Synthesis of Photocrosslinkable Hyperbranched Polyesters with Terminal Methacryloyl Groups by the One-pot Polyaddition of Bis(oxetane)s with 1,3,5-Benzenetricarboxylic Acid and Methacrylic Acid

Tadatomi NISHIKUBO,^{1,†} Hiroto KUDO,¹ Ken MARUYAMA,¹
Takehiko NAKAGAMI,¹ and Hidekazu MIYABE²

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

²*Technical Research Laboratory, Taiyo Ink Mfg. Co., Ltd.,
388 Ohkura, Ranzan-machi, Hiki-gun 355-0222, Japan*

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ABSTRACT: The hyperbranched poly(ester)s with pendant primary hydroxy, methacryloyl, and oxetanyl groups were synthesized by the one-pot method for the polyaddition of bis(oxetane)s with 1,3,5-benzenetricarboxylic acid (TMA) and methacrylic acid (MA) in the presence of tetraphenylphosphonium chloride (TPPC) as a catalyst. A alkaline-developable photo-reactive hyperbranched polymer (**P-4b**) was prepared by the addition reaction of the synthesized hyperbranched poly(ester) **P-4a** with *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA). A resist composed of 58 wt % **P-4b**, 12 wt % dilute monomer, 5 wt % Irgacure907[®] as a photo-initiator, 24 wt % epoxy resin, and 1 wt % dicyandiamide achieved a resolution of a 55 μm line pattern and a 27 μm space pattern by UV irradiation (1000 mJ) when 6 μm thick film is used. [doi:10.1295/polymj.38.447]

KEY WORDS Oxetane / Hyperbranched Polymer / Polyaddition / Photo-radical Polymerization / Photo-resist / UV-curing System /

UV curing systems have been widely used in various applications^{1,2} such as coatings, printing inks, adhesives, photo-resists, and solder masks, because of their low volatile organic compound (VOC), high productivity, excellent physical properties, and energy saving. Recently, these systems have also been applied to electronics and information technology fields³ such as display, CD, DVD, optical-fiber, and optical-device. In these curing systems, acrylate monomers and oligomers are mainly used due to their high reactivity. Most of acrylate oligomers such as acrylated epoxy resins, poly(urethane)s, poly(ester)s, and poly(ether)s have relatively high viscosity, because these oligomers were composed from linear polymer chains in general.

More than 30 years ago, we^{4,5} reported the synthesis of polyesters with pendant hydroxy groups and (meth)acrylate groups by the addition reaction of epoxy resins with (meth)acrylic acid, which have been used as main resins in the fields of coatings and printing inks due to their high photochemical reactivity and excellent mechanical property. Furthermore, these oligomers were modified⁶ with cyclic carboxylic anhydride to form photo-curable oligomer with alkaline developable property. These (meth)acrylated epoxy resin derivatives have been widely used as main resin in solder masks in the world.

Meanwhile, hyperbranched polymers (HBPs) containing a large number of terminal groups possess a randomly branched structure⁷ and have recently attracted a great deal of attention for their unique properties such as lower viscosity, good solubility and many reactive terminal groups compared with the corresponding linear ones. Condensation polymers with hyperbranched structure are mainly synthesized^{8,9} by the one-step self-polycondensation of an AB_m type monomer which has one 'A' functional group and multiple 'B' functional groups. However, these monomers are generally required to process tedious multi-step organic synthesis and are unsuitable for industrial application on a large scale synthesis. To overcome this technical problem, Kakimoto and his co-workers¹⁰ substituted a new method by conventional combination of A_2 and B_3 monomers. Since the reaction system between $\text{A}_2 + \text{B}_3$ monomers produced gel products in general, the control of the reaction condition is an important factor to obtain soluble hyperbranched polymer. However, this method is very convenient in practical applications, because commercially available numerous monomers can be used as starting materials. Recently, based on this concept, we reported¹¹ the synthesis of photo-crosslinkable and alkaline developable hyperbranched poly(imide)s containing many terminal methacryloyl groups and

[†]To whom correspondence should be addressed (E-mail: nishikubot@kanagawa-u.ac.jp).

Scheme 1.

pendant carboxyl groups by the reaction of tris-amine with tetracarboxylic dianhydrides followed by the reaction with glycidyl methacrylate and *cis*-1,2,3,6-tetrahydrophthalic anhydride. Chen and Yin also reported¹² photo-crosslinkable hyperbranched poly(imide)s containing certain photoreactive groups. More recently, Thang *et al.*, reported¹³ the synthesis of photo-curable hyperbranched poly(ester-amine)s with terminal acryloyl groups by the Michail addition reaction of piperazine (A_2 monomer) with trimethylolpropane triacrylate (B_3 monomer).

