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Synthesis and Properties of Photo-Cross-Linkable Hyperbranched Poly(urethane)s Containing Both Terminal Methacryloyl Groups and Carboxyl Groups

Ken Maruyama, Hiroto Kudo, Takayuki Ikehara, and Tadatomi Nishikubo*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Isao Nishimura

Semiconductor Materials Laboratory, Semiconductor Materials Research Laboratories, JSR Corporation, 100, kawajiri-cho, Yokkaichi, Mie 510-8552, Japan

Atsushi Shishido and Tomiki Ikeda

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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ABSTRACT: The synthesis and photopolymerization of alkaline-developable hyperbranched polyurethane (HBPUMA-COOH) were examined. The reaction of dicyclohexylmethane 4,4′-diisocyanate (CMDI) and trimethylolpropane (TMP) in the presence of 2-methacryloyloxyethyl isocyanate (MOI) was carried out to give the soluble hyperbranched polyurethane (HBPUMA) with terminal methacryloyl groups in satisfactory yield. After that, HBPUMA-COOH was synthesized by the reaction of HBPUMA and *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA). The photoradical polymerization of HBPUMA-COOH was examined in the presence of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-2-one (Irgacure 907) as a photoinitiator in the film state upon UV irradiation to afford the corresponding cured film quantitatively. It was found that the tensile strength of the resulting cured film of HBPUMA-COOH was higher than those of the HBPUMA and linear one. The negative patterning property of HBPUMA-COOH also had 5 μm line and space pattern resolution by UV irradiation with 150 mJ/cm^2. Furthermore, it was cleared that the photocured HBPUMA and HBPUMA-COOH showed very low birefringence.

Introduction

UV curing systems have many great interest features from the viewpoints of high productivities, energy saving, and environmental protection and have been used mainly for coatings, adhesives, and printing inks for more than 35 years.[1,2] Recently, these systems were applicable to the electronic materials such as photoresist, solder mask, optical fiber, compact disc (CD), and digital versatile disc (DVD).[3] More recently, these systems were applied to the field of machine processing such as three-dimensional fabrication and micromachining fabrication due to excellent mechanical, electrorical, and chemical properties of their cured materials.

In these systems, (meth)acrylated epoxy resins, poly(urethane)s, poly(ester)s, and poly(ether)s have been used as UV curing materials due to their high photochemical reactivities. The structures of these polymers and oligomers were linear, and their solutions had higher viscosities. Among them, (meth)acrylated polyurethanes[1−4] have excellent frictional resistance and good balance between elasticity and strangeness.

Meanwhile, dendritic polymers such as dendrimers and hyperbranched polymers possess branched structure and have recently attracted a great deal of attention for their unique properties such as lower viscosity, fine solubility, and many reactive terminal groups compared with the corresponding linear ones.[5−7] Therefore, dendritic polymers containing a large number of terminal (meth)acryloyl groups have great possibility as a new high-performance UV curing system. Ranby and Shi reported[8−10] the synthesis of certain dendrimers with many terminal (meth)acryloyl groups. Furthermore, Sangermano et al. reported the photocurable hyperbranched polymers with oxetanyl groups.[11] They also investigated thermal and some mechanical properties of the UV cured films, and it was found that resulting cured films have high glass transition temperatures. However, these dendritic polymers were synthesized by multistep reactions with purification procedures.

On the other hand, hyperbranched polymers are prepared by two differential methods such as the self-condensation of AB$_2$ monomers (AB$_2$-type method)[12,13] and the polycondensation of A$_2$-type monomer with B$_3$-type monomer (A$_2$ + B$_3$ type method),[14] in which the latter method has great ability for the industrial applications, because many commercially available monomers can be used.

Table 1. Synthesis of Hyperbranched Poly(urethane)s Containing Methacryloyl Groups[a]

	feed ratio (mmol)					
run	CMDI	TMP	MOI	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	2	2	2	3 (95)[d]		
2	1	2	2	77	1200	1.43
3	1.5	2	2	93	2900	1.96

[a] The reaction was carried out with CMDI and TMP in the presence of MOI using DBTDL and PT at 50 °C for 6 h. [b] Insoluble parts in hexane/2-propanol: 10/1. [c] Estimated by SEC (DMF) based on polystyrene standards. [d] Insoluble parts in THF.

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* To whom all correspondence should be addressed. E-mail: nishikubot@kanagawa-u.ac.jp.

