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journal or publication title	Reactive and Functional Polymers
volume	131
page range	1-33
year	2018-10
権利	(C)2020. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
URL	http://hdl.handle.net/10112/00020487

doi: 10.1016/j.reactfunctpolym.2018.08.013

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For Reactive and Functional Polymers as an *Original Research Article*

Synthesis of Hyperbranched Polyacetals containing *C*-(4-*t*-butylbenz)calix[4]resorcinarene; Resist Properties for Extreme Ultraviolet (EUV) Lithography

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Abstract

We synthesized the various hyperbranched polyacetals poly(*t*-BCRA[4]-*co*-BVOC), poly(*t*-BCRA[4]-*co*-BVOP), poly(*t*-BCRA[4]-*co*-BVOXP), poly(*t*-BCRA[4]-*co*-BVBC), and poly(*t*-BCRA[4]-*co*-TVCH) by polyaddition of *C*-(4-*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) with 1,4-bis(4-vinyloxy)cyclohexane (BVOC), 1,3-bis(vinyloxy)propane (BVOP), 1,5-bis(vinyloxy)-3-oxapentane (BVOXP), 4,4'-bis(vinyloxy)-1,1'-bicyclohexane (BVBC), and 1,3,5-tris(vinyloxy)cyclohexane (TVCH), respectively. The resist sensitivity of the synthesized polymers using EUV exposure tool was consistent with their structures, and is in the order poly(*t*-BCRA[4]-*co*-BVOC) > poly(*t*-BCRA[4]-*co*-BVOXP) > poly(*t*-BCRA[4]-*co*-TVCH) > poly(*t*-BCRA[4]-*co*-BVOP) >> poly(*t*-BCRA[4]-*co*-BVBC). Furthermore, poly(*t*-BCRA[4]-*co*-BVOC) showed good resist properties such as out-gassing property using EUV exposure tool, film-thickness loss property, and etching durability. Overall, our results indicate that hyperbranched polyacetal poly(*t*-BCRA[4]-*co*-BVOC) has high potential as next-generation resist material for EUV photolithography.

Keywords; positive-type resist, main-chain scission type resist, hyperbranched polyacetal, extreme ultraviolet laser

1. Introduction

The requirement to achieve increasing densities of semiconductor devices has led to great technical advances in photolithography systems using various exposure sources, such as electron beam (EB), KrF excimer laser (λ = 248 nm), ArF excimer laser (λ =193 nm), and extreme ultraviolet (EUV) laser (λ = 13.5 nm)[1] . However, there is a trade-off among resist sensitivity to EUV exposure, resolution, and roughness of the resist pattern, and to achieve resist patterns of less than 16 nm, new materials are required [2,3]. To meet this need, various polymers and oligomers have been synthesized and their resist properties have been examined. Chemical amplification systems using photo-acid generators (PAG) are also available to improve the resist sensitivity and offer higher resolution patterns [4].

Our research group has developed new resist materials for EUV photolithography based on a cyclic oligomer designated as noria (noria = water wheel in Latin) [5]. The synthesis and resist properties of various noria derivatives with pendant *t*-butyl ester groups[6], *t*-butyloxycarbonyl groups [7], adamantyl ester groups [8 -10], cylohexyl acetal moieties [11], and oxetanyl groups [12] were examined, and we found that acetal groups showed higher resist sensitivity with an EUV exposure tool. Furthermore, when we examined other cyclic oligomers such as calixarenes, pillar[5]arene, and cyclic phenols, we found that the resist sensitivity to EUV increased with increasing pore size [13]. This indicates that resist materials having lower density would show higher sensitivity. Very recently, we examined the synthesis and physical properties of hyperbranched polyacetals poly(CRA[4]-*co*-BVOC) and poly(THPE-*co*-BVOC) obtained by the polyaddition of calix[4]resorcinarene (CRA[4]; A_8-type monomer) and tetrahydroxyphenylethane (THPE; A_3-type monomer) with

1,4-bis(4-vinyloxy)cyclohexane (BVOC; B_2-type monomer) as candidate EUV resist materials[14,15]. These results indicated that hyperbranched structures would have lower density, while the acetal groups would decompose easily under EB and EUV exposure, and main-chain scission would decrease the roughness of the resist pattern, i.e., hyperbranched polyacetals might overcome the trade-off issue, and provide high-resolution resist patterns. However, etching-durability of the synthesized poly(CRA[4]-*co*-BVOC) and poly(THPE-*co*-BVOC) were not adequate during transferring process of resist patterns.

In the present paper, based on the idea that the hyperbranched polyacetal might be suitable to provide next generation EUV resist material, we examined the polyaddition of *C*-(4-*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) and several vinyl ethers to synthesize the hyperbranched polyacetals. The structures of *t*-BCRA[4] in the synthesized hyperbranched polyacetals are expected to improve etching durability, due to that *t*-BCRA[4] has more aromatic skeletons compared to those of CRA[4] and THPE. The physical properties and resist properties of the synthesized hyperbranched polyacetals based on *t*-BCRA[4] were examined to offer higher resolution resist material in EUV photolithography system.

2. Experimental

2.1. Materials

Phosphoric acid (H_3PO_4), hexane, triphenylsulfonium perfluoro-l-butanesulfonate (TPS-Nf), and propylene glycol monomethyl ether acetate (PEGMEA) were commercial products. 1,4-Bis(4-vinyloxy)cyclohexane (BVOC), 1,3-bis(vinyloxy)propane (BVOP), 1,5-bis(vinyloxy)-3-oxapentane (BVOXP),

4,4'-bis(vinyloxy)-1,1'-bicyclohexane (BVBC), and 1,3,5-tris(vinyloxy)cyclohexane (TVCH) were gifts from Daicel Co. Tetrahydrofuran (THF) was dried over Na wire. NEt_3 was dried over CaH_2 and distilled before use. *C*-(4-*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) was synthesized as reported [16]. 2.38 wt% of tetramethylammonium hydroxide (TMAH) aqueous solution was used as a developer. Commercial available trioctylamine was used as a quencher in out-gassing property.

2.2. Measurements

Infrared (IR) spectra were taken with a JASCO FT/IR4200. The ^{1}H NMR spectra were recorded on JEOL ECS-400K (400 MHz for ^{1}H NMR) instruments in DMSO-d_6 with Me_4Si (TMS) as an internal standard for ^{1}H NMR. The number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of polymers were estimated by size exclusion chromatography (SEC) with a Tosoh HLC-8220 SEC instrument equipped with refractive-index and ultraviolet detectors. TSK gel columns (TSKgel Super AW3000 and AW2500 x 2) were employed, with DMF as an eluent. Calibration was done with narrow-molecular-weight polystyrene standards. Thermal analysis was performed on a Shimadzu thermogravimetric analyzer (TGA) TGA-50/50H at a heating rate of 10 ^{o}C/min under nitrogen.