On the other hand, we have recently found a new polyaddition reactions of bis(oxetane)s with dicarboxylic acids¹⁴ or bisphenols^{15–17} to produce the high molecular weight polyesters and polyethers with pendant primary hydroxy groups which can be use as the reactive groups for the introduction of functional groups, respectively. Given these background, we designed¹⁸ new hyperbranched poly(ester)s with pendant primary hydroxy groups as reactive groups by the polyaddition reaction of bis(oxetane)s with 1,3,5-benzenetricarboxylic acid (TMA). However, there are no reports on the synthesis of photo-curable and alkaline developable hyperbranched polymers excepting our recent two papers,^{11,19} although alkaline development property is a very important factor in practical application.

This article reports on the synthesis of the hyperbranched poly(ester)s by the polyaddition of bis(oxetane)s with TMA and methacrylic acid (MA) (Scheme 1). Furthermore, we examined the chemical modification of the synthesized hyperbranched poly(ester)s by the reaction of carboxylic anhydride to introduce alkaline developable property for the view point of practical application and its application for the UV curing resist system.

EXPERIMENTAL

Materials

Solvents were dried using CaH_2 and purified in the usual way before use. Tetraphenylphosphonium chloride (TPPC), triphenylphosphine (TPP) were used without further purification. 3-Ethyl-3-phenoxyethyl oxetane (EPMO) (donated from Toagosei Co., Ltd.) was purified by distillation *in vacuo*. 1,4-Bis[(3-ethyl-3-oxetanyl)methoxymethyl] benzene (BEOB), 4,4'-bis[(3-ethyl-3-oxetanyl)methoxy]biphenyl (4,4'-BEOBP) (donated from Toagosei Co., Ltd.) and terephthalic acid (TPA) were purified by recrystallization from appropriate solvents. Reagent grade or commercial grade TMA, MA, *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA), Irgacure907®, 2-hydroxyethyl methacrylate (HEMA), dipentaerythritol hexaacrylate (DPEHA), novolac-type epoxy-resin RE-306CA90 obtained from NIPPON KAYAKU CO. LTD., and other reagents were also used without further purification.

Measurements

Infrared (IR) absorption spectra were measured on a Jasco FT/IR-420 spectrometer. The ^1H NMR spectrum was recorded on JEOL JNM FX-200 instruments in CDCl_3 or dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$) with Me_4Si (TMS) as an internal standard. HPLC analysis was carried out on a Japan Analytical Industry Model HPLC-909 liquid chromatography connected with a JAIGEL-1H-A column using tetrahydrofuran (THF) as an eluent. The purification and isolation of the reaction adducts of EPMO with TMA and MA were carried out using a recycling preparative HPLC (Japan Analytical Industry Co., Ltd.; model HPLC-908 liquid

chromatography) connected with a JAIGEL-1H-AF and JAIGEL-1H-A columns using chloroform as an eluent. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymer were estimated by size exclusion chromatography (SEC; TOSOH model HLC-8220) on TSK gel columns (SuperAW3000 $\times$ 1 and SuperAW2500 $\times$ 3) calibrated by narrow molecular weight distribution polystyrene standards and with a refractive index detector. *N,N*-dimethylformamide (DMF) containing 20 mmolL⁻¹ of lithium bromides and 20 mmolL⁻¹ of phosphoric acids was used as an eluent. Real-time Infrared (RT-IR) absorption spectra were recorded on a BIO-RAD Excalibur FTS-3000MX spectrometer equipped with a HOYA-SCHOTT EX250 UV light source. 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 nitrogen atmosphere. Thermal analysis (TGA) was performed on a Seiko Electronic Instruments model EXSTAR 6000/TG/DTA 6220 at a heating rate of 10 °C/min under nitrogen.

Model Reaction of EP MO with TMA and MA

The measurement of the reaction rate was as follows: The mixture of EP MO (2.304 g; 12 mmol), TMA (0.420 g; 2 mmol), MA (0.517 g; 6 mmol), TPPC (0.225 g; 5 mol % to EP MO as the catalyst), and hydroquinone (HQ) (0.013 g) as an inhibitor in 1-methyl-2-pyrrolidinone (NMP) (5 mL) stirred at 140 °C under nitrogen. The degrees of addition reactions of EP MO with TMA and MA at each time were measured by HPLC (Figure 1).

