Preparation of Acid-Cleavable Branched Polymers for Argon Fluoride Photoresists via Reversible Addition–Fragmentation Chain-Transfer Polymerization

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ABSTRACT: A series of branched polymers for chemically amplified resists (CARs) were prepared through the reversible addition–fragmentation chain-transfer (RAFT) copolymerization of three monomers with lithographic functionalities and an acid-cleavable dimethacrylate monomer. The three monomers with lithographic functionalities were 2-ethyl-2-adamantyl methacrylate, α-γ-butyrolactone methacrylate, and 3-hydroxy-1-adamantyl methacrylate. The acid-cleavable monomer was 2,5-dimethyl-2,5-hexanediol dimethacrylate (DMHDMA), and 2-cyanoprop-2-yl-1-dithionaphthalate was used as a chain-transfer agent. Because DMHDMA contains two methacrylate groups, it induced the branched structures of the polymers. The degree of branching could be controlled by the molar fraction of DMHDMA in the monomer mixtures. The size and structure of the polymers obtained after hydrolysis were very close to those of linear polymers prepared by RAFT copolymerization with the same amount of reagents, only without the acid-cleavable monomer. A preliminary lithography test using an argon fluoride source demonstrated that the acid-cleavable branched polymers could be promising candidates for CAR materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 344–352, 2012

Key words: branched; degradation; living polymerization; photoresists

INTRODUCTION

Argon fluoride (ArF) lithography technology using chemically amplified resists (CARs) and a 193-nm radiation source is widely used for the fabrication of nanosize patterns.[1–5] The polymers for CARs are usually prepared by the copolymerization of more than two monomers having lithographic functionalities, such as a resistance to etching, deprotection for solubility change (positive tone), and adhesion properties. Various polymers for CARs have been developed and used as ArF lithography resins.[1–8] Recently, (hyper)-branched polymers were developed for CARs because of their advantages, such as a low radius of gyration, high density of sterically congested peripheral groups, and low optimum dose for the fabrication of patterns, compared to linear polymers.[3–5]

Branched polymers can be prepared through the free-radical copolymerization of vinyl monomers with a small amount of brancher having two or more vinyl groups.[9,10] However, the fast polymerization cycles of free-radical copolymerization can result in the formation of polymer networks, whereas the brancher can be consumed by cyclization, which prevents the formation of well-defined branched polymers.[10] Living radical polymerization (LRP) can be used to overcome these drawbacks because the polymer chains grow steadily without fast polymerization cycles; this minimizes crosslinking and cyclization.[11,12]

In this study, we prepared branched polymers having an acid-cleavable branching site through reversible addition–fragmentation chain-transfer (RAFT) copolymerization using three methacrylate monomers and one acid-cleavable dimethacrylate monomer. We intentionally used RAFT polymerization to prepare the branched polymers for CARs because this process does not require the use of any metallic reagents and the methacrylate monomers can be easily polymerized.[13–16] Other commonly used techniques, such as atom transfer radical polymerization (ATRP) and stable free-radical polymerization, have drawbacks in the preparation of CAR
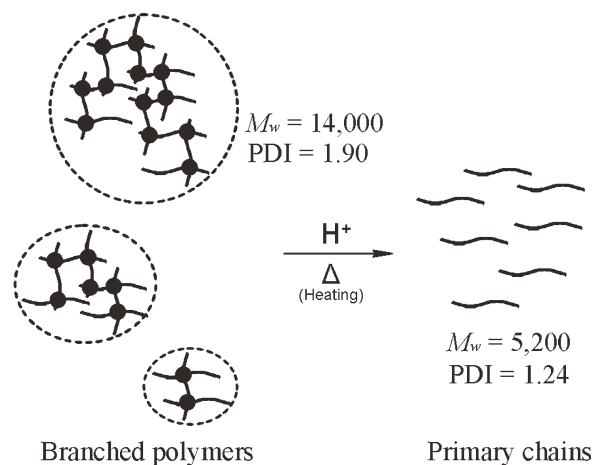
Figure 1 Changes in the acid-cleavable branching polymers in structure and molecular weight during acid hydrolysis. The M_w and PDI values on the branched polymer side and the primary chains are those of entry 4 before and after the acid-hydrolysis steps, respectively.

polymers. ATRP requires the use of metal catalysts, which is not desirable in the lithography process,[4] whereas stable free-radical polymerization cannot be applied to the copolymerization of methacrylate monomers.[13–16] With RAFT polymerization, a series of well-defined branched copolymers composed of methacrylate monomers were prepared without metal contamination. The acid-cleavable branched polymers were hydrolyzed into linear polymers having specific molecular weights. Figure 1 shows the changes in the structure and molecular weight of the acid-cleavable branched polymers by the acid hydrolysis. The molecular weight of the primary chain and the degree of branching were controlled by the molar feed ratio of the monomers to the chain-transfer agent and by the molar fraction of 2,5-dimethyl-2,5-hexanediol dimethacrylate (DMHDMA) in the monomer mixture, respectively. Because the structure and molecular weight of the polymer affect the optimum dose for the fabrication pattern[3,4] and dissolution rate to developer,[1,4] respectively, an acid-cleavable dimethacrylate was used to impart a branched structure to the polymer. Finally, preliminary experiments for the preparation of nanosize patterns through ArF lithography were performed to evaluate the possibility of using the branched polymers as components of CARs.

