Synthesis of Alkaline-Developable, Photosensitive Hyperbranched Polyimides through the Reaction of Carboxylic Acid Dianhydrides and Trisamines

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ABSTRACT: Hyperbranched polyimides (HBPI)s with high glass-transition temperatures and excellent thermal stability were synthesized through the reaction of commercially available carboxylic acid dianhydrides with tris[4-(4-aminophenoxy)phenyl]ethane (TAPE). In particular, hyperbranched polyimide HBPI(TAPE-DSDA), prepared through the reaction of TAPE with 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), showed higher thermal stability and good solubility. Furthermore, alkaline-developable, photosensitive HBPI(TAPE-DSDA)-MA-CA was prepared through the reaction of HBPI(TAPE-DSDA) with glycidyl methacrylate with tetrabutylammonium bromide as a catalyst in *N*-methyl-2-pyrrolidinone (NMP) followed by the addition reaction of *cis*-1,2,3,6-tetrahydrophthalic anhydride with triphenylphosphine as a catalyst in NMP. The glass-transition temperatures of HBPI(TAPE-DSDA)-MA-CA were greater than 300 °C. A resist composed of 74 wt % HBPI(TAPE-DSDA)-MA-CA, 22.2 wt % trimethylpropane triacrylate, and 3.8 wt % Irgacure 907 as a photoinitiator achieved a resolution of a 55-μm line pattern and a 275-μm space pattern by UV irradiation (1000 mJ/cm^2). © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 3697–3707, 2004

Keywords: alkaline-developable photosensitive materials; excellent thermal stability; high glass-transition temperature; hyperbranched polyimides; hyperbranched polymers; lithography; photopolymerization; radical polymerization

INTRODUCTION

It is well known that polyimides are useful high-performance materials because of their excellent thermal stability, high chemical resistance, high breakdown voltage, low thermal expansion, and low dielectric constants.[1] Polyimides are generally prepared through the ring-opening polyaddition of carboxylic dianhydrides with diamines, followed by thermal or chemical imidizations, and they have some significant disadvantages, such as low solubility and intermolecular and intramolecular charge-transfer-complex formation because of their characteristic structures.

Meanwhile, hyperbranched polymers, which are dendritic polymers, have been paid much attention because of their highly branched architecture.[2] Their solubility in common organic solvents is good, and their solution viscosity is low. Furthermore, hyperbranched polymers show interesting functions because they have a large num-

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ber of reactive groups at the ends. Generally, hyperbranched polymers are synthesized with two differential methods: the self-polymerization of an AB_2-type monomer[3] and the copolymerization of an A_2-type monomer with a B_3-type monomer.[4] The latter has a significant advantage for industrial applications because of its one-pot synthesis procedure.

Given this background, hyperbranched polyimides (HBPI)s are expected to have good solubility, high thermal stability, and good film-forming properties. Ueda et al.[5] reported the first synthesis of a photosensitive polyimide based on a hyperbranched poly(ether imide) as a new negative working material. Furthermore, we have reported the first synthesis and reaction of HBPIs containing methacryloyl groups with radically polymerizable photosensitivity.[6]

In this article, we report the first synthesis of an alkaline-developable, photosensitive HBPI containing both (meth)acryloyl and carboxyl groups at the ends. Furthermore, the patterning property of the synthesized HBPI has been evaluated with scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

1,1,1-Tris(4-hydroxyphenyl)ethane, 4-fluoronitrobenzene, hydrazine monohydrate, pyromellitic dianhydride (PMDA), 4,4′-bisphthalic anhydride (BPDA), oxydiphthalic anhydride (ODPA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), tetrabutylammonium bromide (TBAB), and triphenylphosphine (TPP) were purchased from Tokyo Kasei Kogyo Co., Ltd., and TBAB was recrystallized from ethyl acetate. Iron(III) chloride hexahydrate, activated carbon, acetic anhydride, pyridine, glycidyl methacrylate (GMA), *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA), *p*-methoxyphenol, *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), dioxane, and *p*-methoxyphenol were obtained from Kanto Chemical Co., Inc., and NMP was distilled under reduced pressure over CaH_2 before use. Potassium carbonate was purchased from Wako Pure Chemical Industries, Ltd. 4,4′-(4,4′-Isopropylidenediphenoxy)bis(phthalic anhydride) (IDBA) was purchased from Sigma–Aldrich Japan Co., Ltd. Irgacure 907 was purchased from Ciba Speciality Chemicals Co., Ltd.

Measurements

The melting point was measured on a Yanaco MP-500D micro melting-point apparatus. The infrared (IR) spectrum was recorded on a J FT/IR-420 spectrometer with a KBr plate. The ^{1}H NMR spectrum was recorded on a JEOL ECA-600 FT NMR spectrometer in dimethyl sulfoxide-d_6 (DMSO-d_6). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Seiko TG/DTA-6200 and a Seiko DSC-6200, respectively, at a heating rate of 10 °C/min under nitrogen. The number-average molecular weight (M_n) and polydispersity ratios [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were estimated with size exclusion chromatography on a HLC-8220 gel permeation chromatograph with TSK columns (AW2500×3) and were calibrated with polystyrene standards with a narrow molecular weight distribution. DMF containing 20 mmol/L lithium bromide and phosphoric acid was used as the eluent.

Synthesis of 1,1,1-Tris[4-(4-nitrophenoxy)phenyl]ethane (TNPE)

1,1,1-Tris(4-hydroxyphenyl)ethane (10.0 g, 33 mmol), 4-fluoronitrobenzene (15.4 g, 109 mmol), potassium carbonate (15.1 g, 109 mmol), and DMF (100 mL) were charged into a 500-mL flask and stirred at room temperature for 24 h. Then, the produced inorganic salt was filtered off, and the organic phase was washed with ethyl acetate and water. The organic phase was dried over anhydrous magnesium sulfate overnight and was evaporated to remove the solvent. The crude, yellow solid was recrystallized from ethyl acetate.

Yield: 17.0 g (77%). mp: 151–153 °C. IR (KBr, cm^{-1}): 1247 (ν PhOPh), 1343 (ν NO_2), 1587 (ν C=C aromatic). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.20 (s, *3.0 H,* CH_3), 7.15 (d, 6.0 H, J = 8.4 Hz, aromatic), 7.16 (d, 6.0 H, J = 9.0 Hz, aromatic), 7.20 (d, 6.0 H, J = 9.0 Hz, aromatic), 8.24 (d, 6.0 H, J = 9.0 Hz, aromatic). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 30.31 (methyl carbon of triphenyl ethane), 51.34 (quaternary carbon of triphenyl ethane), 117.60, 119.88, 126.24, 130.36, 142.40, 145.52, 152.67, 162.71 (aromatic carbon).

