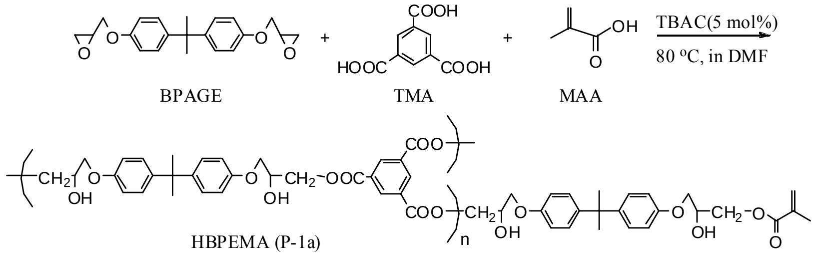
The polyaddition of BPAGE with TMA was examined with 5 mol% of TBAC as a catalyst in DMF at 80 °C for various reaction times (Scheme 1). The yields of the resulting polymers increased until 6 h. At this point, a soluble polymer with M_n = 8800, M_w / M_n = 3.54, which has not any insoluble gel products, was obtained in 84 % yield. However, for longer reaction time than 6 h, the obtained products were partially insoluble in organic solvents. That is, the suitable reaction time to obtain soluble polymer on this polyaddition is 6 h under these conditions. The structure of the obtained products was confirmed by IR and ^{1}H NMR spectroscopy.



Scheme 1

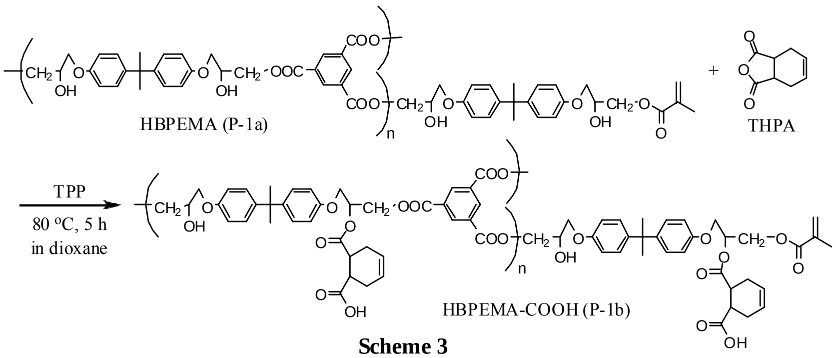
The IR spectrum of the polyester with M_n = 8800 showed characteristic absorption peaks at 3404, 1730, and 913 cm^{-1} assignable to the -O-H, C=O (ester), and C-O-C (cyclic ether due to epoxide), respectively. The ^{1}H NMR spectrum of this product showed assignable proton signals due to methylene protons of epoxide moieties and hydroxyl groups at 2.62 - 2.86 ppm and 5.10 - 5.91 ppm, respectively. This means that the obtained hyperbranched poly(ester) (**HBPE-1**) with M_n = 8800 had small amount of the epoxide groups in the end of polymer chain.

Based on the above results of the synthesis of **HBPE-1**, we also examined the polyaddition of BPAGE with TMA and MAA under similar reaction conditions (Scheme 2). The polyaddition proceeded smoothly, and corresponding soluble hyperbranched epoxy-methacrylates with M_ns = 5100 - 7900 were obtained in good yields.



Scheme 2

In feed molar ratio of BPAGE / TMA / MAA = 6 / 3 / 3, the polymer containing of 98 % of methacryloyl group was obtained in 72 % yield. When the feed ratio of TMA increased, small insoluble gel products were obtained, and the ratio of terminal methacryloyl groups in the polyester decreased. The structure of the resulting polymer was confirmed by IR and ^{1}H NMR spectroscopy. Its IR spectrum showed characteristic absorption peaks at 3406, 1725, and 1637 cm^{-1} assignable to the -O-H, C=O (ester), and C=C (methacryloyl), respectively. The ^{1}H NMR spectrum of this polymer showed proton signals due to methacrylate groups of the ends of the polymer chains at 5.84 - 6.20 ppm. This result shows that hyperbranched epoxy-methacrylate (HBPEMA) with terminal methacryloyl groups at the end of polymer chain was successfully synthesized.



