Characterization and Lithographic Application of Calix[4]resorcinarene Derivatives

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Received August 1, 2007. Revised Manuscript Received October 22, 2007

Calix[4]resorcinarenes were prepared by the condensation of resorcinol and aldehydes (acetaldehyde, benzaldehyde, and 4-isopropylbenzaldehyde), and two isomers, C_{4v} (ccc) and C_{2v} (ctt), were separated by fractional crystallization. The products were characterized by NMR and FTIR, and their dissolution rate in aqueous base was measured. The eight hydroxyl groups of the calix[4]resorcinarenes were protected with acid labile *t*-butoxycarbonyl and *t*-butoxycarbonylmethyl. The protected calixarenes were thoroughly characterized by differential scanning calorimetry, FTIR, and variable-temperature ^{1}H and ^{13}C NMR. Their interaction with 4-isopropylphenol through hydrogen bonding was investigated by ^{13}C NMR and correlated with their inhibition effect of dissolution of poly(4-hydroxystyrene-*co*-*t*-butyl acrylate) in an aqueous base, as studied by quartz crystal microbalance. Finally, the protected calixarenes were employed as a dissolution inhibitor of polyhydroxystyrene-based deep UV and electron beam chemical amplification resists to improve their contrast and performance.

Introduction

It has been a quarter of a century since chemical amplification resists based on photochemically induced acid catalysis were reported.[1] The worldwide implementation of chemical amplification resists in device manufacturing by 248 nm (KrF excimer laser) lithography has enabled the semiconductor industry to follow Moore's law. Miniaturization continues by migrating to a shorter wavelength from 248 to 193 nm (ArF excimer laser). A further shift to 157 nm (F_2 excimer laser) has been given up in spite of large efforts to develop the 157 nm technology including resists. Instead, immersion lithography at 193 nm has emerged as the next-generation technology requiring a resolution below 50 nm, which is the most active area of research and development today. The soft X-ray lithography at 13.4 nm called extreme ultraviolet (EUV) is a contender for the 22 nm node. All of these advanced lithographic technologies are supported by chemical amplification resists primarily through the optimization of resist polymers for each exposure condition. It is noteworthy that 193 nm chemical amplification resists developed for exposure in the air perform well in water by minimal optimization in immersion lithography, where water is placed between the resist film and the last lens element.

The 248 nm resists are built on poly(4-hydroxystyrene) (PHOST) exclusively, which in turn is excluded in the ArF resist design due to excessive absorption at 193 nm. The 157 nm resists required the use of fluoropolymers for good transparency, which contain fluoroalcohol[2–5] as a replacement of phenol and carboxylic acid. The attractive dissolution behavior provided by fluoroalcohol-bearing polymers has prompted their back-integration in the 193 nm resists (wet and dry).[6] As the EUV absorption is determined by the nature of atoms but not by the structure of molecules, PHOST-based resists can be employed, and therefore early EUV lithography development work[7] was performed using 248 nm resists, primarily ESCAP,[8] consisting of a copolymer of 4-hydroxystyrene (HOST) with *t*-butyl acrylate (TBA).

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10.1021/cm7021483 CCC: $40.75

Although chemical amplification resists have demonstrated a 30 nm equal line/space resolution by electron beam[9] and by 193 nm immersion lithography,[10] the challenge is whether or not the resolution can be further extended with an acceptable sensitivity and line edge roughness (LER). Thus, further improvement of chemical amplification resists is critically important.

Small molecules that undergo acid-catalyzed deprotection to generate acidic compounds in an acidic or protected polymer matrix have been also employed as a dissolution inhibitor in the design of chemical amplification resists.[11–18] Furthermore, the use of small molecules that form amorphous glass (molecular glass),[19] instead of polymers, has attracted a great deal of attention recently as a means to overcome the size-related issues (resolution and LER) in lithography below 30 nm. Polyphenolic compounds[20–26] (including calix[4]arenes[21–25]), polyhedral oligomeric silsesquioxane,[27,28] cholates,[29,30] cyclodextrins,[27,31] adamantanes,[32] dendrimers,[33] and fullerenes[34] have been reported as chemically amplified molecular glass resists.

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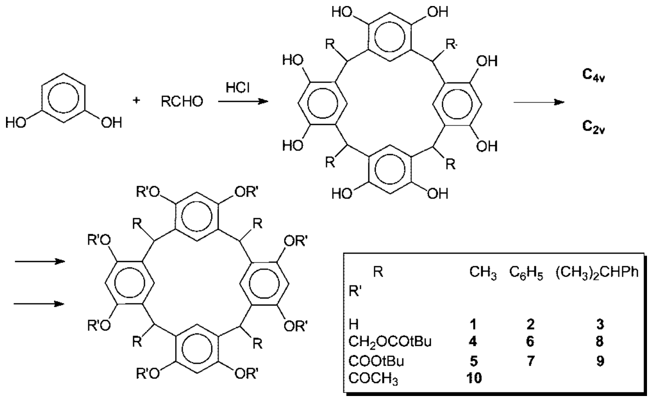

R' \ R	CH_3	C_6H_5	$(CH_3)_2CHPh$
H	**1**	**2**	**3**
$CH_2OCOtBu$	**4**	**6**	**8**
COOtBu	**5**	**7**	**9**
$COCH_3$	**10**		

Figure 1. Synthesis and protection of calix[4]resorcinarenes.

While negative-tone solvent-developed calix[6]arene and calix[7]arene resists were demonstrated by NEC researchers[35] to produce high-resolution patterns (at a very high electron-beam dose), the use of polyphenolic calix[4]resocinarenes as molecular glass chemical amplification resists was pioneered by Ueda and co-workers.[21] Calix[4]resorcinarenes,[36,37] which are produced by the condensation of resorcinol with aldehydes, have eight phenolic hydroxyl groups, which could be protected with acid-labile groups. Initially, we were interested in calix[4]resocinarenes as a platform for molecular glass resists, but because their film-forming property was not high enough, we have decided to evaluate protected calixarenes as dissolution inhibitors in phenolic resists.[18] In this paper, we report the syntheses and fractional recrystallization to separate isomers, detailed characterization (thermal analysis, FTIR, and variable-temperature NMR) of each isomer, their dissolution inhibition effects, and lithographic imaging.

Experimental Section

General Synthetic Procedure of Calix[4]resorcinarenes. A solution of resorcinol and aldehyde (acetaldehyde, benzaldehyde, or 4-isopropylbenzaldehyde) in 50 vol % aqueous ethanol was heated at 75 °C. To the solution was added dropwise concentrated hydrochloric acid. The reaction mixture was continuously stirred at 75 °C for a few hours. Two isomers, C_{4v} (ccc) and C_{2v} (ctt), were separated by fractional crystallization and dried under reduced pressure. We synthesized six calix[4]resorcinarenes (two isomers each of methyl (**1**), phenyl (**2**), and 4-isopropylphenyl (**3**) derivatives, Figure 1).

C-Tetramethyl-calix[4]resorcinarene (ccc Isomer, $\mathbf{1_{ccc}}$*).* A solution of 33.03 g (0.3 mol) of resorcinol and 13.23 mL (0.3 mol) of acetaldehyde in 300 mL of a 50 vol % aqueous ethanol solution was heated at 75 °C. To the solution was added dropwise 75 mL of concentrated hydrochloric acid. The reaction mixture was continuously stirred at 75 °C. After 1 h, the mixture was cooled with an ice bath, and a precipitate was collected with a glass filter and dried under reduced pressure. A filtrate was evaporated, and the second precipitate was filtered. The collected precipitate was recrystallized from a 50 vol % aqueous ethanol solution to yield 23.21 g (57%) of a ccc isomer $\mathbf{1_{ccc}}$. ^{1}H NMR (250 MHz, acetone-d_6, room temperature): CH_3 (1.76, d, $J = 7.3$ Hz), CH (4.52, q, $J = 7.3$ Hz), aromatic CH (6.21, s), aromatic CH (7.65, s), OH (8.46, br). ^{13}C NMR (63 MHz, acetone-d_6, room temperature): CH_3 (20.21), CH (28.63), aromatic CH (103.53), aromatic CH (125.16), aromatic C (126.09), aromatic C−OH (152.24).

C-Tetramethyl-calix[4]resorcinarene (Isomeric Mixture, $\mathbf{1_{ccc}} + \mathbf{1_{ctt}}$*).* To a solution of 33.03 g (0.3 mol) of resorcinol and 13.23 g (0.3 mol) of acetaldehyde in 120 mL of water was added 5 mL of concentrated hydrochloric acid diluted with 5 mL of H_2O over a 15 min period. The reaction mixture was heated at 75 °C for 3 h, and a precipitate was collected with a glass filter every hour. Then, the collected precipitate was recrystallized from CH_3OH/water to give 16.46 g (40%) of a ccc isomer. After the recrystallization, the solution was concentrated by rotary evaporation, and a residue was recrystallized from acetonitrile to give 1.34 g (3%) of a ctt (C_{2v}) isomer. Analytical results for $\mathbf{1_{ctt}}$ are as follows. ^{1}H NMR (250 MHz, acetone-d_6, room temperature): CH_3 (1.36, d, $J = 7.1$ Hz), CH (4.56, q, 7.1 Hz), aromatic CH (6.31, 6.39, s), aromatic CH (6.44, 6.97, s), OH (7.45, 7.95, br). ^{13}C NMR (63 MHz, acetone-d_6, room temperature): CH_3 (20.64), CH (31.32), aromatic CH (103.18, 103.26), aromatic C (123.11, 125.48), aromatic CH (127.27, 127.49), aromatic C−OH (153.38, 153.59).

C-Tetramethyl-calix[4]resorcinarenes ($\mathbf{1_{ccc}} + \mathbf{1_{ctt}}$*) via Corresponding Acetates (*$\mathbf{10_{ccc}}$ *and* $\mathbf{10_{ctt}}$*).* The synthetic procedure was the same as for $\mathbf{1_{ccc}}$. After 1 h, a precipitate formed during the reaction was collected, washed with water, and dried under reduced pressure, to give 13.63 g (100%) of a crude calixarene. The crude calixarene (12.30 g, 22.6 mmol) and a few drops of pyridine were added to 60 mL of acetic anhydride, and the solution was stirred at room temperature for 30 min. Excess acetic anhydride was evaporated, and 20 mL of methanol was added to the residue. A precipitate was collected with a glass filter and washed with methanol. The obtained powderlike product was recrystallized from acetonitrile to give 0.712 g of a "ctt" isomer, $\mathbf{10_{ctt}}$, as the first fraction and 9.735 g of $\mathbf{10_{ccc}}$ as the second fraction. Analysis results for $\mathbf{10_{ccc}}$ are as follows. ^{1}H NMR (250 MHz, $CDCl_3$, room temperature): CH_3 (1.45, d, $J = 7.0$ Hz), CH_3CO (2.06, 2.24, very broad), CH (4.23, q, $J = 7.0$ Hz), aromatic CH (6.01, 7.32, very broad), aromatic CH (6.87, br). ^{13}C NMR (63 MHz, $CDCl_3$, room temperature): CH_3CH (19.70), CH_3CO (20.67), CH_3CH (32.79), aromatic CH (116.62), aromatic CH (125.56), aromatic C (131.71, 136.25), aromatic COH (146.64), CO (168.54). Analysis results for $\mathbf{10_{ctt}}$ are as follows. ^{1}H NMR (63 MHz, $CDCl_3$, room temperature): CH_3 (1.37, d, $J = 7.0$ Hz), CH_3CO (1.92, 2.33), CH (4.24, q, $J = 7.2$ Hz), aromatic CH (5.85, 7.31), aromatic CH (6.72, 6.88). ^{13}C NMR (63 MHz, $CDCl_3$, room temperature): CH_3CH (18.97, 20.96), CH_3CO (20.20), CH_3CH (32.50), aromatic CH (116.16, 118.12), aromatic CH (126.56, 126.32), aromatic C (132.25, 136.62), aromatic COH (145.56, 147.20), CO (168.56, 168.95).

A solution of 4 g of KOH in 50 mL of ethanol was added to a solution of 3.524 g (4 mmol) of $\mathbf{10_{ccc}}$ in 50 mL of ethanol. After the reaction mixture was stirred at 60 °C for 30 min, the solution was neutralized with 4 mL of acetic acid. A precipitate was collected with a glass filter and washed with water. The product was

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recrystallized from a 50 vol % aqueous ethanol solution to yield 1.645 g of $\mathbf{1}_{\mathbf{ccc}}$.

A solution of 0.617 g (0.7 mmol) of $\mathbf{10}_{\mathbf{ctt}}$ and 0.6 g of KOH in 8 mL of ethanol was stirred at 60 °C for 30 min. Then, the solution was neutralized with 0.6 mL of acetic acid. A precipitate was collected, washed with water, and recrystallized from a 50 vol % aqueous ethanol solution to yield 0.145 g of $\mathbf{1}_{\mathbf{ctt}}$.