Synthsis of 1,1,1-Tris[4-(4-aminophenoxy)phenyl]ethane (TAPE)

A mixture of TNPE (8.0 g, 12.0 mmol), activated carbon (1.0 g), iron(III) chloride hexahydrate

(0.07 g, 0.26 mmol), and dioxane (60 mL) in a 200-mL flask was stirred at 80 °C for 8 h. Hydrazine monohydrate (2 mL) was added to the solution. During the reaction, portions of hydrazine monohydrate (2 mL) were added every 2 h. Then, the produced inorganic compound was filtered off, and the organic solution was washed with ethyl acetate and water. The organic phase was dried over anhydrous magnesium sulfate overnight, and was evaporated to remove the solvent. The crude, white powder was washed in boiling acetonitrile.

Yield: 4.9 g (71%). mp: 231–233 °C. IR (KBr, cm^{-1}): 1230 (ν PhOPh), 1497 (ν C═C aromatic), 3445, 3360 (ν NH_2). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.02 (s, *3.0 H,* CH_3), 4.95 (s, 6.0 H, NH_2), 6.57 (d, 6.0 H, J = 9.0 Hz, aromatic), 6.75 (d, 6.0 H, J = 9.0 Hz, aromatic), 6.75 (d, 6.0 H, J = 9.0 Hz, aromatic), 6.94 (d, 6.0 H, J = 9.0 Hz, aromatic). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 30.46 (methyl carbon of triphenyl ethane), 50.47 (quaternary carbon triphenyl ethane), 114.89, 115.70, 120.96, 129.45, 142.41, 145.49, 145.53, 156.98 (aromatic carbon).

Synthesis of Aromatic Hyperbranched Polyimides HBPI(TAPE-ODPA), HBPI(TAPE-DSDA), HBPI(TAPE-6FDA), HBPI(TAPE-IDBA), HBPI(TAPE-PMDA), HBPI(TAPE-BPDA), and HBPI(TAPE-BTDA)

A typical procedure for the polyaddition of TAPE with ODPA was as follows. To a solution of TAPE (0.2898 g, 0.5 mmol) in NMP (10 mL) was added dropwise a solution of carboxylic acid dianhydride ODPA (0.310 g, 1.0 mmol) in NMP (10 mL) at room temperature for 2 h under an argon atmosphere. The mixture was stirred at room temperature for 1 h, and then acetic anhydride (3.0 g) and pyridine (1.0 g) were added to the solution; the solution was stirred at room temperature for 3 h. The reaction mixture was heated at 60 °C and stirred for 5 h. Then, the reaction mixture was poured into excess methanol and stirred at room temperature for 24 h. The precipitate product was dried *in vacuo* at 60 °C for 24 h. The yield of resulting polymer HBPI(TAPE-ODPA) was 0.59 g (99%).

M_n: 32,100. M_w/M_n: 3.99. IR (KBr, cm^{-1}): 1236 (ν PhOPh), 1375 (ν C—N_{imide}), 1498 (ν C═C aromatic), 1695 (ν C═O_{COOH}), 1721, 1788 (ν C═O_{imide}), 3445 (ν OH_{COOH}). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.15–2.18 (m, 6.2 H, CH_3 of TAPE), 3.74–3.80 (m, *3.0 H,* CH_3 of ester), 6.90–7.15 (m, 14.7 H, aromatic of TAPE), 7.25–7.45 (m, 7.3 H, aromatic of TAPE), 7.45–7.65 (m, 4.9 H, aromatic of TAPE), 7.75–8.05 (m, 3.5 H, aromatic of ODPA).

HBPI(TAPE-DSDA)

Yield: 96%. M_n: 35,200. M_w/M_n: 4.36. IR (KBr, cm^{-1}): 1239 (ν PhOPh), 1297 (ν $PhSO_2Ph$), 1377 (ν C═N_{imide}), 1498 (ν C═C aromatic), 1682 (ν C═O_{COOH}), 1725, and 1781 (ν C═O_{imide}), 3443 (ν OH_{COOH}). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.10–2.20 (m, 5.5 H, CH_3 of TAPE), 3.76–3.86 (m, *3.0 H,* CH_3 of ester), 6.98–7.20 (m, 27.1 H, aromatic of TAPE), 7.38–7.46 (m, 8.8 H, aromatic of TAPE), 7.85–7.95 (m, 0.9 H, aromatic of DSDA), 7.95–8.04 (m, 0.5 H, aromatic of DSDA), 8.15–8.25 (m, 4.2 H, aromatic of DSDA), 8.35–8.45 (m, 2.7 H, aromatic of DSDA), 8.50–8.70 (m, 8.4 H, aromatic of DSDA).

HBPI(TAPE-6FDA)

Yield: 93%. M_n: 22,000. M_w/M_n: 217.67. IR (KBr, cm^{-1}): 1242 (ν PhOPh), 1376 (ν C═N_{imide}), 1499 (ν C═C aromatic), 1695 (ν C═O_{COOH}), 1728 and 1784 (ν C═O_{imide}), 3443 (ν OH_{COOH}). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.12–2.20 (m, 7.3 H, CH_3 of TAPE), 3.76–3.84 (m, *3.0 H,* CH_3 of ester), 6.96–7.20 (m, 24.4 H, aromatic of TAPE), 7.38–7.48 (m, 8.2 H, aromatic of TAPE), 7.62–7.88 (m, 8.1 H, aromatic of 6FDA), 7.90–8.04 (m, 3.5 H, aromatic of 6FDA), 8.08–8.20 (m, 4.2 H, aromatic of 6FDA).

HBPI(TAPE-IDBA)

Yield: 96%. M_n: 15,900. M_w/M_n: 3.74. IR (KBr, cm^{-1}): 1237 (ν PhOPh), 1370 (ν C—N_{imide}), 1498 (ν C═C aromatic), 1685 (ν C═O_{COOH}), 1721 and 1776 (ν C═O_{imide}), 3439 (ν OH). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 1.68–1.78 (m, 20.7 H, CH_3 of IDBA), 2.16–2.24 (m, 5.6 H, CH_3 of TAPE), 3.84–3.88 (m, *3.0 H,* CH_3 of ester), 6.96–7.04 (m, 25.8 H, aromatic of TAPE), 7.06–7.14 (m, 24.9 H, aromatic of TAPE and IDBA), 7.28–7.50 (m, 38.4 H, aromatic of TAPE), 7.84–7.90 (m, 6.5 H, aromatic of IDBA), 7.90–7.94 (m, 1.7 H, aromatic of IDBA).