2.3. Synthesis of Hyperbranched Polyacetal [poly(*t*-BCRA[4]-*co*-BVOC)]

A typical procedure; A solution of *C*-(*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) (1.02 g, 1.0 mmol) in THF (15 mL) was stirred until it became clear at room

temperature in the presence of phosphoric acid (H_3PO_4) (0.03 g, 0.30 mmol). Then, 1,4-bisvinyloxycyclohexane (BVOC) (1.34 g, 8.0 mmol) was added, and stirring was continued at 60 ºC. After 3 h, NEt_3 (0.17g, 0.30 mmol) was added. The resulting mixture was poured into a large amount of hexane. The insoluble product were collected by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45 μm), and washed with 2.38 wt% TMAH aq. The obtained product was dried *in vacuo* at room temperature for 24 h to afford a white solid. Yield = 1.13 g (48 %). M_n = 6,790 (M_w/M_n = 2.58). IR (film, cm^{-1}): 3383 (ν O-H), 2949 (ν C-H of methyl), 1456 (ν C=C of aromatic), 1017 (ν C-O of acetal). ^1H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 1.08 - 1.89 (br, $-CH_3$ and $-CH_2-$ of cyclohexyl group), 3.87 - 4.22 (br, >CH), 4.75 - 5.53 (m, CH_2=CH-), 6.38 - 6.94 (m, aromatic proton), 7.93 - 9.25 (m, -OH).

2.4. Synthesis of Hyperbranched Polyacetal [poly(*t*-BCRA[4]-*co*-BVOP)]

A typical procedure; Reaction of *t*-BCRA[4] (1.02 g, 1.0 mmol) and 1,3-bis(vinyloxy)propane (BVOP) (1.54 g, 12 mmol) was carried out in THF (15 mL) using H_3PO_4 (0.03 g, 0.30 mmol) for 6h in the similar way to the synthesis of poly(*t*-BCRA[4]-*co*-BVOC). Yield = 1.03 g (50 %). M_n = 3,670 (M_w/M_n = 1.84). IR (film, cm^{-1}): 3383 (ν O-H), 2949 (ν C-H of methyl), 1507 (ν C=C of aromatic), 1126 (ν C-O of acetal). ^1H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 1.08 - 1.77 (br, $-CH_3$ and $-CH_2-$ of propyl group), 3.35 - 4.10 (br, >CH), 5.10 - 5.54 (m, CH_2=CH-), 6.95 - 6.74 (m, aromatic proton), 7.95 - 9.24 (m, -OH). (Supporting Information Figure S1).

2.5. Synthesis of Hyperbranched Polyacetal [poly(*t*-BCRA[4]-*co*-BVOXP)]

A typical procedure; Reaction of *t*-BCRA[4] (1.02 g, 1.0 mmol) and 1,5-bis(vinyloxy)-3-oxapentane (BVOXP) (1.90 g, 12 mmol) was carried out in THF (15 mL) using H_3PO_4 (0.03 g, 0.30 mmol) for 5 h in the similar way to the synthesis of poly(*t*-BCRA[4]-*co*-BVOC). Yield = 1.19 g (52 %). M_n = 3,600 (M_w/M_n = 2.86). IR (film, cm^{-1}): 3385 (ν O-H), 2949 (ν C-H of methyl), 1506 (ν C=C of aromatic), 1127 (ν C-O of acetal). ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 0.48 - 1.52 (br, $-CH_3$ and $-CH_2-$), 3.50 (br, $-OCH_2-$), 5.19 - 5.59 (m, CH_2=CH- and >CH- of acetal), 6.66 - 7.20 (m, aromatic proton) (Supporting Information Figure. S2).

2.6. Synthesis of Hyperbranched Polyacetal [poly(*t*-BCRA[4]-*co*-BVBC)]

A typical procedure; A typical procedure; Reaction of *t*-BCRA[4] (1.02 g, 1.0 mmol) and 4,4'-bis(vinyloxy)-1,1'-bicyclohexane (BVBC) (2.00 g, 8.0 mmol) was carried out in THF (15 mL) using H_3PO_4 (0.03 g, 0.30 mmol) for 3.5 h in the similar way to the synthesis of poly(*t*-BCRA[4]-*co*-BVOC). Yield = 2.45 g (81 %). M_n = 6,600 (M_w/M_n = 2.20). IR (film, cm^{-1}): 3320 (ν O-H), 2939 (ν C-H of methyl), 1506 (ν C=C of aromatic), 1131 (ν C-O of acetal). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) = 0.69 - 1.98 (br, $-CH_3$ and $-CH_2-$), 3.42 ~ 3.52 (m, -OCH<), 4.83 (s, >CH- of acetal), 6.27 - 7.26 (m, aromatic proton), 9.44 (s, -OH) (Supporting Information Figure. S3).

2.7. Synthesis of Hyperbranched Polyacetal [poly(*t*-BCRA[4]-*co*-TVCH)]

A typical procedure; A typical procedure; Reaction of *t*-BCRA[4] (1.02 g, 1.0 mmol) and 1,3,5-tris(vinyloxy)cyclohexane (TVCH) (0.84 g, 4.0 mmol) was carried out in THF (15 mL) using (H_3PO_4) (0.03 g, 0.30 mmol) for 5 h in the similar way to the synthesis of poly(*t*-BCRA[4]-*co*-BVOC). Yield = 2.43 g (90 %). M_n = 3,100 (M_w/M_n = 1.95).

IR (film, cm^{-1}): 3364 (ν O-H), 2918 (ν C-H of methyl), 1506 (ν C=C of aromatic), 1111 (ν C-O of acetal). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) = 1.09 - 1.77 (m, $-CH_3$ and $-CH_2$-), 2.70 ~2.80 (m, -OCH<), 4.78 (br, >CH-), 6.70 - 6.97 (m, aromatic proton), (Supporting Information Figure S4).

2.8. Preparing Resist Film

All experiments were done with resist films prepared in the following way. A mixture of a resist material and PAG (90 : 9) (wt%) was dissolve in PEGMEA, and the total concentration was adjusted to be 2.5 wt %. The solutions were spin-coated on Si wafers and heated at 90 ^{o}C for 60 s as a prebake.

2.10. Out-gassing

Out-gassing from resists was measured by means of residual gas analysis (RGA) and the witness sample (WS) method at the BL3 station in the NewSUBARU synchrotron radiation facility[17] in Hyogo University. A Ru (5 nm)-capped Mo/Si multilayer mirror was used as the WS-plate, which was placed opposite the resist-coated wafer. Illuminating light was reflected off WS before reaching the wafer. At the wavelength of 13.5 nm, the illumination intensity was 267 mW/cm^2 on the WS, and 85 mW/cm^2 on the resist surface. The exposure chamber was pumped to ultrahigh vacuum in the range between 2×10^{-6} and 4×10^{-6} (Pa) before the exposure to ensure a clean and well-defined analysis environment. The EUV-exposed wafer was developed with 2.38 wt % TMAH aq. for 30 s to confirm that the resist had been completely exposed.

2.9. Resist Sensitivity to EUV

The resist sensitivity was measured using an EUV exposure tool (Smart Field Exposure Tool; SFET) at the Network Joint Research Center for Materials and Devices in Osaka University. The resist film thickness was set at about 100 nm. The EUV-exposed wafer was heated at 90 ºC for 60 s as post exposure bake and soaked in 2.38 wt% TMAH aq. for 30 s (developer) and deionized water for 15 s (rinse). The resist film thickness was measured before and after development by ellipsometry.