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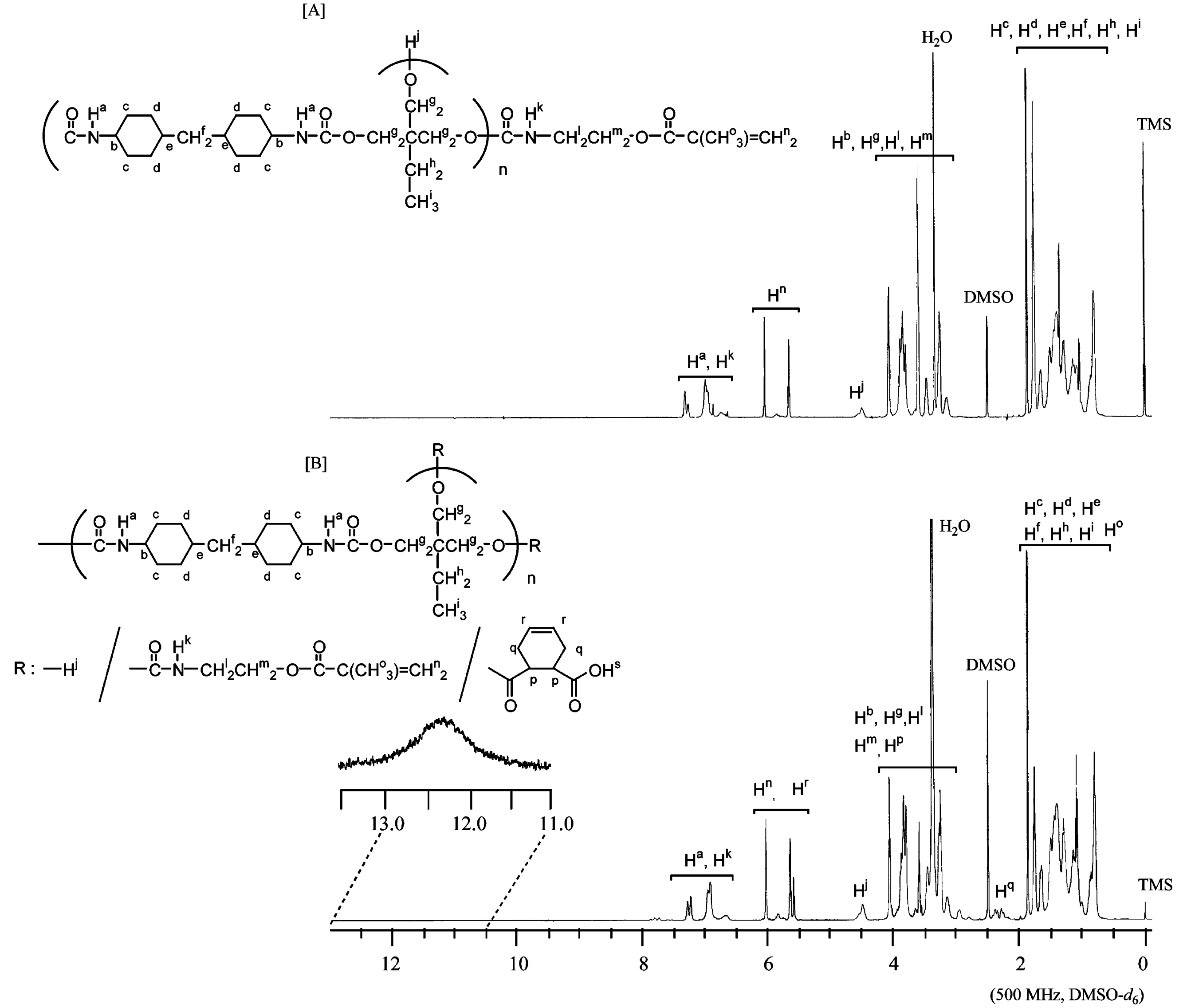


Figure 1. ^{1}H NMR spectra of poly(urethane)s: (a) HBPUMA and (b) HBPUMA-COOH.

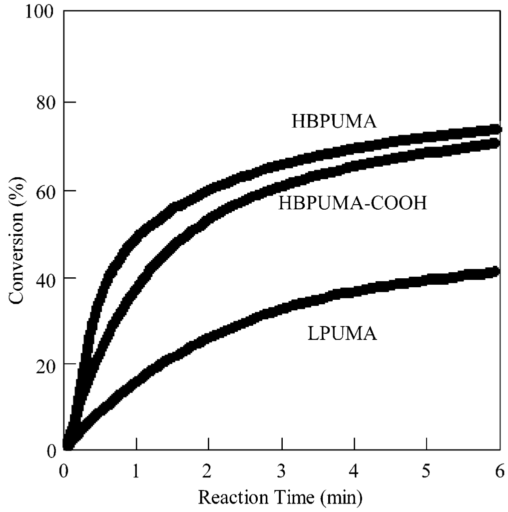


Figure 2. Time−conversion curve of the photoinitiated radical polymerization of HBPUMA, HBPUMA-COOH, and LPUMA in the presence of photoinitiator.