HBPI(TAPE-PMDA)

Yield: 95%. IR (KBr, cm^{-1}): 1237 (ν PhOPh), 1376 (ν C—N_{imide}), 1497 (ν C═C aromatic), 1681 (ν C═O_{COOH}), 1725, 1778 (ν C═O_{imide}), 3482 (ν OH).

HBPI(TAPE-BPDA)

Yield: >99%. IR (KBr, cm^{-1}): 1235 (ν PhOPh), 1373 (ν C—N_{imide}), 1498 (ν C=C aromatic), 1676 (ν C=O_{COOH}), 1720, 1775 (ν C=O_{imide}), 3438 (ν OH_{COOH}).

HBPI(TAPE-BTDA)

Yield: >93%. IR (KBr, cm^{-1}): 1238 (ν PhOPh), 1377 (ν C—N_{imide}), 1498 (ν C=C aromatic), 1671 (ν C=O_{COOH}), 1724, 1779 (ν C=O_{imide}), 3439 (ν OH_{COOH}).

Synthesis of Photosensitive Hyperbranched Polyimide HBPI(TAPE-DSDA)-MA

HBPI(TAPE-DSDA) (0.5962 g, 0.5 mmol as COOH), GMA (0.2132 g, 1.5 mmol), TBAB (8 mg, 0.025 mmol), and a small amount of *p*-methoxyphenol as an inhibitor were dissolved in NMP (20 mL). The mixture was stirred at 80 °C for 24 h under an argon atmosphere. After that, the reaction mixture was poured into a mixed solvent of ethyl acetate and hexane (4:1 v/v). The obtained precipitate was dried *in vacuo*. The yield of photosensitive HBPI(TAPE-DSDA)-MA was 0.54 g (81 %).

IR (KBr, cm^{-1}): 1239 (ν PhOPh), 1297 (ν $PhSO_2Ph$), 1377 (ν C—N_{imide}), 1498 (ν C=C aromatic), 1682 (ν C=O_{COOH}), 1725, 1781 (ν C=O_{imide}), 3443 (ν OH). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 1.80–1.90 (m, 2.8 H, CH_3 of methacryloyl), 2.10–2.12 (m, 6.7 H, CH_3 of TAPE), 3.75–3.85 (m, *3.0 H,* CH_3 of ester), 3.95–4.00 (m, 1.8 H, CH_2 and OH), 4.25–4.35 (m, 0.8 H, CH_2), 5.55–5.60 (m, 0.5 H, vinyl), 6.00–6.05 (m, 0.5 H, vinyl), 6.94–7.18 (m, 35.3 H, aromatic of TAPE), 7.35–7.45 (m, 11.6 H, aromatic of TAPE), 7.85–7.90 (m, 0.2 H, aromatic of TAPE), 7.96–8.00 (m, 0.5 H, aromatic of DSDA), 8.10–8.20 (m, 6.1 H, aromatic of DSDA), 8.35–8.40 (m, 1.6 H, aromatic of DSDA), 8.45–8.70 (m, 11.9 H, aromatic of DSDA).

Synthesis of Alkaline-Developable, Photosensitive Hyperbranched Polyimide HBPI(TAPE-DSDA)-MA-CA

HBPI(TAPE-DSDA)-MA (0.4553 g, 0.5 mmol as OH), THPA (0.4564 g, 3.0 mmol), TPP (6 mg, 0.025 mmol), and a small amount of *p*-methoxyphenol as an inhibitor were dissolved in NMP (20 mL). The mixture was stirred at 60 °C for 24 h under an argon atmosphere. The reaction mixture was poured into a mixed solvent of ethyl acetate and hexane (4:1 v/v). The obtained precipitate was dried *in vacuo* to yield alkaline-developable, photosensitive HBPI(TAPE-DSDA)-MA-CA.

Yield: 0.40 g (76%). IR (KBr, cm^{-1}): 1239 (ν PhOPh), 1297 (ν $PhSO_2Ph$), 1379 (ν C—N_{imide}), 1498 (ν C=C aromatic), 1680 (ν C=O_{COOH}), 1725, 1781 (ν C=O_{imide}), 3486 (ν COOH). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 1.80–1.90 (m, 15.1 H, CH_3 of methacryloyl), 2.10–2.12 (m, 17.3 H, CH_3 of TAPE), 2.30–2.40 (m, 1.1 H, CH_2 of cyclohexenyl), 2.80–2.90 (m, 1.0 H, CH_2 of cyclohexenyl), 3.75–3.85 (m, 3.0 H, CH_3 of ester), 3.95–4.00 (m, 2.6 H, CH_2 and OH), 4.25–4.35 (m, 1.9 H, CH_2), 5.40–5.55 (m, 1.11 H, vinyl of cyclohexenyl), 5.55–5.60 (m, 1.3 H, vinyl of methacryloyl), 6.00–6.05 (m, 1.2 H, vinyl of methacryloyl), 6.90–7.20 (m, 33.4 H, aromatic of TAPE), 7.35–7.45 (m, 10.8 H, aromatic of TAPE), 7.85–8.05 (m, 1.0 H, aromatic of TAPE), 8.10–8.20 (m, 5.9 H, aromatic of DSDA), 8.35–8.55 (m, 5.2 H, aromatic of DSDA), 8.55–8.70 (m, 7.7 H, aromatic of DSDA).