2.10. Thickness Loss

Solutions of hyperbranched polyacetals in PEGMEA were spin-coated on silicon wafers to prepare thin films of about 50 nm thickness. The thickness of the films was measured by ellipsometry before and after soaking in TMAH aq. for 30 sec.

2.11. Etching Durability

Etching durability was examined using the RIE plasma process at the Network Joint Research Center for Materials and Devices in Osaka University. The plasma conditions were 15 sccm CF_4 gas flow, 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. The resist film thickness was measured by ellipsometry before and after RIE plasma etching.

3. Results and Discussion

3.1. Synthesis of Hyperbranched Polyacetals by $A_8 + B_2$-Type Polyaddition

Linear polyacetals are well-known higher thermal-stable polymers that can be synthesized by the polyaddition of dialcohols (A_2-type monomers) and divinyl ethers

(B_2-type monomers) using an acid catalyst[18]. In our previous reports, calix[4]resorcinarene (CRA[4]) and tetrahydroxyphenylethane (THPE) were used as a A_8-type monomer and A_3-type monomer, respectively, i.e., corresponding hyper branched polyacetals could be synthesized by A_n+B_2-type method (n = 3 and 8) by the control of polyaddition conditions [14, 15]. In this time, we examined the polyaddition of *C*-(4-*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) as a A_8-type monomer and several vinyl ethers as B_n-type monomers (n = 2 and 3) for the synthesis of hyperbranched polyacetals (Scheme 1). The structures of *t*-BCRA[4] containing eight aromatic moieties are expected to improve etching durability in the comparison of our previous synthesized hyperbranched polyacetals containing the structures of CRA[4] and THPE in the main chain.

Insert Scheme 1 here

At first, we examined the polyaddition of *t*-BCRA[4] as a A_8-type monomer and 1,4-bis(4-vinyloxy)cyclohexane (BVOC) as a B_2-type monomer (Scheme 1). The reaction of *t*-BCRA[4] and BVOC was carried out in the various feeds ratios of *t*-BCRA[4]/BVOC = 1.0/4.0, 1.0/6.0, 1.0/8.0, 1.0/10.0, and 1.0/12.0 using H_3PO_4 as a catalyst in THF at 60 ^{o}C for 24 h. These results are summarized in Table 1. In the case of the feeds *t*-BCRA[4]/BVOC = 1.0/8.0, 1.0/10.0, and 1.0/12.0, only gel products were obtained (Runs 3 - 5 in Table 1). If polyaddition is stopped before formation of gel products, the corresponding soluble hyperbranched polyacetals should be obtained. Therefore, we chose feed ratio of *t*-BCRA[4]/BVOC as 1.0/8.0 for examination of the reaction time to obtain soluble hyperbranched polymers.

Insert Table 1 here

Next, we examined the effect of reaction time on this polyaddition. The results are summarized in Table 2. Molecular weight (M_n) of the obtained polymers increased up to 9 h. When the reaction time was 1 ~ 2 h, they were soluble in 2.38wt % of TMAH aqueous solution as a developer (Runs 1 and 2). It indicates that polymerization was not enough when the reaction time was 2 h; this reaction gave lower molecular weight oligomer,. Furthermore, when the reaction time was 12 h, only gel product was obtained (Run 7 in Table 2).

Insert Table 2 here

Therefore, we examined large-scale synthesis using the reaction time of Run 3 in Table 2. When the polyaddition of 1.0 mmol of *t*-BCRA[4] with 8.0 mmol of BVOC was carried out in the presence of 0.3 mmol of H_3PO_4 as a catalyst in THF (15 mL) at 60 °C for 3 h, the corresponding polymer with M_n = 6,790 (M_w/M_n = 2.58) was obtained in 48 % yield (Run 1 in Table 3). Its structure was confirmed by ^{1}H-NMR spectroscopy. Figure 1 shows the ^{1}H-NMR spectrum of the obtained polymer. Methyl and methylene protons of cyclohexyl groups and aromatic protons of *t*-BCRA[4] were seen at 1.08 ~ 1.89 ppm and 6.38 ~ 6.94 ppm, respectively. Methine proton of *t*-BCRA[4], acetal moieties, and cyclohexyl groups were seen at 3.87 ~ 4.22 ppm. These results indicate that polyaddition proceeded to give hyperbranched polyacetal poly(*t*-BCRA[4]-*co*- BVOC).

Insert Figure 1 here

3.2. Polyaddition of *t*-BCRA[4] with another divinyl ethers (BVOP, BVOXP, BVBC) and trivinyl ether (TVCH)

In the similar way for the synthesis of poly(*t*-BCRA[4]-*co*-BVOC), we examined the polyaddition of *t*-BCRA[4] with certain divinyl ethers such as BVOP, BVOXP and BVBC as B_2 type monomers, and a trivinyl ether (TVCH) as a B_3 type monomer as shown in Scheme 1. Reaction time and feed ratios were examined using H_3PO_4 as a catalyst in THF, and corresponding hyperbranched polyacetals poly(*t*-BCRA[4]-*co*-BVOP), poly(*t*-BCRA[4]-*co*-BVOXP), poly(*t*-BCRA[4]-*co*-BVBC), and poly(*t*-BCRA[4]-*co*-TVCH) were obtained with M_n = 3,100 - 6,600 (M_w/M_n = 1.84 - 2.86) in 50 - 90 % yields, respectively (Runs 2 ~ 5 in Table 3). Their structures were confirmed by ^{1}H NMR spectroscopy, and the ratio of copolymers compositions were close to the feed molar ratios in each case (Figures S1 ~ S4).

Insert Table 3 here

The physical properties of the obtained polymers such as film forming ability, thermal stability and solubility in 2.38 wt% TMAH aq. were examined. These polymers were insoluble in 2.38 wt% TMAH aq. and have good film forming ability by the spin-coating on the silicon wafer. Their decomposition temperatures (T_d^i) were determined by TGA, to be T_d^i = 111 - 193 ºC. These results indicate that the

synthesized hyperbranched polyacetals have good physical properties which are relevant to the application for resist materials.

3.3. Resist sensitivity of hyperbranched polyacetals under EUV exposure tool

The resist sensitivity of synthesized hyperbranched polyacetals poly(*t*-BCRA[4]-*co*-BVOC), poly(*t*-BCRA[4]-*co*-BVOP), poly(*t*-BCRA[4]-*co*-BVOXP), poly(*t*-BCRA[4]-*co*-BVBC), and poly(*t*-BCRA[4]-*co*-TVCH) were examined under EUV exposure tool. Solution of these polymers in the presence of TPS-Nf as a PAG were spin coated on silicon wafer to prepare corresponding thin films with about 100 nm thickness. The post exposure baking (PEB) temperatures and time were 90 ^{o}C and 60 sec, respectively. After that, the corresponding wafer was soaked in 2.38 wt% TMAH aq. for 30 s (developer) and deionized water for 15 s (rinse). Main-chain scission reaction of the synthesized hyperbranched polyacetals would proceed to give the corresponding products, which are soluble in 2.38 wt% aq. as shown in Scheme 2, i.e., unexposed part can offer resist pattern after developing process.

