SUPPORTING INFORMATION

Dendronized Macromonomers for Three-Dimensional Data Storage

Anzar Khan,[†] Anders E. Daugaard,[‡] Andrea Bayless,[†] Shogo Koga,[§] Yasuaki Miki,[§] Ken Sato,[§]

Jun Enda,[§] Søren Hvilsted,[‡] Galen D. Stucky, and Craig J. Hawker[†],*

Departments of Chemistry and Biochemistry, Materials Department, Materials Research Laboratory, and Mitsubishi Chemical Center for Advanced Materials, University of California, Santa Barbara, California 93106-9510. Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 423 Produktionstorvet, DK-2800 Kgs, Lyngby, Denmark. Mitsubishi Chemical Group Science and Technology Research Center, Inc.1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

E-mail: hawker@mrl.ucsb.edu

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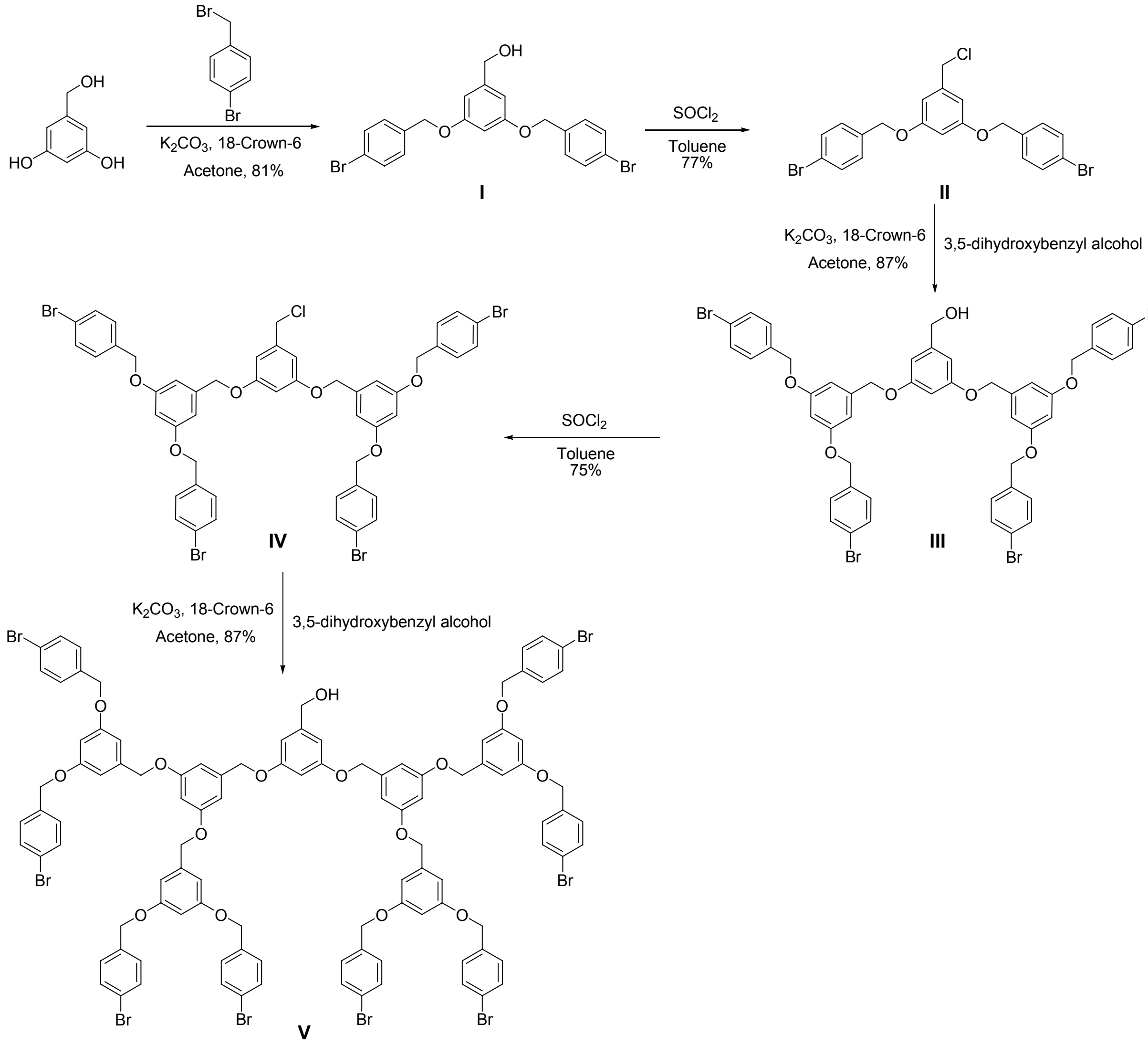
General Methods and Materials

Materials. 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirine TPO) was purchased from BASF. Hexamethylenediisocyanate was purchased from Wako. Dioctyltin dilaurate (U810) was purchased from Nitto Kasei. Tribromophenyl acrylate (BR-30) was purchased from Dai-Ichi Kogyo Seiyaku. Polypropylene-triol (GP1000) (average molecular weight is 1000) was purchased from Sanyo Chemical Industries. All these chemicals were used as received. Analytical TLC was performed on commercial Merck plates coated with silica gel GF254 (0.24 mm thick). Column chromatography was performed on a Biotage SP1 Flash Purification System using FLASH 40+M and FLASH 25+M cartridges. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with a Universal ATR sampling accessory. ^{1}H NMR (400 MHz and 200 MHz) and ^{13}C NMR (100 MHz) measurements were performed on a Bruker AC 400 and 200 spectrometers at 23 ± 2 ^{o}C using residual protonated solvent signal as internal standard (^{1}H: $\delta(CHCl_3)$ = 7.26 ppm and ^{13}C: $\delta(CHCl_3)$ = 77.0 ppm. Differential Scanning Calorimetry (DSC) measurements were performed with a TA Instruments DCS 2920 with temp rate of 5 degrees per minute. Data was collected during third cycle in the selected temperature ranges. Calibrations were made using indium as a standard for both temperature transitions and the heats of fusion. Melting transition temperatures (Tm) were determined by peak maxima of the transition.