The identification of the reaction products was as follows: EP MO (2.304 g; 12 mmol), TMA (0.420 g; 2 mmol), MA (0.517 g; 6 mmol), and TPPC (0.225 g; 5 mol % to EP MO) were dissolved in NMP (5 mL), and stirred at 140 °C for 6 h in the presence of HQ (0.013 g) as an inhibitor under nitrogen. The reaction mixture was diluted with chloroform, and then washed

Figure 1. HPLC chromatogram for the reaction of EP MO with TMA and MA using TPPC as a catalyst at 140 °C for 6 h in NMP.

with water. The obtained organic layer was dried with MgSO₄, and then resulting organic phase was evaporated. The obtained crude residues were separated using a recycling preparative HPLC to give three products (A, B, and C), which structures were confirmed by IR and ¹H NMR spectroscopy.

Adduct A from TMA with three EP MO: IR (bulk, cm⁻¹): 3440 (ν OH), 1731 (ν C=O, ester), 1599 and 1497 (ν C=C of aromatic), and 1239 (ν C–O–C, ester). ¹H NMR (200 MHz, CDCl₃, TMS) δ = 0.96 (t, J = 7.5 Hz, 9.0H, CH₂CH₃), 1.63 (q, J = 7.5 Hz, 6.0H, CH₂CH₃), 2.20–2.40 (brs, 3.0H, OH), 3.73 (s, 6.0H, C–CH₂–OH), 3.97 (s, 6.0H, O–CH₂–C), 4.49 (s, 6.0H, CO₂–CH₂–C), and 6.85–7.40 (m, 15.0H, aromatic H in EP MO unit), 8.70–8.80 ppm (m, 3.0H, aromatic H in TMA unit).

Adduct B from TMA with two EP MO: IR (bulk, cm⁻¹): 3600–3500 (ν OH and COOH), 1729 (ν C=O, ester and carboxyl group), 1599 and 1497 (ν C=C of aromatic), and 1239 (ν C–O–C, ester). ¹H NMR (200 MHz, CDCl₃, TMS) δ = 0.98 (t, J = 7.5 Hz, 6.0H, CH₂CH₃), 1.65 (q, J = 7.5 Hz, 4.0H, CH₂CH₃), 3.81 (s, 4.0H, C–CH₂–OH), 3.99 (s, 4.0H, O–CH₂–C), 4.49 (s, 4.0H, CO₂–CH₂–C), 5.00–5.60 (brs, 1.9H, OH), 6.70–7.40 (m, 10.0H, aromatic H in EP MO unit), and 8.60–8.90 ppm (m, 3.0H, aromatic H in TMA unit).

Adduct C from MA with EP MO: IR (bulk, cm⁻¹): 3448 (ν OH), 1732 (ν C=O, ester), 1637 (ν C=C, vinyl), 1599 and 1497 (ν C=C of aromatic), 1245 (ν C–O–C, ester), and 810 (ν C–H, vinyl). ¹H NMR (200 MHz, CDCl₃, TMS) δ = 0.94 (t, J = 7.5 Hz, 3.0H, CH₂CH₃), 1.58 (q, J = 7.5 Hz, 2.0H, CH₂CH₃), 1.94 (s, 3.0H, CH₃), 2.20–2.60 (brs, 1.0H, OH), 3.64 (s, 2.0H, C–CH₂–OH), 3.92 (s, 2.0H, O–CH₂–C), 4.27 (s, 2.0H, CO₂–CH₂–C), 5.58 and 6.11 (s, 2.0H, C=CH₂), and 6.80–7.40 ppm (m, 5.0H, aromatic H in EP MO unit).

Polyaddition of BEOB with TMA and MA

A typical procedure for the polyaddition of BEOB with TMA and MA was as follows: BEOB (1.002 g; 3 mmol), TMA (0.210 g; 1 mmol), MA (0.254 g; 3 mmol), TPPC (0.056 g; 0.15 mmol), HQ (0.017 g; 0.15 mmol), and NMP (2 mL) were charged into a round-bottomed flask under a stream of dried air. The reaction was performed at 140 °C for 24 h under stirring, and then the solution was poured into a large amount of water to precipitate the polymer. The resulting polymer was reprecipitated from THF into *n*-hexane, reprecipitated from THF into diethyl ether, and then dried *in vacuo* to yield a brown-colored solid. The yield of polymer (**P-2a**) was 0.86 g (58%). M_n of the polymer estimated by SEC was 4200 (M_w/M_n = 3.02). The ratio of methacryloyl groups in the end of polymer chain (RM) was 16%, which was cal-