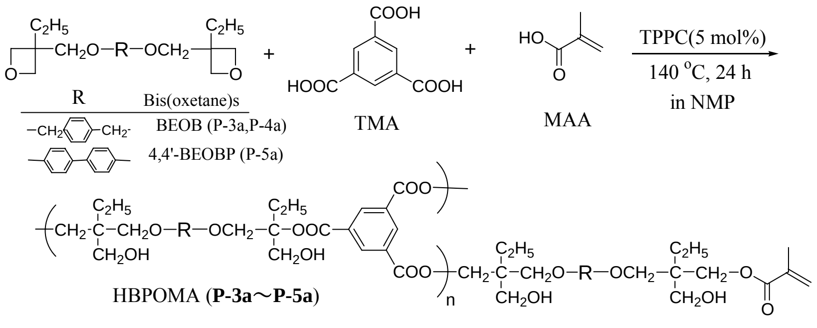
Scheme 3

Since alkali aqueous solutions have been practically used as the developer for negative type photo-resists, the introduction of the carboxyl groups into the HBPEMA was examined to induce alkaline-develop ability by the addition reaction of HBPEMA (**P-1a**) with 0.5 equiv of THPA using TPP as a catalyst in 1,4-dioxane at 80 °C for 5 h, and corresponding HBPEMA-COOH (**P-1b**) was obtained. The structure of HBPEMA-COOH was confirmed by ^{1}H NMR spectroscopy, and it was found that the degree of introduction of carboxyl groups was calculated to be 49% (Scheme 3).

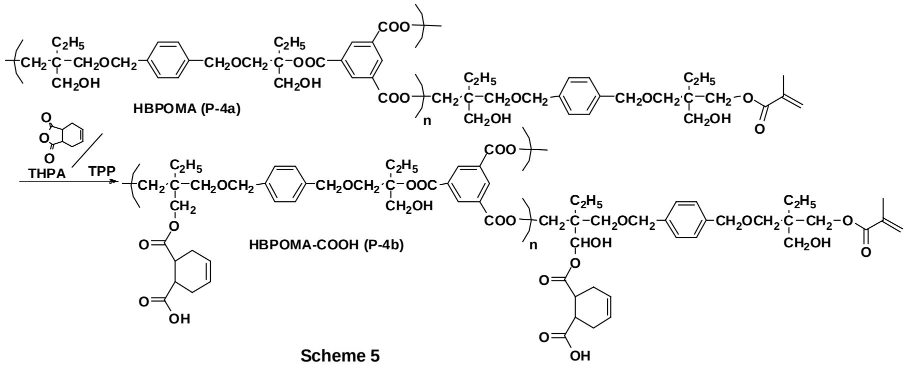
The solubilities of the resulting hyperbranched polymers (HBPEMA and HBPEMA-COOH) and linear polymers (LPEMA and LPEMA-COOH) were examined. All the obtained polymers were soluble in common organic solvents such as 1,4-dioxane, methanol, THF, and DMF, but were insoluble in aromatic solvents such as anisole and chlorobenzen. Furthermore, HBPEMA (**P-1a**) and LPEMA (**P-2a**) were insoluble in a 10 wt% TMAH aqueous solution; however both HBPEMA-COOH (**P-1b**) and LPEMA-COOH (**P-2b**) were soluble in 10 wt% TMAH aqueous solution. This means that solubility of polymer reasonably changed by the introduction of carboxyl groups into the polymer side chain.

Synthesis of the Hyperbranched Oxetane-methacrylate

Based the above result for the synthesis of **HBPE-1**, the polyaddition of BEOB and TMA with the feed ratio of 3/1 in feed was examined at 140 °C for 24 h, and soluble polymer with $M_n = 4000$ ($M_w/M_n = 2.90$) was obtained in 68 % yield. The structure of the polymer was confirmed by IR and ^{1}H NMR spectroscopy, and it was found that the obtained polymer was **HBPE-2** with pendant primary hydroxyl groups in the side chain and some oxetanyl groups at the ends of polymer chains. This result shows that the control of the reaction time and feed ratios of these Polyaddition is important factor to obtain the soluble products on the reaction of bis(oxetane) with TMA. Then, we examined the polyaddition of BEOB with TMA and MAA under the similar conditions. In feed ratio of BEOB/TMA/MAA=3/1/3, the hyperbranched oxetane-methacrylate, **P-3a** containing of 16% of methacryloyl groups was obtained in 58 % yield. In feed ratio of BEOB/TMA/MAA=3/1/9, the hyperbranched oxetane-methacrylate, **P-4a** containing of 54% of methacryloyl groups was obtained. This result also shows that the ratio of methacryloyl groups in oxetane-methacrylate (HBPOMA) increased with increase of the concentration of MAA in feed. HBPOMA, **P-5a** with rigid structure, pendant primary hydroxyl groups and terminal methacryloyl groups were synthesized by the polyaddition of 4,4'-BEOBP with TMA and MAA (feed ratio of BEOBP/TMA/MA=3/1/9) under the same conditions, and the structure of the resulting **P-5a** was also



Scheme 4



Scheme 5

confirmed by IR and ^{1}H NMR spectroscopy. These results showed that the hyperbranched oxetane-methacrylates (HBPOMA)s with pendant primary hydroxyl groups and terminal methacryloyl groups were synthesized by the one-pot method of the polyaddition of bis(oxetane)s with TMA and MAA (Scheme 4).