Synthesis of the dendritic monomers:[1]



Scheme S1

Typical procedure for the synthesis of bromo substituted dendritic alcohols;

Br_2-G1-OH (I): A mixture of 4-bromobenzyl bromide (28.90 g, 116 mmol), 18-crown-6-ether (3.06 g, 12 mmol) and 3,5-dihydroxybenzyl alcohol (6.48 g, 46 mmol) in dry acetone (90 mL) was refluxed under nitrogen for 12 h. The mixture was cooled and the solvent was removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2/H_2O and extracted with CH_2Cl_2 (x3). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography using CH_2Cl_2 as eluent to afford benzyl alcohol **I** as a white solid (18.00 g, 81%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 1.95 (t, 1 H, -CH_2OH, $^3J = 6.0$ Hz), 4.61 (d, 2 H, -CH_2OH, $^3J = 6.0$ Hz), 4.98 (s, 4 H, (Br)Ar-CH_2-OAr), 6.48 (t, 1 H, Ar*H*, ^4J = 2.1 Hz), 6.60 (d, 2 H, Ar*H*, ^4J = 2.1 Hz), 7.27 and 7.50 (ABq, 8 H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 65.2 (1 C, Ar-*C*H_2OH), 69.4 (2 C, (Br)Ar-*C*H_2O-Ar), 101.5 (1 C, arom. *C*H), 106.0 (2 C, arom. *C*H), 122.0 (2 C, arom. *C*Br), 129.2 (4 C, (Br)arom. *C*H), 131.8 (4 C, (Br)arom. *C*H), 135.9 (2 C, (Br)arom. *C*-CH_2O), 143.7 (1 C, arom. *C*-CH_2OH), 160.0 (2 C, arom. *C*-O-); IR (cm^{-1}): 3290 (OH), 2920, 2875 (C-H), 1610, 1595 (C=C), 1160, 1010 (C-O); 825, 800 (1,4-Ar), 690 (1,3,5-Ar); MS (m/z, EI): 476, 478, 480 (1:2:1, M$^+$); T_m = 98-99°C.

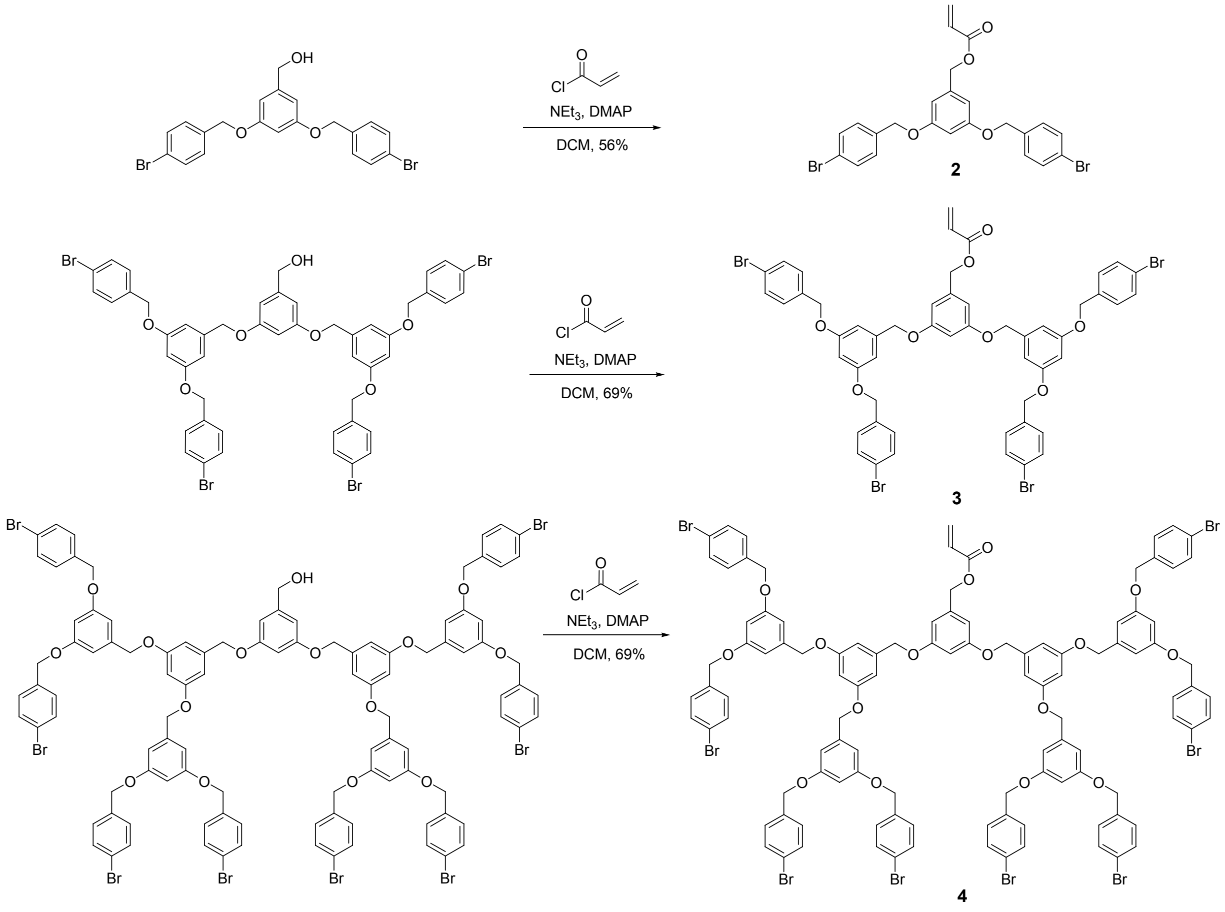
Typical procedure for the synthesis of bromo substituted dendritic chlorides;

Br_2-G1-Cl (II): A solution of **I** (0.50 g, 1.0 mmol) in dry toluene (6.5 mL) was cooled to 0°C and pyridine (0.09 g, 1.1 mmol) was added. To the stirred mixture a solution of $SOCl_2$ (0.14 g, 1.1 mmol) in toluene (0.2 mL) was added dropwise. After addition the mixture was heated to reflux for 30 min. The reaction mixture was concentrated *in vacuo* and the residue was dissolved in CH_2Cl_2 and filtered through a silica gel plug. The obtained solid was recrystallized from hexane and the product was isolated as a white solid (0.40 g, 77%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 4.51 (s, 2 H, -C*H*$_2$Cl), 4.99 (s, 4 H, (Br)Ar-C*H*$_2$-OAr), 6.51 (t, 1 H, Ar*H*, ^4J = 2.1 Hz), 6.63 (d, 2 H, Ar*H*, ^4J = 2.1 Hz), 7.29 and 7.52 (ABq, 8 H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 46.3 (1 C, Ar-*C*H_2Cl), 69.5 (2 C, (Br)Ar-*C*H_2O-Ar), 102.2 (1 C, arom. *C*H), 107.9 (2 C, arom. *C*H), 122.1 (1 C, arom. *C*Br), 129.2 (4 C, (Br)arom. *C*H), 131.9 (4 C, (Br)arom. *C*H), 135.8 (2 C, (Br)arom. *C*-CH_2O), 139.9 (1 C, arom. *C*-CH_2Cl), 160.0 (2 C, arom. *C*-O-); IR (cm^{-1}): 2920, 2875 (C-H); 1595 (C=C), 1170, 1060, 1010 (C-O), 835, 800 (1,4-Ar), 705 (C-Cl); MS (m/z, EI): 494, 496, 498, 500 (1:2:1.5:0.5, M$^+$); T_m = 83-84°C.