culated by the intensity ratio of ^1H NMR. The content of COOH groups in the polymer chain was 4.57%, which was measured by neutralization titration of the carboxyl groups using 0.01-N ethanolic aqueous solution in THF. IR (film, cm^{-1}): 3388 (ν O–H), 1729 (ν C=O, ester), 1636 (ν C=C, vinyl), 1461 (ν C=C, aromatic), 1241 (ν C–O–C, ester), 1096 and 1051 (ν C–O–C, ether), and 992 (ν C–O–C, cyclic ether of oxetane), and 817 (ν C–H, vinyl). ^1H NMR (200 MHz, DMSO- d_6 , TMS): 0.75–1.05 (m, 12.4H, $\text{CH}_2\text{--CH}_3$), 1.20–1.70 (m, 8.2H, $\text{CH}_2\text{--CH}_3$), 1.70–1.85 (s, 1.0H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 3.00–3.75 (m, 16.8H, $\text{C--CH}_2\text{--O}$, $\text{C--CH}_2\text{--OH}$, and OH), 4.10–4.80 (m, 19.3H, $\text{COO--CH}_2\text{--C}$, $\text{O--CH}_2\text{--Ar}$, and $\text{CH}_2\text{--O}$ in oxetane ring), 5.57 and 5.94 (s, 0.7H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 6.95–7.40 (m, 8.3H, aromatic H in BEOB unit), and 8.40–8.80 ppm (m, 3.0H, aromatic H in TMA unit).

Polyaddition of 4,4'-BEOBP with TMA and MA

The polyaddition of 4,4'-BEOBP (1.15 g; 3 mmol), TMA (0.210 g; 1 mmol) and MA (0.775 g; 9 mmol) was performed in NMP (2 mL) using TPPC (0.056 g; 0.15 mmol) as a catalyst and HQ (0.017 g) as a radical polymerization inhibitor at 140 °C for 24 h. The resulting mixture was poured into a large amount of water to precipitate the polymer. The resulting polymer was reprecipitated from THF into *n*-hexane, reprecipitated from THF into diethyl ether, and then dried *in vacuo* to yield a brown-colored solid. The yield of polymer (**P-6a**) was 1.25 g (53%). RM was 57%, which was calculated by the intensity ratio of ^1H NMR. $M_n = 3800$, $M_w/M_n = 2.20$. IR (film, cm^{-1}): 3430 (ν O–H), 1725 (ν C=O, ester), 1636 (ν C=C, vinyl), 1500 (ν C=C, aromatic), 1237 (ν C–O–C ester), 997 (ν C–O–C, cyclic ether of oxetane), and 821 (ν C–H, vinyl). ^1H NMR (200 MHz, DMSO- d_6 , TMS) δ = 0.82–1.05 (m, 6.0H, $\text{CH}_2\text{--CH}_3$), 1.30–1.75 (m, 4.0H, $\text{CH}_2\text{--CH}_3$), 1.75–1.85 (s, 1.5H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 3.10–4.80 (m, 14.0H, $\text{C--CH}_2\text{--O}$ -biphenyl unit, $\text{C--CH}_2\text{--OH}$, $\text{COO--CH}_2\text{--C}$, $\text{CH}_2\text{--O}$ in oxetane ring, and OH), 5.58 and 6.02 (s, 1.0H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 6.55–7.64 (m, 8.0H, aromatic H in bisphenol), and 8.55–8.72 ppm (m, 1.5H, aromatic H in TMA unit).

Polyaddition of BEOB with TPA and MA

The mixture of BEOB (2.01 g, 6 mmol), TPA (0.83 g, 5 mmol), TPPC (0.23 g, 0.6 mmol) in NMP (2 mL) was stirred at 140 °C for 30 h. Then, MA (2.58 g, 30 mmol) and HQ (0.17) were added to the reaction mixture and stirred for additional 18 h. The resulting mixture was poured into a large amount of water to precipitate the polymer. The resulting polymer was reprecipitated twice from THF into diethyl ether, and then dried *in vacuo* to yield a brown-colored solid. The yield of polymer (**P-7a**) was 2.37 g (88%). RM

was 95%, which was calculated by the intensity ratio of ^1H NMR. $M_n = 3800$, $M_w/M_n = 2.30$. IR (film, cm^{-1}): 3388 (ν O–H), 1730 (ν C=O, ester), 1636 (ν C=C, vinyl), 1463 (ν C=C, aromatic), 1243 (ν C–O–C, ester), 1100 and 1055 (ν C–O–C, ether), and 816 (ν C–H, vinyl). ^1H NMR (200 MHz, DMSO- d_6 , TMS): 0.65–0.95 (m, 6.0H, $\text{CH}_2\text{--CH}_3$), 1.11–1.68 (m, 4.0H, $\text{CH}_2\text{--CH}_3$), 1.71–1.85 (s, 0.9H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 3.10–3.72 (m, 7.9H, $\text{C--CH}_2\text{--O}$ and $\text{C--CH}_2\text{--OH}$), 3.80–4.81 (m, 9.5H, $\text{COO--CH}_2\text{--C}$, $\text{O--CH}_2\text{--Ar}$, and OH), 5.41 and 6.00 (s, 0.6H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 6.94–7.33 (m, 4.0H, aromatic H in BEOB unit), and 7.82–8.20 ppm (m, 3.7H, aromatic H in TPA unit).