C-Tetraphenyl-calix[4]resorcinarene (ccc, $\mathbf{2}_{\mathbf{ccc}}$*).* A solution of 2.76 g (0.025 mol) of resorcinol and 2.65 g (2.55 mL, 0.025 mol) of benzaldehyde in 20 mL of ethanol was heated at 75 °C under nitrogen. To the solution was immediately added 2.1 mL (0.025 mol) of concentrated hydrochloric acid, and then the reaction mixture was stirred at 75 °C for 20 h. The mixture containing a yellow precipitate formed during the reaction was poured into 250 mL of a 50 vol % aqueous methanol solution to remove acid. The precipitate was collected with a glass filter and dried under reduced pressure to give 4.637 g (94%) of a crude product.

C-Tetraphenyl-calix[4]resorcinarene (ccc−ctt Mixture, $\mathbf{2}_{\mathbf{ccc}} + \mathbf{2}_{\mathbf{ctt}}$*).* A solution of 2.76 g (0.025 mol) of resorcinol and 2.65 g (2.55 mL, 0.025 mol) of benzaldehyde in 20 mL of a 50 vol% aqueous methanol solution was heated at 75 °C under nitrogen. To the solution was slowly added 2.1 mL (0.025 mol) of concentrated hydrochloric acid, and then the reaction mixture was stirred at 75 °C for several days. The reaction mixture was poured into 250 mL of a 50 vol % aqueous methanol solution to remove acid. The precipitate was collected with a glass filter and dried under reduced pressure. The ctt isomer was isolated by recrystallization from dimethylformamide (DMF).

C-Tetra-4-isopropylphenyl (iPrPh)-Calix[4]resorcinarene (ctt, $\mathbf{3}_{\mathbf{ctt}}$*).* The reaction between resorcinol and 4-isopropylbenzaldehyde was carried out in a fashion similar to the synthesis of the phenyl derivative. After 15 h at 75 °C, a precipitate formed during the reaction was collected with a glass filter after the reaction mixture was cooled down with an ice bath. The collected precipitate was washed in 50 mL of refluxing methanol, filtered, and dried under reduced pressure to yield 15.42 g (80%) of $\mathbf{3}_{\mathbf{ctt}}$. ^{1}H NMR (250 MHz, acetone-d$_6$, room temperature): CH$_3$ (1.17, d, $J = 6.9$ MHz, 1.18, d, $J = 6.9$ Hz), CH (2.77, q, $J = 6.9$ Hz), CH (5.76, s), aromatic CH (6.22, 6.28), aromatic CH (6.50, 6.66), aromatic CH−CH (6.78, 6.86, AB q, $J = 8.2$ Hz), OH (7.30, 7.57). ^{13}C NMR (63 MHz, acetone-d$_6$, room temperature): CH$_3$CH (24.35, 24.44), CH$_3$CH (34.11), CH (43.35), aromatic CH (102.93, 103.29), aromatic C (122.91, 122.44), iPrPh aromatic CH (125.94), iPrPh aromatic CH (130.25), aromatic CH (130.57, 132.25), iPrPh aromatic C (141.71), iPrPh aromatic C (145.54), aromatic COH (154.08).

C-Tetra-4-isopropylphenyl-calix[4]resorcinarene (Mixture of ccc and ctt, $\mathbf{3}_{\mathbf{ccc}} + \mathbf{3}_{\mathbf{ctt}}$*).* The synthetic procedure was similar to the one above. After 7 h at 75 °C, a precipitate formed during the reaction was collected with a glass filter after the reaction mixture was cooled down with an ice bath. The precipitate ($\mathbf{3}_{\mathbf{ctt}}$) was washed in 70 mL of refluxing methanol for 30 min, separated with a glass filter, and dried under reduced pressure. The filtrate was placed in a refrigerator overnight, and a mixture of isomers was given as a crystal. Recrystallization from acetonitrile gave 5.88 g of $\mathbf{3}_{\mathbf{ccc}}$. Analysis results for $\mathbf{3}_{\mathbf{ccc}}$ are as follows. ^{1}H NMR (250 MHz, acetone-d$_6$, room temperature): CH$_3$ (1.28, d, $J = 6.9$ Hz), CH (2.87, q, $J = 6.9$ Hz), CH (5.84, s), aromatic CH (6.27, s), aromatic CH (6.65, s), aromatic CH−CH (6.87, 6.97, AB q, $J = 8.2$ Hz), OH (7.49, s). ^{13}C NMR (63 MHz, acetone-d$_6$, room temperature): CH$_3$CH (24.62), CH$_3$CH (34.47), CH (42.51), ring aromatic CH (103.40), ring aromatic C (122.22), iPrPh aromatic CH (126.27), iPrPh aromatic CH (128.89), ring aromatic CH (132.21), iPrPh aromatic C (143.34), iPrPh aromatic C (145.76), ring aromatic C−OH (154.02).

General Protection Procedure. All eight of the OH groups of calix[4]resorcinarenes **1**, **2**, and **3** were fully protected with *t*-butoxycarbonyl (tBOC) or *t*-butoxycarbonylmethyl (tBOCCH$_2$) (Figure 1). Calixresorcinarene was reacted with di-*t*-butyl dicarbonate in the presence of pyridine. For the reaction of *t*-butyl bromoacetate with calixresorcinarene, potassium carbonate/18-crown-6 or sodium hydride was employed. The protected calixresorcinarenes were purified by recrystallization.

*O-Octa-*t*-butoxycarbonylmethyl-C-tetramethyl-calix[4]resorcinarene (ccc,* $\mathbf{4}_{\mathbf{ccc}}$*).* To a solution of 1.63 g (3 mmol) of $\mathbf{1}_{\mathbf{ccc}}$ in 30 mL of dry acetone was added 4.56 g (33 mmol) of potassium carbonate, 0.70 g (2.64 mmol) of 18-crown-6, and 5.15 g (26.4 mmol) of *t*-butyl bromoacetate. The reaction mixture was refluxed with vigorous stirring. After 72 h, the mixture was poured into 200 mL of water, and then a precipitate was collected with a glass filter, washed with water and methanol, and recrystallized from 2-propanol to give 2.65 g (61%) of $\mathbf{4}_{\mathbf{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (1.45, s), CH$_3$−CH (1.45), OCH$_2$ (4.18, br), CH$_3$−CH (4.67, q, $J = 7.0$ Hz), aromatic CH (6.18, s), aromatic CH (ca. 6.5, very br). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (19.60), *t*-butyl CH$_3$ (28.02), CH$_3$−CH (30.91), OCH$_2$ (67.43), O−C (81.59), aromatic CH (99.96, br), aromatic C (125.70), aromatic CH (129.13, br), aromatic C (154.20), C=O (168.42).

*O-Octa-*t*-butoxycarbonylmethyl-C-tetramethyl-calix[4]resorcinarene (ctt,* $\mathbf{4}_{\mathbf{ctt}}$*).* Sodium hydride (0.576 g, 60 wt % in oil) was dispersed in a mixed solvent of DMF and tetrahydrofuran (THF) (2.5 mL/7 mL). To the mixture was added in a 30 min period a suspension of 0.817 g (1.5 mmol) of $\mathbf{1}_{\mathbf{ctt}}$ and 2.808 g (14.4 mmol) of *t*-butyl bromoacetate in a mixture of DMF and THF (2.5 mL/1 mL), and then the reaction mixture was vigorously stirred for 12 h. An insoluble part was filtered off, and a filtrate was evaporated. The white solid thus obtained was washed with water and methanol and recrystallized from toluene/cyclohexane to give 1.266 g (58%) of the ester. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): CH$_3$−CH (1.33, d, $J = 7.0$ Hz), *t*-butyl CH$_3$ (1.39, 1.49), OCH (4.03, AB quartet, $J = 15.3$ Hz), OCH (4.54, AB quartet, $J = 14.8$ Hz), CH$_3$−CH (4.73, q, $J = 6.8$ Hz), aromatic CH (5.97, 6.25), aromatic CH (6.31, 7.10). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (20.06), *t*-butyl CH$_3$ (27.97, 28.10), CH$_3$−CH (30.72), OCH$_2$ (67.52), O−C (81.50, 81.74), aromatic CH (99.32, 101.24), aromatic CH (125.45, 126.38), aromatic C (127.36, 130.66), aromatic C (153.56, 155.03), C=O (168.14, 168.65).

*O-Octa-*t*-butoxycarbonyl (tBOC)-C-tetramethyl-calix[4]resorcinarene (ccc,* $\mathbf{5}_{\mathbf{ccc}}$*).* Pyridine (0.08 mL) was added to a solution of 6.76 g (1.5 mmol) of $\mathbf{1}_{\mathbf{ccc}}$ and 2.881 g (13.2 mmol) of di-*t*-butyl dicarbonate in 20 mL of dry acetone. The reaction mixture was refluxed for 15 h and concentrated by rotary evaporation to give a yellow solid. Recrystallization from acetone yielded 1.910 g (95%) of $\mathbf{5}_{\mathbf{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): CH$_3$−CH (1.42, d), *t*-butyl CH$_3$ (1.46, s), CH$_3$−CH (4.43, q, $J = 7.1$ Hz), aromatic CH (6.89, very br). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (20.52), *t*-butyl CH$_3$ (27.66), CH$_3$−CH (31.41), *t*-butyl C (82.80), aromatic CH (116.40, br), aromatic C (125.71), aromatic CH (134.40), aromatic C (146.94), C=O (151.47).

O-Octa-tBOC-C-tetramethyl-calix[4]resorcinarene (ctt, $\mathbf{5}_{\mathbf{ctt}}$*).* $\mathbf{1}_{\mathbf{ctt}}$ was protected with tBOC in a fashion similar to the above procedure for $\mathbf{1}_{\mathbf{ccc}}$. The yellow solid obtained by rotary evaporation of the reaction mixture was subjected to recrystallization from acetone to provide 1.910 g (95%) of $\mathbf{5}_{\mathbf{ctt}}$. ^{1}H NMR (250 MHz, CDCl$_3$): CH$_3$−CH (1.36, d, $J = 7.1$ Hz), *t*-butyl CH$_3$ (1.32, 1.54), CH$_3$−CH (4.48, q, $J = 7.0$ Hz), aromatic CH (6.02, 7.33), aromatic CH (6.77, 7.17). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH

(19.70), *t*-butyl CH$_3$ (27.37, 27.76), CH$_3$−CH (31.98), *t*-butyl C (82.80, 82.96), aromatic CH (115.56, 117.59), aromatic C (126.52, 126.71), aromatic CH (132.93, 134.93), aromatic C (146.72, 147.59), C=O (146.72, 147.59).

O-*Octa*-t-*butoxycarbonylmethyl*-C-*tetraphenyl-calix[4]resorcinarene (ccc,* $\mathbf{6_{ccc}}$*)*. The synthetic procedure was similar to that of $\mathbf{4_{ccc}}$. A precipitate formed by pouring the reaction mixture in water was collected with a glass filter, washed with water and methanol, and recrystallized from 2-propanol/acetone to give 2.290 g (67%) of $\mathbf{6_{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (1.37, 1.45), OCH (4.03, AB quartet, J = 15.0 Hz), OCH (4.11, AB quartet, J = 15.8 Hz), tetra-substituted benzene CH (5.85, 6.12), Ph−CH−Ph (5.88, s), tetra-substituted benzene CH (6.16, 6.30), aromatic CH (6.79, m), aromatic CH (6.97, m). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (27.98, 28.08), Ph−CH−Ph (43.13), OCH$_2$ (67.51, 67.85), O−C (81.60), tetra-substituted benzene CH (100.15, 100.35), aromatic CH (125.42), tetra-substituted benzene C (125.46, 127.22), aromatic CH (127.63), aromatic CH (128.99), tetra-substituted benzene CH (128.49, 132.69), aromatic C (143.02), tetra-substituted benzene C (154.86), C=O (168.31).

O-*Octa*-t-*butoxycarbonylmethyl*-C-*tetraphenyl-calix[4]resorcinarene (ctt,* $\mathbf{6_{ctt}}$*)*. $\mathbf{6_{ctt}}$ was prepared in a procedure similar to those of $\mathbf{4_{ccc}}$ and $\mathbf{6_{ccc}}$. A precipitate obtained by pouring the reaction mixture in water was collected with a glass filter, washed with water and methanol, and recrystallized from acetone to give 2.500 g (73%) of $\mathbf{6_{ctt}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (1.38, 1.47), OCH$_2$ (4.17, AB quartet, J = 15 MHz, 4.20, AB quartet, J = 15 MHz), tetra-substituted benzene CH (5.66, 6.19), Ph−CH−Ph (5.90, s), tetra-substituted benzene CH (6.269, 6.272), aromatic CH (6.64, m), aromatic CH (6.90, m). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (27.995, 28.020), Ph−CH−Ph (42.89), OCH$_2$ (67.22, 67.86), *t*-butyl C (81.51, 81.65), tetra-substituted benzene CH (99.03, 100.87), aromatic C (125.42), tetra-substituted benzene C (126.38, 127.05), aromatic CH (127.48), aromatic CH (128.99), tetra-substituted benzene CH (128.85, 132.16), aromatic C (142.31), tetra-substituted benzene C (154.68, 154.86), C=O (167.84, 168.30).