Br_4-G2-OH (III): Compound **III** was prepared from **II** by the method reported for synthesis of molecule **I** and purified by column chromatography furnishing a white solid (12.80 g, 87%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 1.75 (t, 1 H, -CH_2O*H*, ^3J = 6.0 Hz), 4.62 (d, 2 H, -C*H*$_2$OH, ^3J = 6.0 Hz), 4.96, 4.97 (2 x s, 12 H, Ar-C*H*$_2$-OAr), 6.51 (2 x t, 3H, Ar*H*, ^4J = 2.0 Hz, ^4J = 2.0 Hz), 6.59 (d, 2 H, Ar*H*, ^4J = 2.0 Hz), 6.65 (d, 4H, Ar*H*, ^4J = 2.0 Hz), 7.27 and 7.50 (ABq, 16H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 65.3 (1 C, Ar-*C*H_2OH), 69.5 (4 C, (Br)Ar-*C*H_2O-Ar), 69.9 (2 C, Ar-*C*H_2O-Ar), 101.5 (1 C, arom. *C*H), 101.7 (2 C, arom. *C*H), 105.9 (2 C, arom. *C*H), 106.5 (4 C, arom. *C*H), 122.0 (4 C, arom. *C*Br), 129.2 (8 C, (Br)arom. *C*H), 131.8 (8 C, (Br)arom. *C*H), 135.9 (4 C, (Br)arom. *C*-CH_2O), 139.6 (2 C, arom. *C*-CH_2O), 143.6 (1 C, arom. *C*-CH_2OH), 160.0 (4 C, arom. *C*-O-), 160.1 (2 C, arom. *C*-O-); IR (cm^{-1}): 3325 (OH), 2920, 2880 (C-H), 1590 (C=C), 1150, 1070, 1010 (C-O), 825, 795 (1,4-Ar), 675 (1,3,5-Ar); MS (m/z, ESI/TOF): 1083 $\{M+Na\}^+$, 1099 $\{M+K\}^+$; T_m = 103-104°C.

Br_4-G2-Cl (IV): Compound **IV** was prepared from **III** by the general method described above for molecule **II** and purified by precipitation into hexanes from CH_2Cl_2, giving a white solid (7.69 g, 75%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 4.50 (s, 2 H, -CH_2Cl), 4.96, 4.98 (2 x s, 12 H, Ar-CH_2-OAr), 6.51 (2 x t, 3H, Ar*H*, ^4J = 2.2 Hz, ^4J = 2.2 Hz), 6.61 (d, 2 H, Ar*H*, ^4J = 2.2 Hz), 6.64 (d, 4H, Ar*H*, ^4J = 2.2 Hz), 7.27 and 7.49 (ABq, 16H, (Br)Ar*H*, ^3J = 8.4 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 46.4 (1 C, Ar-CH_2Cl), 69.5 (4 C, (Br)Ar-CH_2O-Ar), 70.1 (2 C, Ar-CH_2O-Ar), 101.9 (2 C, arom. *C*H); 102.3 (1 C, arom. *C*H), 106.6 (4 C, arom. *C*H), 107.9 (2 C, arom. *C*H), 122.1 (4 C, arom. *C*Br), 129.2 (8 C, (Br)arom. *C*H), 131.9 (8 C, (Br)arom. *C*H), 135.9 (4 C, (Br)arom. *C*-CH_2O), 139.4 (2 C, arom. *C*-CH_2O), 139.8 (1 C, arom. *C*-CH_2Cl), 160.0 (6 C, arom. *C*-O-); IR (cm^{-1}): 3060, 2870 (C-H), 1590 (C=C), 1150, 1045, 1010 (C-O), 830, 800 (1,4-Ar), 710 (C-Cl), 680 (1,3,5-Ar); MS (m/z, ESI/TOF): 1079$\{M+H\}^+$, 1101 $\{M+Na\}^+$, 1117 $\{M+K\}^+$; T_m = 104-105°C.

Br_8-G3-OH (V): Molecule **V** was synthesized from compound **IV** as described for compound **I** and purified by column chromatography (Solvent) furnishing an off-white glassy solid (0.51 g, 87%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 1.68 (br-t, 1 H, -CH_2O*H*, ^3J = 6.0 Hz), 4.61 (d, 2 H, -CH_2OH, ^3J = 5.8 Hz), 4.97 (s, 28 H, Ar-CH_2-OAr), 6.51 (m, 7 H, Ar*H*), 6.61 (d, 2 H, Ar*H*, ^4J = 1.9 Hz), 6.65 (m, 12 H, Ar*H*), 7.28 and 7.50 (ABq, 32 H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 65.3 (1 C, Ar-CH_2OH), 69.5 (8 C, (Br)Ar-CH_2O-Ar), 70.0 (6 C, Ar-CH_2O-Ar), 101.5 (1 C, arom. *C*H), 101.7 (2 C, arom. *C*H), 101.8 (4 C, arom. *C*H), 105.9 (2 C, arom. *C*H), 106.5 (4 C, arom. *C*H), 106.6 (8 C, arom. *C*H), 122.1 (8 C, arom. *C*Br), 129.2 (16 C, (Br)arom. *C*H), 131.8 (16 C, (Br)arom. *C*H), 135.9 (8 C, (Br)arom. *C*-CH_2O), 139.50 (2 C, arom. *C*-CH_2O), 139.53 (4 C, arom. *C*-CH_2O), 143.7 (1 C, arom. *C*-CH_2OH), 160.0 (8 C, arom. *C*-O-), 160.10 (4 C, arom. *C*-O-), 160.14 (2 C, arom. *C*-O-); IR (cm^{-1}): 3325 (OH), 3060, 2870 (C-H), 1590 (C=C), 1150, 1040, 1010 (C-O), 830, 800 (1,4-Ar), 680 (1,3,5-Ar); T_g = 51.4°C.