Recently, it was reported that photocurable hyperbranched polymers containing photopolymerizable groups were synthesized via the $A_2 + B_3$ type method.[15−17]

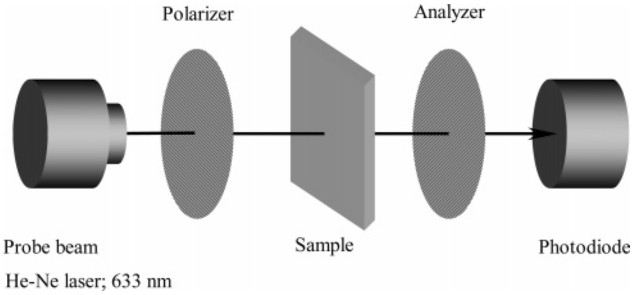
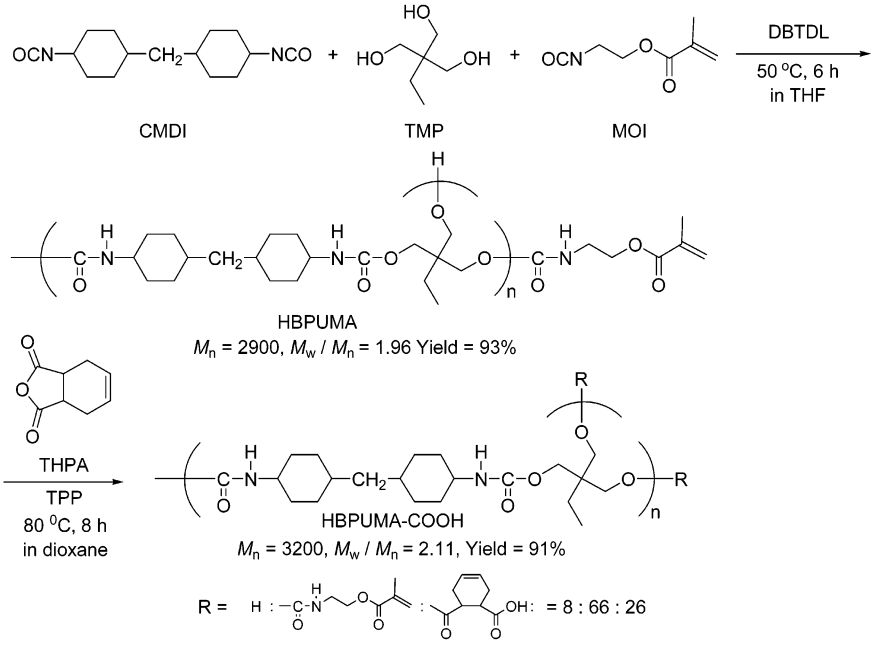


Figure 3. Schematic illustration of an experimental setup for the birefringence measurement.

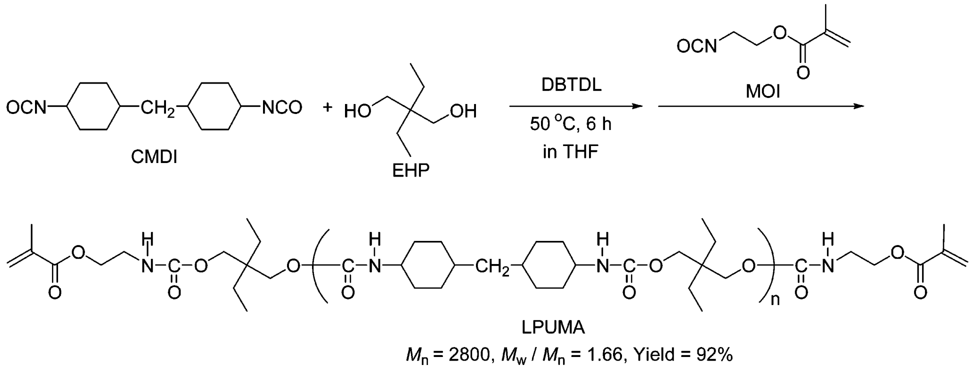
More recently, we[18] examined the photochemical reaction and properties of photocurable hyperbranched polyesters containing methacryloyl group at the ends, and it was found a new exciting result that birefringence of the cured hyperbranched polymer was lower than that of linear one. This shows that photocurable hyperbranched polymers are useful UV curing materials for the application in the new field of electronics industries.