Insert Scheme 2 here

The value of the remained films thickness was measured by means of ellipsometer after the lithography process. These results are depicted in Figure 2. Their resist sensitivities (E_0) were in the range between 1.0 and 7.0 mJ/cm^2 exposure doses. In the case of poly(*t*-BCRA[4]-*co*-BVBC), its thin film was remained after the lithography process and E_0 could not be determined. This means that the resulting products

insoluble in 2.38 wt% aq. after main-chain scission reaction, due to dicyclohexyl skeletons of BVBC.

The resist sensitivity is consistent with the structures of the synthesized polymers and is in the order poly(*t*-BCRA[4]-*co*-BVOC) > poly(*t*-BCRA[4]-*co*-BVOXP) > poly(*t*-BCRA[4]-*co*-BVOP) > poly(*t*-BCRA[4]-*co*-TVCH), i.e., poly(*t*-BCRA[4]-*co*-BVOC) is expected to have adequate resist-sensitivity for application in EUV photoresist system. In our previous reports, the synthesized hyperbranched polycetals poly(CRA[4]-*co*-BVOC) (M_n = 7,200, M_w/ M_n = 1.60) and poly(THPE-*co*-BVOC) (M_n = 3,900, M_w/ M_n = 1.23) also showed higher resist sensitivities using EUV exposure tool, i.e., Eo were about 0.25 mJ/cm^2[14. 15]. These mean that BVOC might be an appropriate B_2-type monomer in these hyperbranched polyacetals, showing higher resist sensitivities on EUV exposure tool.

Insert Figure 2 here

3.4. Out-gassing property of hyperbranched polyacetals under EUV exposure

If out-gassing can occur during EUV exposure of resist materials, it could contaminate the mirror in the EUV photolithography equipment and lead to image distortion and loss of irradiation power. The out-gassing behavior of the synthesized poly(*t*-BCRA[4]-*co*-BVOC) was examined using EUV exposure tool. A resist material prepared from 5 wt% of poly(*t*-BCRA[4]-*co*-BVOC) in the presence of TPS-Nf as a PAG and trioctylamine as a quencher were spin-coated on 8-inch bare silicon wafers and baked at 90 ºC for 90 s. Out-gassing was detected by the RGA method, followed by WS testing, and the vacuum pressure were recorded before and after EUV

exposure. The results of quadrupole-mass analysis of out-gassed fragments using poly(*t*-BCRA[4]-*co*-BVOC) is shown in Figure 3[A] in the comparison of those of poly(CRA[4]-*co*-BVOC) (Figure3[B]) and poly(THPE-*co*-BVOC), which were synthesized in our previous reports [14,15] (Figure 3[C]).

Insert Figure 3 here

In the case of poly(THPE-*co*-BVOC), many fragments were formed in various amounts during EUV exposure of its film, suggesting that it cannot be applicable to EUV resist material (Figure 1[C]). However, the resist materials of poly(*t*-BCRA[4]-*co*-BVOC) and poly(CRA[4]-*co*-BVOC) produced smaller amounts of fragments than poly(THPE-*co*-BVOC), suggesting that they can be applicable to EUV resist materials.

3.5. Thickness Loss of poly(*t*-BCRA[4]-*co*-BVOC) on Silicon Wafer after Soaking in TMAH aq

The synthesized poly(*t*-BCRA[4]-*co*-BVOC) is expected to undergo main-chain scission due to decomposition of acetal units in the main-chain, acting as positive photoresists (i.e., the unexposed part must remain on the silicon wafer after development). Poly(*t*-BCRA[4]-*co*-BVOC) was insoluble in 2.38 wt% TMAH aq, solution, so TMAH aq. might be available as a developer. Its resist film was prepared on silicon wafer by spin-coating solutions in PEGMEA. The thickness of the films was determined by ellipsometry before and after soaking in 2.38 wt% TMAH aq. for 30 sec. The ratios of decrease of the thickness of poly(*t*-BCRA[4]-*co*-BVOC) was 0.3%,

indicating that it can be used as positive resist material with 2.38 wt% TMAH aq. as the developer.

3.6. Etching Durability

Etching durability of the film prepared from poly(*t*-BCRA[4]-*co*-BVOC) was examined. The plasma conditions were 15 sccm CF_4 gas flow, 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. Figure 4 shows the etching rates of thin films prepared from poly(*t*-BCRA[4]-*co*-BVOC) in the comparison for those of polymethyl methacrylate (PMMA) and polyhydroxy styrene (PHS). PMMA and PHS are typical resist materials. In our previous reports, etching rates of poly(CRA[4]-*co*-BVOC) and poly(THPE-*co*-BVOC) were similar to that of PMMA [14, 15]. However, in this time, poly(*t*-BCRA[4]-*co*-BVOC) showed exceptional etching durability, similar to that of PHS. This means that poly(*t*-BCRA[4]-*co*-BVOC) has high durable property during etching process in the photo-lithography system. It is presumably because of that *t*-BCRA[4] has eight aromatic skeletons which would increase etching durability.

Insert Figure 4 here

4. Conclusions

We synthesized hyperbranched polyacetals, poly(*t*-BCRA[4]-*co*-BVOC), poly(*t*-BCRA[4]-*co*-BVOP), poly(*t*-BCRA[4]-*co*-BVOXP), poly(*t*-BCRA[4]-*co*-BVBC), and poly(*t*-BCRA[4]-*co*-TVCH) by polyaddition of *C*-(4-*t*-butylbenz)calix[4]resorcinarene (*t*-BCRA[4]) with

1,4-bis(4-vinyloxy)cyclohexane (BVOC), 1,3-bis(vinyloxy)propane (BVOP), 1,5-bis(vinyloxy)-3-oxapentane (BVOXP), 4,4'-bis(vinyloxy)-1,1'-bicyclohexane (BVBC) and 1,3,5-tris(vinyloxy)cyclohexane (TVCH), respectively. The synthesized polymers had appropriate solubility, film-forming ability, and thermal stability relevant to applicable for photo-resist materials. Their resist sensitivities (E_0) using EUV exposure tool were examined in the film sates and were consistent with the structures. Poly(*t*-BCRA[4]-*co*-BVOC) showed highest resist sensitivity ($E_0 = 1.0$ mJ/cm^2). Furthermore, the resist properties (out-gassing on EUV exposure, thickness loss after soaking in TMAH aq., etching durability) of the thin films prepared from poly(*t*-BCRA[4]-*co*-BVOC) were also examined, and lower out-gassing property, lower thickness-loss property, and higher etching durability were observed. These mean that poly(*t*-BCRA[4]-*co*-BVOC) appears to be a promising candidate for providing resist patterns with exceptional resolution in EUV photolithography. The resist patterns using poly(*t*-BCRA[4]-*co*-BVOC) under electron beam and extreme ultraviolet laser exposure tools are under consideration.

Acknowledgements

This work was partly supported by the Cooperative Research Program "Network Joint Research Center for Materials and Devices".