Scheme S2

Br$_2$-G1-Acrylate (**2**)**:** Compound **I** (0.150 g, 0.3 mmol) was dissolved in CH_2Cl_2 (2 mL) after which DMAP (0.016 g, 0.1 mmol) and Et_3N (0.5 g, 0.7 mL, 5 mmol) were added. To this stirring mixture acryloyl chloride (0.114 g, 0.1 mL, 1.2 mmol) was added dropwise, and the resulting slurry was stirred for 16 h at room temperature under nitrogen atmosphere. The reaction mixture was filtered and the organic layer was extracted with $NaHSO_4$ (1 M, x3), $NaHCO_3$ (x3) and brine (x1). The organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The product was obtained as an oil (0.093 g, 56%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 4.98 (s, 4 H, (Br)Ar-CH_2-OAr), 5.12 (s, 2 H, -CH_2OCO-), 5.87 (dd, 1 H, CH_2=C, ^{2}J=1.3 Hz, ^{3}J=10.4 Hz), 6.16 (dd, 1 H, CH_2=C*H*-, ^{3}J=10.4 Hz, ^{3}J=17.3 Hz), 6.44 (dd, 1 H, CH_2=C*H*-, ^{2}J=1.3 Hz, ^{3}J=17.3 Hz), 6.51 (t, 1 H, Ar*H*, ^4J = 2.2 Hz), 6.59 (d, 2 H, Ar*H*, ^4J = 2.2 Hz), 7.28 and 7.50 (ABq, 8H, (Br)Ar*H*, ^3J = 8.4 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 66.1 (1 C, Ar-*C*H_2OH), 69.5 (2 C, (Br)Ar-*C*H_2O-Ar), 102.0 (1 C, arom. *C*H), 107.3 (2 C, arom. *C*H), 122.1 (1 C, arom. *C*-Br), 128.3 (1 C, -*C*H=CH_2), 129.2 (4 C, (Br)arom. *C*H), 131.4 (1C, *C*H_2=CH), 131.9 (4 C, (Br)arom.

*C*H), 135.8 (2 C, (Br)arom. *C*-CH_2O), 138.5 (1 C, arom. *C*-CH_2OCO), 159.9 (2 C, arom. *C*-O-), 166.0 (1 C, C-*C*OO-); IR (cm^{-1}): 3056, 2926, 2875 (C-H), 1722 (C=O), 1610, 1595 (C=C), 1152, 1011 (C-O), 832, 800 (1,4-Ar), 727 (1,3,5-Ar); MS (m/z, ESI/TOF): 552 $\{M+Na\}^+$.

Br_4-G2-Acrylate (3): The product was obtained from compound **III** by the general procedure reported for compound **2** and the product was obtained as a solid (0.109 g, 69%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 4.96, 4.98 (2 x s, 12 H, Ar-C*H*$_2$-OAr), 5.13 (s, 2 H, -C*H*$_2$OCO-), 5.84 (dd, 1 H, C*H*$_2$=C, ^{2}J=1.3 Hz, ^{3}J=10.4 Hz), 6.16 (dd, 1 H, CH_2=C*H*-, ^{3}J=10.4 Hz, ^{3}J=17.3 Hz), 6.44 (dd, 1 H, CH_2=C*H*-, ^{2}J=1.3 Hz, ^{3}J=17.3 Hz), 6.50 (m, 3H, Ar*H*), 6.59 (d, 2 H, Ar*H*, ^4J = 2.1 Hz), 6.64 (d, 4H, Ar*H*, ^4J = 2.1 Hz), 7.27 and 7.49 (ABq, 16H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 Mhz) $CDCl_3$, δ_C (ppm): 66.2 (1 C, Ar-*C*H_2OH), 69.5 (4 C, (Br)Ar-*C*H_2O-Ar), 70.0 (2 C, Ar-*C*H_2O-Ar), 101.8 (1 C, arom. *C*H), 101.9 (2 C, arom. *C*H), 106.6 (4 C, arom. *C*H), 107.2 (2 C, arom. *C*H), 122.1 (4 C, arom. *C*-Br), 128.3 (1 C, OOC-*C*H=CH_2), 129.2 (8 C, (Br)arom. *C*H), 131.4 (1 C, -CH=*C*H_2), 131.9 (8 C, (Br)arom. *C*H), 135.9 (4 C, (Br)arom. *C*-CH_2O), 138.4 (1 C, arom. *C*-CH_2OCO), 139.5 (2 C, arom. *C*-CH_2O), 160.0 (6 C, arom. *C*-O-), 166.0 (1 C, *C*OO-); IR (cm^{-1}): 3063, 2920, 2880 (C-H); 1724 (C=O); 1592 (C=C), 1150, 1050, 1010 (C-O); 827, 800 (1,4-Ar); 680 (1,3,5-Ar).MS (m/z, ESI/TOF): 1132 $\{M+Na\}^+$; T_m = 101°C.