EXPERIMENTAL

Materials

2,2′-Azobisisobutyronitrile (AIBN; Junsei) was purified by recrystallization from ethanol. Three monomers, 2-ethyl-2-adamantyl methacrylate (EAdMA), 3-hydroxy-1-adamantyl methacrylate (HAdMA), and γ-butyrolactone methacrylate (GBLMA), were sup-

plied by Dongjin Semichem Co., Ltd., and were used as received. Tetrahydrofuran (THF) was distilled under sodium and benzophenone. All other reagents and solvents were used as received without further purification. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN)[6,17] and DMHDMA[18] were synthesized according to the literature.

^{1}H-NMR of CPDN (CDCl$_3$, ppm, δ): 8.17 (m, 1H), 7.88 (m, 2H), 7.50 (m, 4H), 1.97 (s, 6H). ^{1}H-NMR of DMHDMA (CDCl$_3$, ppm, δ): 6.01 (s, 2H), 5.49 (s, 2H), 1.90 (s, 6H), 1.84 (s, 4H), 1.48 (s, 12H).

Preparation of the polymers

The feed molar ratios of components for the polymerization solutions are listed in Table I. All of the polymers were prepared from the same polymerization procedures, except for the amount of branching reagent. Entry 4 is given as an example reaction as follows: 5.96 g (24.0 mmol) of EAdMA, 4.08 g (24.0 mmol) of GBLMA, 2.84 g (12.0 mmol) of HAdMA, 1.04 g (3.69 mmol) of DMHDMA, 0.814 g (3.00 mmol) of CPDN, and 0.0990 g (0.600 mmol) of AIBN were dissolved in 10 mL of THF in a 100-mL Schlenk flask equipped with a magnetic stirring bar and a condenser. The flask was subjected to three freeze–pump–thaw cycles to remove oxygen and then placed in an 80°C oil bath. Samples were taken at different reaction times for gel permeation chromatography [GPC; molecular weight and polydispersity index (PDI)] and ^{1}H-NMR (monomer conversion) analysis. Polymerization was ceased when the stirring bar stopped because of the high viscosity of the reacting solution. The product was diluted by THF before it was precipitated into excess diethyl ether to remove unreacted components. Finally, the resulting polymer was dried *in vacuo* at 30°C for 24 h.

Thiocarbonylthionaphthalate moieties at the end of the polymers were removed through a procedure reported previously[19] as follows. For entry 4, 6.50 g of polymer was dissolved in 80 mL of methyl ethyl ketone with 9.85 g (60.0 mmol) of AIBN. The solution was placed in a 250-mL, round-bottom flask equipped with a magnetic stirring bar and a condenser and refluxed for 8 h. The final product was isolated by precipitation in diethyl ether and dried *in vacuo* at 30°C for 24 h.

Hydrolysis and methylation

The branched polymers were hydrolyzed according to a procedure reported previously.[20,21] Amounts of 200 mg of the polymer and 2.00 g of p-toluenesulfonic acid were dissolved in 40.0 g of 1,4-dioxane in a 100-mL, round-bottom flask equipped with a magnetic stirring bar and a condenser. After 40 min of refluxing, the hydrolyzed polymer was isolated by

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TABLE I
Reaction Conditions of the RAFT Polymerization of EAdMA (24.0 mmol), GBLMA (24.0 mmol),
and HAdMA (12.0 mmol)

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Entry[a]	DMHDMA (mmol)	Molar fraction of DMHDMA[b]	Reaction time (h)	Conversion (%)[c]	Composition (%)[d]	DMHDMA (mol %)[e]	M_w (Da)[f]	PDI[f]	Number of primary chains per polymer[g]
1	0	0	4	75/96/94	31/43/26	0	6,500	1.09	1.00
2	0.900	0.0148	3	65/92/—	34/45/21	1.9	8,800	1.30	1.35
3	1.89	0.0305	2.5	67/92/—	33/46/21	3.8	13,100	1.58	2.02
4	3.69	0.0579	2	64/88/—	30/45/25	7.4	21,400	2.04	3.29

[a] Amounts of 3.00 mmol of CPDN, 0.600 mmol of AIBN, and 10 mL of THF was used in the RAFT polymerization. We performed the polymerization by refluxing the THF solution.

[b] The molar fractions of DMHDMA in the monomer mixture were calculated as follows: Molar fraction of DMHDMA = $\{f_{DMHDMA}/(f_{EAdMA} + f_{GBLMA} + f_{HAdMA} + f_{DMHDMA})\}$, where $f_{monomer}$ is the feed amount of each monomer (mmol).

[c] The conversions (%) of the monomers were measured by ^{1}H-NMR. The three values were EAdMA, GBLMA, and HAdMA, respectively. The conversion of HAdMA in entries 2–4 could not be obtained because of the peak of HAdMA overlapped with those of DMHDMA.

[d] The compositions of the polymers measured from the ^{1}H-NMR spectra of the polymers. The values represent the molar fractions of the EAdMA, GBLMA, and HAdMA monomeric units, respectively, in the polymers.

[e] The molar percentages of DMHDMA compared to other monomers in the polymers were calculated as follows: Molar percentage of DMHDMA = $\{f_{DMHDMA}/(f_{EAdMA} \times Conversion_{EAdMA} + f_{GBLMA} \times Conversion_{GBLMA} + f_{HAdMA} \times Conversion_{HAdMA} + f_{DMHDMA})\} \times 100$, where $f_{monomer}$ is the feed amount of each monomer (mmol) and $Conversion_{monomer}$ is the conversion of each monomer. The $Conversion_{HAdMA}$ values for entries 2–4 were evaluated from the conversion ratio of HAdMA to the other monomers in entry 1.