Chemical Modification of the Hyperbranched Polymer 4a (**P-4a**)

The reaction of **P-4a** (0.199 g; 1.0 mmol as hydroxyl group, $M_n = 3600$, $M_w/M_n = 2.01$, RM = 54%), with THPA (0.091 g; 0.6 mmol) was carried out in the presence of TPP (0.05 g; 0.20 mmol) as a catalyst in 1,4-dioxane (0.3 mL) at 80 °C for 4 h. Then, the reaction mixture was diluted with THF, washed thrice with large amount of water to remove TPP and poured into *n*-hexane to precipitate the polymer, and dried *in vacuo*. The yield of polymer (**P-4b**) was 0.23 g (79%). The degree of conversion of hydroxyl groups was 55%, which was calculated by the intensity ratio of ^1H NMR. The content of COOH groups in the polymer chain was 11.4%, which was measured by neutralization titration of the pendant carboxyl groups using 0.01-N ethanolic aqueous solution in THF. IR (film, cm^{-1}): 2500–3500 (O–H, COOH), 1733 (C=O, ester, carboxylate), 1462 (C=C, aromatic), 1238 (C–O–C, ester), and 992 (C–O–C, cyclic ether of oxetane). ^1H NMR (200 MHz, DMSO- d_6 , TMS): 0.75–1.05 (m, 6.1H, $\text{CH}_2\text{--CH}_3$), 1.20–1.70 (m, 4.0H, $\text{CH}_2\text{--CH}_3$), 1.70–1.85 (m, 1.4H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 2.20–2.65 (m, 3.0H, $\text{CH--CH}_2\text{--CH=}$ in THPA unit), 2.80–3.75 (m, 9.5H, OCO--CH--CH_2 in THPA unit, $\text{C--CH}_2\text{--O}$, $\text{C--CH}_2\text{--OH}$, and OH), 4.10–4.80 (m, 10.2H, $\text{COO--CH}_2\text{--C}$, $\text{O--CH}_2\text{--Ar}$, and $\text{CH}_2\text{--O}$ in oxetane ring), 5.40–5.70 (m, 2.0H, $\text{CH}_2\text{--CH=}$ in THPA unit and $\text{C}(\text{CH}_3)=\text{CH}_2$), 5.94 (s, 0.5H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 6.95–7.40 (m, 4.0H, aromatic H in BEOB unit), and 8.40–8.80 ppm (m, 1.5H, aromatic H in TMA unit).

Photo-initiated Radical Polymerization

A typical procedure for the photo-initiated radical polymerization was as follows: 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 follows. **P-4a** (97 wt %) and Irgacure907[®] (3 wt %) as a photo-initiator were dissolved in THF and dried to make film on the plate. The film, containing a photo-initiator on the plate, was irradiated

Scheme 2.

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 $\text{C}=\text{C}$ stretching near 1636 cm^{-1} due to methacryloyl group in **P-4a** was measured by RT-IR.

Preparation and Evaluation of Solder Resist

Typical procedure for the preparation of solder resist was as follows. The solution of solder resist (**Sample 1**) was prepared from 58 wt % of **P-4b** as a main resin, 12 wt % of DPEHA as a diluent, 5 wt % of Irgacure907[®] as a photo-initiator, 24 wt % of novolac type epoxy resin as a thermal curing agent, 1 wt % of dicyandiamide as an additive, and diethylene glycol monoethyl ether acetate as a solvent (40 wt % to **P-4b**), and this solution was coated onto a substrate with a bar coater with a wet film. The coated substrate was heated at 80°C for 20 min to remove the solvent and exposed by broad-band UV light (500 mJ/cm^2). After that, the exposed resist film on the substrates was developed by putting spray with 1 wt % of Na_2CO_3 aqueous solution for 60 min, being rinsed with water, and dried. The obtained negative pattern was measured with a scanning electron micrograph (SEM) image.

RESULTS AND DISCUSSION

Model Reaction

As a model reaction for the polyaddition of bis(oxetane)s with TMA and MA, the reaction of EPPO (12 mmol) with TMA (2 mmol) and MA (6 mmol) was examined in NMP using 5 mol % of TPPC as a catalyst at 140°C (Scheme 2). As shown in Figure 1, new appearances of certain peaks were conformed in HPLC chromatogram, when the reaction was carried

out for 6 h. Therefore, these three fractions corresponding to three peaks A, B, and C were separated by recycling HPLC, and their structures were confirmed by ^1H NMR and IR spectroscopy. As the result, the fraction A was a compound obtained by the addition reaction of one-equivalent of TMA with three-equivalent of EPPO. The fraction B consisted of the compound obtained by the addition reaction of one-equivalent of TMA with two-equivalent of EPPO, and fraction C was done of that by the equivalent addition reaction of MA with EPPO, respectively. These reactions and structures are illustrated in Scheme 2. Furthermore, although we could not isolate a product obtained by the equivalent addition reaction of TMA with EPPO, peak D seems to be a corresponding adduct. This means that the addition reaction of EPPO with TMA and MA proceeded to give the targeted products.