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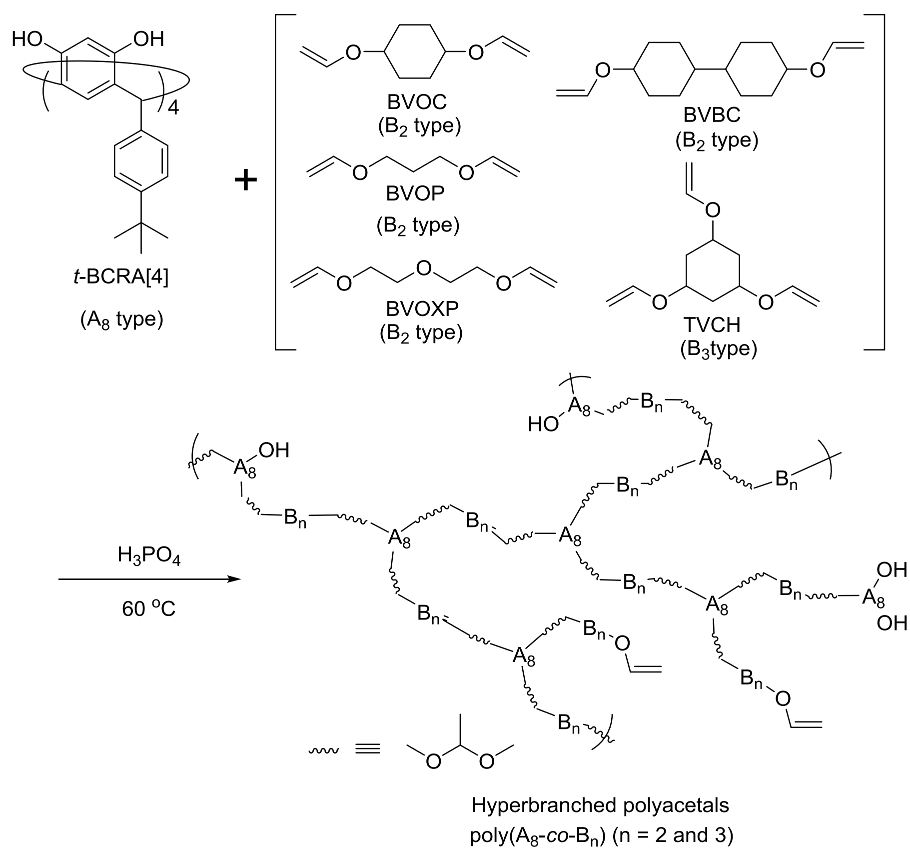
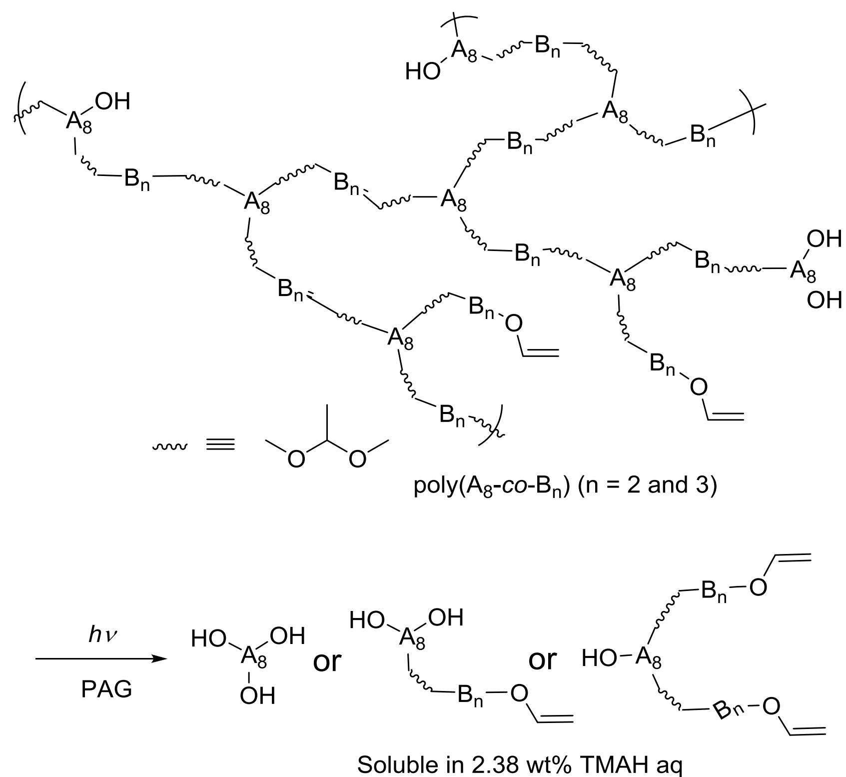


Scheme 1. Synthesis of hyperbranched polyacetals



Scheme 2. Main-chain scission reaction of poly(A_8-*co*-B_n) (n = 2 and 3).

Table 1

Effect of feed ratio in the polyaddition of *t*-BCRA[4] and BVOC[a)]

Run	Feed ratio	Yield	$M_n(M_w/M_n)$[b)]
	t-BCAR[4]/BVOC	%	
1	1.0/4.0	25	2,530 (1.01)
2	1.0/6.0	35	3,590 (1.10)
3	1.0/8.0	>99	Gel[c)]
4	1.0/10.0	>99	Gel[c)]
5	1.0/12.0	>99	Gel[c)]

[a)]Conditions; *t*-BCRA[4] (0.10 mmol), BVOC (4.0 ~ 12.0 mmol), H_3PO_4 (0.10 mmol) at 60 °C in THF (5 mL). [b)]Estimated by SEC based on polystyrene standards; LiBr and H_3PO_4 solution in DMF (20 mM). [c)]Could not be determined.

Table 2

Effect of reaction time in the polyaddition of *t*-BCRA[4] and BVOC[a)]

Run	Reaction Time	Yield	$M_n(M_w/M_n)$[b)]	Solubility of
	h	%		TMAHaq. [c)]
1	1	20	3,200 (1.03)	soluble
2	2	75	3,200 (1.02)	soluble
3	3	>99	6,500 (1.36)	insoluble
4	4	>99	6,800 (1.40)	insoluble
5	6	>99	68,000 (1.66)	insoluble
6	9	>99	918,000 (1.41)	insoluble
7	12	>99	Gel[c)]	-[c)]

[a)]Conditions; *t*-BCRA[4] (0.10 mmol), BVOC (0.80 mmol), H_3PO_4 (0.10 mmol) at 60 °C in THF (5 mL). [b)]Estimated by SEC based on polystyrene standards; LiBr and H_3PO_4 solution in DMF (20 mM). [c)]Solubility test used 2.38 wt% TMAH aq. [d)]Could not be determined.

Table 3

Polyadditionof t-BCRA[4] with divinyl ethers B_2-type monomers and trivinyl ether B_3-type monomer[a)]

Run	B_n	Feed ratio t-BCRA[4]/B_n	Reaction time (h)	Yield %	$M_n(M_w/M_n)$[b)]	T_d^i (°C)[c)]
1	BVOC (B_2)	1.0 / 8.0	3.0	48	6,790 (2.58)	193
2	BVOP (B_2)	1.0 / 12.0	6.0	50	3,670 (1.84)	111
3	BVOXP (B_2)	1.0 / 12.0	5.0	52	3,600 (2.86)	165
4	BVBC (B_2)	1.0 / 8.0	3.5	81	6,600 (2.20)	176
5	TVCH (B_3)	1.0 /4.0	5.0	90	3,100 (1.95)	189

[a)] Conditions; THF was used as solvent at 60 °C. [b)] Estimated by SEC based on polystyrene standards; LiBr and H3PO4 solution in DMF (20 mM). [c)]Intial decomposition temperature determined by TGA.