Br_8-G3-Acrylate (4): Compound **4** was prepared from **V** by the general procedure reported for compound **2** and the product was obtained as a solid (0.105 g, 69%). ^{1}H-NMR (500 MHz) $CDCl_3$, δ_H (ppm): 4.95 (s, 28 H, Ar-C*H*$_2$-OAr), 5.11 (s, 2 H, -C*H*$_2$OCO-), 5.82 (dd, 1 H, C*H*$_2$=C, ^{2}J=1.3 Hz, ^{3}J=10.4 Hz), 6.15 (dd, 1 H, CH_2=C*H*-, ^{3}J=10.4 Hz, ^{3}J=17.3 Hz), 6.42 (dd, 1 H, CH_2=C*H*-, ^{2}J=1.3 Hz, ^{3}J=17.3 Hz), 6.51 (m, 6 H, Ar*H*), 6.54 (t, 1 H, Ar*H*, ^{4}J=2.1 Hz), 6.59 (d, 2 H, Ar*H*, ^4J = 2.1 Hz), 6.63 (m, 12 H, Ar*H*), 7.24 and 7.47 (ABq, 32H, (Br)Ar*H*, ^3J = 8.3 Hz); ^{13}C-NMR (125 MHz) $CDCl_3$, δ_C (ppm): 66.2 (1 C, Ar-*C*H_2OCO), 69.4 (8 C, (Br)Ar-*C*H_2O-Ar), 70.0 (4 C, Ar-*C*H_2O-Ar), 70.1 (2 C, Ar-*C*H_2O-Ar), 101.8 (6 C, arom. *C*H), 101.9 (1 C, arom. *C*H), 106.6 (12 C, arom. *C*H), 107.2 (2 C, arom. *C*H), 122.0 (8 C, arom. *C*-Br), 128.3 (1 C, OOC-*C*H=CH_2), 129.2 (16 C, (Br)arom. *C*H), 131.4 (1 C, -CH=*C*H_2), 131.8 (16 C, (Br)arom. *C*H), 135.9 (8 C, (Br)arom. *C*-CH_2O), 138.4 (1 C, arom. *C*-CH_2OCO), 139.3 (2 C, arom. *C*-CH_2O), 139.5 (4 C, arom. *C*-CH_2O), 160.0 (10 C, arom. *C*-O-), 160.1 (4 C, arom. *C*-O-), 166.0 (1 C, *C*OO-); MS (m/z, ESI/TOF): 2294 $\{M+Na\}^+$; IR (cm^{-1}): 3060, 2870 (C-H), 1723 (C=O), 1590 (C=C), 1155, 1040, 1010 (C-O), 825, 800 (1,4-Ar), 680 (1,3,5-Ar); T_m = 86°C.

Formulations.

	Polyols (wt%)			Isocyanate (wt%)	Monomer (wt%)	Initiator (wt%)	Catalyst (wt%)
	polycarbonate-diol	polypropylene-triol	trimethyl-olpropane	HMDI	**1**, **2**, **3**, or **4**	TPO	dioctyltin-dilaurate
Polyurethane matrix formulation	0.0	77.2	0.0	19.48	3	0.3	0.02
polycarbonate matrix formulation	63.0	0.0	7.0	26.68	3	0.3	0.02

Sample Preparation. To fabricate optical films, several drops of the mixture of solutions A and B were placed between two 3 x 1 inch glass plates separated by Teflon spacers of 0.5mm thicknesses. Clips were placed on both ends of the glass slides to hold them in proper position. The whole assembly was then placed in a heating oven set at 60 ºC for 15 hrs. After curing the films, the sample sandwiched between two glass slides was mounted on the holographic setup and exposed.

Hologram Recording and Evaluation. Experimental setup for recording of holograms was assembled on an optical table suspended on vibration damping supports. The output of a blue diode laser (SONY SBL-N001A, 407 nm, 45 mW, single longitudinal mode) was split into two beams with equal power using a continuously adjustable beam splitter consisting of two half-wavelength plates and a polarizer cube.[2] The resulting beams passed through spatial filters and collimating lenses, which produced beams with diameter of ~ 5 mm. The angle between the recording beams was 37.4^{o}. Optical power density in a single recording beam was ~6 mW/cm^2. A sample was placed at the intersection point of the recording beams on a computer-controlled rotation stage (Sigma Koki SGSP-120YAW, 0.025^{o} positioning accuracy). Intensities of the diffracted and transmitted beams were measured by Si photodiodes protected from ambient light by interference filters. Exposure of a sample to the recording beams was controlled by a computer-operated shutter (Suruga Seiki F77-4). Overall controls over the experiment and data acquisition were carried out by a home-brew program running on a PC. The experimental setup allowed us to control the amount of optical energy used for recording of a hologram, record multiple diffraction gratings, determine their diffraction efficiency (M# measurements), and measure angular selectivity of diffraction gratings to evaluate the amount of volume shrinkage due to the recording.

Diffraction efficiency was determined using the following formula:

$$\eta = \frac{I_D}{I_D + I_T}$$

here I_D and I_T are intensities of diffracted and transmitted beams, respectively. Holograms recorded in our experiments are transmission volume holograms (transmission Bragg holograms).[2]

Sensitivity of the material was estimated using the following equation:

$$S = \frac{\sqrt{\eta}}{dtI}$$

where t is the recording time, d is the thickness of a hologram and I is the combined intensity of recording beams.

Multiplexing capabilities of the recording material were evaluated using M# parameter:

$$M\# = \sum_{i=1}^{N} \sqrt{\eta_i}$$

In these experiments, we recorded consecutively N holographic gratings on the same spot on the sample. The sample was rotated by a certain angle between the recordings. For each hologram, we measured diffraction efficiency η_i.

M/# and Angular selectivity curves of data storage systems in polyurethane matrix.