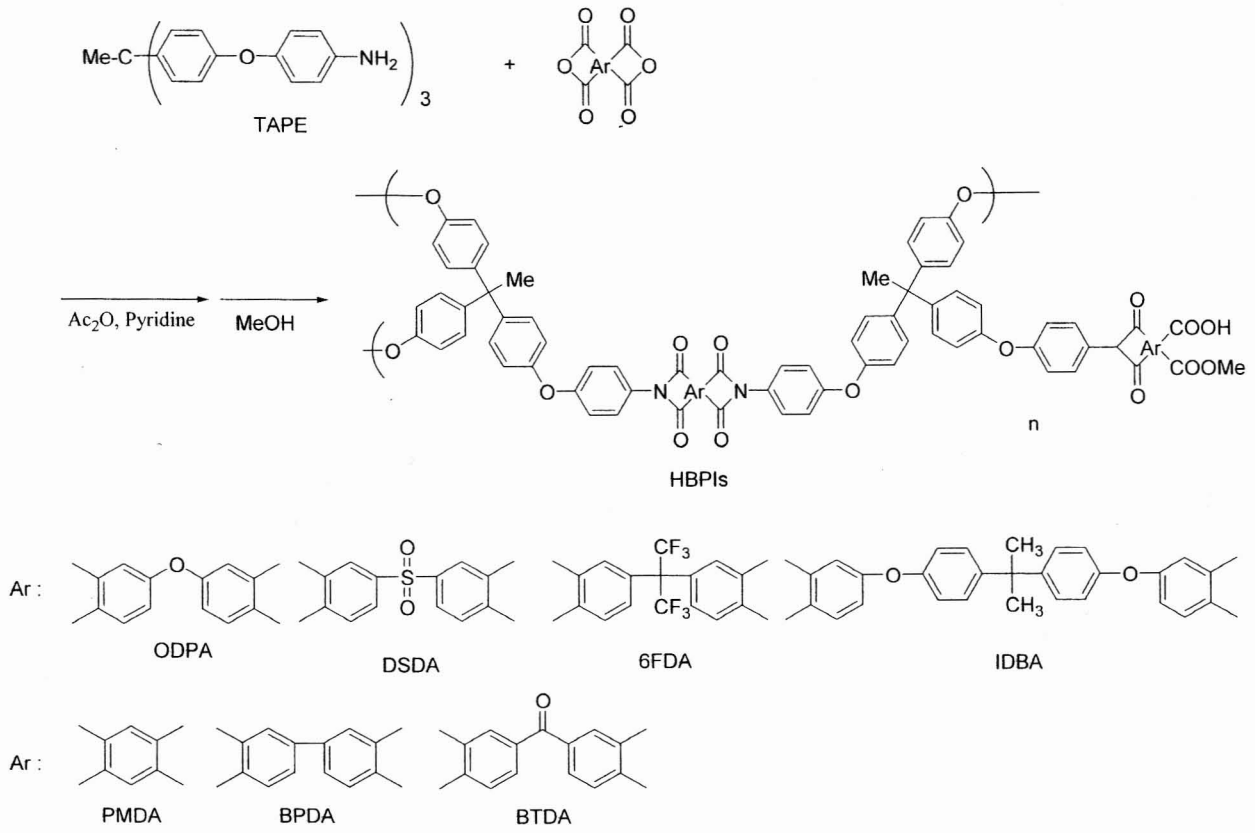
Patterning Property of HBPI(TAPE-DSDA)-MA-CA

A photoresist was prepared from 74.0 wt % HBPI(TAPE-DSDA), 22.2 wt % tirmethylolpropane triacrylate (TMPTA) as a diluent, 3.8 wt % Irgacure 907 as a photoinitiator, and 400 mL of dimethylacetamide (DMAc) as a solvent, and it was coated onto a substrate with a bar coater with a wet film thickness of 100 μm. The coated substrate was heated at 80 °C for 20 min to remove the solvent and was exposed to UV light (1000 mJ/cm^2). After that, the exposed polymer film on the substrate was developed with 10 wt % tetramethylamonium hydroxide (TMAH) for 5 min.

RESULTS AND DISCUSSION

Synthesis of TAPE

We examined the synthesis of the HBPIs through the reaction of TAPE and certain carboxylic dianhydrides. We designed the monomer TAPE containing triamine groups and an aromatic moiety. As illustrated in Scheme 1, TAPE was synthesized by a two-step reaction. The substitution reaction of 1,1,1-tris(4-nitrophenyl)ethane with 4-fluoronitrobenzene was carried out in the presence of potassium carbonate at room temperature for 24 h in DMF to afford the corresponding compound TNPE. The nitro groups of TNPE were reduced by hydrazine monohydrate, activated carbon, and iron(III) chloride hexahydrate in di-



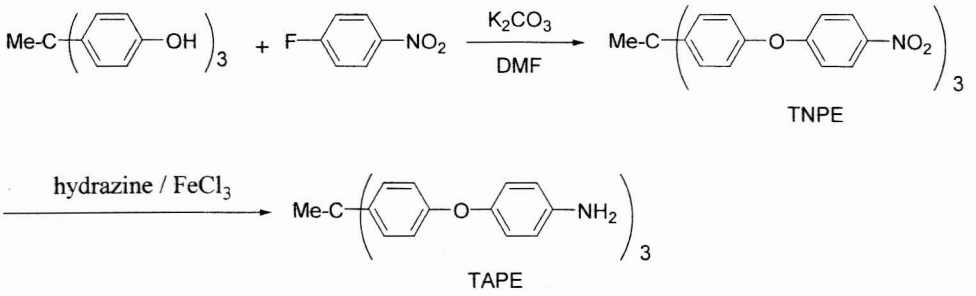
Scheme 2. Synthesis of HBPIs.

NMR spectrum of HBPI(TAPE-DSDA), the characteristic signals were observed at 2.10–2.20 due to CH_3 of TAPE, at 3.76–3.86 due to CH_3 of the ester at the polymer ends, at 6.98–7.46 due to the aromatic of TAPE, and at 7.85–8.70 due to the aromatic of DSDA [Fig. 2 (a)]. No apparent proton

Table 1. Synthesis of HBPIs[a]

					Before Annealing[c]			After Annealing[c]		
Polymer	Dianhydride	Yield (%)[b]	M_n^d	M_w/M_n^d	T_g (°C)[c]	$T_d^{5\%}$ (°C)[f]	$T_d^{10\%}$ (°C)[f]	T_g (°C)[e]	$T_d^{5\%}$ (°C)[f]	$T_d^{10\%}$ (°C)
HBPI(TAPE-ODPA)	ODPA	99	32,100	3.99	—[h]	146	192	237	490	525
HBPI(TAPE-DSDA)	DSDA	96	35,200	4.36	—[h]	145	181	310	477	502
HBPI(TAPE-6FDA)	6FDA	93	22,000	217.67	—[h]	150	240	284	501	530
HBPI(TAPE-IDBA)	IDBA	80	15,900	3.74	—[h]	124	170	212	518	530
HBPI(TAPE-PMDA)	PMDA	95	—[g]	—[g]	—[h]	201[i]	255[i]	285[i]	503[i]	530[i]
HBPI(TAPE-BPDA)	BPDA	>99	—[g]	—[g]	—[h]	127[i]	165[i]	264[i]	498[i]	536[i]
HBPI(TAPE-BTDA)	BTDA	93	—[g]	—[g]	—[h]	182[i]	229[i]	248[i]	500[i]	527[i]

[a] The reaction of TAPE (0.5 mmol) and aromatic dianhydrides (1.0 mmol) in NMP (20 mL) was carried out with Ac_2O (3.0 g) and pyridine (1.0 g) at room temperature and 60 °C for 7 and 5 h, respectively.
[b] Insoluble parts in MeOH.
[c] Annealing condition. 300 °C for 1 h.
[d] Measured by GPC (DMF) based on polystyrene standards.
[e] Measured by DSC at a heating rate of 10 °C/min under nitrogen.
[f] Measured by TG/DTA at a heating rate of 10 °C/min under nitrogen.
[g] Insoluble in DMF.
[h] Not detected.
[i] The value was obtained from a gel compound.