O-*Octa-tBOC*-C-*tetraphenyl-calix[4]resorcinarene (ccc,* $\mathbf{7_{ccc}}$*)*. One drop of pyridine was added to a suspension of 1.586 g (2 mmol) of $\mathbf{2_{ccc}}$ and 3.841 g (17.6 mmol) of di-*t*-butyl dicarbonate in 30 mL of dry acetone, and then the reaction mixture was refluxed. An insoluble part completely disappeared. The reaction was continued for 20 h, and then the solvent evaporated. A residue was subjected to recrystallization from acetone/2-propanol to give 1.153 g (40%) of $\mathbf{7_{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (1.15, 1.40, s), Ph−CH−Ph (5.64, s), tetra-substituted benzene CH (6.04, 6.31), aromatic CH (6.69, br), tetra-substituted benzene CH (6.88, 7.03), aromatic CH (6.98, m). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (27.26, 27.56), Ph−CH−Ph (43.70), *t*-butyl C (82.59, 82.85), tetra-substituted benzene CH (116.94, 117.25), aromatic C (126.09), aromatic CH (128.09), aromatic CH (128.60), tetra-substituted benzene C (129.18, 133.26), tetra-substituted benzene C (131.13, 131.43), aromatic C (144.28), tetra-substituted benzene C (147.37, 147.52), C=O (150.35, 151.12)

O-*Octa-tBOC*-C-*tetraphenyl-calix[4]resorcinarene (ctt,* $\mathbf{7_{ctt}}$*)*. One drop of pyridine was added to a suspension of 1.586 g (2 mmol) of $\mathbf{2_{ctt}}$ and 3.841 g (17.6 mmol) of di-*t*-butyl dicarbonate in 30 mL of dry acetone, and then the reaction mixture was refluxed for 20 h. In this case, an insoluble part still remained after 20 h. A residue obtained after evaporation of the solvent was recrystallized from acetone to give 1.463 g (46%) of $\mathbf{7_{ctt}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (1.19, 1.35), Ph−CH−Ph (5.75, s), tetra-substituted benzene CH (6.00, 6.45), aromatic CH (6.68, d), aromatic CH (6.90, m), tetra-substituted benzene CH (6.98, 7.09). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): *t*-butyl CH$_3$ (27.33, 27.57), Ph−CH−Ph (43.48), *t*-butyl C (82.41, 83.36), tetra-substituted benzene CH (116.46, 116.82), aromatic C (126.00), aromatic CH (127.95), aromatic CH (129.14), tetra-substituted benzene C (129.64, 132.64), tetra-substituted benzene C (131.67, 132.44), aromatic C (139.65), tetra-substituted benzene C (147.33), C=O (150.52, 151.12).

O-*Octa*-t-*butoxycarbonylmethyl*-C-*tetra-4-isopropylphenyl-calix[4]resorcinarene (ccc,* $\mathbf{8_{ccc}}$*)*. $\mathbf{8_{ccc}}$ was prepared in a fashion similar to $\mathbf{4_{ccc}}$. A precipitate formed by pouring the reaction mixture in water was collected with a glass filter, washed with water and methanol, and recrystallized from 2-propanol to give 4.16 g (74%) of $\mathbf{8_{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): CH$_3$−CH (1.22, br), *t*-butyl CH$_3$ (1.37, 1.44), OCH (3.97, m), OCH (4.07, q, J = 16 Hz), tetra-substituted CH (3.85, 6.23), tetra-substituted CH (6.16, 6.30, br), aromatic CH (6.78, d, J = 8.1 Hz), aromatic CH (6.90, d, J = 8.2 Hz). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (23.96, 24.20), *t*-butyl CH$_3$ (28.03), CH$_3$−CH (33.55), Ph−CH−Ph (42.67), OCH$_2$ (67.41, 67.96), *t*-butyl C (81.49), tetra-substituted benzene CH (100.65, 101.93), iPrPh aromatic CH (125.58), tetra-substituted benzene C (126.26, 128.26), iPrPh aromatic CH (129.16), tetra-substituted benzene CH (132.23), iPrPh aromatic C (140.47), iPrPh aromatic C (145.36), tetra-substituted benzene C (154.69), C=O (168.37).

O-*Octa*-t-*butoxycarbonylmethyl*-C-*tetra-4-isopropylphenyl-calix[4]resorcinarene (ctt,* $\mathbf{8_{ctt}}$*)*. For the synthetic procedure, see $\mathbf{8_{ccc}}$ above. A precipitate obtained by pouring the reaction mixture in water was collected with a glass filter, washed with water and methanol, and recrystallized from 2-propanol to give 10.49 g (56%) of $\mathbf{8_{ctt}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): CH$_3$−CH (1.12, d, J = 6.8 Hz, 1.14, d, J = 6.9 Hz), *t*-butyl CH$_3$ (1.38, 1.43), CH$_3$−CH (2.70, m), OCH (4.05, AB quartet, J = 5.0 Hz), OCH (4.20, AB quartet, J = 4.5 Hz), Ph−CH−Ph (5.89, s), tetra-substituted benzene CH (6.22, 6.26), tetra-substituted benzene CH (6.29, 6.35), iPrPh aromatic CH (6.66, d, J = 8.0 Hz), iPrPh aromatic CH (6.81, d, J = 8.2 Hz). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (23.67, 24.09), *t*-butyl CH$_3$ (28.01, 28.05), CH$_3$−CH (33.31), Ph−CH−Ph (42.69), OCH$_2$ (67.49, 68.04), *t*-butyl C (81.43, 81.56), tetra-substituted benzene CH (100.03, 101.57), iPrPh aromatic CH (125.38), tetra-substituted benzene C (126.40, 128.48), tetra-substituted benzene CH (128.11, 131.38), iPrPh aromatic CH (129.36), iPrPh aromatic C (139.58), iPrPh aromatic C (145.14), tetra-substituted benzene C (154.56, 155.03), C=O (168.01, 168.44).

O-*Octa-tBOC*-C-*tetra-4-isopropylphenyl-calix[4]resorcinarene (ccc,* $\mathbf{9_{ccc}}$*)*. $\mathbf{9_{ccc}}$ was prepared as described for $\mathbf{4_{ccc}}$. After 20 h of the reaction, the solvent was evaporated and a residue was recrystallized from 2-propanol to give 4.303 g (81%) of $\mathbf{9_{ccc}}$. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature): CH$_3$−CH (1.18, d, J = 7.0 Hz, 1.21, d, J = 7.0 Hz), *t*-butyl CH$_3$ (1.41, 1.15), CH$_3$−CH (2.78, m, J = 6.9 Hz), Ph−CH−Ph (5.61), tetra-substituted benzene CH (6.31, 6.36), iPrPh aromatic CH (6.60, d, J = 8.0 Hz), iPrPh aromatic CH (6.88, d, J = 8.3 Hz), tetra-substituted benzene CH (6.88, 6.99). ^{13}C NMR (63 MHz, CDCl$_3$, room temperature): CH$_3$−CH (23.91), *t*-butyl CH$_3$ (27.41, 27.54), CH$_3$−CH (33.41), Ph−CH−Ph (43.31), *t*-butyl C (82.28, 83.28), tetra-substituted benzene CH (117.06), iPrPh aromatic CH (126.12), iPrPh CH (128.71), tetra-substituted benzene CH (128.87, 132.81), tetra-substituted benzene C (131.46, 131.60), iPrPh aromatic C (138.56), iPrPh aromatic C (146.04), tetra-substituted benzene C (147.20, 147.26), C=O (150.38, 151.11)

*O-Octa-tBOC-*C*-tetra-4-isopropylphenyl-calix[4]resorcinarene (ctt, $\mathbf{9}_{\mathbf{ctt}}$).* The synthetic procedure was the same as above. After 20 h of the reaction, the solvent was evaporated and a residue recrystallized from a mixed solvent of cyclohexane and toluene to give 2.193 g (68%) of $\mathbf{9}_{\mathbf{ctt}}$. ^{1}H NMR (250 MHz, $CDCl_3$, room temperature): CH_3−CH (1.07, d, $J = 7.1$ Hz, 1.10, d, $J = 7.6$ Hz), *t*-butyl CH_3 (1.18, 1.34), CH_3−CH (2.67, m, $J = 6.9$ Hz), Ph−CH−Ph (5.72, s), tetra-substituted benzene CH (6.50, 6.52), iPrPh aromatic CH (6.70, d, $J = 8.2$ Hz), iPrPh aromatic CH (6.81, d, $J = 8.2$ Hz), tetra-substituted benzene CH (6.92, 7.14). ^{13}C NMR (63 MHz, $CDCl_3$, room temperature): CH_3−CH (23.91), *t*-butyl CH_3 (27.41, 27.54), CH_3−CH (13.41), Ph−CH−Ph (43.31), *t*-butyl C (82.28, 83.28), tetra-substituted benzene CH (116.61), iPrPh aromatic CH (129.41), tetra-substituted benzene CH (128.89, 131.91), iPrPh aromatic CH (129.95), tetra-substituted benzene C (132.32, 132.43), iPrPh aromatic C (137.01), iPrPh aromatic C (145.79), tetra-substituted benzene C (147.04, 147.46), C=O (150.50, 151.15).

Conversion of *t*-Butyl Ester to Carboxylic Acid. $\mathbf{4}_{\mathbf{ccc}}$, $\mathbf{4}_{\mathbf{ctt}}$, and $\mathbf{8}_{\mathbf{ctt}}$ were treated with *p*-toluenesulfonic acid in toluene at 90 °C to convert the eight peripheral ester groups to carboxylic acid. The precipitated products ($\mathbf{11}_{\mathbf{ccc}}$ from $\mathbf{4}_{\mathbf{ccc}}$, $\mathbf{11}_{\mathbf{ctt}}$ from $\mathbf{4}_{\mathbf{ctt}}$, and $\mathbf{12}_{\mathbf{ctt}}$ from $\mathbf{8}_{\mathbf{ctt}}$) were washed with toluene or hexane, and then with boiling methanol. Analysis results for $\mathbf{11}_{\mathbf{ccc}}$ are as follows. ^{13}C NMR (63 MHz, acetone-d$_6$, room temperature): CH_3−CH (20.08), CH_3−CH (31.58), OCH_2 (66.82, 67.10), aromatic CH (100.83), aromatic C (126.12), aromatic CH (129.59), aromatic C (155.16), C=O (170.23, 170.41). Analysis results for $\mathbf{11}_{\mathbf{ctt}}$ are as follows. ^{13}C NMR (63 MHz, acetone-d$_6$, room temperature): CH_3−CH (20.58), CH_3−CH (31.39), OCH_2 (66.79, 67.03, 67.14), aromatic CH (99.66, 101.52), aromatic CH (126.12, 127.05), aromatic C (127.59, 130.81 m), aromatic C (154.60, 155.78/155.94), C=O (170.05, 170.22, 170.38, 170.68).

Measurements. NMR spectra were obtained on a Bruker AC250 or AM300 spectrometer. IR spectra were measured on a Nicolet Magna-IR 550 spectrometer. UV spectra were recorded on a Hewlett-Packard model 8452A diode array spectrophotometer using thin films cast on quartz discs. Thermogravimetric analysis (TGA) was performed at a heating rate of 5 °C/min in N_2 on a TA Instrument Hi-Res TGA 2950 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C/min on a TA Instruments DSC 2920 modulated differential scanning calorimeter. A quartz crystal microbalance (QCM)[38] (Maxtek TPS-550 sensor probe and PI-70 driver, Phillips PM6654 programmable high-resolution frequency counter) was used to study the dissolution behavior of the polymer films in aqueous tetramethylammonium hydroxide (TMAH) by measuring frequency and resistance using 5 MHz crystals. The space-filling models of the optimum conformation of calixresorcinarenes were produced with HyperChem using the Amber 1 semiempirical method and the Polak-Ribiere algorithm.

Dissolution Inhibition Effect. The calixarene ester or carbonate was added to a solution of PolyE (a copolymer of TBA and HOST) dissolved in propylene glycol methyl ether acetate (PGMEA) at a varying loading from 5 to 25 wt %. The PolyE[39] employed in this study had a composition of HOST/TBA = 70/30 and was useless for the Shipley (now Rohm & Haas Electronic Materials) UVIIHS formulation[40] due to its excessive dissolution rate, even in the presence of a dissolution-inhibiting photochemical acid generator (PAG) such as di-4-*t*-butylphenyliodonium camphorsulfonate. The spin-cast films were baked at 120 °C for 60 s. The dissolution kinetics of the PolyE films[39] containing the protected calixarenes were studied using QCM in a 0.26 N TMAH aqueous solution (CD-26).