In this article, we report the synthesis and photoinduced radical polymerization of hyperbranched polyurethanes containing both terminal metacryloyl and carboxyl groups. Furthermore,

Scheme 1



Scheme 2



we examined the mechanical and optical properties of the photocured film of obtained hyperbranched polyurethane.

Experimental Section

Materials. All solvents were dried and purified in the usual way before use. Dicyclohexylmethane 4,4′-diisocyanate (CMDI) and 2-methacryloyloxyethyl isocyanate (MOI) were distilled before use. Trimethylolpropane (TMP), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (EHP), *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA), dibutyltin dilaurate (DBTDL), triphenylphosphine (TPP), Irgacure 907 2-benzl-2-*N*,*N*-dimethylamino-1-(4-morpholinophenyl)butanone (Irgacure 369), pentaerythritol tetramethacrylate, and phenothiazine (PH) were used without further purification.

Measurements. Infrared absorption spectra (IR) were measured on a Jasco FT/IR-420 spectrometer. The ^{1}H NMR spectrum was recorded on a JEOL model JNM α-500 (500 MHz for ^{1}H NMR) in DMSO-d_6 with Me_4Si (TMS) as an internal standard. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a TOSO HLC-8220 SEC equipped with refractive index and ultraviolet detectors using TSK gel columns [eluent: solution of LiBr and phosphoric acid (20 mM) in DMF], calibrated with narrow molecular weight polystyrene standards. Glass transition temperatures (T_g's) were measured on a Seiko Electronic Instruments model EXSTAR 6000/DSC6200 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min under a nitrogen atmosphere. Real-time infrared (RT-IR) absorption spectra were recorded on BIO-RAD Excalibur FTS-3000MX spectrometer equipped with a HOYA-SCHOTT EX250 UV light source. The tensile strength was tested on a TENSILON/RTC-1250A machine with a strain rate of 5 mm/min at room temperature. The size of the specimens for the tensile test was 50 × 5 mm with the thickness of ca. 0.3 mm. The setup for birefringence measurement is shown in Figure 3. The cured films or drawn cured films were placed between a pair of crossed polarizers. The intensity of the probe light at 633 nm from He−Ne laser transmitted through the crossed polarizers and the films was measured with a photodiode. Drawn cured films were prepared elongating cured films by about 3%.

Synthesis of Hyperbranched Polyurehane Containing Terminal Methacryloyl Groups (HBPUMA). The mixture of CMDI (15.7 g, 60 mmol), TMP (10.7 g, 80 mmol), MOI (12.4 g, 80 mmol), DBTDL (1.26 g, 2 mmol), and a small amount of PT in THF (110 mL) was stirred at 50 °C for 6 h. The resulting mixture was poured into a large amount of hexane to precipitate the polymer. The resulting polymer was reprecipitated twice from THF into mixed solvent of *n*-hexane and 2-propanol (vol/vol = 10/1) and dried in vacuo at room temperature for 24 h. The yield of HBPUMA was 36.1 g (93%). The M_n of HBPUMA estimated by SEC was 2900 (M_w/M_n = 1.96). IR (film, cm^{-1}): 3404 (ν O−H), 3316 (ν N−H), 1709 (ν C═O of urethane), 1637 (ν C═C of methacryloyl). ^{1}H NMR (500 MHz, DMSO-d_6): 0.78−1.80 (m, 40.0 H, $-CH_2-CH-CH_2-CH_2-$CH$-$NH$-$ and C$-CH_2-CH_3$), 1.80−1.92 (m, 6.0 H, $C(CH_3)=CH_2$), 3.19−4.25 (m, 23.0 H, $-CH-$NH$-$, $-$C$-CH_2-$OH, and $-$NH$-CH_2-CH_2-$O$-$), 4.25−4.87 (m, 1.0 H, $-OH$), 5.62−6.32 (m, 4.0 H, $C(CH_3)=CH_2$), 6.82−7.45 (m, 5.0 H, NH).