Scheme 1. Synthesis of TAPE.

oxane to give TAPE in a 71% yield. The structure of TAPE was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

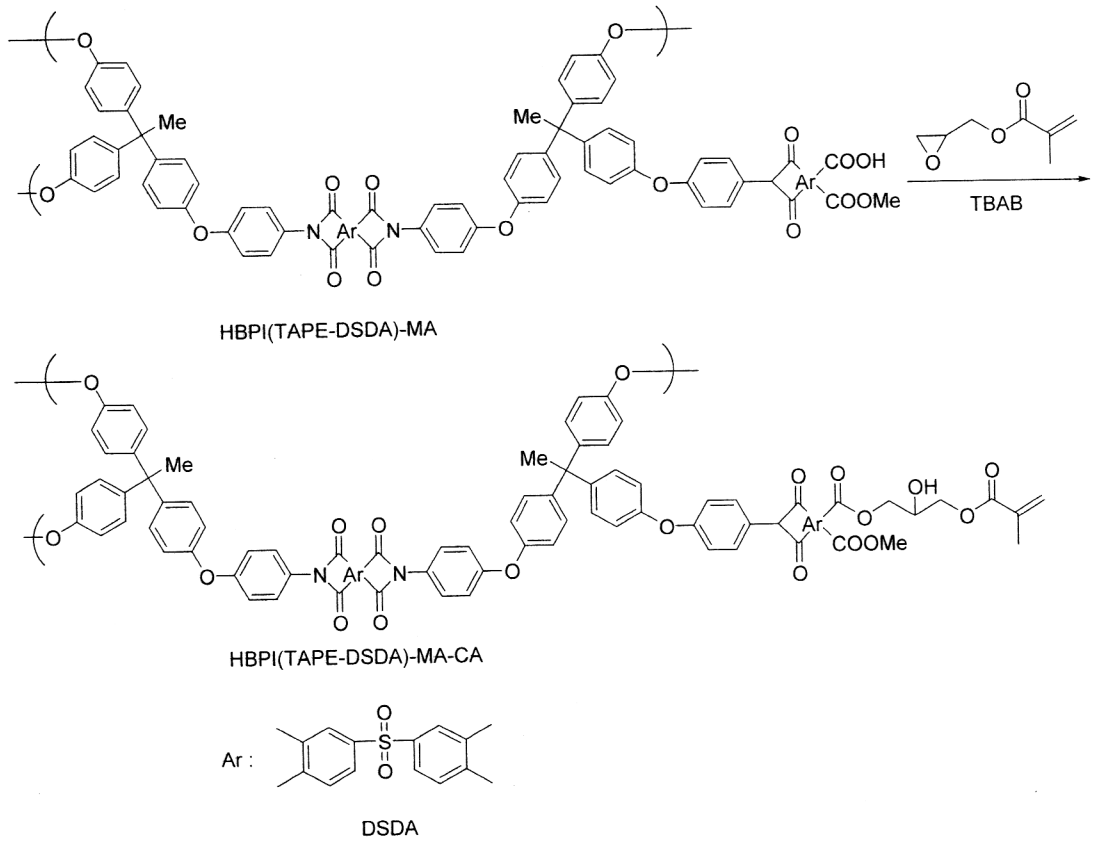
Synthesis of HBPIs through the Reaction of TAPE with Carboxylic Acids PMDA, BPDA, BTDA, ODPA, DSDA, 6FDA, and IDBA

Okamoto et al.[7] reported the synthesis of HBPIs with two different terminal groups, such as anhydride groups or amino groups, through the reaction of tris(4-aminophenyl)amine (TAPA) and acetic dianhydride 6FDA. They reported the synthesis of amine-terminated and carboxy anhydride terminated HBPIs by the two synthetic methods. They obtained amine-terminated HBPIs when a solution of TAPA was added dropwise to a solution of 6FDA in a monomer feed ratio of TAPA/6FDA = 1:1, and they obtained anhydride-terminated HBPIs when a solution of 6FDA was added dropwise to a solution of TAPA in a monomer feed ratio of TAPA/6FDA = 1:2.

In this study, we synthesized HBPIs with terminal carboxylic acid groups through the reaction of TAPE with certain commercially available carboxylic dianhydrides, such as ODPA, DSDA, OFDA, IDBA, PMDA, BPDA, and BTDA, as shown in Scheme 2. First, the carboxylic acid terminated HBPIs were obtained through the reaction of TAPE with ODPA. This reaction was prepared as follows. A TAPE solution in NMP was added dropwise to a solution of carboxylic dianhydride ODPA in NMP at room temperature for 2 h under argon, and the mixture was stirred at room temperature for 1 h more to afford corresponding poly(amide acid)s. Then, acetic anhydride and pyridine were added under stirring at 60 °C for 5 h to form imide groups in the polymer chains and anhydride groups in the polymer ends. After that, excess methanol was added to the solution, and the solution was stirred at room temperature for 24 h for the methanolysis of the terminal carboxylic anhydride groups in the polymer to obtain HBPI(TAPE-ODPA) containing carboxylic acid and monomethyl phthalate groups at the ends. In the same manner, HBPI(TAPE-DSDA), HBPI(TAPE-6FDA), and HBPI(TAPE-IDBA) were obtained through the reaction of TAPE with DSDA, 6FDA, and IDBA, respectively. These conditions and results are summarized in Table 1.

In the case of the reactions of TAPE with PMDA, BPDA, and BTDA, the resulting products were not soluble in any organic solvents. These results mean that gelation occurred in the stage of the addition reaction of TAPE with PMDA, BPDA, and BTDA. Through the reaction of 6FDA, a wide polydispersity ratio of HBPI(TAPE-6FDA) was obtained (M_w/M_n = 217.67; Table 1). For this polymerization, the reaction mixture was consistently homogeneous, with all strating materials and products remaining in the solution. It seems that microgel products might be obtained in this polymerization system. Other resulting HBPIs—HBPI(TAPE-ODPA), HBPI(TAPE-DSDA), and HBPI(TAPE-IDBA)—were soluble in common organic solvents, such as $CHCl_3$, THF, DMF, DMAc, NMP, and DMSO (Table 2), and their yields and M_n's were 93–99% and 22,000–32,100, respectively.