[f] M_w and PDI values were obtained from GPC with the LS detector.

[g] The number of primary chains per a polymeric unit was calculated from $(M_{w.\ polymer})/(M_{w.\ linear\ polymer})$.

precipitation in diethyl ether and then dried *in vacuo* at 30°C for 6 h.

For GPC measurement, the carboxylic acid groups derived from EAdMA and DMHDMA were methylated as follows.[22–24] The hydrolyzed polymer was dissolved in a mixture of THF (10.0 mL) and MeOH (3.00 mL) in a 100-mL, round-bottom flask equipped with a stirring bar. Then, 1.00 mL of a diethyl ether solution of trimethylsilyl diazomethane (2.0*M*) was added to the solution. After 12 h of reaction at room temperature, a small amount of acetic acid was added to the solution to quench the methylation. Finally, the modified polymer was isolated by precipitation in diethyl ether and dried *in vacuo* at 30°C for 24 h.

Lithographic performance evaluation

CAR solutions were prepared by Dongjin Semichem Co., Ltd., by dissolution of 2 g of the polymers, 0.02 g of triphenylsulfornium triflate, and 0.01 g of triethanolamine in 10 g of propylene glycol methyl ether acetate (PGMEA). The crude resist solutions were filtered through a 0.2-μm filter. The CAR solutions were spin-coated on Si wafers, and the film thicknesses were about 150 nm. The wafers were soft-baked at 110°C for 60 s, and after the exposure, they were postexposure baked under the same conditions as the soft-baked wafers and then developed. The 70-nm node process was applied, and the exposure was carried out with a 0.85-NA tool. The cross sections of the developed patterns were obtained with scanning electron microscopy (SEM).

Analysis

^{1}H-NMR spectra were measured with a JEOL JNM LA-300 spectrometer (300 MHz for ^{1}H-NMR) or a Bruker Avance 600 spectrometer (600 MHz for ^{1}H-NMR) with CDCl$_3$ as the solvent. The conversion of the monomers was determined by the former, and the composition of the polymers was determined by the latter. The molecular weight and PDI values were measured by GPC with refractive-index (RI) and light-scattering (LS) detectors. GPC for the RI detector was equipped with a Waters 510 high-performance liquid chromatography (HPLC) pump and three columns (PLgel 5.0-μm guard, MIXED-C, and MIXED-D, Polymer Laboratories). The RI detector was a Viscotek LR125 (Viscotek Corporation in Houston, TX, USA) laser refractometer, analyzed by Omnisec software, and calibration was established with polystyrene standards from Polymer Laboratories in Amherst, MA, USA. GPC for the LS detector was performed with a Waters 510 HPLC pump and two columns (PLgel 5.0-μm guard and MIXED-D, Polymer Laboratories). The LS detector was a Wyatt mini-DAWN multiangle laser LS detector (690 nm), analyzed by Astra software (Wyatt Technology Corp). The *dn/dc* values of the polymers were obtained from an RI detector (OPTILAB DSP, Wyatt Technology Corporation in Milford, MA, USA) connected to an LS detector. The *dn/dc* values of the polymers after the

AIBN treatment and after the hydrolysis–methylation steps were around 0.142 and 0.120 mL/g, respectively. HPLC-grade THF (J. T. Baker) was used as the eluent at a flow rate of 1.0 mL/min at 35°C.

RESULTS AND DISCUSSION

Three monomers having lithographic functionalities, EAdMA, GBLMA, and HAdMA, were copolymerized with DMHDMA to prepare branched polymers and without DMHDMA to prepare linear polymers. Because DMHDMA has two methacrylate groups, it can induce a branched structure in a polymer. Table I shows the four sets of polymerization conditions with the same amounts of monomers, CPDN, and AIBN and a different amount of DMHDMA. The molar fraction of DMHDMA in the monomer mixture was changed from 0 to 0.0579. It was expected that an increase in the molar fraction of DMHDMA in the monomer mixture would increase the degree of branching of the polymers.[12,25] The molar ratio of the monomer to CPDN was fixed at 20 to make the weight-average molecular weights (M_w's) of the linear polymer and primary chains about 5000. The molar ratio of CPDN to AIBN was fixed at 5, as this ratio has been found to be optimal for the copolymerization of these monomers.[26]