Synthesis of Linear Polyurethane Containing Terminal Methacryloyl Groups (LPUMA). The mixture of CMDI (0.695 g, 2.7 mmol), EHP (0.397 g, 3.0 mmol), and DBTDL (0.033 g, 0.053 mmol) was stirred at 50 °C for 6 h. MOI (0.543 g, 3.5 mmol) and a small amount of PT were added to the reaction mixture and stirred for an additional 24 h. The resulting mixture was poured into a large amount of hexane to precipitate the polymer. The resulting polymer was reprecipitated twice from THF into mixed solvent of *n*-hexane and 2-propanol (vol/vol = 10/1) and dried in vacuo at room temperature for 24 h. The yield of LPUMA was 1.10 g (92%). The M_n of LPUMA estimated SEC was 2800 ($M_w/M_n = 1.66$). IR (film, cm^{-1}): 3316 (ν N−H), 1709 (ν C═O of urethane), 1637 (ν C═C of methacryloyl). ^{1}H NMR (500 MHz, DMSO-d_6): 0.56−0.94 (m, 6.0 H, $\mathrm{C{-}CH_2{-}C}H_3$), 0.97−1.90 (m, 22.4 H, $-\mathrm{C}H_2-\mathrm{C}H-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{CH}-\mathrm{NH}-$ and $\mathrm{C}-\mathrm{C}H_2-\mathrm{C}H_3$, and $\mathrm{C(C}H_3\mathrm{)}{=}\mathrm{CH_2}$), 3.05−4.38 (m, 2.9 H, $-\mathrm{C}H-\mathrm{NH}-$, and $-\mathrm{NH}-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{O}-$), 5.63−6.35 (m, 0.5 H, $\mathrm{C(CH_3)}{=}\mathrm{C}H_2$), 6.92−7.95 (m, 2.1 H, N*H*).

Chemical Modification of the HBPUMA. The mixture of HBPUMA (12.0 g, 12 mmol of hydroxyl group, $M_n = 2900$, $M_w/M_n = 1.96$), THPA (3.65 g, 24 mmol), TPP (0.047 g, 0.18 mmol), and small amount of PT in 1,4-dioxane (16 mL) was stirred at 80 °C for 8 h. The resulting mixture was poured into a large amount of water to precipitate the polymer. The resulting polymer (HBPUMA-COOH) was reprecipitated twice from THF into diethyl ether and dried in vacuo at room temperature for 24 h. The yield of HBPUMA-COOH was 12.1 g (91%). The M_n of HBPUMA-COOH estimated by SEC was 3200 ($M_w/M_n = 2.11$). IR (film, cm^{-1}): 2500−3500 (ν O−H of carboxylic acid), 3324 (ν N−H), 1714 (ν C═O of urethane), 1637 (ν C═C of methacryloyl). ^{1}H NMR (500 MHz, DMSO-d_6) : 0.62−1.99 (m, 46.0 H, $-\mathrm{C}H_2-\mathrm{C}H-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{CH}-\mathrm{NH}-$, $\mathrm{C}-\mathrm{C}H_2-\mathrm{C}H_3$, and $\mathrm{C(C}H_3\mathrm{)}{=}\mathrm{CH_2}$), 2.20−2.45 (m, 2.8 H, $\mathrm{CH}-\mathrm{C}H_2-\mathrm{CH}{=}$), 2.81−4.25 (m, 10.0 H, $-\mathrm{C}H-\mathrm{NH}-$, $-\mathrm{C}-\mathrm{C}H_2-\mathrm{OH}$, $-\mathrm{NH}-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{O}-$, and $\mathrm{O}-\mathrm{CO}-\mathrm{C}H-\mathrm{CH_2}$), 4.25−4.75 (m, 0.3 H, −O*H*), 5.40−6.34 (m, 5.4 H, $\mathrm{C(CH_3)}{=}\mathrm{C}H_2$ and $-\mathrm{CH_2}-\mathrm{C}H{=}$), 6.82−7.15 (m, 5.0 H, N*H*), 11.00−13.50 (br, 0.7 H, COO*H*).

Solubility of Hyperbranched Polymer and Linear Polymer. 2 mg of the resulting polymers was dissolved in 2 mL of the solvents.

Photoinitiated Radical Polymerization. A typical procedure for the photoinitiated radical polymerization was as follows: The photoinitiated radical polymerization of HBPUMA was performed in the film state as follows. HBPUMA (97 wt %) and Irgacure 907 (3 wt %) were dissolved in THF. The solution was cast on a KBr plate and dried to make film on the plate. The film, containing a photoinitiator 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 3 mW/cm^2 (at 254 nm). The rate of decrease in the C═C stretching near 1637 cm^{-1} due to methacryloyl group in HBPUMA was measured by RT-IR.