The structure of the obtained HBPIs was confirmed with IR and ^{1}H NMR spectroscopy. Figure 1 presents the IR spectrum of HBPI(TAPE-DSDA) before and after annealing at 300 °C for 1 h. The characteristic absorption peaks based on the imide and carboxylic acid groups of HBPI-(TAPE-DSDA) can be observed at 1377 (ν C═N$_{imide}$), 1682 (ν C═O$_{COOH}$), 1725 and 1781 (ν C═O$_{imide}$), and 3443 cm^{-1} (ν OH$_{COOH}$) [Fig. 1(a)]. After 1 h of annealing at 300 °C, a new peak assignable to anhydride groups appeared around 1850 cm^{-1} [Fig. 1(b)]. As illustrated in the ^{1}H



Scheme 3. Synthesis of hyperbranched polyimide HBPI(TAPE-DSDA)-MA-CA.

Synthesis of Alkaline-Developable, Photosensitive HBPI(TAPE-DSDA)-MA-CA

To introduce alkaline-developable carboxyl groups, we examined the addition reaction of HBPI(TAPE-DSDA)-MA and THPA and in the presence of TPP as a catalyst in NMP at 60 and 70 °C for 24 h; it afforded hyperbranched polyimide HBPI (TAEA-BTDA)-MA-CA in 68 and 76% yields, as shown in Scheme 4 and Table 4. The structure of the resulting hyperbranched polyimide HBPI-(TAPE-DSDA)-MA-CA was confirmed with IR and ^{1}H NMR spectroscopy. Figure 2(C) presents the ^{1}H NMR spectrum of HBPI(TAPE-DSDA)-MA-CA, which shows signals assignable to the

Table 3. Synthesis of HBPI(TAPE-DSDA)-MA[a]

Run	Temperature (°C)	Time (h)	Yield (%)[b]	DR (%)[c]	$M_n \times 10^{-4}$[d]	M_w/M_n[d]	T_g (°C)[e]	$T_d^{5\%}$ (°C)[f]	$T_d^{10\%}$ (°C)[f]
1	70	24	83	34	4.59	10.40	—[g]	254	398
2	70	48	88	46	4.70	15.41	—[g]	298	419
3	80	24	81	49	4.18	8.09	—[g]	323	438
4	80	48	83	27	4.29	92.15	—[g]	186	270

[a] The reaction was carried out with HBPI(TAPE-DSDA) (0.5 mmol as COOH) and GMA (1.5 mmol) in the presence of TBAB (0.025 mmol) in NMP.
[b] Insoluble part in 1:4 AcOEt/hexane.
[c] Calculated by ^{1}H NMR.
[d] Estimated by GPC (DMF) based on polystyrene standards.
[e] Measured by DSC at heating rate of 10 °C/min under nitrogen (second scan).
[f] Measured by TG/DTA at a heating rate of 10 °C/min under nitrogen.
[g] Not detected.

Table 2. Solubility of HBPIs[a]

Solvent	HBPI(TAPE-ODPA)	HBPI(TAPE-DSDA)	HBPI(TAPE-6FDA)	HBPI(TAPE-IDBA)
MeOH	−	−	−	−
$CHCl_3$	+−	+−	++	++
THF	++	++	++	++
AcOEt	−	−	+−	−
Toluene	−	−	−	−
Chlorobenzene	−	−	−	+−
DMF	++	++	++	++
DMAc	++	++	++	++
NMP	++	++	++	++
DMSO	++	++	++	++
1 wt % $Na_{2C}O_3$	−	−	−	−
3 wt % Na_2CO_3	−	−	−	−
2.38 wt % TMAH	−	+−	+−	−

[a] ++ = soluble at room temperature; + = soluble by heating; +− = partially soluble; − = insoluble.

signals for amide groups of poly(amide acid) were observed. These results mean that HBPI(TAPE-DSDA) had monomethyl phthalate groups at the ends of the polymer.

Furthermore, the glass-transition temperatures (T_g's), 5% weight—loss temperatures ($T_d^{5\%}$'s), and 10% weight-loss temperatures ($T_d^{10\%}$'s) of the resulting HBPIs were determined before and after annealing at 300 °C for 1 h. The cyclization of terminal monomethyl phthalate groups at the end proceeded in the solid state at 300 °C to form anhydride groups. As summarized in Table 1, the $T_d^{5\%}$ and $T_d^{10\%}$ values of the HBPIs increased after annealing. However, no significant changes in the T_g values were observed after annealing.

According to the aforementioned results, we examined the chemical modification of HBPI-(TAPE-DSDA) because both its thermal properties and solubility were good.

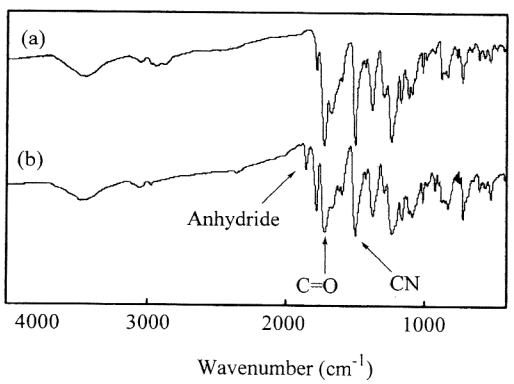


Figure 1. IR spectra of HPBI(TAPE-DSDA) (a) before and (b) after annealing at 300 °C.

Synthesis of Photosensitive HBPI(TAPE-DSDA)-MA

Nishikubo and coworkers'[8,9] reported the addition reaction of epoxide with carboxylic acid, using quaternary onium salts as catalyst.[6] In this study, we examined the addition reaction of GMA with HBPI(TAPE-DSDA) to introduce photosensitive (meth)acryloyl groups at the ends (Scheme 3). The reaction of HBPI(TAPE-DSDA) and GMA was carried out in the presence of TBAB as a catalyst in NMP at 70 and 80 °C for 24 and 48 h, affording the corresponding product HBPI(TAPE-DSDA)-MA containing methacryloyl groups at the ends in 81–83% yields. These results and conditions are summarized in Table 3.

Figure 2 presents ^{1}H NMR spectra before and after the reaction of GMA and HBPI(TAPE-DSDA). Signals assignable to methacrylate groups at the ends of the polymer chains can be observed around 5.55–5.60 ppm. This result shows that HBPI(TAPE-DSDA)-MA had (meth)acryloyl groups at the chain ends. The degrees of reaction (DRs) were also calculated to be 27–49 by the ^{1}H NMR integration of the signals for methyl protons of ester and vinyl protons of methacryloyl groups. DR increased with increasing reaction temperature and time. However, when the reaction was performed at 80 °C for 48 h, a reduction of DR was observed (Table 3). This result means that microgelation proceeded at a higher reaction temperature.

Furthermore, no apparent T_g's of HBPI(TAPE-DSDA)-MA were observed up to 300 °C; $T_d^{5\%}$ and $T_d^{10\%}$ were found at 254–323 and 398–438 °C, respectively.