Furthermore, to compare the photochemical reactivity between the hyperbranched polymer and corresponding linear polymer, linear oxetane-methacrylate, LPOMA (**P-6a)** with M_n=3800, M_w/M_n=2.30 were prepared by the polyaddition of BEOB with TPA and MAA under the same reaction conditions.

The introduction of the carboxyl groups into HBPOMA (**P-4a)** was performed. The reaction of **P-4a** (M_n=3600, M_w/M_n=2.01, RM=54 %) and 0.6 equiv. of THPA was carried out with TPP as a catalyst at 80 ^{o}C for 4 h, and the corresponding HBPOMA-COOH (**P-4b)** containing 55 % of the pendant carboxyl groups was obtained in 79 % yield (Scheme 5). The structure of **P-4b** was confirmed by ^{1}H NMR and IR spectroscopy.

The solubility of **P-4a** both containing pendant primary hydroxyl and terminal methacryloyl groups and **P-4b** both containing pendant carboxyl and terminal methacryloyl groups were examined. These polymers were soluble in 1,4-dioxane, chloroform, ethanol, methanol, THF, acetone, DMF, NMP, and DMSO, and were insoluble in diethyl ether, hexane, and toluene. **P-4a** was partly soluble in anisole and chlorobenzene; however, **P-4b** was insoluble in the same solvents. On the other hand, although **P-4b** with pendant carboxyl groups was soluble in 1.0 wt% of $NaHCO_3$ aqueous solution, 1.0 wt% of Na_2CO_3 aqueous solution, and 2.38 wt% of TMAH, **P-4a** was insoluble in the same aqueous solutions. These results suggested that the alkali-solubility of polymers was dramatically changed by the introduction of certain carboxyl groups into the polymer.

We examined 5 wt % loss temperatures ($T_d^{5\%}$) of **P-4a** and **P-4b**. $T_d^{5\%}$s of **P-4a** and **P-4b** were 268 and 258 ^{o}C, respectively. This result suggests that the weight-loss temperatures of **P-4a** with pendant hydroxyl groups were fallen by the introduction of the pendant carboxyl groups. That is, lower $T_d^{5\%}$ of **P-4b** was caused by the elimination of low molecular weight THPA from pendant ester linkage of the polymer.

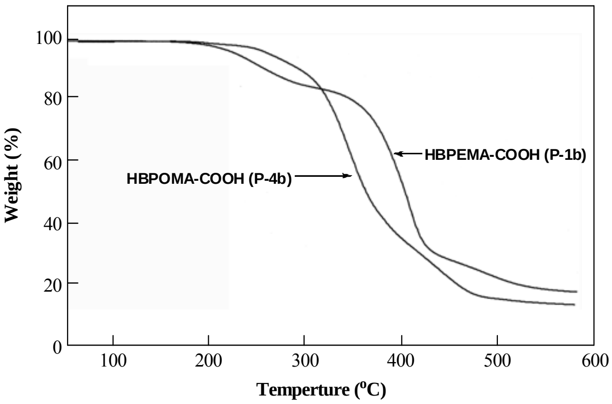
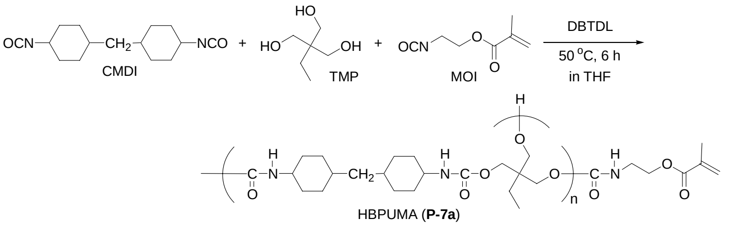


Figure 1. TGA profiles of polymers containing pendant carboxyl gropus.