Based on the above result, conversion rates of TMA and MA on the reaction with EPPO were measured by HPLC. As shown in Figure 2, conversions of TMA and MA gradually increased and reached 40 and 9% at 12 h, respectively. This result means that the reaction rate of TMA to EPPO was higher than that of MA to EPPO under competition conditions. Therefore, the one pot polyaddition of bis(oxetane) and TMA in the presence of MA can proceed under appropriate conditions to afford the corresponding hyperbranched polyesters with pendant primary hydroxy groups in the side chain and terminal methacryloyl groups at the ends.

Synthesis of Novel Hyperbranched Poly(ester)s with Terminal Methacryloyl Groups

The polyaddition of equimolar BEOB with TMA (3/2 as feed ratio) was carried out in the presence of TPPC as a catalyst (5 mol %) at 140°C for 24 h

Figure 2. Conversion rate of TMA and MA on the reaction with EPMO. (■): TMA, (●): MA.

to obtain the corresponding polymer in 96% yield. However, all of the reaction products were insoluble in common organic solvents, which means that the gelation occurred during the polyaddition of BEOB with TMA under the above conditions.

On the other hand, when the polyaddition of BEOB and TMA was performed with the feed ratio of 3/1 in feed at 140 °C for 24 h, soluble polymer **P-1a** with $M_n = 4000$ ($M_w/M_n = 2.90$) was obtained in 68% yield (run 1 in Table I). The structure of **P-1a** was confirmed by IR and ^1H NMR spectroscopies. It was found that **P-1a** was hyperbranched polymer with pendant primary hydroxy groups in the side chain. Detail reaction conditions and results have been reported¹⁸ in the previous paper. This means that the controlled reaction time and feed ratios of these polyaddition can offer the soluble hyperbranched polymer on the reaction of bis(oxetane) with TMA.

Based on the results of model reaction and the

above reaction of BEOB with TMA, we examined the polyaddition of BEOB and TMA in the presence of MA under the similar conditions (Scheme 1). In feed ratio of BEOB/TMA/MA = 3/1/3, the hyperbranched poly(ester), **P-2a** containing 16% of terminal methacryloyl groups was obtained in 58% yield (run 2 in Table I). The structure of **P-2a** was confirmed by IR and ^1H NMR spectroscopy. It was also observed that the ratio of methacryloyl groups in the obtained hyperbranched poly(ester)s increased with increase of the concentration of MA in feed (runs 3–5 in Table I). **P-6a** which had rigid structure, with pendant primary hydroxy groups and terminal methacryloyl groups was also synthesized by the polyaddition of 4,4'-BEOBP with TMA and MA (feed ratio of BEOBP/TMA/MA = 3/1/9) under the same reaction conditions. Furthermore, as shown in Figure 2, the rate of addition reaction of oxetane groups with TMA was much higher than that of oxetane groups with MA.

From all these results, it was concluded that the hyperbranched poly(ester)s with pendant primary hydroxy groups and certain terminal methacryloyl groups were synthesized by the one-pot method of the polyaddition of bis(oxetane)s with TMA and MA, although terminal oxetane groups were remained in the obtained polymers.

Furthermore, to compare the photochemical reactivity between the hyperbranched polymer and linear polymer, we synthesized the linear polyester **P-7a** with $M_n = 3800$, $M_w/M_n = 2.30$ by the polyaddition of BEOB with TPA and MA under the same reaction conditions as mentioned above.

Photo-initiated Radical Polymerization of the Hyperbranched Polyester with Terminal Methacryloyl Groups

The photo-initiated radical polymerization of **P-4a** ($M_n = 3600$, $M_w/M_n = 2.01$, RM = 54%) was per-

Table I. Synthesis of hyperbranched poly(ester)s containing methacryloyl groups

Run	Polymer	Feed ratio (mmol)			Yield (%) ^c	$M_n \times 10^{-3}$ ^d	M_w/M_n ^d	RM (%) ^e
		Bis(oxetane)s	TMA	MA				
1 ^a	P-1a	BEOB 3	1	0	68	4.0	2.90	—
2 ^a	P-2a	BEOB 3	1	3	58	4.2	3.02	16
3 ^a	P-3a	BEOB 3	1	6	55	3.9	2.55	37
4 ^a	P-4a	BEOB 3	1	9	54	3.6	2.01	54
5 ^a	P-5a	BEOB 3	1	15	39	2.2	1.45	57
6 ^b	P-6a	4,4'-BEOBP 3	1	9	53	3.8	2.20	57