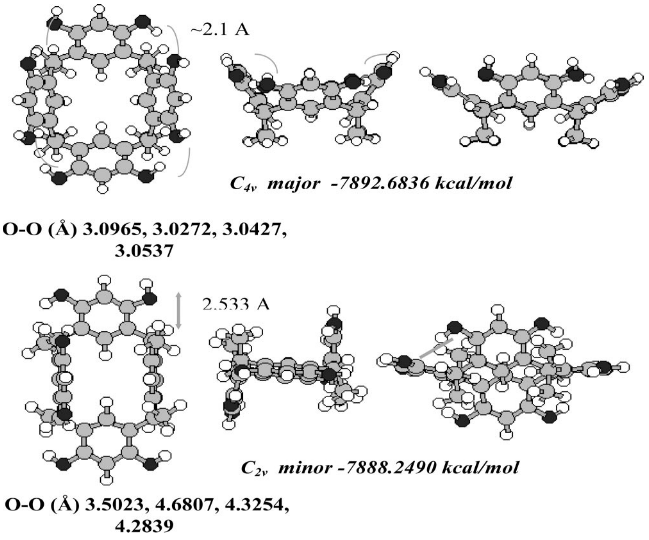

Figure 2. Two configurations (ccc and ctt) of methyl-calix[4]resorcinarene **1**.

Lithographic Imaging. The lithographic performance of the ESCAP 248 nm resist containing $\mathbf{4}_{\mathbf{ccc}}$ as a dissolution inhibitor has been reported elsewhere.[41] In this study, we added $\mathbf{4}_{\mathbf{ccc}}$ to the IBM KRS electron-beam resist,[42] which is based on ketal-protected PHOST. Electron-beam exposures were done under a vacuum at 10^{-10} to 10^{-9} Torr on a Leica VB6 direct write exposure system (100 keV).

Results and Discussion

Synthesis and Characterization. The isomeric structures of **1** are presented in Figure 2. Calix[4]resocinarenes could exist in principle in four configurations, cis−cis−cis (ccc), cis−cis–trans (cct), cis–trans−trans (ctt), and trans–cis–trans (tct).[43] However, two isomers, ccc and ctt, are typically the main products,[44] although isolation of the cct isomer was reported in a limited case (R = CH_3).[45] The ccc and ctt isomers have C_{4v} and C_{2v} symmetries, respectively, and the distribution of the isomers can be controlled slightly by modifying the condensation reaction conditions but is strongly affected by the aldehyde structure (R in Figure 1). In **1**, the ccc isomer is more stable than the ctt isomer, and the degree of hydrogen bonding is larger in the ccc isomer and with a smaller R, as the IR spectra in Figure 3 indicate. The O−O distance in $\mathbf{1}_{\mathbf{ccc}}$ is shorter than that in $\mathbf{1}_{\mathbf{ctt}}$, and essentially all of the OH groups of $\mathbf{1}_{\mathbf{ccc}}$ can undergo hydrogen

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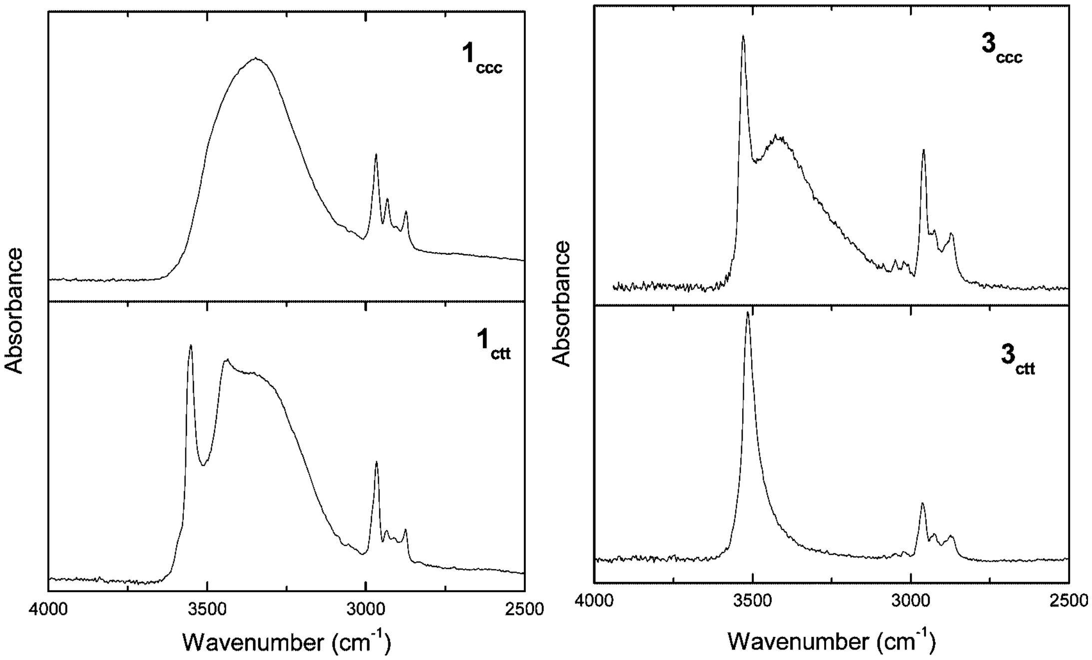

Figure 3. IR spectra of calix[4]resocinarenes **1** and **3** cast from 2-ethoxyethanol on a NaCl plate.

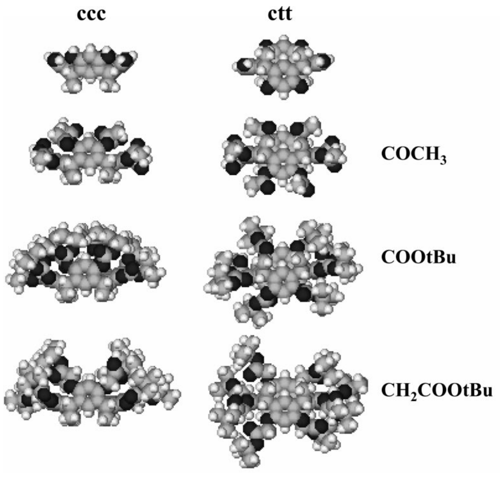

Figure 4. Space-filling models of **1** and its derivatives.

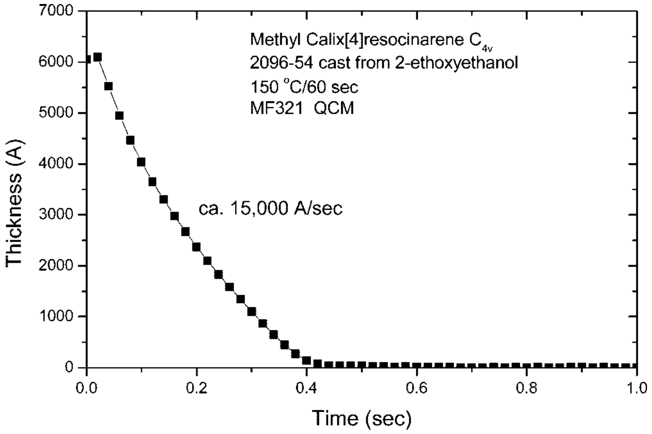

Figure 5. Dissolution kinetics of $\mathbf{1}_{ccc}$ in 0.21 N TMAH as measured by QCM.

bonding in the solid phase, while $\mathbf{1}_{ctt}$ has a significant amount of free OH groups. More free OH groups are present in the sterically bulky **3**, and $\mathbf{3}_{ctt}$ does not possess any significant concentrations of hydrogen-bonded OH.

^{1}H and ^{13}C NMR spectra at room temperature (see the Experimental Section) indicate that all of the protons and carbons of the repeat unit of $\mathbf{1}_{ccc}$ are magnetically equivalent, providing only one set of resonances for each proton and carbon, as it has a calix (vase) structure (Figure 4). In contrast, $\mathbf{1}_{ctt}$ no longer assumes the vase structure (Figure 4), and only the phenyl rings facing each other are magnetically equivalent, thus giving rise to two sets of the aromatic and OH resonances. Replacement of the four CH_3 groups in **1** with a bulkier isopropylphenyl (iPrPh) group maintains the magnetic equivalence of the protons and carbons of the four ring benzenes and four pendant iPrPh groups, although the stable conformation is no longer calix-shaped. In the synthesis of **3**, the ctt isomer is a major product in contrast to **1**. In $\mathbf{3}_{ctt}$, only the two facing benzene groups in the ring are magnetically equivalent, giving rise to two sets of resonances for each proton and carbon. The four pendant phenyl groups are equivalent, showing only one set of resonances for each proton and carbon, while the iPrPh CH_3 groups resonate at slightly different chemical shifts (1.17 and 1.18 ppm in ^{1}H NMR and 24.35 and 24.44 ppm in ^{13}C NMR). Acetylation of the eight OH groups of $\mathbf{1}_{ccc}$ results in significant broadening of ^{1}H and ^{13}C resonances at room temperature due to some restriction of the chain mobility. Variable-temperature NMR studies on the chain mobility of the protected calixresorcinarenes are described in detail in the next section.

A film of $\mathbf{1}_{ccc}$, cast from 2-ethoxyethanol and baked at 150 °C for 60 s, dissolves rapidly at ca. 15 000 Å/sec in 0.21 N TMAH (Figure 5), much faster than PHOST (200–2000 A/sec depending on the molecular weight).

Variable-Temperature NMR Studies on Protected Calixresorcinarenes. An ^{1}H NMR investigation of calix[4]-resocinarenes with R = CH_3 and R′ = H, $COCH_3$, and COC_2H_5 was reported by Högberg.[44] Variable-temperature ^{1}H NMR measurements were performed by Gutsche et al.

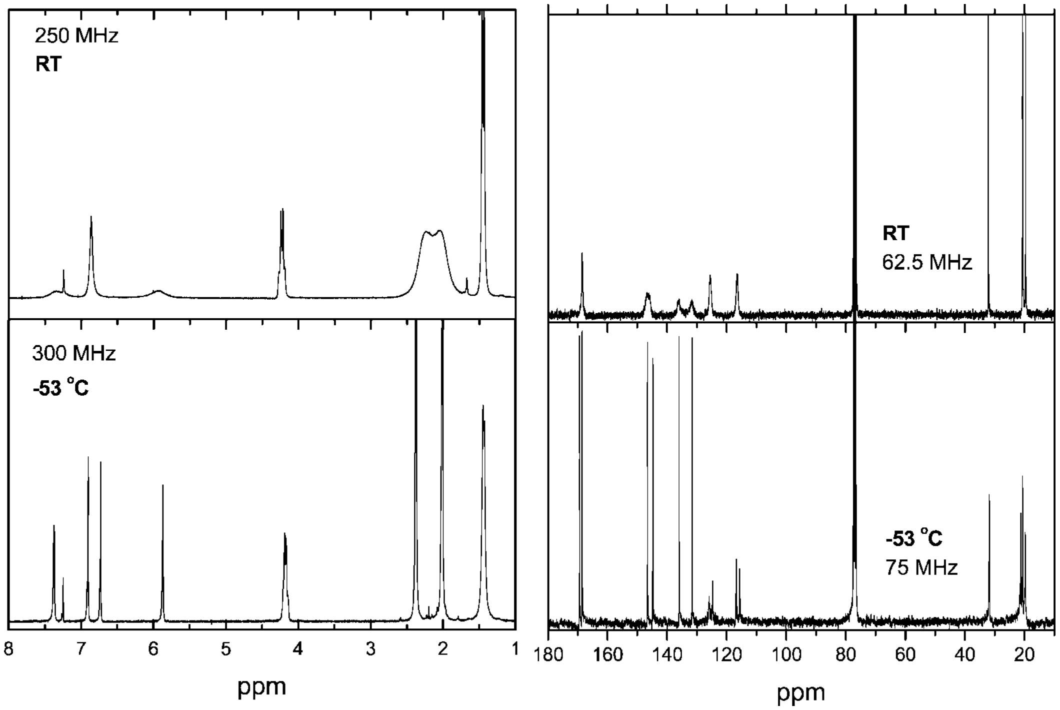

Figure 6. ^{1}H (left) and ^{13}C (right) NMR spectra of $\mathbf{10}_{\mathrm{ccc}}$ in $CDCl_3$ at room temperature (top) and –53 °C (bottom).

on esters and ethers of calix[4]arenes prepared by the condensation of phenol (not resorcinol) and aldehyde.[46] All eight OH groups of the calixresorcinarenes can be protected with acetyl or acid-labile functionalities. The protection, even with a small acetyl, reduces the flexibility of the ccc isomers, giving rise to broad ^{1}H and ^{13}C resonances at room temperature. Furthermore, the aromatic CH ^{1}H resonances split into two well-separated, broad peaks at room temperature. When the NMR solution in $CDCl_3$ of $\mathbf{10}_{\mathrm{ccc}}$ is cooled down to −53 °C, the acetyl CH_3 and aromatic CH resonances, broad at room temperature, become sharpened, and the other aromatic CH resonance splits into two peaks (Figure 6). It is interesting to note that the ^{1}H NMR spectrum of $\mathbf{10}_{\mathrm{ccc}}$ at −53 °C is almost identical to the spectrum of $\mathbf{10}_{\mathrm{ctt}}$ at room temperature (see the chemical shifts in the Experimental Section). In agreement with the ^{1}H NMR studies, the aromatic CH carbons inside the calixarene ring are not magnetically equivalent, even at room temperature (Figure 6). Cooling the ^{13}C NMR sample of $\mathbf{10}_{\mathrm{ccc}}$ to −53 °C sharpens the aromatic and carbonyl resonances, and they all split into two sharp peaks, due to the freezing of two conformers. Again, the ^{13}C NMR spectrum of $\mathbf{10}_{\mathrm{ccc}}$ at −53 °C resembles the spectrum of $\mathbf{10}_{\mathrm{ctt}}$ at room temperature (compare the chemical shifts in the Experimental Section).