Crude polymers were obtained as a pink powder because CPDN moieties were included at the end of the polymer chains. Figure 2(a) shows the ^{1}H-NMR spectrum of the crude polymer of entry 4 obtained after 2 h of polymerization. The proton peaks of the naphthyl group between 7.7–8.3 ppm indicated that the thiocarbonylthionaphthalate group from CPDN was covalently bonded to the chain end of the crude polymer; this proved that CPDN worked as a RAFT agent.[6,19] The thiocarbonylthionaphthalate group in the polymer was intentionally removed through reaction with an excess amount of AIBN, as described in the Experimental part, because this group could absorb the 193-nm wavelength used in the ArF lithography process.[6] The removal of the thiocarbonylthionaphthalate group was confirmed by a color change from pink to white and the disappearance of the proton peaks attributed to the naphthyl group [Fig. 2(b)]. In the case of entry 4, a tiny amount of unreacted vinyl groups from DMHDMA was observed in the polymer structures [proton peaks at 5.45 and 6.01 ppm in Fig. 2(a)]; this was due to the large amount of DMHDMA used.[12,27] The vinyl group in the polymer was found to be saturated by the reaction of the crude polymer with an excess amount of AIBN during the process to remove the thiocarbonylthionaphthalate groups at the chain end, as shown in Figure 2(b); the proton peaks from the vinyl groups were not seen. The molecular weight and PDI values of the polymer before and after reaction with AIBN did not change
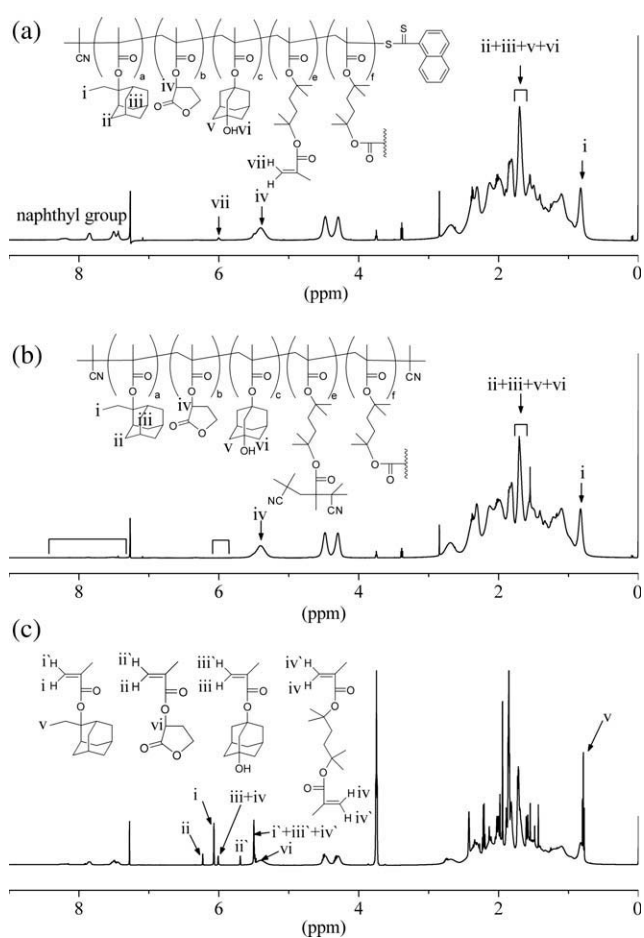

Figure 2 Chemical structure and ^{1}H-NMR spectra of the polymer of entry 4 (a) before and (b) after the CPDN removal step. The polymer was reacted with 60 mmol of AIBN under methyl ethyl ketone (MEK) reflux state. (c) ^{1}H-NMR spectrum of the polymerization solution of entry 4 at 2 h. The ^{1}H-NMR samples for measuring the real-time concentration or the conversions of monomers were prepared by the evaporation of THF from extracted polymerization solutions followed by their dissolution in CDCl$_3$.

significantly; this indicated that no further crosslinking reactions occurred during the reactions. This was probably due to the use of an excess amount of AIBN.[19] Because the concentration of radicals generated from AIBN was much higher than those of the thiocarbonylthionaphthalate groups and vinyl groups contained in polymer, the thiocarbonylthionaphthalate groups and vinyl groups should have been substituted or reacted with 2-cyano-2-propyl radicals generated from AIBN. Therefore, the molecular weights and PDI values shown in Table I were obtained with the polymers after reaction with AIBN, and they were similar with those of the crude polymers.

Figure 3 shows the plot of ln([M]$_0$/[M]) versus time, where [M]$_0$ is the initial concentration of each monomer and [M] is the real-time concentration of each monomer. The real-time concentration of monomers could be measured by ^{1}H-NMR [Fig. 2(c)]. The
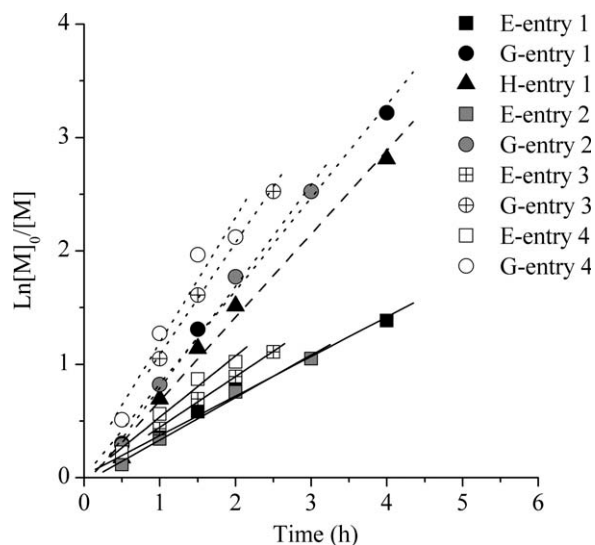
Figure 3 $Ln([M]_0/[M])$ values with respect to the reaction time of entries 1–4. The capital letters E, G, and H in the legend indicate EAdMA, GBLMA, and HAdMA, respectively. The $\ln([M]_0/[M])$ values of HAdMA are indicated only for entry 1, which did not contain DMHDMA.