H. Kudo et al. Figure 1

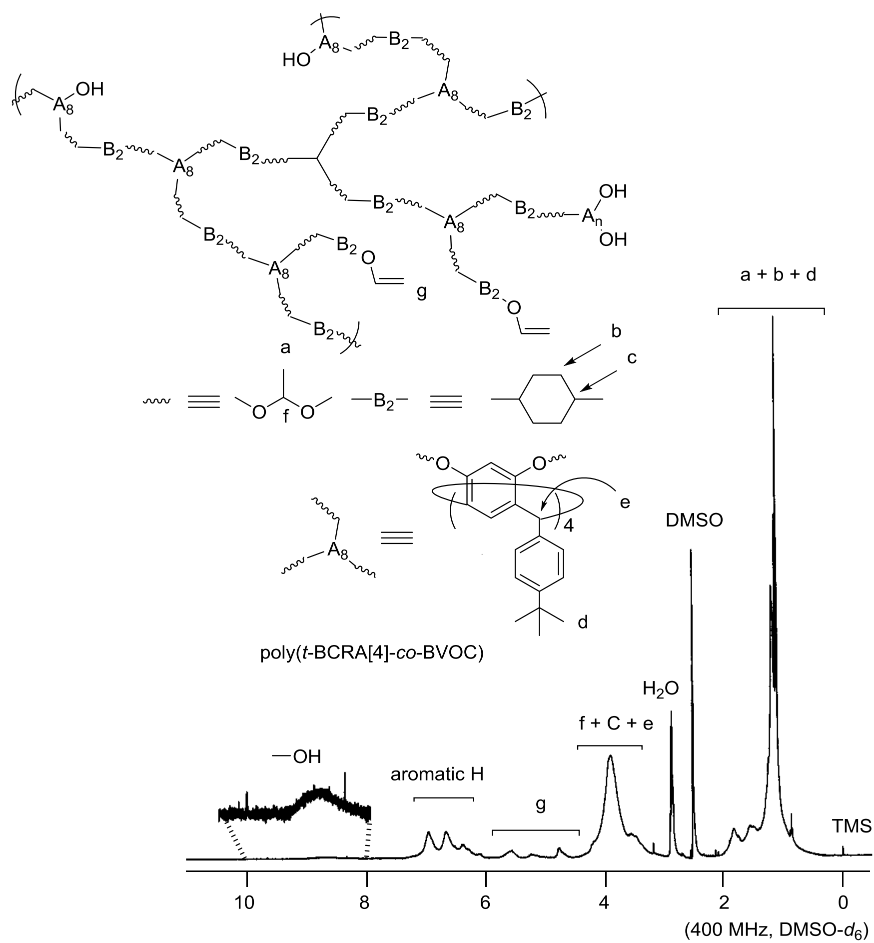


Fig. 1 ^{1}H NMR spectrum of poly(*t*-BCRA[4]-*co*-BVOC).

H. Kudo et al. Figure 2

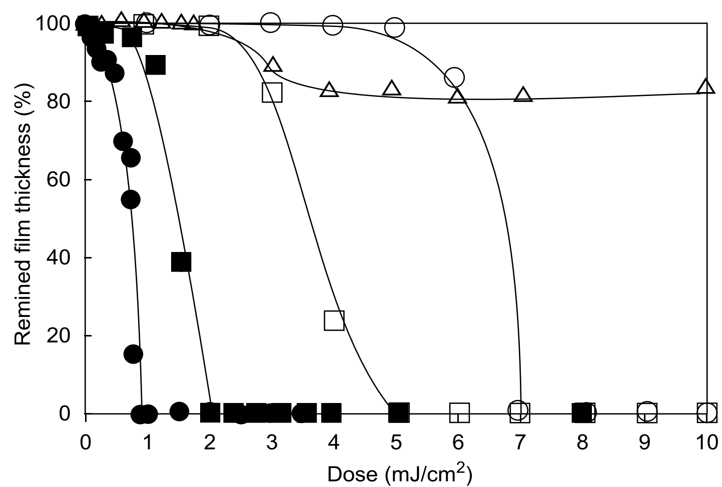


Fig.2 Sensitivity curves of hyperbranched polyacetals based on *t*-BCRA[4] using EUV exposure tool. ●; poly(*t*-BCRA[4]-*co*-BVOC), ■; poly(*t*-BCRA[4]-*co*-BVOXP), □; poly(*t*-BCRA[4]-*c*o-BVOP), Δ; poly(*t*-BCRA[4]-*c*o-BVBC), ○; poly(*t*-BCRA[4]-*c*o-TVCH).

H. Kudo et al. Figure 3

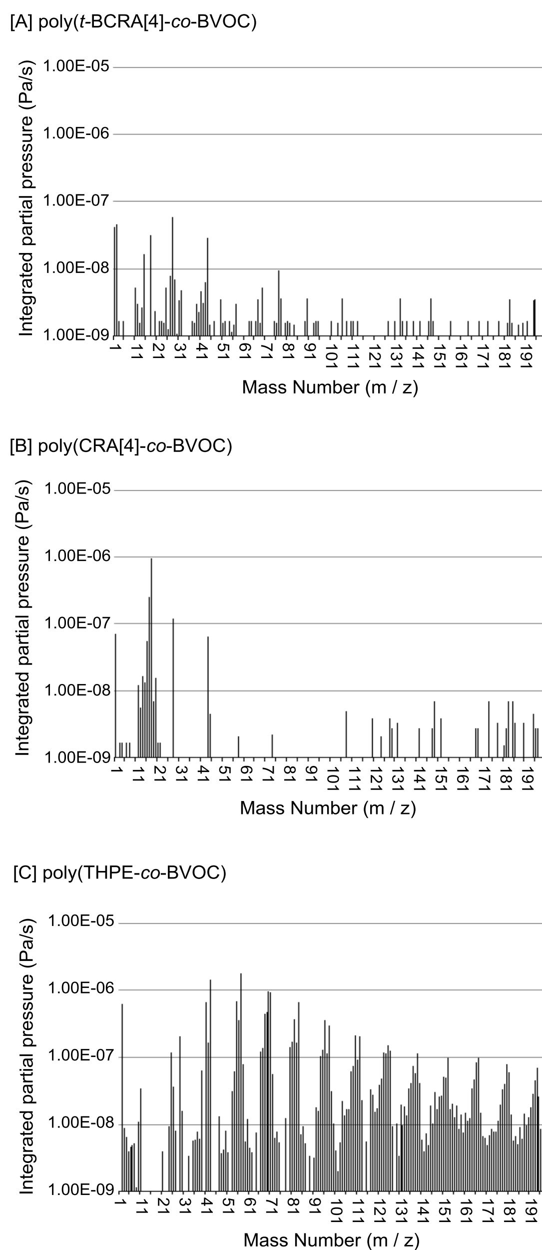


Fig.3 Out-gassed fragments from resist films prepared with poly(*t*-BCRA-*co*-BVOC) [A], poly(CRA[4]-*co*-BVOC) [B], and poly(THPE-*co*-BVOC)[C].