^aThe reaction was carried out with BEOB and TMA in the presence of MA using 5 mol % of TPPC and HQ at 140 °C for 24 h. ^bThe reaction was carried out with 4,4'-BEOBP and TMA in the presence of MA using 5 mol % of TPPC and HQ at 140 °C for 24 h. ^cInsoluble parts in diethyl ether. ^dEstimated by SEC (DMF) based on polystyrene standards. ^eThe ratio of methacryloyl groups (RM) were calculated by ^1H NMR as followed. [Terminal methacryloyl groups/(Terminal methacryloyl groups + Terminal oxetanyl groups + Terminal carboxyl groups)] $\times$ 100.

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-7a** (97 wt %) and Irgacure907[®] (3 wt %).

formed in the film state. As shown in Figure 3, the reaction rapidly proceeded, and conversions reached to 59 and 88% in 2 and 10 min, respectively. Furthermore, the photo-irradiated polymer film became insoluble in any organic solvents. On the other hand, when the photochemical reaction of **P-7a** ($M_n = 3800$, $M_w/M_n = 2.30$) with linear structure was performed under the same irradiation conditions, the conversions were 43 and 76% in 2 and 10 min, respectively. Furthermore, it was observed that the rate of photochemical reaction of **P-4a** was strongly enhanced by the addition of low molecular weight monomer HEMA under the same irradiation conditions, and the conversions of the mixture of **P-4a** (70 wt %), HEMA (27 wt %), and photo initiator (3 wt %) reached to 78

and 95% at 2 and 10 min, respectively. This means that the molecular motion and content of methacryloyl groups of the film prepared from **P-4a**, HEMA, and photo-initiator increased by the addition of low molecular weight monomer HEMA.

These results showed that this hyperbranched polyester with terminal methacryloyl groups had higher photochemical reactivity than the corresponding linear polyester with terminal methacryloyl groups, because the former polymer had many photo reactive groups in the end of polymer chain.

Chemical Modification of the Hyperbranched Polyester with THPA

Ordinarily, alkali aqueous solutions have been used as developers for negative resists. Therefore, the introduction of the carboxyl groups into **P-4a** was examined (Scheme 3). The reaction of **P-4a** ($M_n = 3600$, $M_w/M_n = 2.01$, RM = 54%) with 0.6 equiv. of THPA was carried out using TPP as a catalyst at 80 °C for 4 h, and it was found that the corresponding polymer **P-4b** containing 55% of the pendant carboxyl groups was obtained in 79% yield. The structure of **P-4b** was confirmed by ¹H NMR and IR spectroscopy.

Solubilities of **P-4a** containing pendant primary hydroxy and terminal methacryloyl groups, and **P-4b** containing pendant carboxyl and terminal methacryloyl groups were evaluated. Both polymers were well 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. Furthermore, **P-4b** with pendant carboxyl groups was soluble in 1.0 wt % of NaHCO₃ aqueous solution, 1.0 wt % of Na₂CO₃ aqueous solution, and 2.38 wt % of tetramethylammonium hydroxide (TMAH) aque-

Scheme 3.

Table II. Solubility of poly(ester)s with pendant hydroxyl or carboxyl groups^a

Solvent	P-4a	P-4b
Hexane	—	—
Toluene	—	—
Diethyl ether	—	—
1,4-Dioxane	++	++
Chloroform	++	++
Anisole	+-	—
Chlorobenzene	+-	—
Ethanol	++	++
Methanol	++	++
THF	++	++
Ethyl acetate	+-	+-
Acetone	++	++
DMF	++	++
NMP	++	++
DMSO	++	++
1.0 wt % NaHCO ₃	—	++
1.0 wt % Na ₂ CO ₃	—	++
2.38 wt % TMAH	—	++

^a++: soluble at room temperature, +-: partially soluble, —: insoluble.

ous solution; however, **P-4a** was insoluble in the same aqueous solutions (Table II). These results showed that the alkali-solubility of both polymers was dramatically changed by the introduction of certain carboxyl groups into the polymer.