integration of the peak at 0.83 ppm was a standard and was set to 3. The real-time concentrations of EAdMA, GBLMA, and HAdMA were obtained from the integrations of the peaks at 6.07, 6.23, and 6.01 ppm in the case of the preparation of the linear polymer (entry 1). In the preparation of the branched polymers, the real-time concentrations of EAdMA and GBLMA could be measured by ^{1}H-NMR with the peaks at 6.07 and 6.23 ppm, respectively, whereas those of HAdMA and DMHDMA could not be measured because the proton peaks of the vinyl groups of DMHDMA and HAdMA overlapped at the same positions, 5.45 and 6.01 ppm, respectively. Accordingly, the $\ln([M]_0/[M])$ values of HAdMA in the copolymerization with DMHDMA could not be indicated (entries 2–4). Because DMHDMA was not used in entry 1, the $\ln([M]_0/[M])$ values of HAdMA of entry 1 are indicated in Figure 3. The values of $\ln([M]_0/[M])$ increased linearly with time; this indicated that the radical concentration was almost constant during the polymerization. The $\ln([M]_0/[M])$ values, depending on reaction time for entry 1, showed that the monomer reactivity ratio was in the order GBLMA > HAdMA ≫ EAdMA, and this may have affected the composition distribution of the polymers, as reported previously.[13–16,26] Figure 3 also shows that the polymerization rate increased as the amount of DMHDMA in the reaction increased. This was attributed to an increase in the pseudokinetic constant with an increase in the amount of dimethacrylate monomer, which has a higher kinetic coefficient.[28]

Figure 4 shows the relative fractions of EAdMA and GBLMA (f_{EAdMA} and f_{GBLMA}, respectively) in

the polymers with respect to the conversion of EAdMA. f_{EAdMA} and f_{GBLMA} were calculated through the following equations:

$$f_{EAdMA} = [\text{Conversion}_{EAdMA}/(\text{Conversion}_{EAdMA} + \text{Conversion}_{GBLMA})] \times 100 \qquad (1)$$

$$f_{GBLMA} = [\text{Conversion}_{GBLMA}/(\text{Conversion}_{EAdMA} + \text{Conversion}_{GBLMA})] \times 100 \qquad (2)$$

where $\text{Conversion}_{EAdMA}$ and $\text{Conversion}_{GBLMA}$ are the conversion of EAdMA and GBLMA, respectively, and they were measured by ^{1}H-NMR. Because the conversion of HAdMA could not be obtained, as mentioned previously, f_{EAdMA} and f_{GBLMA} could only be obtained from the ratio of each monomer to the sum of both monomers. Figure 4 shows that f_{EAdMA} increased as the polymerization proceeded, whereas f_{GBLMA} decreased. This result could be ascribed to the different reactivity ratios of the two monomers, as mentioned previously.[13–16,26] GBLMA was better incorporated into the polymer chains than EAdMA in the early stage of polymerization because of the higher reactivity of GBLMA compared to that of EAdMA. Because the side group of GBLMA was smaller than that of EAdMA, there should have been less steric hindrance for the polymerization of GBLMA, which in turn, gave a higher reactivity.[29] As the polymerization proceeded, the molar ratio of the two monomers, GBLMA/EAdMA, in the polymerization solution decreased; this indicated that EAdMA became the main component in the polymerization solution in the later stage. Therefore, the majority of EAdMA was likely incorporated into the polymer chain in the later stage of
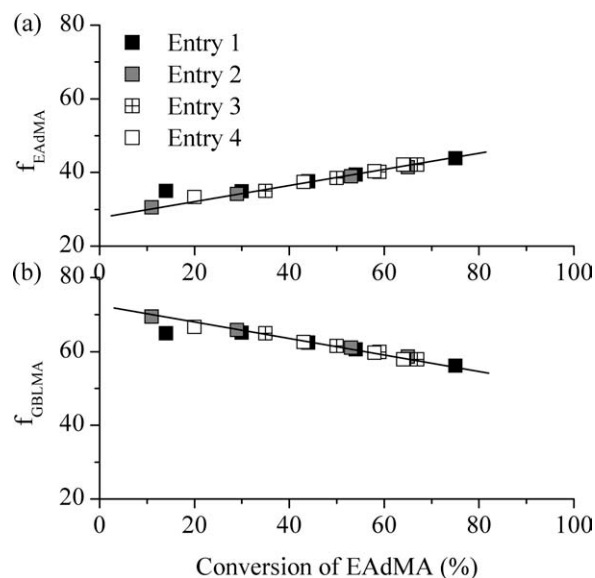

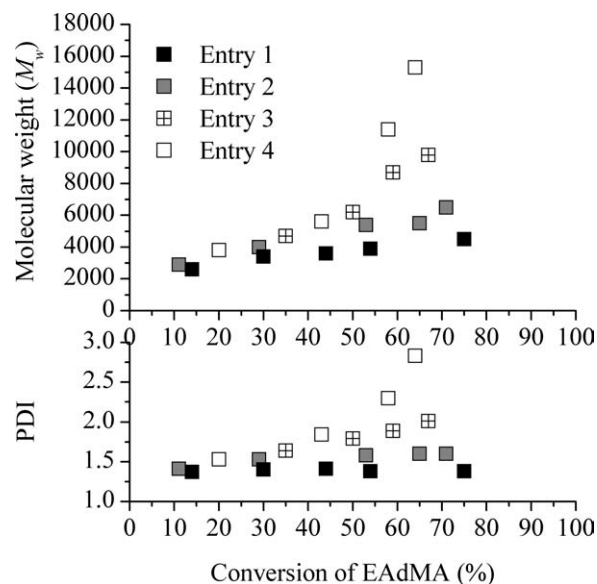**Figure 4** (a) f_{EAdMA} and (b) f_{GBLMA} versus the conversion of EAdMA.