^{1}H and ^{13}C NMR spectra at variable temperatures of $\mathbf{4}_{\mathrm{ccc}}$ in $CDCl_3$ are presented in Figure 7. The OCH_2 (4.18 ppm) and aromatic CH (6.18 and 6.5 ppm) ^{1}H resonances are broad at room temperature. Raising the temperature to 55 °C sharpens the peak ascribed to the aromatic CH between the two oxygen-substituted carbons, but the OCH_2 and aromatic CH inside the calixarene ring remain quite broad even at this high temperature. ^{13}C resonances of the aromatic CH groups at 99.96 and 129.13 ppm are broad at room temperature and become sharp at 55 °C (Figure 7). Cooling the sample solutions to −53 °C freezes the bond rotation and restricts the interchange between two isomeric states, thus giving rise to two separate resonances for the aromatic CH protons. The extremely broad signal of the aromatic CH in the calixarene ring at room temperature becomes two widely separated (ca. 1.5 ppm) peaks at −53 °C. What is noteworthy also is that the two protons of each OCH_2 group are magnetically nonequivalent at −53 °C due to the restricted rotation of the bond and appear as two sets of well-separated (ca. 0.7 ppm) AB quartets. In accordance with the ^{1}H NMR, all the aromatic and OCH_2 carbon resonances split into two peaks at −53 °C (Figure 7).

Figure 8 presents ^{1}H and ^{13}C NMR spectra of $\mathbf{4}_{\mathrm{ctt}}$ at temperatures ranging from room temperature to 131 °C. The 250 MHz (63 MHz for ^{13}C) spectra at room temperature and 55 °C were measured in $CDCl_3$, and higher-boiling $CDCl_2CDCl_2$ was employed for measurements at 104 and 131 °C at 300 MHz (75 MHz for ^{13}C). At 131 °C, there is evidence that a trace acid in the chlorinated solvent starts to cleave the protecting group. Nevertheless, it is interesting to note that the ^{1}H and ^{13}C spectra remain essentially the same from room temperature to 131 °C, with all the aromatic protons and carbons appearing as two peaks. The peaks at 7.5 and 6.9 ppm in Figure 8 are due to $CHCl_3$ and $CHCl_2CHCl_2$ in the NMR solvents, respectively. The OCH_2 protons resonate as well-separated and distinct AB quartets even at 131 °C, indicating that the two CH_2 protons are magnetically nonequivalent due to the restricted bond rotation even at this high temperature. The ^{13}C resonances of the quaternary (81.74 and 81.50 ppm at room temperature) and carbonyl (168.14 and 168.65 ppm at room temperature)

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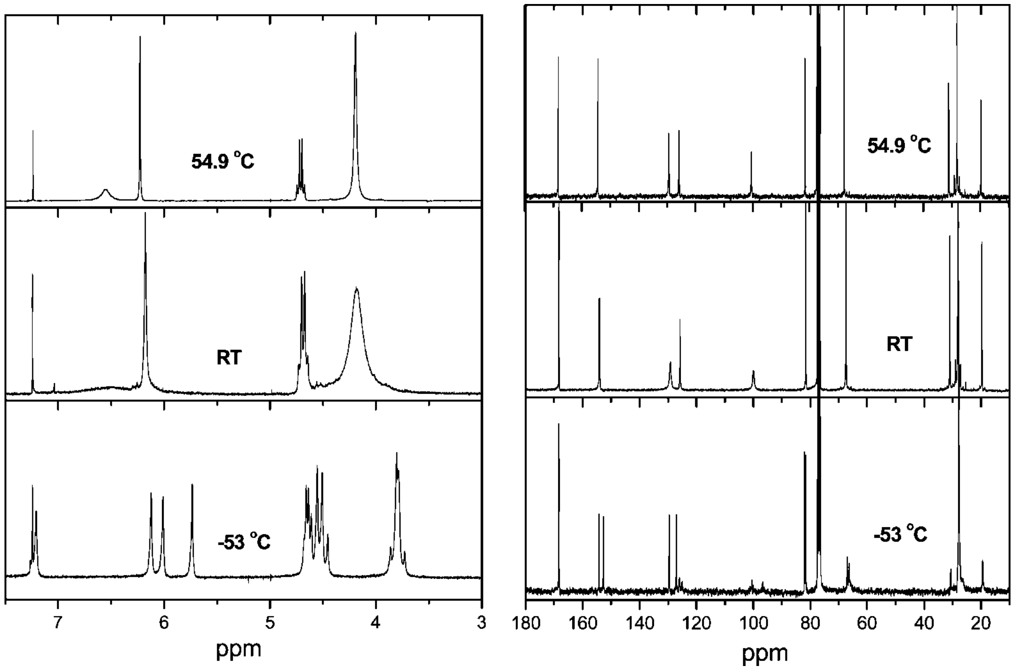

Figure 7. ^{1}H and ^{13}C NMR spectra of $\mathbf{4}_{\mathrm{ccc}}$ in $CDCl_3$ at various temperatures.

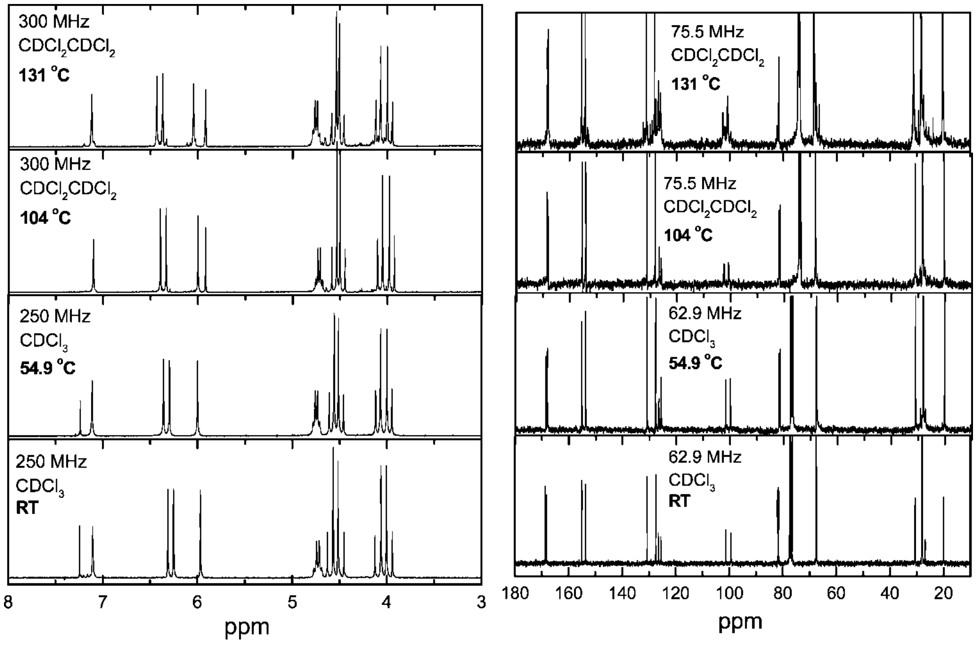

Figure 8. ^{1}H and ^{13}C NMR spectra of $\mathbf{4}_{\mathrm{ctt}}$ in $CDCl_3$ at room temperature and 54.9 °C and in CD_2ClCD_2Cl at 104 and 131 °C.

carbons in $\mathbf{4}_{\mathrm{ctt}}$ are split into two at temperatures ranging from room temperature to 131 °C.

The replacement of CH_3 with Ph increases the steric hindrance, and even the ccc isomer $\mathbf{6}_{\mathrm{ccc}}$ shows two peaks for *t*-butyl methyl protons (1.37 and 1.45 ppm) and carbons (27.98 and 28.08 ppm), OCH_2 protons (two AB quartets at 4.03 and 4.11 ppm) and carbons (67.51 and 67.85 ppm), and tetra-substituted benzene CH protons (5.85 and 6.12 ppm and 6.16 and 6.30 ppm) and carbons (100.15 and 100.35 ppm and 128.49 and 132.69 ppm) at room temperature (Figure 9). The ctt isomer exhibits splitting in the *t*-butyl quaternary (81.51 and 81.65 ppm) and carbonyl (168.30 and 167.84 ppm) carbon resonances at room temperature (Figure 9). ^{1}H and ^{13}C NMR spectra of $\mathbf{8}_{\mathrm{ccc}}$ at three different temperatures are presented in Figure 10. The two sets of distinct AB quartet signals of the OCH_2 protons at −53 °C become broader at room temperature and almost coalesce to a single peak at 131 °C. The CH proton signals of the tetra-substituted benzene rings are broader at room temperature than at −53 °C and coalesce to a single peak at 131 °C. One of the iPrPh CH protons becomes almost frozen at −53 °C. The single carbonyl carbon peak at 168.37 ppm at room temperature splits into two at −53 °C.

The effect of protecting all eight of the OH groups with tBOC on the NMR spectra is very similar to the protection with CH_3CO or bulkier $tBOCCH_2$. In the case of $\mathbf{1}_{\mathrm{ccc}}$, the tBOC protection renders the aromatic CH ^{1}H and ^{13}C resonances very

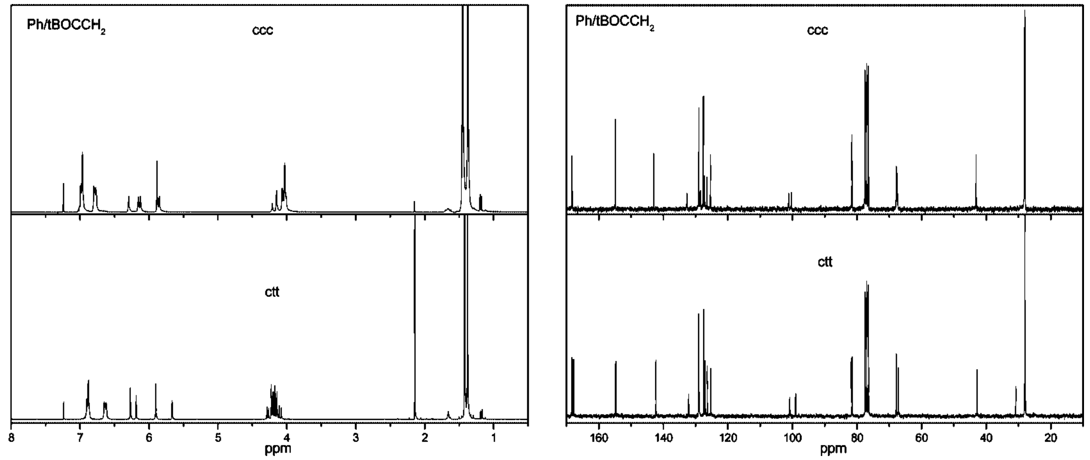

Figure 9. ^{1}H (left) and ^{13}C (right) NMR spectra of $\mathbf{6}_{ccc}$ (top) and $\mathbf{6}_{ctt}$ (bottom) in $CDCl_3$ at room temperature.

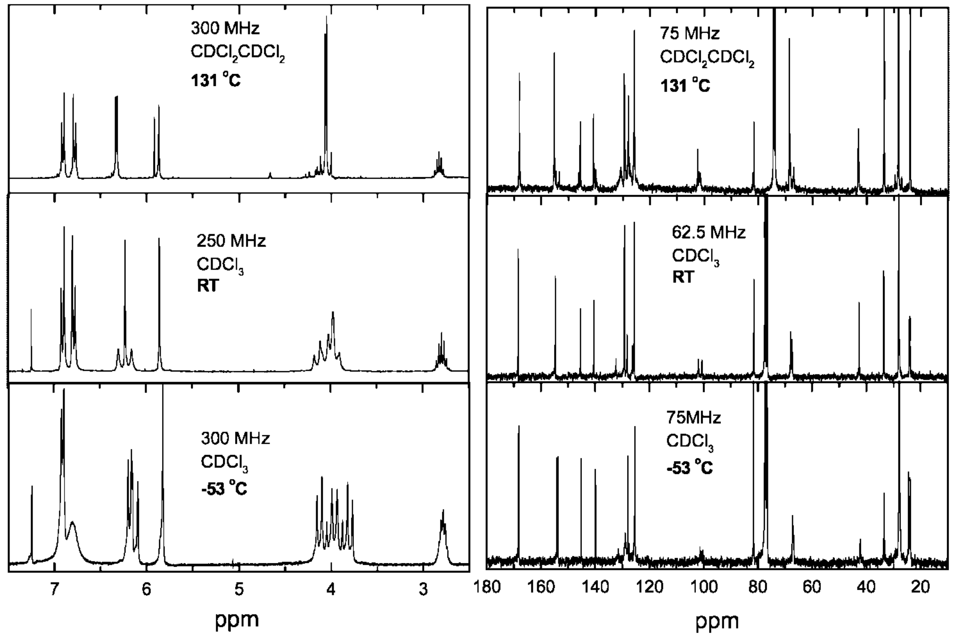

Figure 10. ^{1}H and ^{13}C NMR spectra of $\mathbf{8}_{ccc}$ in $CDCl_3$ at –53 °C and room temperature and in CD_2ClCD_2Cl at 131 °C.