H. Kudo et al. Figure 4

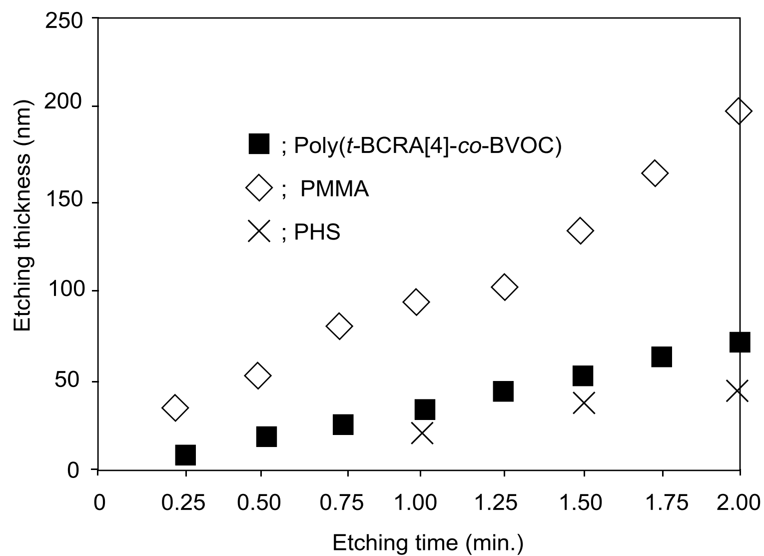
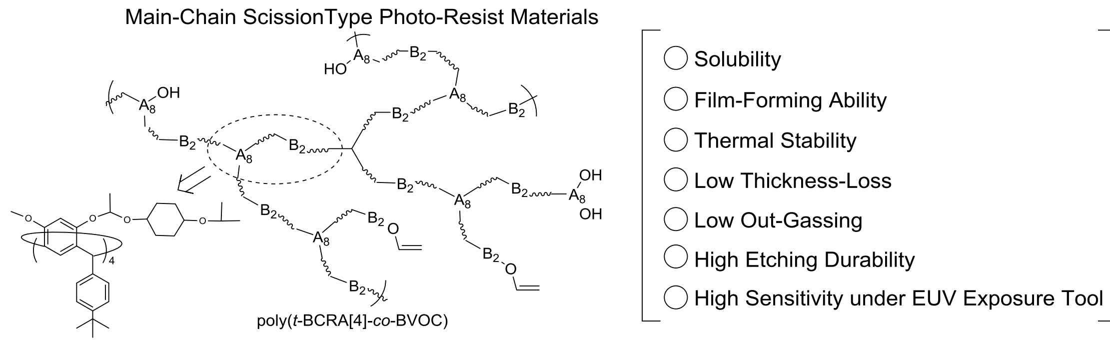


Fig. 4 Etching durability of the thin films on the silicon wafer prepared from poly(*t*-BCRA[4]-*co*-BVOC), poly(methyl methacrylate)(PMMA), and poly(hydroxystyrene)(PHS).

Graphical Abstract

(H. Kudo et al)



Supporting Information

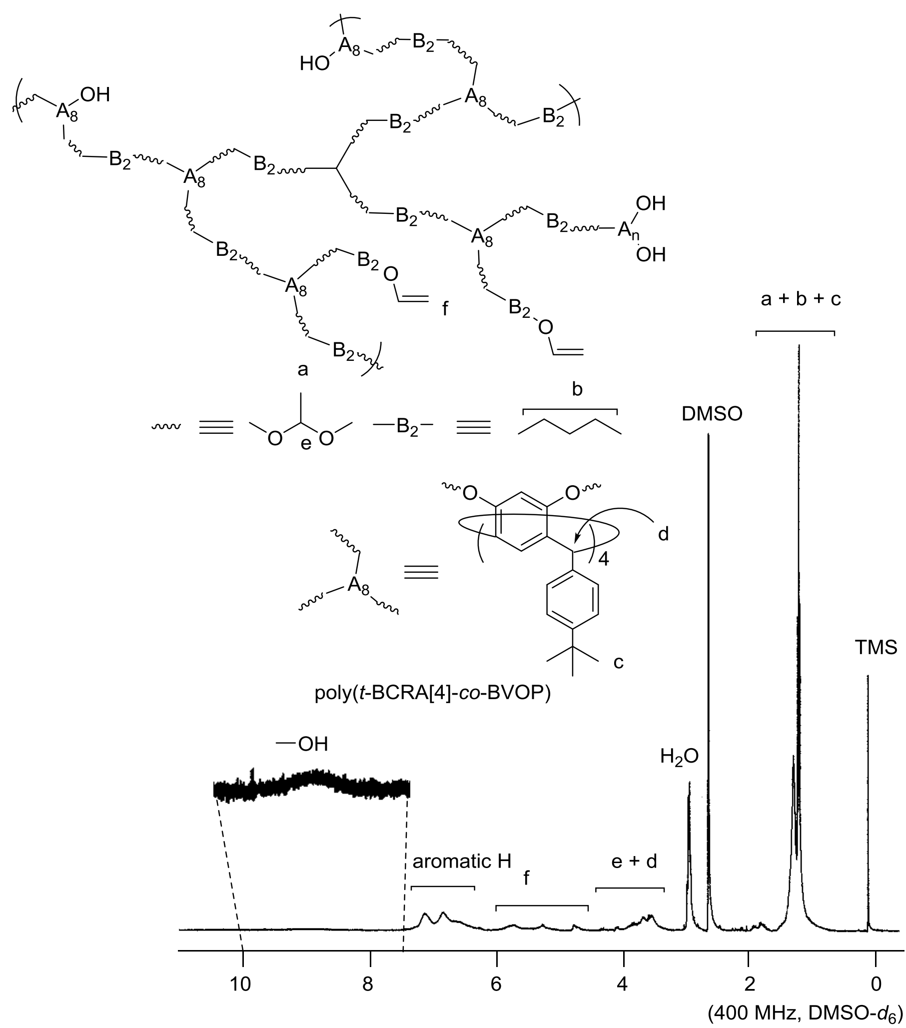


Figure. S1 ^{1}H NMR spectrum of poly(*t*-BCRA[4]-*co*-BVOP).