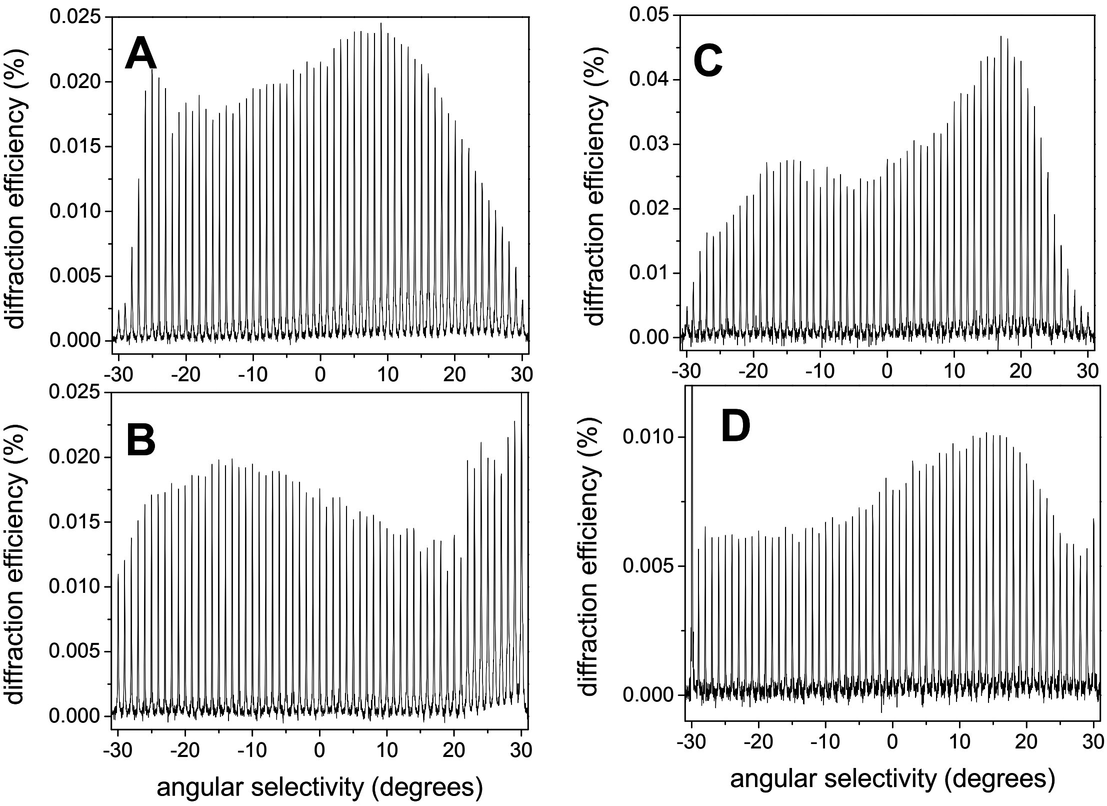


Figure S1. Angular selectivity curves of the holograms recorded in 0.5 mm thick films containing; a) monomer **1**, b) monomer **2**, c) monomer **3**, and d) monomer **4**.

M/# and Angular selectivity curves of data storage systems in polycarbonate matrix.

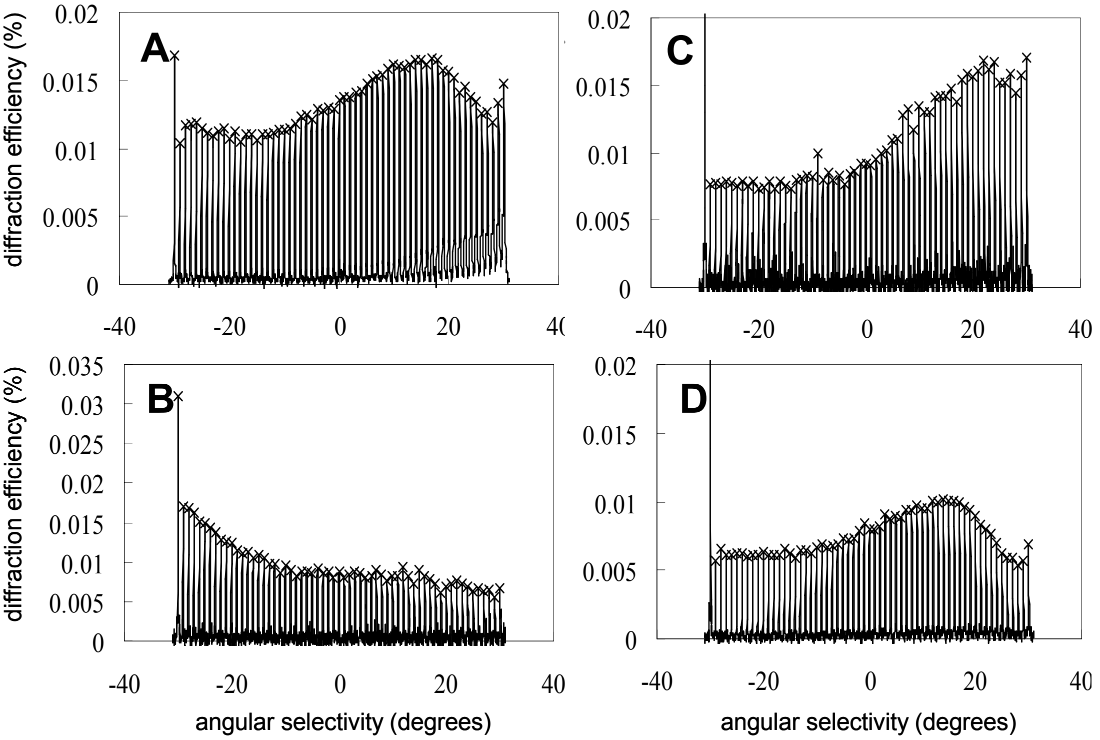


Figure S2. Angular selectivity curves of the holograms recorded in 0.5 mm thick films containing; a) monomer **1**, b) monomer **2**, c) monomer **3**, and d) monomer **4**.

Table S1. Holographic properties of the different data storage systems in the polycarbonate matrix.

Monomer	Storage Capacity (M/#)	Sensitivity (cm/mJ)	Volume Shrinkage (%)
1	7	0.14	0.23
2	6	0.06	0.1
3	6.5	0.04	0.04
4	6	0.05	0.03

Shrinkage Calculation. Shrinkage due to the recording was evaluated in accordance with Dhar's report.[3] A set of fifteen holograms was angle multiplexed from -28° to +28° by 4° step. After recording of the holograms, the material was post-cured for 5 minutes with LEDs (Bivar Inc., 400 nm, 10 mW/cm^2). In order to evaluate the volume shrinkage taken place in the out-of-plane direction, σ, the shift in the Bragg angle, $\Delta\theta_{Bragg}$, experimentally obtained was fitted to the following equation:

$$\Delta\theta_{Bragg} = \arcsin\left[n_1 \sin\left\{ \phi_1 - \frac{\pi}{2} + \arcsin\left(\frac{\lambda}{2\Lambda_1 n_1} \right) \right\} \right] - \arcsin\left[n_0 \sin\left\{ \phi_0 - \frac{\pi}{2} + \arcsin\left(\frac{\lambda}{2\Lambda_0 n_0} \right) \right\} \right],$$

where λ, ϕ, Λ and n are the recording laser wavelength, the grating tilt angle, the grating fringe spacing and the refractive index, respectively. The subscripts 1 and 0 represent the states with and without the volume shrinkage. ϕ_1 and Λ_1 are the functions of σ and described, respectively, as $\phi_1 = \pi/2 - \arctan\{\tan(\pi/2 - \phi_0)/(1+\sigma)\}$ and $\Lambda_1 = \Lambda_0 \sin\phi_1 / \sin\phi_0$. In this study, $n_0 = n_1 = 1.510$ was used for the shrinkage evaluation.