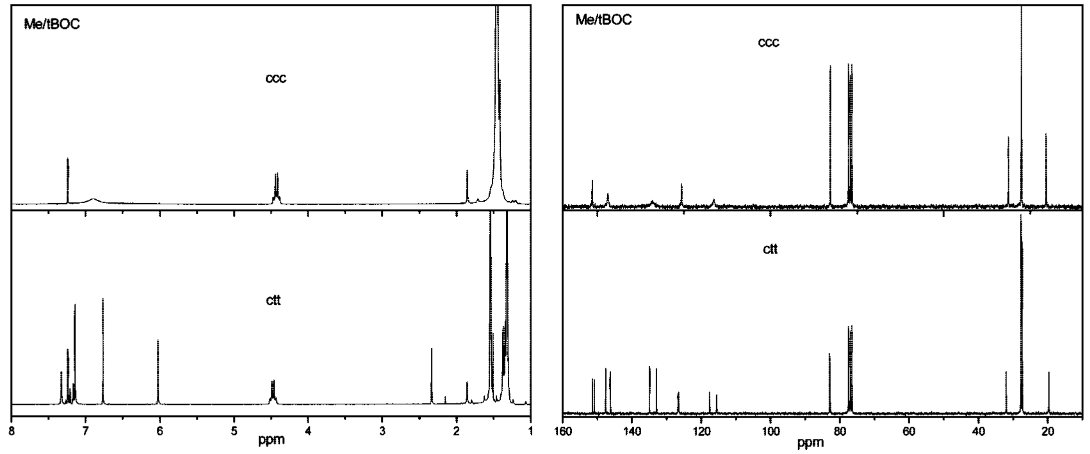

Figure 11. ^{1}H (left) and ^{13}C (right) NMR spectra of $\mathbf{5}_{ccc}$ (top) and $\mathbf{5}_{ctt}$ (bottom) in $CDCl_3$ at room temperature.

broad (Figure 11). The replacement of CH_3 with Ph or iPrPh results in splitting of the calixarene aromatic CH ^{1}H and ^{13}C resonances as well as the resonances of the pendant groups such as the *t*-butyl CH_3, *t*-butyl quaternary C, and iPr. Only two calixarene benzene rings facing each other are magnetically equivalent in $\mathbf{5}_{ccc}$, $\mathbf{7}_{ccc}$, and $\mathbf{9}_{ccc}$ at room temperature. The ctt isomers of the tBOC-protected calixarenes show two sets of resonances for many of the protons and carbons. The ^{1}H and

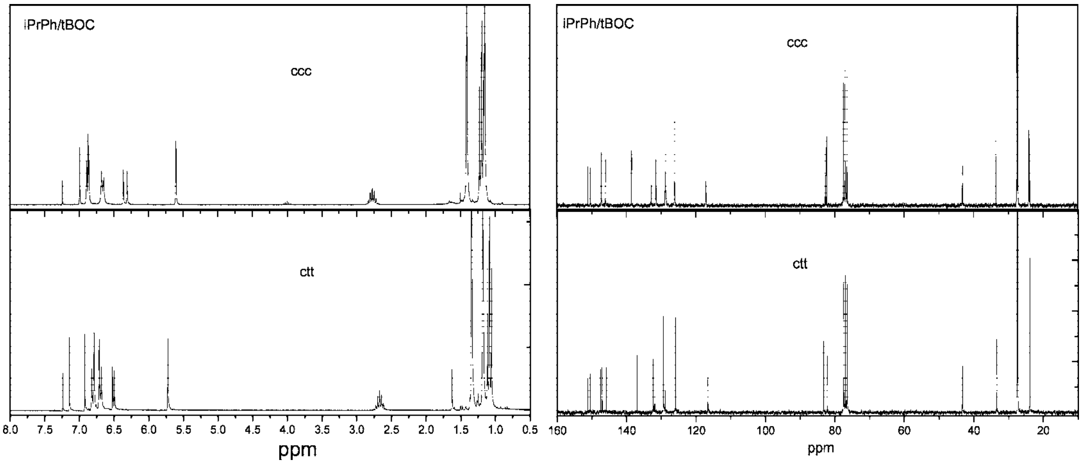

Figure 12. ^{1}H (left) and ^{13}C (right) NMR spectra of $\mathbf{9}_{ccc}$ (top) and $\mathbf{9}_{ctt}$ (bottom) in CDCl$_3$ at room temperature.

^{13}C NMR spectra of $\mathbf{9}_{ccc}$ and $\mathbf{9}_{ctt}$ are presented in Figure 12.

According to our ^{1}H and ^{13}C NMR studies, while the ccc isomer of the tBOCCH$_2$-protected tetramethyl-calix[4]resorcinarene $\mathbf{4}_{ccc}$ has some flexibility at room temperature, its ctt isomer does not exhibit any rotational averaging of NMR spectra even at 130 °C. The two methylene protons in the ester side chains are magnetically nonequivalent even at 130 °C in the ctt isomers.

NMR Spectra of Deprotected Calixresorcinarenes Bearing Carboxylic Acid on Periphery. In chemically amplified resists, *t*-butyl ester is converted to carboxylic acid upon a postexposure bake by reaction with photochemically generated aid. In an attempt to understand the effect of the structural modification on the conformation of calix[4]resorcinarenes, $\mathbf{4}_{ccc}$ and $\mathbf{4}_{ctt}$ were reacted with *p*-toluenesulfonic acid in toluene to cleave the *t*-butyl ester, and ^{13}C NMR was run on the deprotected samples. Chemical shifts are presented in the Experimental Section. Beside complete disappearance of the peaks due the *t*-butyl methyl, *t*-butyl quaternary carbon, and ester carbonyl, the spectral change is fairly small. In the case of $\mathbf{11}_{ccc}$ (from $\mathbf{4}_{ccc}$), OCH$_2$ and carbonyl resonances split into two peaks [66.82 (smaller) and 67.01 ppm for OCH$_2$ and 170.23 and 170.41 ppm (smaller) for C=O]. In the case of $\mathbf{11}_{ctt}$ (from $\mathbf{4}_{ctt}$), the splitting is observed in the aromatic carbon resonances also. One of the aromatic C (ring-forming carbon) resonances at 130.81 ppm shows multiplicity, and the other aromatic C−O carbon peak shows a smaller second peak (155.78 ppm) very close to the main peak at 155.94 ppm. The OCH$_2$ peak splits into three peaks (66.79, 67.03, and 67.14 ppm) and the C=O resonance into four peaks (170.05, 170.22, 170.04, and 170.68 ppm). These NMR data suggest that the limited rotation around the OCH$_2$ group in **4**, **6**, and **8** is not due to the bulky *t*-butyl group. The peak multiplicity observed in $\mathbf{11}_{ctt}$ suggests that this calixresorcinarene consists of more than two stable conformers at room temperature, perhaps due to strong hydrogen bonding between the peripheral carboxylic acid groups.

FTIR Spectroscopy of Protected Calix[4]resorcinarenes. FTIR spectra of the carbonyl region of the tBOCCH$_2$-protected calix[4]resorcinarenes and 6F-bisphenol A (6FBPACH$_2$tBOC) are presented in Figure 13. Two major carbonyl peaks are observed in all the cases. The absorption at a longer wavenumber may not be a single peak in the case of sterically more crowded $\mathbf{4}_{ctt}$ and $\mathbf{8}_{ctt}$. Furthermore, the smaller absorption appears to shift to a lower wavenumber and increases in intensity as the steric hindrance is increased. It is interesting that even 6FBPACH$_2$tBOC shows two carbonyl peaks, while only one peak is observed in methyl phenoxyacetate, the smallest model compound. No extra splitting is observed in ^{1}H and ^{13}C resonances of 6FBPACH$_2$tBOC in CDCl$_3$ at room temperature. In the case of the tBOC-protected calixresorcinarenes ($\mathbf{5}_{ccc}$ and $\mathbf{9}_{ctt}$), only one carbonyl peak is observed at 1758.3 and 1762.5 cm^{-1}, respectively.

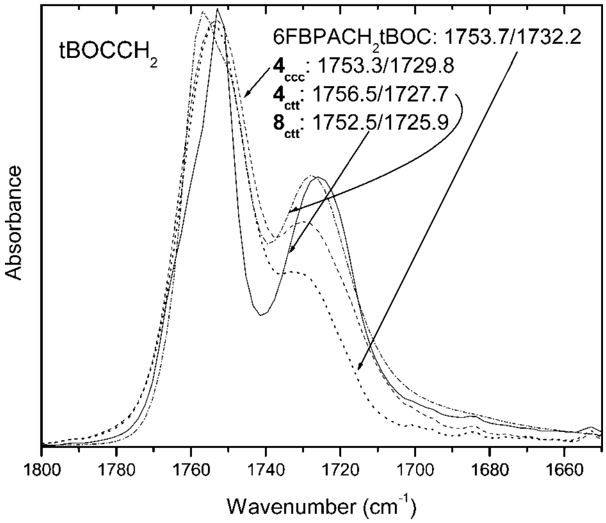

Figure 13. FTIR spectra of the carbonyl region of $\mathbf{4}_{ccc}$, $\mathbf{4}_{ctt}$, $\mathbf{8}_{ctt}$, and 6FBPACH$_2$tBOC.

Thermal Properties of Protected Calixresorcinarenes. The calixresorcinarenes protected with tBOC and tBOCCH$_2$ lose a significant amount of weight upon heating to 175–220 °C due to the loss of isobutene and carbon dioxide in the former and isobutene in the latter. The thermal properties of these protected calixarenes can be quite complex, as demonstrated by the DSC curve of $\mathbf{8}_{ctt}$ in Figure 14. The sample was first heated from room temperature to 150 °C at 10 °C/min, which showed glass transition at 55 °C and crystallization at 75 °C. The sample was cooled down to room temperature and then heated to 300 °C. On the second heating, glass transition or crystallization was not observed, but melting was detected

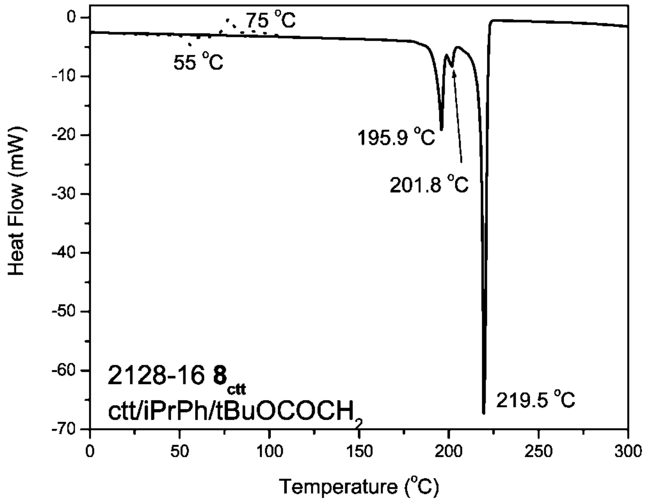

Figure 14. DSC curves of $\mathbf{8}_{\mathbf{ctt}}$ (10 °C/min).

at 195.5 and 201.8 °C before deprotection at 219.5 °C. In the case of $\mathbf{4}_{\mathbf{ccc}}$, the first heating exhibited only melting at 140.1 °C, and glass transition was observed at 51 °C upon a second heating, followed by deprotection at 215.8 °C. $\mathbf{7}_{\mathbf{ccc}}$ exhibited glass transition at 63 °C upon the first heating and 66 °C upon the second heating, and melting was immediately followed by deprotection at 190 °C. Glass transition temperatures (T_g), crystallization temperatures (T_c), melting points (T_m), and deprotection temperatures (T_d) of the protected calix[4]resocinarenes are presented in Table 1. We observed some batch-to-batch variations, especially in T_g and T_c. The thermal data should be useful in selecting the calixarene derivatives as film-forming molecular glass resists and also in selecting heating conditions to form amorphous glass.

Interaction of Protected Calixresorcinarenes with Phenol. In order to investigate the interaction of the calixarene-based dissolution inhibitor with the phenolic OH group, a shift of aromatic C1 and C4 ^{13}C resonances of 4-isopropylphenol induced by addition of the protected calixarenes was measured in CDCl$_3$ (Figure 15), as described for PAG−phenol interaction.[39] The degree of the interaction, as measured by the shift caused by 1 mol % of an additive as summarized in Figure 16, was about 4 times greater with the calixarene systems than with the classical bispheol-A protected with tBOC (BISBOC)[11] or 6FBPACH$_2$tBOC (Figure 17). The *t*-butyl ester protected calixarenes appear to interact with isopropylphenol more strongly than the tBOC-protected systems, but $\mathbf{5}_{\mathbf{ccc}}$ and $\mathbf{7}_{\mathbf{ccc}}$ are as good as the tBOCCH$_2$ systems. Among the tBOCCH$_2$-protected calixarenes, the structural modifications (ccc vs ctt and Me vs iPrPh) do not affect the interaction much. In the case of the tBOC-protected calixarenes, the ccc isomers seem to have a stronger affinity toward isopropylphenol except for **9**.