We also compared the $T_d^{5\%}$ of HBPOMA-COOH, **P-4b** with that of HBPEMA-COOH, **P-1b**. As shown in Figure 1, the $T_d^{5\%}$s of **P-4b** and **P-1b** were 258 and 225 ^{o}C, respectively. That is, HBPOMA-COOH had better thermal stability than epoxy-methacrylate (HBPEMA-COOH) in the initial stage. These might come from differences of the ester linkage of pendant carboxyl moieties. That is, the pendant ester linkage composed from *sec*-alcohol unit in HBPEMA-COOH **(P-1b)** decomposed easily at lower temperature to remove THPA molecule than the ester linkage composed from *primary*-alcohol unit in **P-4b**.

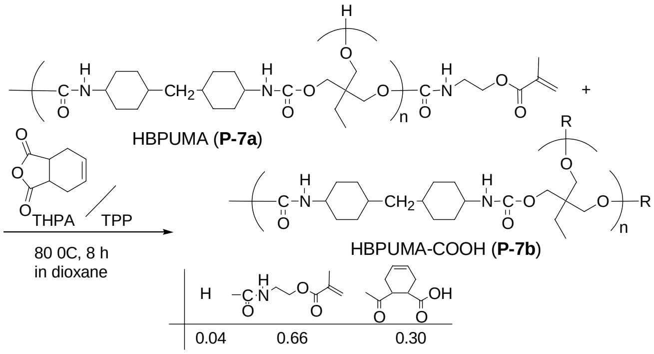
Synthesis of the Hyperbranched Poly(urethane)methacrylate (HBPUMA)

The polyaddition of CMDI with TMP and MOI was examined with 2 mol % DBTDL as a catalyst in THF at 50 °C for 6 h (Scheme 6). The polyaddition proceeded smoothly, and corresponding soluble hyperbranched poly(urethane)-methacrylate (HBPUMA) (**P-7a**) with M_n = 2900 was obtained in 93 % yield. The structure of the resulting polymer was confirmed by IR and ^{1}H NMR spectroscopy. The IR spectrum of this material showed characteristic absorption peaks at 3404, 1709, and 1637 cm^{-1} assignable to the -O-H, C=O (urethane) and C=C (methacryloyl), respectively. The ^{1}H NMR spectrum of this polymer also showed proton signals due to methacrylate groups of the ends of the polymer chains around at 5.62 - 6.32 ppm and hydroxyl groups of ends of polymer chains around at 4.25 – 4.87 ppm. This result showed that HBPUMA with terminal methacryloyl groups and hydroxyl groups at the end of polymer chain was obtained.



Scheme 6

The introduction of the carboxyl groups into the HBPUMA containing partly terminal hydroxyl groups (**P-7a**) was carried out to achieve alkaline-developability (Scheme 7).



Scheme 7

The reaction of HBPUMA with THPA was performed using TPP as a catalyst in 1,4-dioxane at 80 °C for 8 h, and the corresponding HBPUMA-COOH (**P-7b**) was obtained in 90 % yield. The structure of the synthesized HBPUMA-COOH was confirmed by IR and ^{1}H NMR spectroscopy. The IR spectrum of this material showed characteristic absorption peaks around 2500 - 3500 cm^{-1} assignable to the -O-H (carboxylic Acid). The ^{1}H NMR spectrum of this polymer showed proton signals due to carboxylic acid groups of the ends of the polymer chains around 11.0 – 13.50 ppm. This result suggests that HBPUMA-COOH (**P-7b**) with terminal methacryloyl groups and the carboxylic acid groups in the polymer chain was obtained.

Photochemical Reaction of Resulting HBPS

The photo-initiated radical polymerization of HBPEMA film was performed using Irgacure 907® (3 wt %) as a photo-initiator upon UV irradiation with a 250-W high pressure mercury lamp (Intensity: 8.0 mW/cm^2 at 254 nm). The rate of conversion of the methacryloyl groups was confirmed from the decrease of the absorbance at 1637 cm^{-1} due to C=C bond in the film state by the real-time FT-IR spectra.

Figure 2 showed the relationships between the conversion of C=C bond (%) and irradiation time. This result showed that the reaction proceeded smoothly, and the conversions of HBPEMA

(*Mn*=5900), Ref-1 (prepared by the reaction of BPAGE with MAA), and LPEMA (**P-2a**) (*Mn*=6000, prepared by the reaction with BPGE, terephthalic acid (TPA), and MAA were 21, 28, and 16 % at 40 sec., respectively. However, HBPEMA showed the highest conversion at 240 sec. That is, the conversion of Ref-1 was the highest until 70 sec., because Ref-1 has the highest motility of methacryloyl groups.