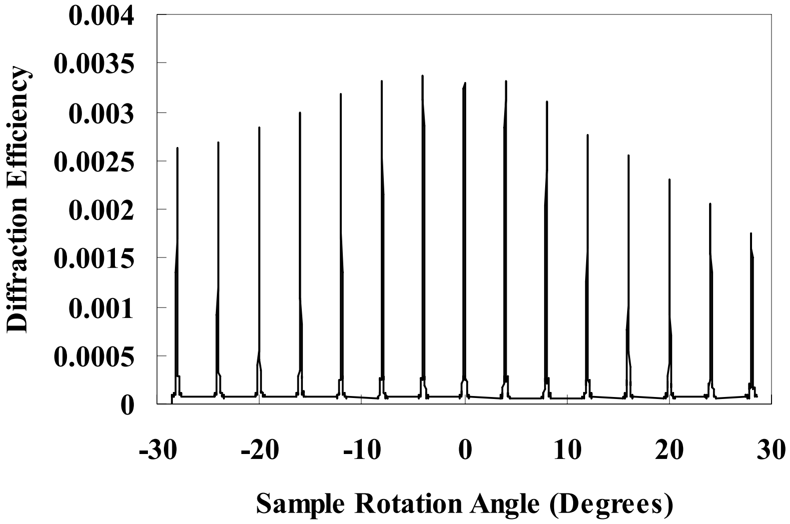


Figure S3. Diffraction efficiency of the fifteen recorded holograms as a function of sample rotation angle for holographic system containing monomer **1**. The angle of the maximum diffraction efficiency for each hologram was found by fitting each peak to a Gaussian line shape.

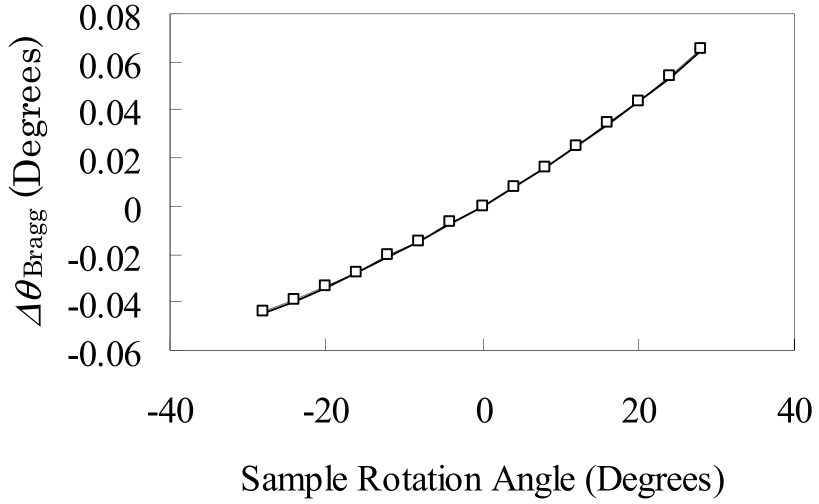


Figure S4. Shift in the Bragg angle as a function of sample rotation angle for **1**.

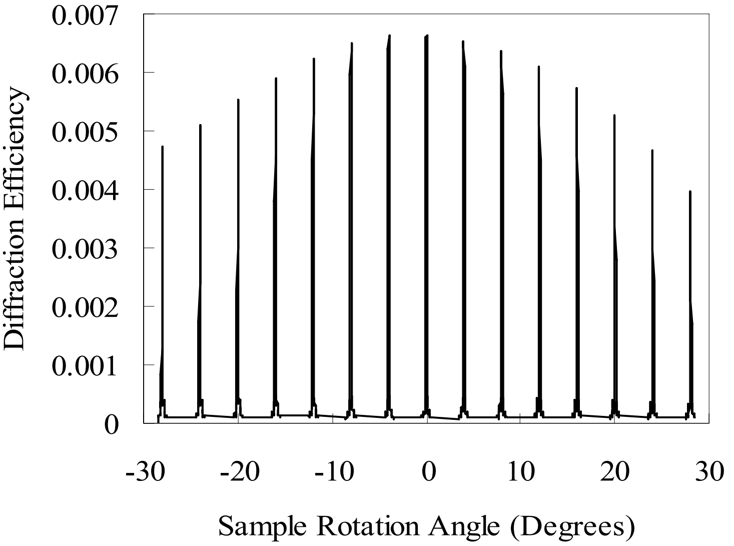


Figure S5. Diffraction efficiency of the fifteen recorded holograms as a function of sample rotation angle for holographic system containing Monomer **2**. The angle of the maximum diffraction efficiency for each hologram was found by fitting each peak to a Gaussian line shape.

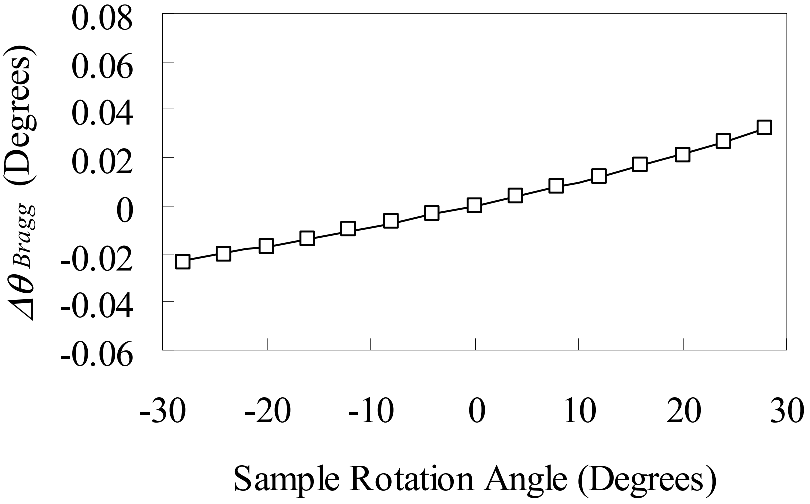


Figure S6. Shift in the Bragg angle as a function of sample rotation angle for Monomer **2** system. The solid line represents the fit to the Bragg shift using the theoretical equation.

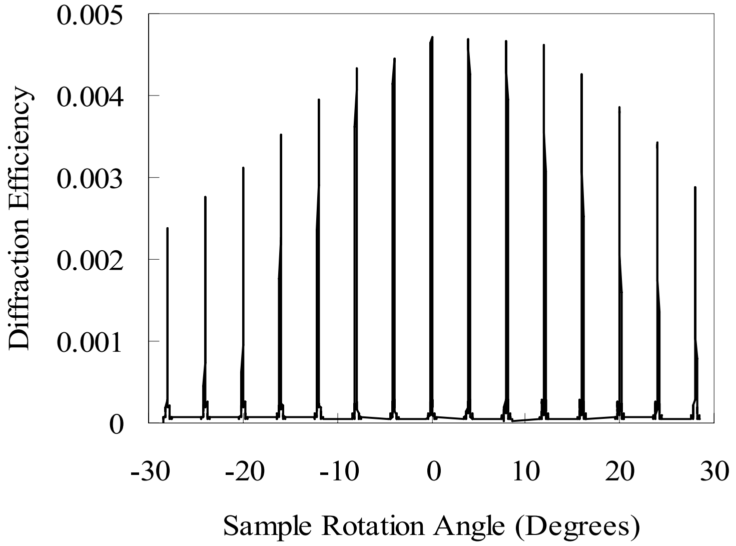


Figure S7. Diffraction efficiency of the fifteen recorded holograms as a function of sample rotation angle for holographic system containing Monomer **3**. The angle of the maximum diffraction efficiency for each hologram was found by fitting each peak to a Gaussian line shape.