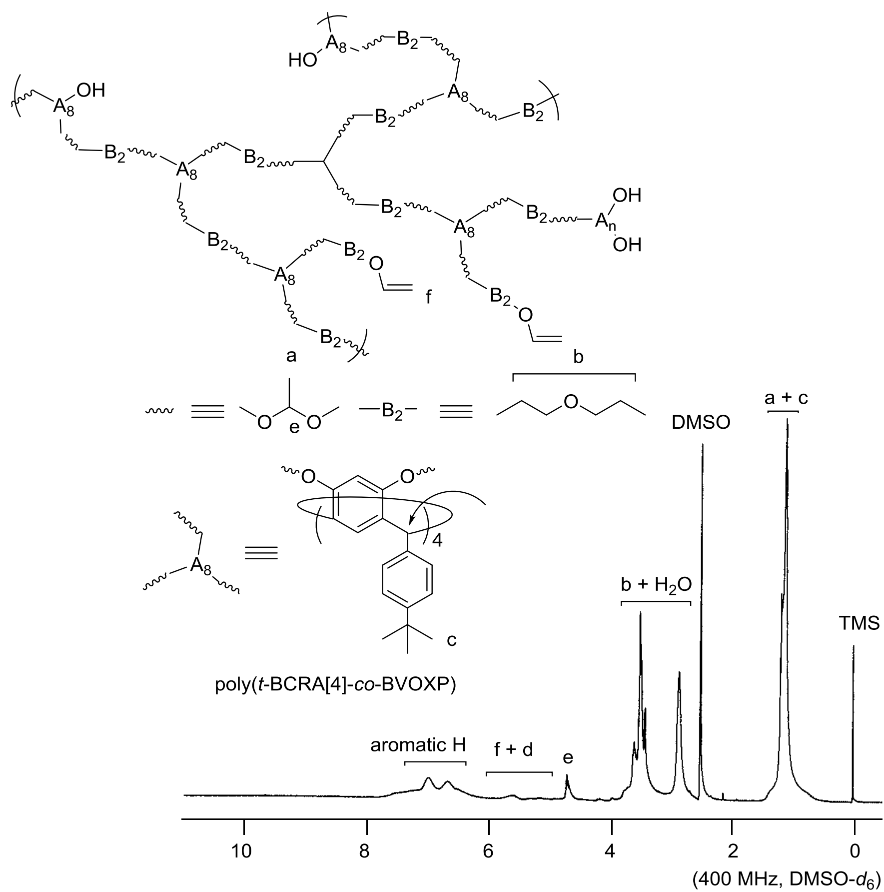


Figure. S2 ^{1}H NMR spectrum of poly(*t*-BCRA[4]-*co*-BVOXP).

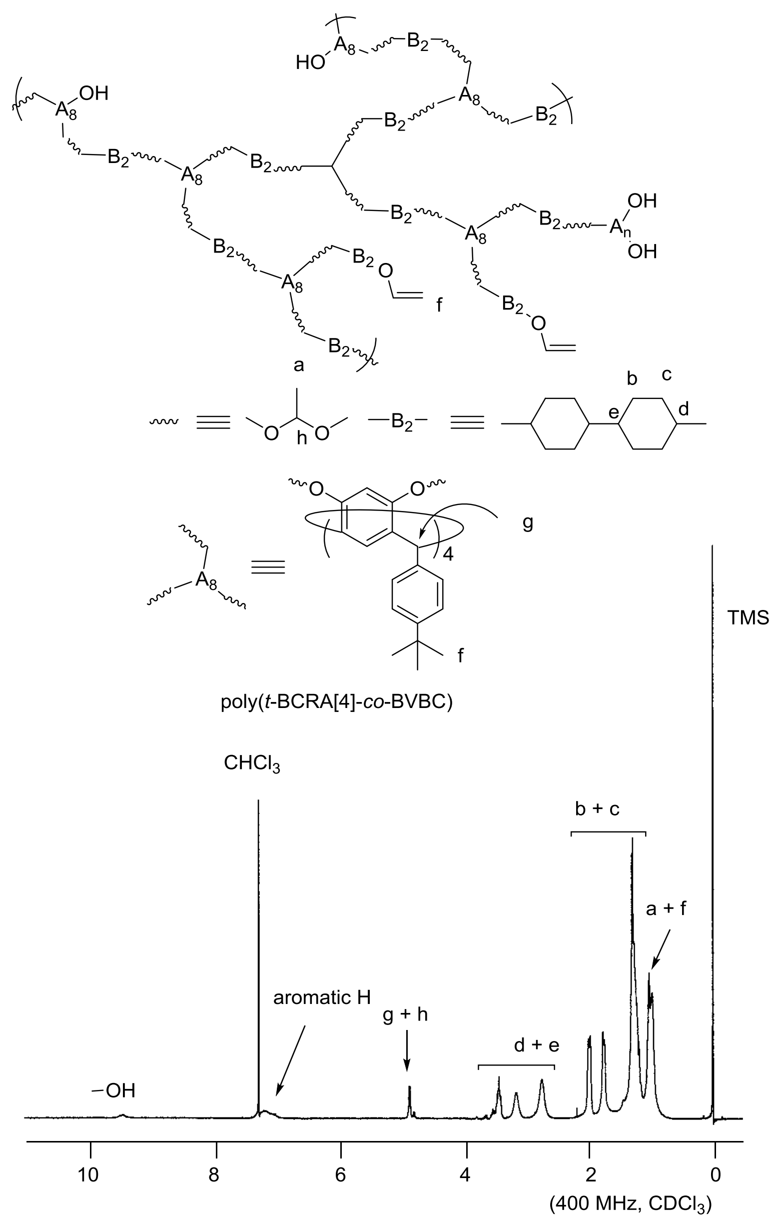


Figure. S3 ^{1}H NMR spectrum of poly(*t*-BCRA[4]-*co*-BVBC).

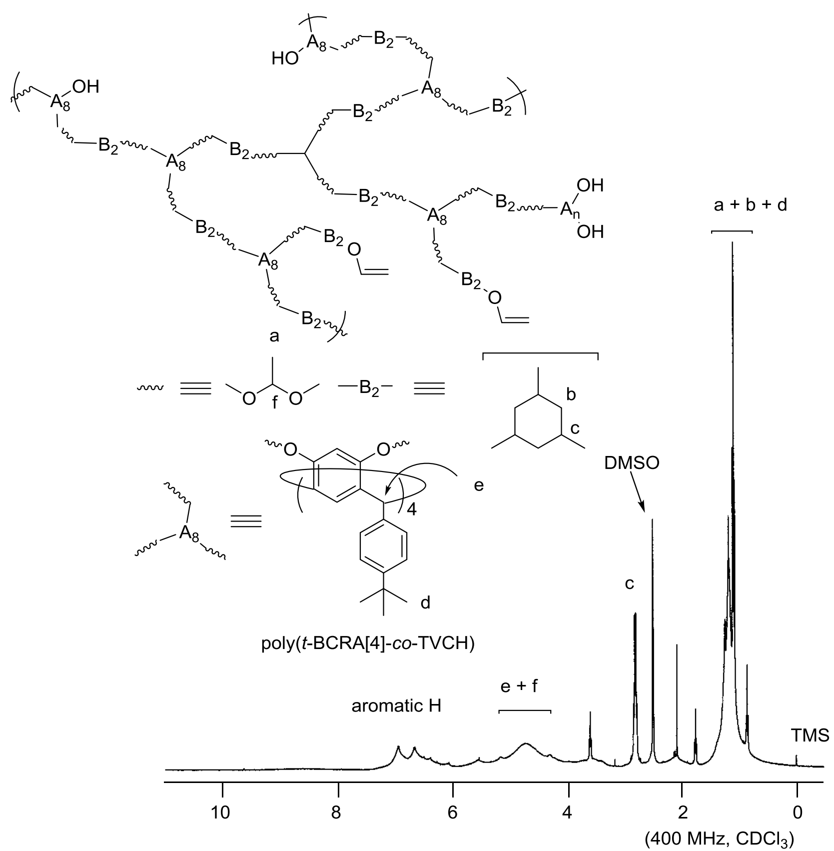


Figure. S4 ^{1}H NMR spectrum of poly(*t*-BCRA[4]-*co*-TVCH).