Figure 5 M_w and PDI values of the polymers, which were measured by GPC with an RI detector. GPC samples were prepared by dilution of the extracted polymerization solution with HPLC-grade THF and their filtration through 0.2-μm pore syringe filters.

polymerization. As a result, the composition gradient of the resulting polymer could be predicted.[14,15] In addition, it should be noted that f_{EAdMA} and f_{GBLMA} with respect to the conversion of EAdMA were similar in all of the entries; this indicated that the addition of DMHDMA did not affect the relative reactivities of the monomers or the compositions of the polymers.

Figures 5 and 6 show the GPC results measured with the RI detector, including the M_w and PDI values and the GPC curves. Although four monomers were copolymerized, only the conversions of EAdMA were used for standard values. Because each conversion ratio of EAdMA and GBLMA at a certain conversion of EAdMA in all of the entries was similar in this study (Fig. 4) regardless of the molar feeding ratio of DMHDMA and each conversion ratio of EAdMA, GBLMA, and HAdMA at a certain conversion of EAdMA in the preparations of linear polymers was very similar in a previous work,[26] the use of EAdMA conversions as standard values seemed to be reasonable. The molecular weight of the linear polymer increased as the conversion of EAdMA increased, whereas the PDI values were less than 1.30 throughout the polymerization; this indicated that the polymerization proceeded through an LRP mechanism, more or less.[14–17] For the branched polymers, both the molecular weights and PDI values increased as the conversion of EAdMA increased. Particularly, very large increases in the molecular weight and PDI value were observed for entry 4 about halfway through

EAdMA conversion; this indicated that a highly branched structure was obtained in the later stage of the polymerization.[27] In addition, the molecular weights and PDI values increased as the molar fraction of DMHDMA in the monomer mixture increased. For example, the molecular weights of the branched polymers increased from 5500 to 7300, 8700, and 14,000, whereas the PDI values increased from 1.20 to 1.38, 1.69, and 1.90, respectively, as the molar fraction of DMHDMA in the monomer mixture for each increased from 0 to 0.0148, 0.0305, and 0.0579, respectively (Table II). The GPC curves became broader as the conversion of EAdMA increased or the molar fraction of DMHDMA in the monomer mixture increased, and the high-molecular-weight shoulders of the GPC curves indicated the formation of a large number of branches (Fig. 6).[12,27] These results indicate that DMHDMA was incorporated into the polymers as the brancher, and the degree of branching increased as polymerization proceeded and as the molar fraction of DMHDMA in the monomer mixture increased.

Figure 7 shows the GPC traces of the polymers measured by LS and RI. Because the hydrodynamic volume of the branched polymer was smaller than that of the linear polymer when they had the same molecular weight, the relative molecular weight measured by RI should have been smaller than the
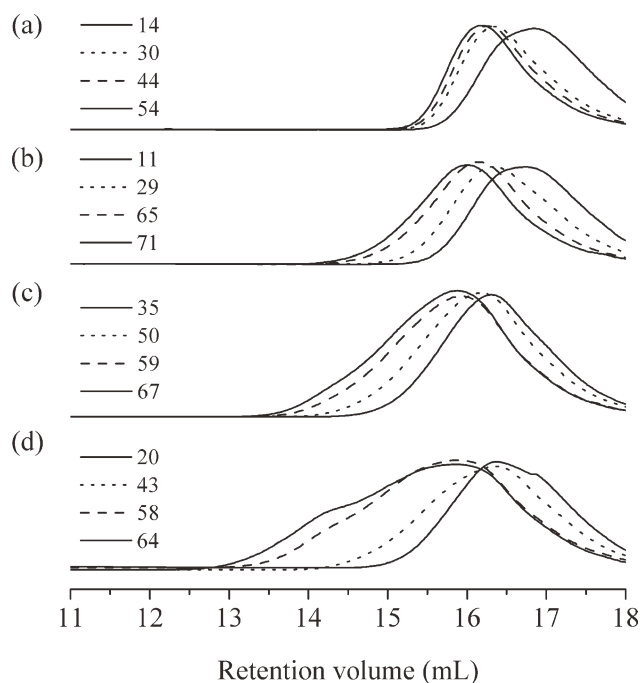

Figure 6 GPC traces of entries (a) 1, (b) 2, (c) 3, and (d) 4 versus the conversion of EAdMA. The numbers next to the lines in the legends are the conversions of EAdMA. The GPC traces were measured by an RI detector. The GPC samples were prepared by dilution of the extracted polymerization solution with HPLC-grade THF and their filtration through a 0.2-μm pore syringe filters.

TABLE II
M_w and PDI Values of the Products Before and After the Acid Hydrolysis and Methylation Steps

Entry	Before		After	
	M_w (Da)[a]	PDI[a]	M_w (Da)[a]	PDI[a]
1	5,500	1.20	5,700	1.18
2	7,300	1.38	4,800	1.24
3	8,700	1.69	5,100	1.16
4	14,000	1.90	5,200	1.24

[a] M_w and PDI values were obtained from GPC with an RI detector.