Table 4. Synthesis of HBPI(TAPE-DSDA)-MA-CA[a]

Run	THPA (mmol)	Temperature (°C)	Yield (%)[b]	DR (%)[c]	$M_n \times 10^{-4}$[d]	M_w/M_n[d]	T_g (°C)[e]	$T_d^{5\%}$ (°C)[f]	$T_d^{10\%}$ (°C)[f]
1	3.0	60	76	45	4.06	18.07	—[g]	197	322
2	3.0	70	68	88	4.07	74.41	—[g]	227	330

[a] The reaction was carried out with photosensitive HBPI(TAPE-DSDA) (0.5 mmol as OH) and THPA in the presence of TPP (0.025 mmol) in NMP for 24 h.
[b] Insoluble part in 1:4 AcOEt/hexane.
[c] Estimated by ^{1}H NMR.
[d] Estimated by GPC (DMF) based on polystyrene standards.
[e] Measured by DSC at a heating rate of 10 °C/min under nitrogen (second scan).
[f] Measured by TG/DTA at a heating rate of 10 °C/min under nitrogen.
[g] Not detected.

4. The DRs were calculated to be 45 and 88 through the ^{1}H NMR integration of the signals of the methyl protons of ester and the vinyl protons of THPA moieties. By this addition reaction at 70 °C, a wide polydispersity ratio was observed (M_w/M_n = 74.41) (Run 2 in Table 4). This result indicates that the microgelation reaction proceeded at a higher reaction temperature.

Thermal Properties of HBPI(TAPE-DSDA), HBPI(TAPE-DSDA)-MA, and HBPI(TAPE-DSDA)-MA-CA

Figure 3 shows TGA curves of HBPI(TAPE-DSDA), HBPI(TAPE-DSDA)-MA, and HBPI-(TAPE-DSDA)-MA-CA. HBPI(TAPE-DSDA) did not show a significant initial-weight-loss temperature (T_d^{init}) until about 470 °C [Fig. 3(a)]. On the other hand, the T_d^{init} values of HBPI(TAPE-DSDA)-MA and HBPI(TAPE-DSDA)-MA-CA were about 180 and 150 °C, respectively [Fig. 3(b,c)]. These results mean that the thermal decomposition of terminal (meth)acryloyl groups and carboxyl groups in the polymer ends occurred.

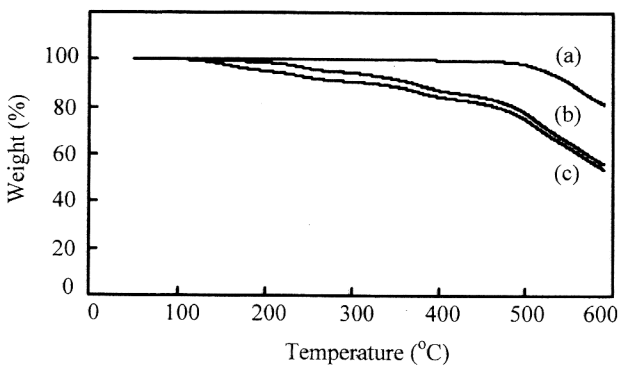


Figure 3. TGA curves of polyimides: (a) HPBI(TAPE-DSDA), (b) HPBI(TAPE-DSDA)-MA, and (c) HPBI-(TAPE-DSDA)-MA-CA.

Patterning Property of HBPI(TAPE-DSDA)-MA-CA

The patterning property of HBPI(TAPE-DSDA)-MA-CA was measured with an SEM image obtained from a polymer film prepared as follows. The photoresist was prepared from 74.0 wt % HBPI(TAPE-DSDA)-MA-CA, 22.2 wt % TMPTA as a diluent, 3.8 wt % Irgacure 907 as a photoinitiator, and 400 mL of DMAc as a solvent, and it was coated onto a substrate with a bar coater with a wet film thickness of 100 μm. The coated substrate was heated at 80 °C for 20 min to remove the solvent and was exposed to UV light (1000 mJ/cm^2). After that, the exposed polymer film on the substrate was developed with 10 wt % TMAH for 5 min. As a result, a clear pattern with a 55-μm line width was obtained (Fig. 4).

CONCLUSIONS

From all these results, the following conclusions can be drawn. First, certain HBPIs with monomethyl phthalate groups at the ends of the polymer chains were synthesized through the reaction of commercially available carboxylic acid dianhydrides with TAPE. Second, the obtained HBPI-(TAPE-DSDA) had a high T_g, excellent thermal stability, and good solubility in common organic solvents. Third, alkaline—developable, photoreactive HBPI(TAPE-DSDA)-MA-CA containing both methacyloyl and carboxylic acid groups at