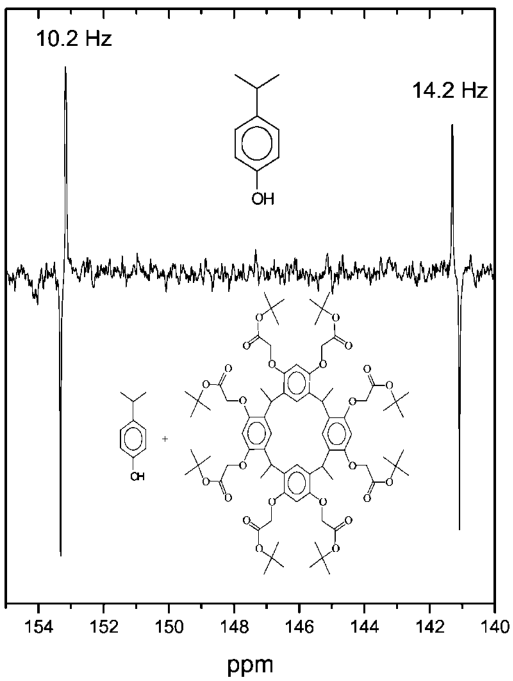

Figure 15. ^{13}C NMR spectra of 4-isopropylphenol (top) and its mixture with $\mathbf{4}_{\mathbf{ccc}}$ (bottom, inversed) in CDCl$_3$ at room temperature.

Dissolution Inhibition Effects of Protected Calixresorcinarenes. As mentioned in the Introduction, the calix[4]-resorcinarene derivatives did not form good films in our experiments.[18] When the film contained a significant amount of residual casting solvent, it looked like a good film. Upon further drying, however, the film became hazy. The poor film quality might have been due to our use of pure isomers instead of mixtures or our use of fully protected compounds instead of partially protected materials. We decided to use our fully protected calix[4]resorcinarene derivatives as a dissolution inhibitor of phenolic resists.

Table 1. Thermal Properties of Protected Calix[4]resorcinarenes

number	structure	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)
2096-60	ccc/Me/tBOCCH$_2$ $\mathbf{4}_{\mathbf{ccc}}$	51.4 (second)		140.1 (first)	215.8 (second)
2128-25	ccc/Me/tBOCCH$_2$ $\mathbf{4}_{\mathbf{ccc}}$	50.9 (second)		140.6 (first)	204.8 (second)
2128-12	ctt/Me/tBOCCH$_2$ $\mathbf{4}_{\mathbf{ctt}}$			183.7 (second)	216.3 (second)
2096-69	ccc/Me/tBOC $\mathbf{5}_{\mathbf{ccc}}$				179.2 + shoulder (second)
2128-42	ccc/Me/tBOC $\mathbf{5}_{\mathbf{ccc}}$				174 (second)
2128-43	ctt/Me/tBOC $\mathbf{5}_{\mathbf{ctt}}$		137.2 (first)	184.1 (second)	203.4 (second)
2128-60	ctt/Ph/tBOCCH$_2$ $\mathbf{6}_{\mathbf{ctt}}$		108.3 (first)	211.1 (second)	215.2 (second)
2128-66	ctt/Ph/tBOCCH$_2$ $\mathbf{6}_{\mathbf{ctt}}$			199.0 (second)	215.3 (second)
2128-61	ccc/Ph/tBOC $\mathbf{7}_{\mathbf{ccc}}$	63.8 (first), 66.3 (second)		190 (second), shoulder of Td	190.0 (second)
2128-65	ccc/Ph/tBOC $\mathbf{7}_{\mathbf{ccc}}$			176.3 (second)	189.6 (second)
2128-28	ccc/iPrPh/tBOCCH$_2$ $\mathbf{8}_{\mathbf{ccc}}$			215.4 (second)	220.7 (second)
2128-16	ctt/iPrPh/tBOCCH$_2$ $\mathbf{8}_{\mathbf{ctt}}$	55 (first)	75 (first)	201.8 (second)	219.5 (second)
2170-07	ctt/iPrPh/tBOCCH$_2$ $\mathbf{8}_{\mathbf{ctt}}$			191.8 (second)	207.5 (second)
2128-29	ccc/iPrPh/tBOC $\mathbf{9}_{\mathbf{ccc}}$			175.6 (second)	182.7 (second)
2128-01	ctt/iPrPh/tBOC $\mathbf{9}_{\mathbf{ctt}}$			191.7 (second)	206.3 (second)

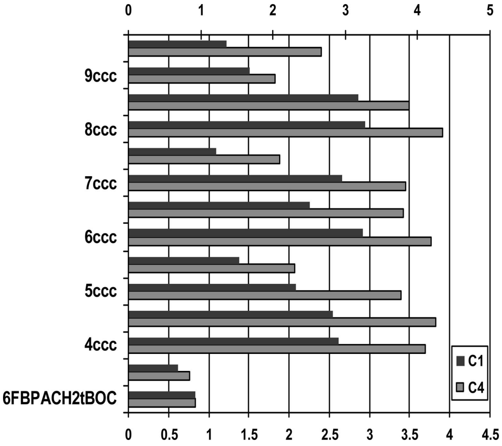

Figure 16. Shifts (Hz) of aromatic C1 and C4 resonances of 4-isopropylphenol induced by 1 mol % of acid-labile dissolution inhibitors.

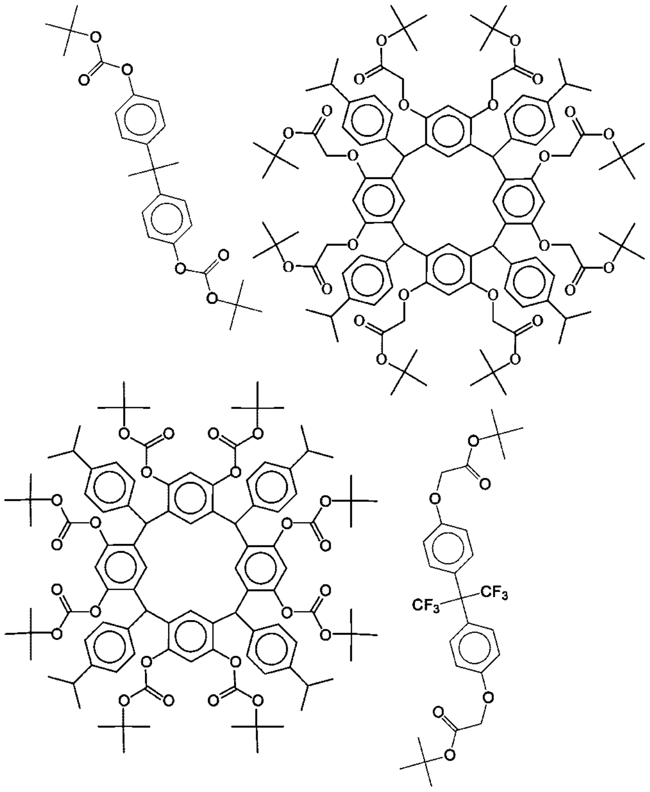

Figure 17. Structures of dissolution inhibitors employed in this study.

The protected calixarenes were added at 5, 10, 15, and 20 wt % to a PGMEA solution of a copolymer of HOST with TBA (70/30 composition).[8] The dissolution rates of the films cast on Au-coated quartz wafers and baked at 120 °C for 60 s were measured in a 0.26 N TMAH developer (CD-26) on a QCM. This copolymer composition offers too high a dissolution rate of 85 Å/sec to be used as a positive resist resin. The dissolution kinetics curves for the phenolic polymer films doped with $\mathbf{5}_{ccc}$ and BISBOC (Figure 16) are compared in Figure 18. $\mathbf{5}_{ccc}$ slows down the dissolution of the HOST−TBA copolymer much more profoundly than BISBOC.

All 12 of the derivatives we had prepared with different isomeric structures, substituents, and acid-labile protecting groups were subjected to the dissolution behavior investigation. Only a couple of the dissolution kinetics curves are presented (Figures 18 and 19). It is clear that the protected ccc methyl-calixarene exhibits a much stronger inhibition effect than BISBOC and that the calixarene system provides an induction period, as long as 5 min at the 20 wt % loading (Figure 18). In Figure 19 are compared the *t*-butyl ester protection group **4** with tBOC **5** using the ccc isomer of methyl-calixarene. While the tBOC group tends to show a longer induction period, the *t*-butyl ester functionality is more effective in reducing the dissolution rate at the same weight or mole percent loading.

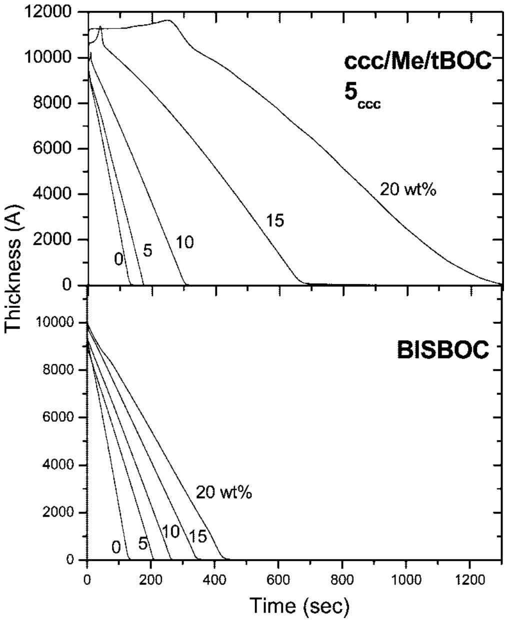

Figure 18. Dissolution kinetic curves of poly($HOST_{0.7}$-co-$TBA_{0.3}$) containing $\mathbf{5}_{ccc}$ (top) and BISBOC (bottom) in 0.26 N TMAH.

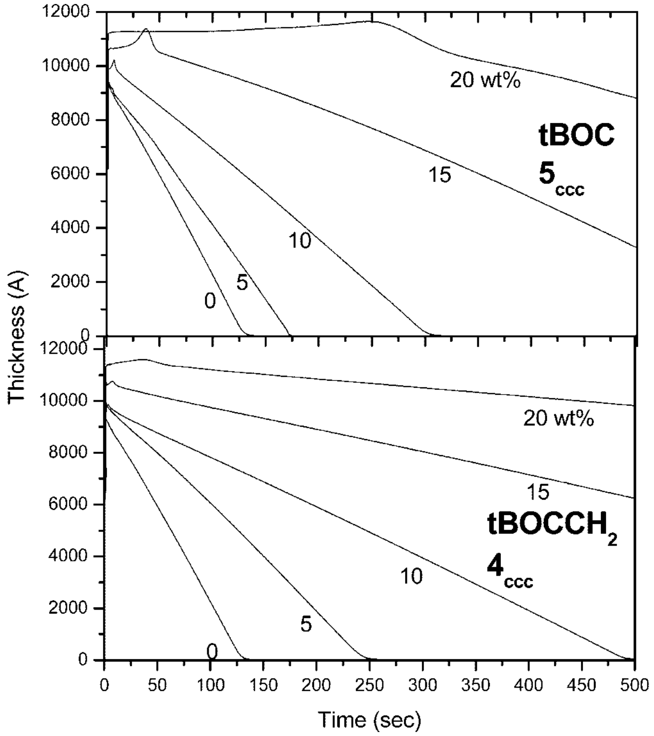

Figure 19. Dissolution kinetic curves of poly($HOST_{0.7}$-co-$TBA_{0.3}$) containing $\mathbf{5}_{ccc}$ (top) and $\mathbf{4}_{ccc}$ (bottom) in 0.26 N TMAH.

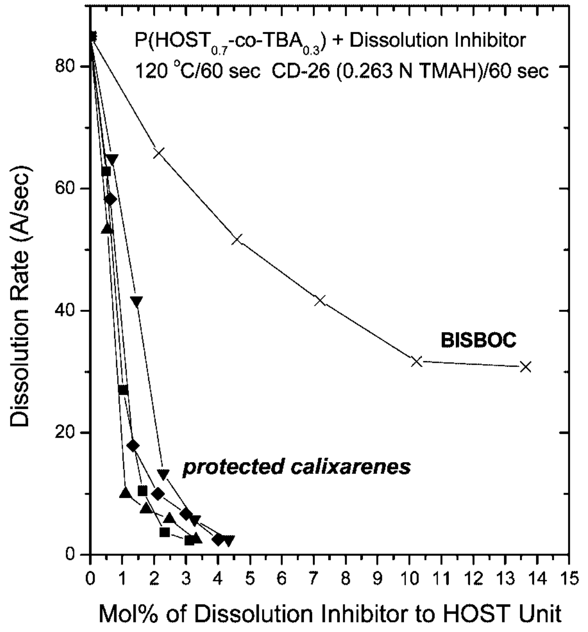

Figure 20. Dissolution inhibition effect of protected calixarenes and BISBOC in 0.26 N TMAH.