absolute molecular weight measured by LS.[30,31] As the molar fraction of DMHDMA in the monomer mixture increased, the shapes of the GPC curves obtained from LS and RI became more different. In addition, the numbers of primary chains per polymer increased as the molar fraction of DMHDMA in the monomer mixture increased, as shown in Table I. The number of primary chains per polymer was calculated by division of the absolute molecular weight of the polymers by the absolute molecular weight of the linear polymer. Because all of the polymers had similar molecular weights after the hydrolysis and methylation steps, as described later, the molecular weight of the primary chains of the branched polymers should have been similar to that of the linear polymer. These results confirm the effect of the molar fraction of DMHDMA in the
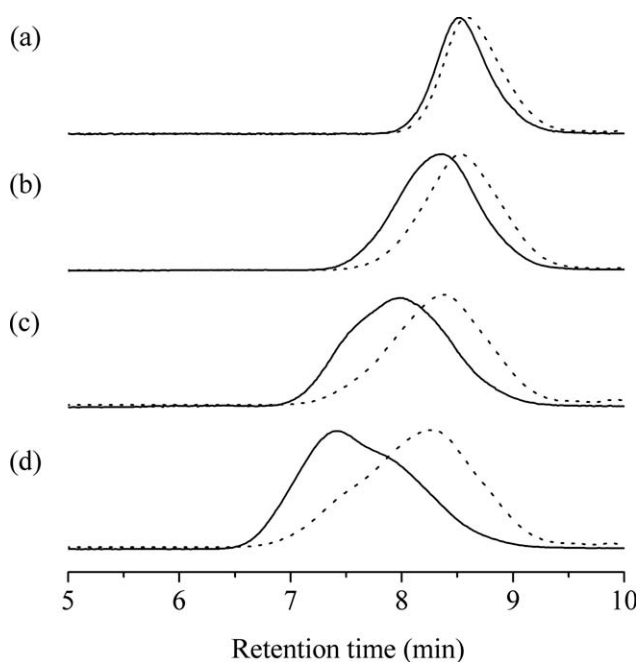
monomer mixture on the degree of branching in the polymers.

The polymer sample treated with AIBN was further acid-hydrolyzed and then methylated to study the changes in the structure and molecular weight of the branched polymers during the lithography process. Table II shows the changes in the molecular weight and PDI values after the hydrolysis and methylation steps. The molecular weights and PDI values of the branched polymers decreased after the reactions, and these values were close to those of the linear polymer (Table II). Particularly, the PDI values of the polymers after the reactions were less than 1.3; this indicated that the primary chains of the branched polymers grew through LRP.[30,32] The molecular weights of the linear polymers prepared without DMHDMA did not decrease and even increased after the hydrolysis and methylation reactions, although the ethyladamantyl group was replaced by a methyl group (Table II). Possibly, the polymers obtained after the reactions had similar or slightly larger hydrodynamic volumes to those having bulky side groups. This was probably due to the hydrolysis of butyrolactone of GBLMA into a carboxylic acid and primary alcohol followed by the methylation of the carboxylic acid.[33–35] Figure 8 shows the changes in the chemical structure of polymer entry 4 after the acid hydrolysis and methylation steps. For example, the ethyladamantyl group in the polymers was replaced with a methyl group. A portion of the butyrolactone group in the polymer was hydrolyzed to a carboxylic acid and primary alcohol under acidic conditions through a reverse Fischer reaction,[33–35] and the carboxylic acid group was methylated during the methylation step; the proton peak at 0.83 ppm of the crude polymer disappeared, and new peaks appeared at 3.61, 3.73, and 4.94 ppm after the hydrolysis and methylation steps. The peak at 3.61 ppm, labeled i in Figure 8, was ascribed to the methyl group attached to acrylic acid derived from EAdMA and DMHDMA incorporated in the polymer. The peaks at 3.73 and 4.94 ppm, labeled iv and iii, respectively, were due to the
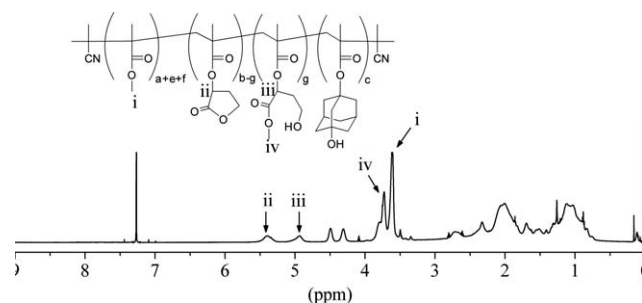

Figure 7 GPC traces of polymers for entries (a) 1, (b) 2, (c) 3, and (d) 4 measured by the LS (solid line) and RI (dashed line) detectors. The RI detector was connected with the LS detector.

Figure 8 Chemical structure and the ^{1}H-NMR spectrum of polymer of entry 4 after acid hydrolysis and methylation steps.
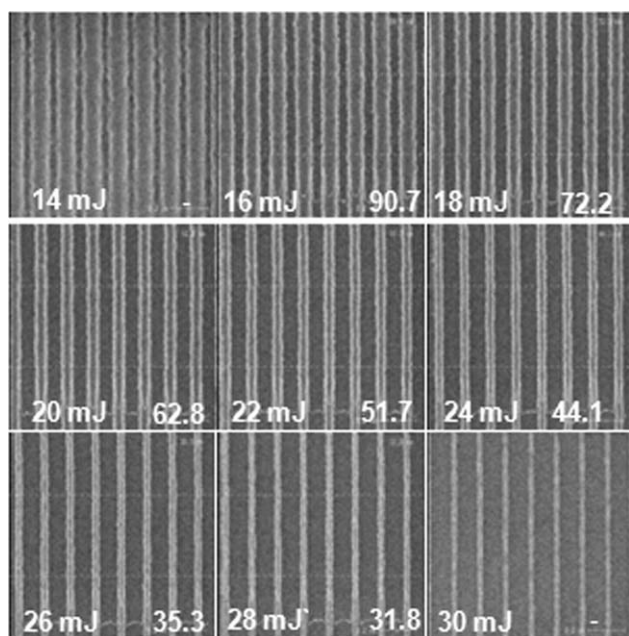
Figure 9 Cross-sectional SEM images of patterns from the CAR containing the polymer of entry 4, depending on dose. The values on the left lower part and right lower part in the images are the dose (mJ/cm^2) and thickness of the patterns (nm), respectively. A dash represents inaccessible data.