This means that the motility of Ref-1 with low molecular weight is superior in the first step cross-linking reaction; however, HBPEMA arrived at the highest conversion after 70 seconds, because the motility of the polymer chain of HBPEMA was higher than Ref-1 on the last stage of the photo-crosslinking reaction. Furthermore, HBPEMA (**P-1a**) showed higher photo-reactivity than LPEMA (**P-2a**). This is because hyperbranched epoxy-methacrylate HBPEMA has many methacryloyl groups in the end of polymer chain.

Table I. Physical properties of the cured polymers.

Sample$^{a)}$	$T_g^{b)}$ (°C)	Crosslinking density$^{b)}$ (mol/m^3)	Tensile strength (MPa)	Elongation at break (%)	Δn (x 10^{-4})$^{c)}$
Cured HBPEMA	**83**	**1156**	**32.6**	**3.02**	**2.9**
Cured LPEMA	**94**	**213**	**16.2**	**2.89**	**4.2**

a) Cured films were obtained by exposure for 4 min followed by heating at 100 °C for 1 h.
b) Measured by DMS at heating rate of 4 °C/min under N_2.
c) Birefringence of drawn cured film was analyzed with a polarizing optical microscope

As summarized in Table 1, the *Tg* of the cured HBPEMA was slightly lower than the cured LPEMA. However, the cured hyperbranched polymer had higher cross-linking density, higher tensile strength, and higher elongation at break than the corresponding cured liner one. This means that the cured HBPEMA had strong mechanical property.

The optical property of the cured polymer was also examined. Interestingly enough, the cured HBPEMA showed relatively low birefringence, which is about half value of the cured LPEMA. This means that birefringence of the cured hyperbranched polymer film has been regulated by the cross-linking of terminal methacryloyl groups in the polymer chain of HBPEMA.

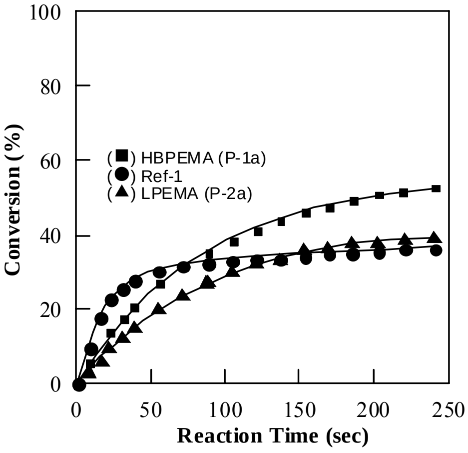


Figure 2. Time-conversion curve of the photo-initiated radical polymerization of HBPEMA, Ref-1 and LPEMA in the presence of photo-initiator.

The photo-initiated radical polymerization of **P-4a** (M_n=3600, M_w/M_n=2.01, RM=54%) was performed in the film state. As shown in Figure 3, the reaction proceeded rapidly, and the conversion reached to 88% after 10 min. Furthermore, the photo-irradiated polymer film became insoluble in any organic solvents. On the other hand, when the photochemical reaction of **P-6a** (M_n=3800, M_w/M_n=2.30) with linear structure was performed under the same irradiation conditions, the conversion was 76% at 10 min. Furthermore, it was observed that the rate of photochemical reaction of **P-4a** was strongly enhanced by the addition of a monomer HEMA under the same conditions, and the conversions of the mixture of **P-4a** (70 wt %), HEMA (27 wt %), and photo initiator (3 wt %) reached to 95 % after 10 min. These results showed that HBPOMA with terminal methacryloyl groups had higher photochemical reactivity than the corresponding linear oxetane-methacrylate (LPOMA, P-6a) with terminal methacryloyl groups, because the former had many photo-reactive groups in the end of polymer chain.

The photo-initiated radical polymerization of HBPUMA, HBPUMA-COOH, and the corresponding LPUMA (**P-8a**) was examined in the presence of 3 wt% of Irgacure 907® as a photo-initiator under UV irradiation with a 250-W high pressure mercury lamp (Intensity: 8.0 mW/cm^2 at 254 nm). The conversion of the methacryloyl groups was calculated from the decrease of the absorbance at 1637 cm^{-1} due to C=C bond in the film state by the real-time FT-IR spectra. The conversions of HBPUMA, HBPUMA-COOH, and LPUMA are 76, 72, and 42 % after 6 min., respectively. This means that HBPUMA (**P-7a**) and HBPUMA-COOH (**P-7b**) showed higher photochemical reactivity than the corresponding linear LPUMA (**P-8a**), because the formers had many photoreactive groups in the end of polymer chain. However, HBPUMA-COOH (**P-7b**) shows lower photochemical reactivity than HBPUMA (**P-7a**), because the motility of the polymer chain of HBPUMA-COOH was lower than HBPUMA due to introduction of the carboxyl group.