Patterning Property of HBPUMA-COOH. A photoresist was prepared from 65 wt % HBPEAc-COOH as a main resin, 26 wt % pentaerythrtol tetraacrylate as a diluent, and 9 wt % Irgacure 369 as a photoinitiator, and it was coated onto a substrate with a spin-coater with a wet film of 1.5 μm thick. The coated substrate was heated at 100 °C for 2 s and exposed upon UV light (150 mJ/cm^2 at 365 nm) under nitrogen. After that, the exposed polymer film on the substrate was developed with 0.3 wt % tetramethylamonium hydroxide (TMAH) aqueous solution.

Results and Discussion

Synthesis of Hyperbranched Polyurethane Containing Carboxyl Groups and Methacryloyl Groups at the Ends (HBPUMA-COOH) and Linear Polyurethanes Containing Methacryloyl Groups (LPUMA). It was reported that hyperbranched polyurethanes were synthesized by the AB$_2$-type method, and their physical properties were examined compared with the corresponding linear ones.[19] In this time, we examined the reaction of diisocyanate (A$_2$-type monomer, CMDI), triol (B$_3$-type monomer, TMP), and monoisocyanate (A-type monomer, MOI) in the presence of DBTDL as a catalyst in THF at 50 °C for 6 h in the certain feeds ratios to afford the soluble polymers and gel products. These conditions and results are summarized in Table 1. In the case of the feed ratios of CMDI/TMP/MOI = 2/2/2, the gel product was obtained in 95% yield (run 1). However, in the feeds of CMDI/TMP/MOI = 1/2/2 and 1.5/2/2, the soluble polymers were obtained with M_n's = 1200 and 2900 in 77 and 93% yields, respectively (runs 2 and 3).

Table 2. Solubility of Poly(urethane)s[a]

solvent	HBPUMA	HBPUMA-COOH	LPUMA
water	−	−	−
DMSO	++	++	++
DMAc	++	++	++
DMF	++	++	++
methanol	++	++	++
acetone	++	++	++
THF	++	++	++
ethyl acetate	−	−	−
chlorobenzene	−	−	−
chloroform	++	++	++
anisole	+-	+−	++
hexane	−	−	−
2.38 wt % THAH[c]	−	++	−

[a] ++: soluble at room temperature; +−: partially soluble or swelling; −: insoluble. [b] TMAH: tetramethylammonium hydroxide.

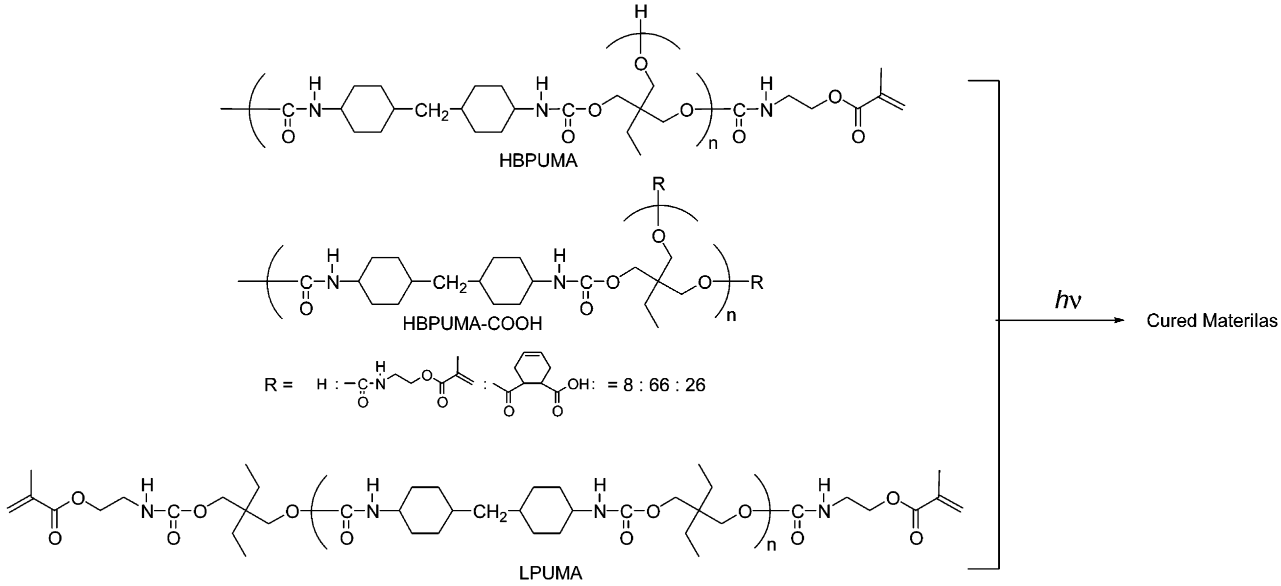
The structure of the resulting polymers was confirmed by IR and ^{1}H NMR spectroscopies. The IR spectrum showed characteristic absorption peaks at 3404, 3316, 1709, and 1637 cm^{-1} assignable to the −O−H, N−H, C═O (urethane), and C═C (methacryloyl), respectively. Figure 1A depicts the ^{1}H NMR spectrum of the polymer with $M_n = 2900$ (run 3 in Table 1) showing signals due to methacrylate groups at the ends around 5.62−6.32 ppm and hydroxyl groups at the ends around 4.25−4.87 ppm. These results showed that these polyadditions produced the hyperbranched polyurethane (HBPUMA) containing both hydroxyl groups and methacryloyl groups at the ends.