methyl group attached to the carboxylic acid derived from GBLMA and the tertiary proton next to the carboxylic acid, respectively. In the case of entry 4, about 46% of γ-butyrolactone was hydrolyzed. We compared the absolute molecular weights of the linear polymer (entry 1) before and after the hydrolysis and methylation steps with LS. It was found that M_w of the linear polymer after the reactions was 5700 (PDI = 1.09), compared to 6500 (PDI = 1.09) before the reactions. Therefore, the decrease in the molecular weight after the reactions was confirmed.

The thermal properties of the polymers were characterized. Because the decomposition temperature (T_d) of the polymers, around 175°C (measured by thermogravimetric analysis, TGA-7, PerkinElmer), was much higher than the lithography processing temperature (105–130°C), the unexposed branching site of the polymers was safe during the lithography process. The glass-transition temperatures (T_g) of the polymers could not be obtained with a differential scanning calorimeter (DSC, TA Instruments 2920) because the T_g values were larger than the T_d values.[36] Ismailova et al.[36] measured the T_d and T_g values of polymers composed of 2-methyl-2-adamantyl methacrylate, GBLMA, and HAdMA. The T_d values ranged from 148.5 to 201°C, depending on the molecular weight of the polymer, whereas the T_g values were about 220°C. Because the chemical structure of EAdMA is very similar to that of

2-methyl-2-adamantyl methacrylate, similar thermal properties were expected.

CARs containing the polymers were prepared, and the ArF lithography performance of these samples was tested. The optimal dose for each CAR was obtained from the pattern size under a 70-nm node process and with various doses of light. For example, the optimal dose for the CAR containing the entry 4 polymer was 18 mJ; when an 18-mJ dose under a 70-nm node mask was used, 72.2-nm patterns were obtained, as shown in Figure 9, whereas thicker or thinner patterns were obtained when smaller or larger doses were used because of insufficient or excess acid generation from the photoacid generator. Figure 10 shows the SEM images of the patterns from the CARs containing the polymers. The line width roughness (LWR) values of the patterns from the polymers were all about 6.5 nm. Therefore, polymers having primary chains with similar molecular weights showed similar lithography performances, although their molecular weights were different. The optimum doses for the CARs containing the branched polymers (entries 2–4) were smaller than that for the CAR containing the linear polymer (entry 1). This was probably due to the higher compaction (or smaller free volume) of the linear polymer compared to those of the branched polymers.[1,4] We are currently pursuing the development of acid-cleavable branched polymers with
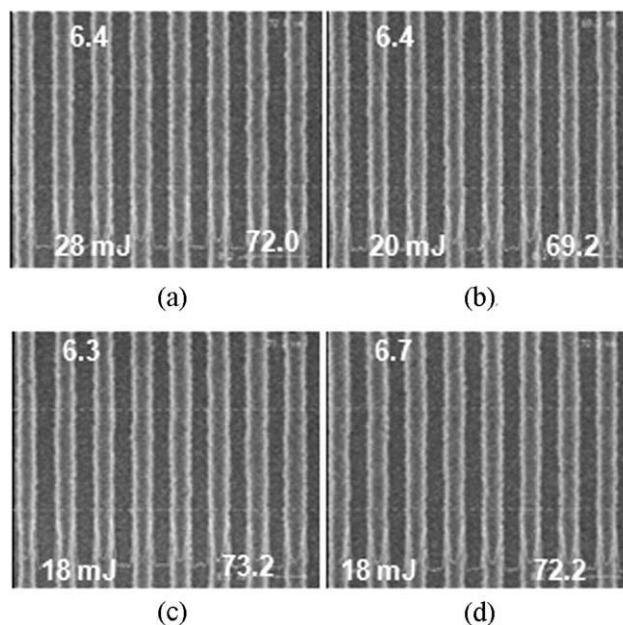

Figure 10 Cross-sectional SEM images of patterns from the CARs containing the polymers of entries (a) 1, (b) 2, (c) 3, and (d) 4. The values on the left upper part, left lower part, and right lower part in the images are LWR (nm), dose (mJ/cm^2), and thickness of the patterns (nm), respectively.

optimal characteristics with regard to the size of the primary chains and the degree of branching.

CONCLUSIONS

A series of acid-cleavable branched polymers having primary chains with the same molecular weight and different degrees of branching were prepared by the adjustment of the molar fraction of DMHDMA in the monomer mixture at a constant monomer/ CPDN ratio through RAFT copolymerization. The LWR of the patterns obtained from CARs containing the branched polymers were comparable to that obtained from CAR containing the linear polymer, whereas the optimum doses for the former were comparably smaller. Therefore, the acid-cleavable branched polymers obtained from RAFT polymerization could be promising alternatives to conventional CAR materials. Currently, we are working to determine the molecular weights of the branched polymers having optimally sized primary chains that would allow for more defined lithographic patterns with smaller LWR values.

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