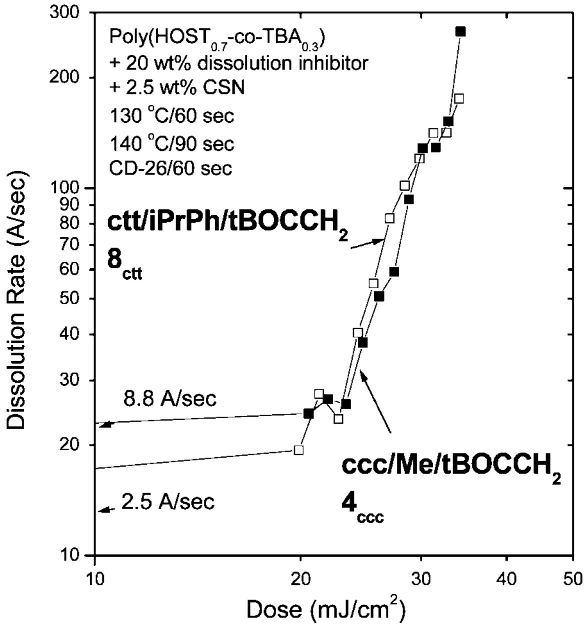

Figure 21. Development contrast curves of three-component resists employing poly($HOST_{0.7}$-co-$TBA_{0.3}$), $\mathbf{4}_{ccc}$ and $\mathbf{8}_{ctt}$, and CSN PAG in 0.26 N TMAH.

The calixarene esters and carbonates are bulky and heavy molecules (molecular weight ranging from 1345 to 1874) and are more impressive in their dissolution inhibition capability when compared with smaller difunctional dissolution inhibitors such as BISBOC (Figure 17) on the basis of mole percent. Figure 20 presents the effect of the loading in mole percent of the five protected calixarenes on the dissolution rate of PolyE (TBA/HOST = 30/70) in CD-26 in comparison with BISBOC and 6FBPACH$_2$tBOC (Figure 17). All of the calixarene derivatives investigated in this study show a mutually similar and strong loading effect, much stronger than the small bifunctional inhibitors. Furthermore, the calixarene derivatives can bring the dissolution rate of PolyE down to <5%, while the maximum dissolution rate reduction achieved with the bifunctional compounds is only 75–65%.

Unfortunately, our detailed variable-temperature NMR studies did not provide insight in the dissolution inhibition behavior of the fully protected calix[4]resorcinarene derivatives. Our IR data on unprotected calix[4]resorcinarenes clearly indicate that two isomers have highly different hydrogen-bonding interactions, which also depend on the type of aldehyde employed in synthesis. Furthermore, our NMR work indicates that the core structures of two isomers are very much different and that the pendant chains carrying protecting groups are highly restricted in motion. All of these observations on isomerically pure calixresorcinarenes could become very useful when one pushes the dissolution limit of the calixarene resists and tries to understand the film-forming properties of such compounds.

Development Contrast. ESCAP-type deep UV resists were formulated by dissolving the HOST/TBA (70/30) copolymer, 20 wt % of tBOCCH$_2$-protected calix[4]resorcinarenes ($\mathbf{4}_{ccc}$ and $\mathbf{8}_{ctt}$), and 2.5 wt % of *N*-camphorsulfonyloxynaphthalimide (CSN) in PGMEA. This acid generator was selected in this investigation because its noninhibiting character[28] would reveal more clearly the dissolution inhibition effect of the calixarenes. No other additives were employed, as this study was an attempt to understand the dissolution inhibition effect of the calixarene derivatives in a fundamental way. The contrast curves are presented in Figure 21. The resist films were prebaked at 130 °C for 60 s, exposed to 254 nm radiation, postbaked at 140 °C for 90 s, and developed with CD-26 (0.26 N TMAH) for 60 s. While the unexposed films have only small and acceptable thinning of 2.5 and 8.8 Å/sec, the films exposed to >20 mJ/cm^2 begin to dissolve rapidly in the developer, providing good contrasts. Thus, the use of the calixarene-based dissolution inhibitors successfully minimizes the unexposed thinning of the fast dissolving resin and provides good lithographic contrast. The optical density of $\mathbf{4}_{ccc}$ and $\mathbf{8}_{ctt}$ is 1.1/μm and 1.6/μm at 248 nm, respectively. The TBA–HOST copolymer films containing 20 wt % of $\mathbf{4}_{ccc}$, $\mathbf{5}_{ccc}$, and BISBOC have 248 nm absorptions of 0.32/μm, 0.14/μm, and 0.16/μm, respectively. The calixarene-based dissolution inhibitors can be expected to improve the lithographic performance of chemically amplified positive resists such as APEX and ESCAP resists. In fact, improvement in contact hole patterning of the ESCAP resist by the contrast enhancement effect of $\mathbf{4}_{ccc}$ has been reported.[41]

Lithographic Imaging. Electron-beam patterning of a resist based on the IBM KRS resist containing $\mathbf{4}_{ccc}$ is presented in Figure 22. The resist film was prebaked at 110 °C for 60 s, exposed to 115 μC/cm^2 of 100 keV electron beams, postbaked at 60 °C for 60 s, and developed with CD-26 (0.26 N TMAH) for 60 s. Dense and semidense 40 nm line/space patterns are presented.

Summary

Calix[4]resorcinarenes were prepared by the condensation of resorcinol and aldehydes (acetaldehyde, benzaldehyde, and 4-isopropylbenzaldehyde), and two isomers, C_{4v} (ccc) and C_{2v} (ctt), were separated by fractional crystallization.

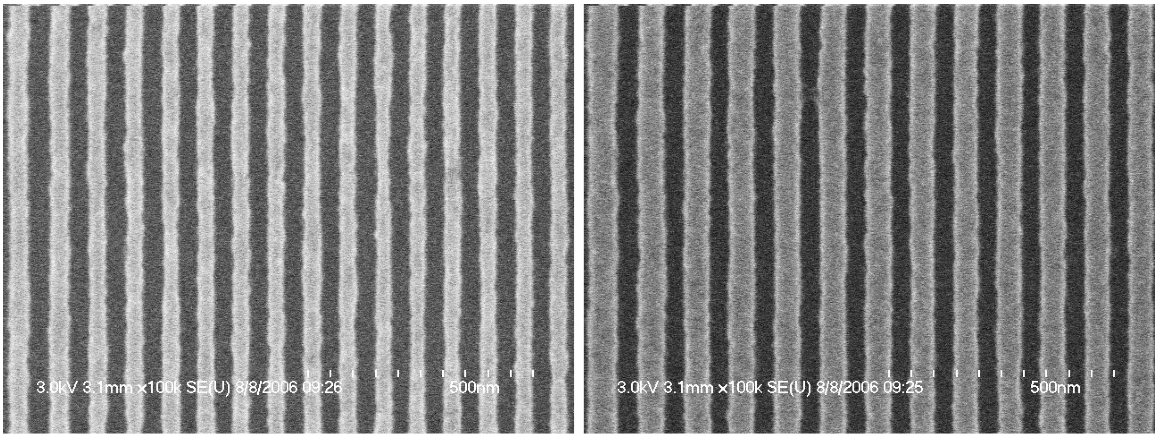

Figure 22. Scanning electron micrographs of 40 nm dense and semidense patterns printed by electron beam in IBM KRS resist containing **4**$_{\text{ccc}}$.

FTIR indicates that the degree of hydrogen bonding is very different between the two isomers and depends also on the aldehyde employed in the synthesis.

The ccc isomer of C-tetramethyl-calix[4]resorcinarene dissolves at ca. 15 000 Å/sec in 0.21 N TMAH, much faster than poly(4-hydroxystyrene) (200–2000 Å/sec).

All eight OH groups of the calix[4]resorcinarenes were protected with acetyl and acid-labile functionalities such as tBOC and tBOCCH$_2$.

The protection, even with small acetyl, reduces the flexibility of the ccc isomers, at room temperature, and the ^{1}H and ^{13}C NMR spectra of the ctt isomer at room temperature resemble those of the ccc isomer at −53 °C in the calix[4]resorcinarene derived from acetaldehyde. This indicates that the chain mobility is more restricted in the ctt isomer than the ccc isomer. In the case of the ctt isomer, the aromatic CH carbons inside the calixarene ring are not magnetically equivalent even at room temperature.

In the case of the ccc isomer of the CH$_2$tBOC-protected calix[4]resorcinarene derived from acetaldehyde, some of the ^{1}H and ^{13}C resonances remain broad even at 55 °C. Cooling the NMR sample solution to −53 °C freezes the bond rotation and restricts the interchange between two isomeric states, thus giving rise to two separate resonances for some of the protons and carbons. The two protons of each OCH$_2$ group are magnetically nonequivalent at −53 °C due to the restricted rotation of the bond and appear as two sets of well-separated AB quartets.

In the case of the ctt isomer of the CH$_2$tBOC-protected calix[4]resorcinarene derived from acetaldehyde, ^{1}H and ^{13}C NMR spectra remain essentially the same from room temperature to 130 °C, with all the aromatic protons and carbons appearing as two peaks, the OCH$_2$ protons resonating as well-separated and distinct AB quartets, and the quaternary and carbonyl carbons splitting into two peaks. **4**$_{\text{ctt}}$ is rigid even at 130 °C.

Replacement of CH$_3$ with Ph (or iPrPh) increases the steric hindrance, and even the ccc isomer shows two NMR peaks for many of the protons and carbons at room temperature. The ctt isomer of the tBOCCH$_2$-protected C-tetraphenyl-calix[4]resorcinarene exhibits splitting in the *t*-butyl quaternary and carbonyl carbon resonances at room temperature.

The effect of protecting all eight OH groups with tBOC on the NMR spectra is very similar to protection with CH$_3$CO or the bulkier tBOCCH$_2$. Only two calixarene benzene rings facing each other are magnetically equivalent in **5**$_{\text{ccc}}$, **7**$_{\text{ccc}}$, and **9**$_{\text{ccc}}$ at room temperature.

FTIR spectra of the tBOCCH$_2$-protected calixresorcinarenes exhibit two carbonyl peaks, and the smaller absorption appears to shift to a lower wavenumber and increases in intensity as the steric hindrance is increased.

The calixresorcinarenes protected with tBOC and tBOCCH$_2$ lose a significant amount of weight upon heating to 175–220 °C due to the loss of isobutene and carbon dioxide in the former and isobutene in the latter. The thermal properties of these protected calixarenes are quite complex, exhibiting sometimes glass transition and melting, sometimes only melting, and sometimes crystallization and melting. The thermal data should be useful in selecting the calixarene derivatives as film-forming molecular glass resists and also in selecting heating conditions to from amorphous glass.

Interaction between the protected calixarenes with 4-isopropylphenol was investigated by ^{13}C NMR. The degree of the interaction as measured by the shift caused by 1 mol % of an additive has been found to be about 4 times greater with the calixarene systems than the classical dissolution inhibitor such as bisphenol-A protected with tBOC. The *t*-butyl ester protected calixarenes appear to interact with isopropylphenol more strongly than the tBOC protected systems. Among the tBOCCH$_2$-protected calixarenes, the structural modifications (ccc vs ctt and Me vs iPrPh) do not affect the interaction much.

Dissolution inhibition effects of the protected calixarenes were investigated using a 70/30 copolymer of HOST with TBA as a matrix polymer and 0.26 N TMAH as a developer. All the calixarene derivatives investigated in this study show a mutually similar and strong loading effect, much stronger than the small bifunctional inhibitors. Furthermore, the calixarene derivatives can bring the dissolution rate of the copolymer down to <5%, while the maximum dissolution rate reduction achieved with the bifunctional compounds is only 75–65%.

ESCAP-type deep UV resists were formulated by dissolving the HOST/TBA (70/30) copolymer, 20 wt % of tBOCCH$_2$-protected calix[4]resorcinarenes, and 2.5 wt % of nondissolution-inhibiting *N*-camphorsulfonyloxynaphthalimide. The resists showed high development contrasts and only small and acceptable thinning of <10 Å/sec in the unexposed areas.

Electron-beam patterning of a resist based on the IBM KRS containing C-tetramethyl-calix[4]resorcinarene protected with $tBOCCH_2$ provided dense and semidense 40 nm line/space patterns.

Although our detailed NMR analysis of the calixarene derivatives did not shed light on their dissolution inhibition behavior, the in-depth knowledge of their structures and properties as investigated on the isomerically pure compounds by FTIR, variable-temperature ^1H and ^{13}C NMR, and DSC could become useful in understanding and improving the lithographic performance of molecular glass resists based on calix[4]resorcinarenes.

Acknowledgment. The authors thank J. Hamilton for his thermal analyses and M. Sanchez for her electron beam patterning.

CM7021483