Next, chemical modification of HBPUMA for the synthesis of the alkaline-developable hyperbranched polymer was examined. The addition reactions of HBPUMA (run 3 in Table 1) with THPA was examined using TPP as a catalyst in 1,4-dioxane at 80 °C for 8 h, affording the corresponding HBPUMA-COOH with $M_n = 3200$ and $M_w/M_n = 2.11$ in 91% yield. The structure of synthesized HBPUMA-COOH was confirmed by IR and ^{1}H NMR spectroscopies. The IR spectrum showed a characteristic absorption peak around 2500−3500 cm^{-1} assignable to −OH (carboxylic acid). The ^{1}H NMR spectrum of HBPUMA-COOH showed proton signals due to carboxylic acid groups of the ends of the polymer chains around 11.00−13.50 ppm, as shown in Figure 1B. This result shows that HBPUMA-COOH has both methacryloyl groups and carboxyl groups at the ends as illustrated in Scheme 1.

Furthermore, the linear photocurable polyurethane containing methacryloyl groups at the ends was prepared by the polyaddition of CMDI and EHP in the presence of MOI in the similar fashion as mentioned above, to give the corresponding linear polyurethane (LPUMA) with $M_n = 2800$ and $M_w/M_n = 1.66$ in a 92% yield, as shown in Scheme 2.

Solubility of Hyperbranched Polymer and Linear Polymer. The solubilities of the resulting hyperbranched polymers (HBPUMA and HBPUMA-COOH) and corresponding linear polymer (LPUMA) were examined. These results are summarized in Table 2. All the obtained polymers were well soluble

Scheme 3



in chloroform, methanol, THF, and DMF but insoluble in hexane and chlorobenzene. Though HBPUMA was insoluble in 2.38 wt % of TMAH aqueous solution, HBPUMA-COOH was well soluble in these aqueous solutions. This means that solubility of polymer reasonably changed by the introduction of carboxyl groups into the end of polymer chain. Furthermore, the solubility of LPUMA was that same as that of HBPUMA.

Photoinitiated Radical Polymerization. The photoinitiated radical polymerization of HBPUMA, HBPUMA-COOH, and LPUMA was performed in the film state, which was prepared with Irgacure 907 (3 wt %) as a photoinitiator under UV irradiation with a 250 W high-pressure mercury lamp (intensity: 8.0 mW/cm^2 at 254 nm) (Scheme 3). The conversion rate 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.

Figure 2 illustrates the relationships between the conversion rate of the radical polymerization and reaction time. It is observed that the reaction proceeded smoothly, and the conversion of HBPUMA, HBPUMA-COOH, and LPUMA reached at 76, 72, and 42% after 6 min. HBPUMA and HBPUMA-COOH showed higher photochemical reactivity than LPUMA. This result indicates that the photochemical reactivity of hyperbranched polymer (HBP) is higher than that of linear one (LP) due to that HBP has many photoreactive groups at the ends. Furthermore, HBPUMA-COOH shows a lower photochemical reactivity than HBPUMA. This indicated that the motility of the polymer chain of HBPUMA-COOH was lower than HBPUMA due to the carboxyl group.

Thermal and Mechanical Properties of Cured Films. Thermal and mechanical properties of the cured films were investigated. The cured films were obtained by exposure for 10 min followed by heating at 80 °C for 30 min. T_g, tensile strength, and elongation at break are summarized in Table 3.