Thermal Properties of Hyperbranched Polymers

Glass transition temperatures (T_g s) and 5 wt % weight loss temperatures ($T_d^{5\%}$ s) of the synthesized polymer **P-4a**, which had pendant primary hydroxy groups and terminal methacryloyl groups, and **P-4b** with pendant carboxyl groups and terminal methacryloyl groups were measured by DSC and TGA, respectively. As summarized in Table III, **P-4a** with hy-

Table III. Thermal properties of **P-4a** and **P-4b**

Run	Polymer	T_g (°C) ^a	$T_d^{5\%}$ (°C) ^b
1	P-4a	18	268
2	P-4b	21	258

^aMeasured by DSC at a heating rate of 10 °C/min under nitrogen. ^bMeasured by TG/DTA at a heating rate of 10 °C/min under nitrogen.

droxy groups showed T_g at 18 °C. On the other hand, the T_g of **P-4b** with carboxyl groups was 21 °C. This result shows that T_g of the hyperbranched polymer with pendant hydroxy groups increased by the introduction of pendant carboxyl groups, although the expected dramatical rise was not found.

Furthermore, we examined 5 wt % loss temperatures ($T_d^{5\%}$) of **P-4a** and **P-4b**. As summarized in Table III, $T_d^{5\%}$ of **P-4a** and **P-4b** were 268 and 258 °C, respectively. This result suggests that the weight-loss temperatures of the hyperbranched polymer **P-4a** with pendant hydroxy groups was 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 the polymer.

We also compared the $T_d^{5\%}$ of **P-4b** with that of the other type of hyperbranched polyester¹⁹ (**ref 1**) with pendant carboxyl groups and terminal methacryloyl groups, which was prepared by the polyaddition of di(glycidyl ether) of bisphenol-A with TMA and MA followed by the reaction with THPA under similar reaction conditions, from the view point of the practical application as solder resist. As shown in Figure 4, although the $T_d^{5\%}$ of **P-4b** was 258 °C, the $T_d^{5\%}$ of **ref 1** was 225 °C. This means that **P-4b** prepared from the reaction of bis(oxetane) had better thermal stability than **ref 1** prepared from the reaction of bis(epoxide) in the initial stage. These differences might come

Figure 4. TGA profiles of polymer.

Table IV. Composition of solder resists^a

Composition		Sample 1	Sample 2	ref 2
Main resin	58 wt %	P-4b	P-6b	SP-3500
Diluents	12 wt %	DPEHA	DPEHA	DPEHA
Photo-initiator	5 wt %	Irgacure 907	Irgacure 907	Irgacure 907
Curing agent	24 wt %	Epoxy resin	Epoxy resin	Epoxy resin
Additive	1 wt %	Dicyandiamine	Dicyandiamine	Dicyandiamine

^aDiethylene glycol monoethyl ether acetate (40 wt % to P-4b) was used as a solvent.

from the ester linkage of pendant carboxyl moieties. That is, the pendant ester linkage composed from *sec*-alcohol unit in **ref 1** decomposed easily at lower temperature to remove THPA molecule than the ester linkage composed from *primary*-alcohol unit in **P-4b**.

Evaluation of Solder Resist Based on Polyester P-4b with both Photoreactive Methacryloyl Groups and Alkaline Developable Carboxyl Groups

The patterning property of the prepared solder resist was measured with a SEM image.

The resist solution composed from the mixture of main resin (**P-4b** with 55% of the pendant carboxyl groups), diluents, photo-initiator, thermal-curing agent, and additive are summarized in Table IV. The resist solution coated on the substrate was dried to form the resist film (50 μm thick) and exposed by the UV light. After that, the exposed resist film on the substrates was developed with 1 wt % of Na_2CO_3 aqueous solution. Figure 5 showed a SEM image of the contact-printed negative pattern, which was post-baked at 150 $^\circ\text{C}$ for 60 min after lithography process. This result showed that the solder resist composed mainly from **P-4b** was capable of very high resolving such as 55 μm line width.

Figure 5. SEM image of the pattern.

CONCLUSIONS

We have investigated synthesis and photo-initiated radical polymerization of hyperbranched poly(ester)s with both photosensitive groups and alkali-developable groups. Novel hyperbranched poly(ester)s with methacryloyl groups were synthesized by the poly-addition of bis(oxetane)s with TMA and MA. The chemical modification of the synthesized hyperbranched poly(ester)s was carried out with THPA to afford the alkali developable polymer containing pendant carboxyl groups. It was also found that the polymer (**P-4b**) prepared from the reaction of BEOB with TMA and MA followed by the reaction with THPA had higher $T_d^{5\%}$ than other type of hyperbranched polyester (**ref 1**) prepared from the reaction of bis(epoxide) with TMA and MA followed by the reaction with THPA. Negative-type solder resist based on **P-4b**, photo-initiator, diluents, curing agent, and additive was prepared, and lithographic behavior was evaluated. As a result, it was found that this solder resist has excellent resolution such as 55 μm line width when 50 μm thick film is used.

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