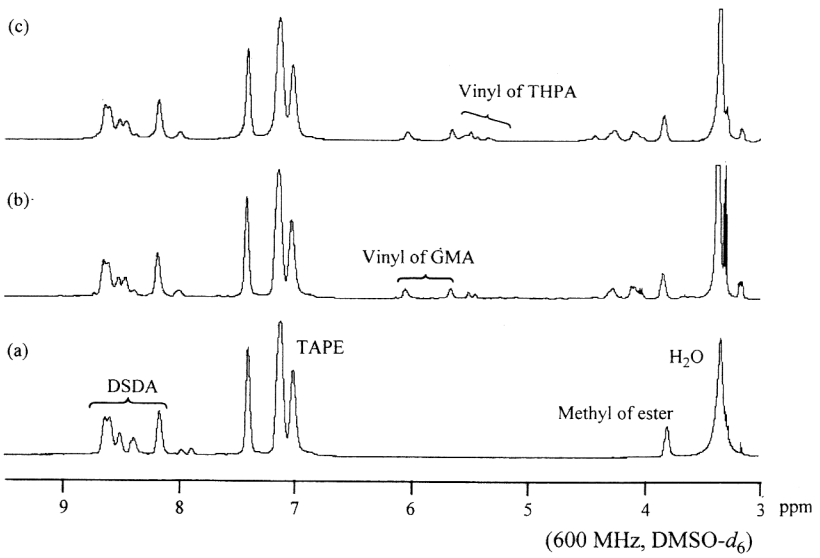
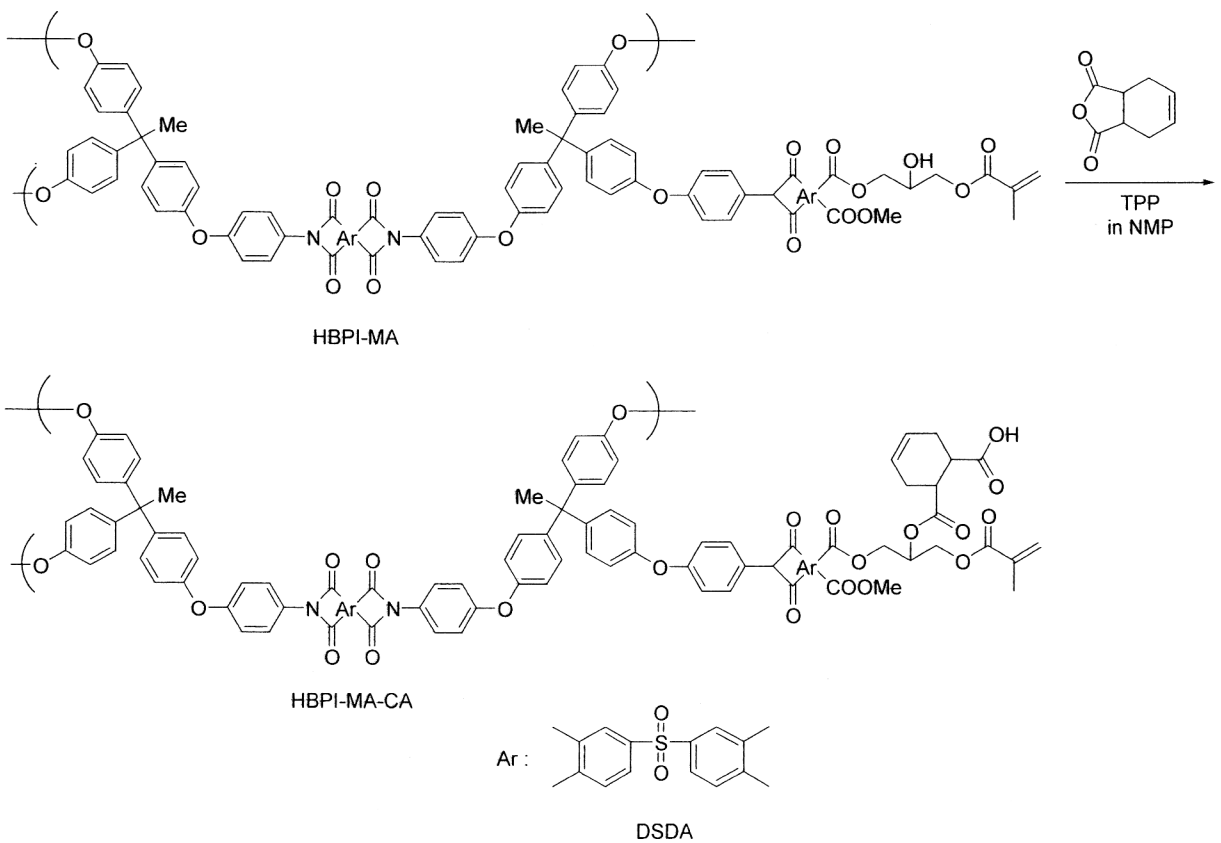


Figure 2. ^{1}H NMR spectra of polyimides: (a) HPBI(TAPE-DSDA), (b) HPBI(TAPE-DSDA)-MA, and (c) HPBI(TAPE-DSDA)-MA-CA.

methacrylate groups of the THPA units around 5.40–5.55 ppm. With IR spectroscopy, the characterstic absorption peaks of carboxylic acid groups were observed at 1680 and 3484 cm^{-1}. These results strongly support the structure of HBPI(TAPE-DSDA)-MA-CA, as shown in Scheme



Scheme 4. Synthesis of hyperbranched polyimides HBPI-MA-CA containing methacryloyl and carboxyl groups.

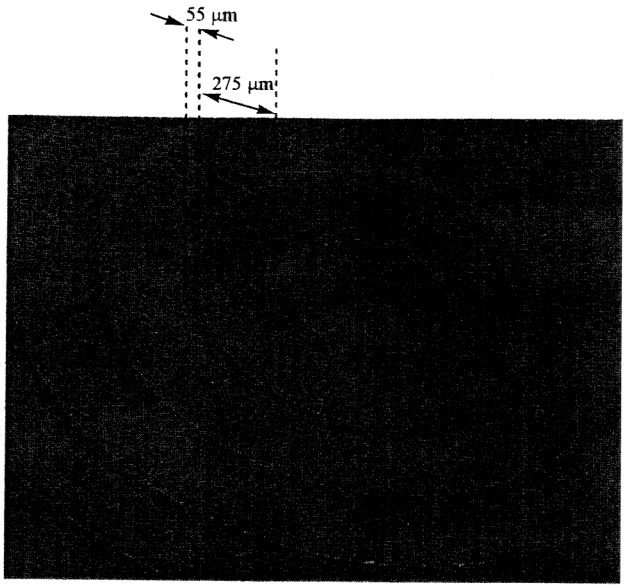


Figure 4. SEM image obtained from a HPBI(TAPE-DSDA)-MA-CA film prepared from HBPI(TAPE-DSDA), TMPTA, as a diluent, and Irgacure 907 as a photoinitiator.

the ends was synthesized through the addition reaction of HBPI(TAPE-DSDA) with GMA with TBAB as a catalyst in NMP, followed by an addition reaction with THPA with TPP as a catalyst in NMP. Fourth, a resist composed of HBPI(TAPE-DSDA)-MA-CA, trimethylpropane triacrylate, and Irgacure 907 as a photoinitiator achieved a resolution of a 55-μm line pattern and a 275-μm space pattern by UV irradiation (1000 mJ/cm^2).

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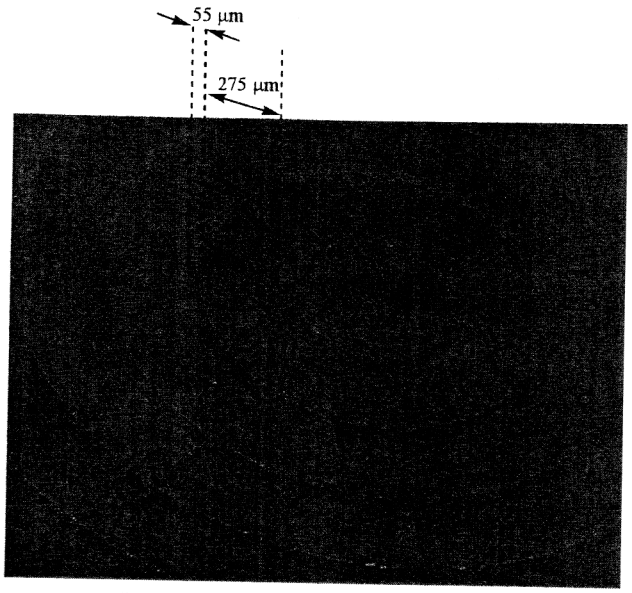

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