The values of T_g's increased after curing reaction in all the cases of the polymers. The cured films of HBPUMA and HBPUMA-COOH had higher T_g's and higher tensile strength than those of LPUMA. This means that the cured film of HBPUMA and HBPUMA-COOH had higher cross-linking densities. Furthermore, those of cured film of HBPUMA-COOH were higher than those of HBPUMA due to the intermolecular and intramolecular effect of carboxyl groups.

Optical Properties of the Cured Film. It seems that a polymer chain of hyperbranched polymer is hard to align due to their structure. Therefore, we examined birefringence of the cured film of HBPUMA, HBPUMA-COOH, and LPUMA. The birefringence measurement in the cured films was carried out at room temperature with the experimental setup represented in Figure 4. The intensity (I) of the probe light transmitted through crossed polarizer was measured. The relationship between I and birefringence (Δn) is given by the following equation:

$$I = I_0 \sin^2(\pi d \Delta n/\lambda)$$

where I_0 is the intensity transmitted under parallel polarizer, d is the film thickness, and λ is the wavelength of the probe light. The calculated values of Δn of the cured films are summarized in Table 4. The cured film of HBPUMA, HBPUMA-COOH, and LPUMA had little birefringence. Furthermore, the drawn cured film of HBPUMA had little birefringence, too, but the drawn cured film of LPUMA had birefringence. Birefringence is caused by polymer chain orientation. Therefore, it seems that the orientation of the polymer chain of the photocured HBPUMA did not occur easily because of their highly branched structures. This means that the photocured hyperbranched polymer is an essentially low-birefringence material. However, the drawn cured film of HBPUMA-COOH generated small birefringence. This indicated that small orientation was caused due to the carboxyl groups at the ends of polymer.

Patterning Properties. The patterning property of HBPUMA-COOH was measured with an SEM image obtained

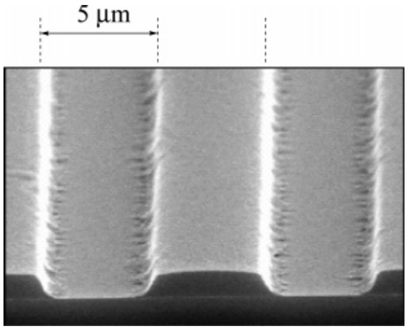


Figure 4. SEM image of the pattern.

Table 3. Physical Properties of Polymers and Cured Materials[a]

polymers and cured films	T_g (°C)[b]	tensile strength (MPa)	elongation at break (%)
HBPUMA	20	*c*	*c*
HBPUMA-COOH	28	*c*	*c*
LPUMA	31	*c*	*c*
cured film of HBPUMA	61	23.1[c]	5.0
cured film of HBPUMA-COOH	65	25.5[d]	4.5
cured film of LPUMA	50	15.4[c]	9.0

[a] Cured films were obtained were obtained by exposure for 10 min of the polymers followed by heating at 80 °C for 30 min. [b] Measured by DSC at a heating rate of 10 °C/min under nitrogen. [c] Not determined.

Table 4. Birefringence (Δn) of the Cured Films

run	cured film	Δn ($\times 10^{-4}$)
1	cured film of HBPUMA	0.3
2	cured film of HBPUMA-COOH	0.4
3	cured film of LPUMA	0.7
4	draw cured film of HBPUMA	0.9
5	draw cured film of HBPUMA-COOH	1.6
6	draw cured film of LPUMA	2.9

from polymer film prepared as follows. The photoresist was prepared from 65 wt % of HBPUMA-COOH, 26 wt % of pentaerythritol tetramethacrylate as a diluent, and 9 wt % of Irgacure 369 as a photoinitiator. The resist solution coated on the substrate was dried to form the resist film (1.5 μm thick) and exposed by the UV light. After that, the exposed resist film on the substrates was developed with 0.3 wt % of TMAH aqueous solution. As a result, a clear pattern with a 5 μm line and space was obtained (Figure 4), which is high resolution as photocurable material.

Conclusion

From all these results, the following conclusions can be drawn. (1) HBPUMA was synthesized through the polyaddition of CMDI with TMP and MOI. (2) Alkaline-developable HBPUMA-COOH was synthesized through the addition reaction of HBPUMA with THPA. (3) The obtained hyperbranched had high photoreactivity. (4) The cured film of HBPUMA had a high tensile strength. (5) Birefringence of the cured film of HBPUMA was lower than that of the cured film of LPUMA. (6) The negative resist composed of HBPUMA-COOH, diluents, and photoinitiator showed good resolution such as 5 μm line and space.

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