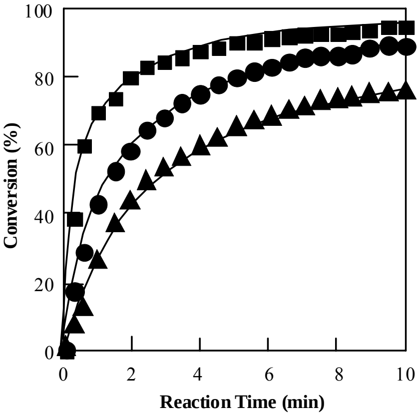


Figure 3. Time-conversion curve of the photo-initiated radical polymerization: (●) P-4a (97 wt%) and Irgacure907 (3 wt%); (■) P-4a (70 wt%), Irgacure907 (3 wt%) and HEMA (27 wt%); (▲) P-6a (97 wt%) and Irgacure907 (3 wt%).

4. CONCLUTION

From all results, it was concluded that high performance hyperbranched polymers such as HBPEMA, HBPOMA, and HBPUMA were synthesized, and photochemical reactivities and some physical properties were examined. Then, it was found that hyperbranched polymers have higher photochemical reactivity than the corresponding liner-type polymers. In addition, it was also found that HBPOMA-COOH with pendant carboxyl groups has higher thermal stability than HBPEMA-COOH with pendant carboxyl groups.

5. References

1) T. Nishikubo Ed., *Synthesis and Application of Photosensitive Polymers*, CMC. Tokyo. 1979.
2) Y. Tabata, Y. Takimoto, Y. Tominaga, H. Nakamoto, and T. Nishikubo Eds. *Ultraviolet and Electron Beam Curable Materials*, CMC. Tokyo. 1989.
3) Y. Tabata, T. Isobe, T. Otaka, M. Sato, M. Takayama, Y. Tominaga, and T. Nishikubo, Eds., *Technology & Application of UV/EB Curing*, CMC, Tokyo, 1997.
4) S. R. Turner, B. I. Voit, and T. H. Mourey, *Macromolecules*, **26**, 4617 (1993).

5) S. R. Turner, F. Walter, B. I. Voit, and T. H. Mourey, *Macromolecules*, **37**, 1611 (1994).
6) Y. H. Kim, and O. W. Webster, *Macromolecules*, **25**, 5561 (1992).
7) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, **17**, 117 (1985).
8) G. R. Newkome, Z. Yao, G. R. Baker, and V. K. Gupta, *J. Org. Chem..*, **50**, 2003 (1985).
9) Y. H. Kim, and O. W. Webster, *J. Am. Chem. Soc.*, **112**, 4592 (1990).
10) W-F. Shi and B. Ranby, *J. Appl. Polym. Sci.*, **59**, 1937, 1945, 1952 (1995).
11) K. Matyjaszewski, S. G. Gaynor, A. Kulfan, and M. Podwike, *Macromolecules*, **30**, 5192 (1997).
12) A. Sunder, R. Hanselmann, H. Frey, and R. Mulhaupt, *Macromolecules*, **32**, 4240 (1999).
13) M. Okazaki, I. Washio, Y. Shibasaki, and M. Ueda, *J. Am. Chem. Soc*. **125**, 8120 (2003).
14) R. Spindler, and J. M. J. Fréchet, *Macromolecules*, **26**, 4809 (1993).
15) J. Hao, M. Jikei, and M. Kakimoto, *Macromolecules* **36**, 3519 (2003).
16) S. Makita, H. Kudo, and T. Nishikubo, *J. Polym. Sci. Part A. Polym. Chem.*, **42**, 3697 (2004).
17) K. Maruyama, H. Kudo, and T. Nishikubo et al., *J. Polym. Sci. Part A. Polym. Chem.*, **43**, 4642 (2005).
18) T. Nishikubo, H. Kudo, and K. Maruyama et al., *Polym. J.,* **38**, 447 (2006).
19) K. Maruyama, H. Kudo, and T. Nishikubo, *Macromolecules*, **40**, 4895 (2007).