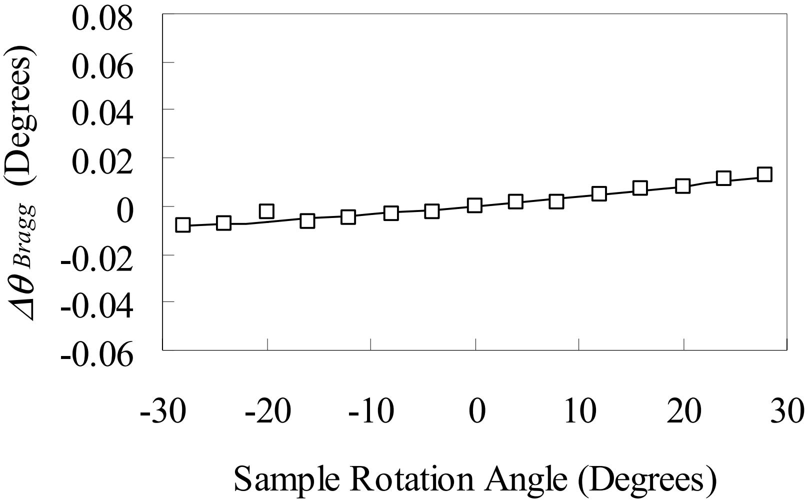


Figure S8. Shift in the Bragg angle as a function of sample rotation angle for Monomer **3** system. The solid line represents the fit to the Bragg shift using the theoretical equation.

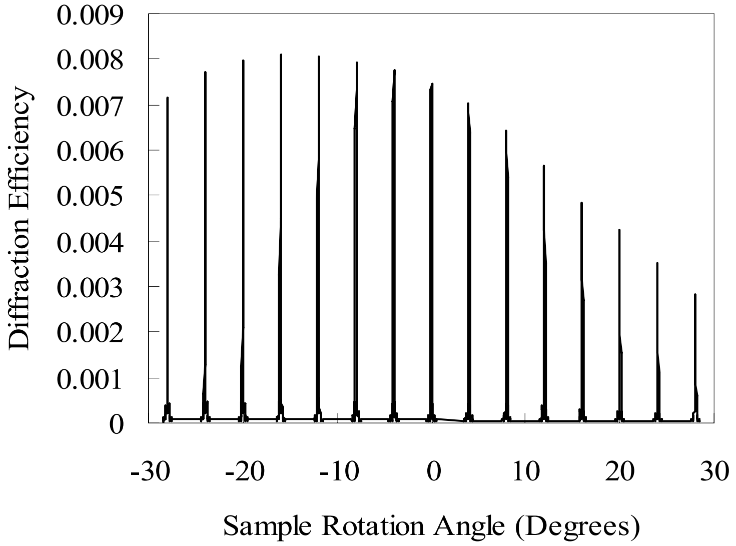


Figure S9. Diffraction efficiency of the fifteen recorded holograms as a function of sample rotation angle for holographic system of Monomer **4**. The angle of the maximum diffraction efficiency for each hologram was found by fitting each peak to a Gaussian line shape.

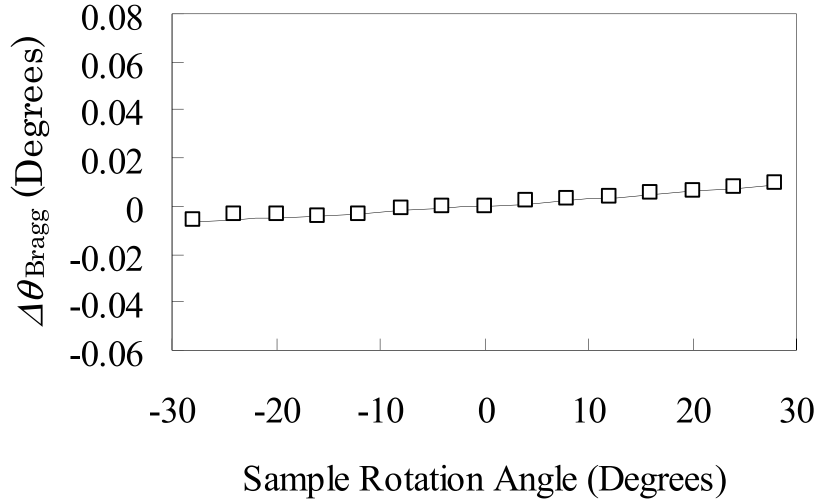


Figure S10. Shift in the Bragg angle as a function of sample rotation angle for Monomer **4**.

Refractive index calculation;

Theoretical refractive indices of the acrylate monomers **1**, **2**, **3**, and **4** were calculated using software by Polymer-Design Tools$^{\mathrm{TM}}$ (http://www.hallogram.com/polymerdesign/index.html).

Exposure time for each hologram;

	Monomer **1**	Monomer **2**	Monomer **3**	Monomer **4**
Recording Angle	Exposure time (msec)	Exposure time (msec)	Exposure time (msec)	Exposure time (msec)
-30	4000	8000	10000	15000
-29	720	2120	2180	2500
-28	720	2080	2180	2500
-27	720	2040	2180	2520
-26	720	2020	2180	2520
-25	720	2020	2200	2520
-24	720	2000	2200	2540
-23	720	2020	2220	2560
-22	740	2020	2240	2580
-21	740	2020	2260	2620
-20	740	2020	2280	2640
-19	760	2040	2320	2680

-18	760	2060	2340	2720
-17	780	2080	2380	2760
-16	800	2100	2420	2820
-15	800	2120	2460	2880
-14	820	2140	2520	2940
-13	840	2180	2580	3000
-12	860	2200	2620	3080
-11	880	2240	2700	3160
-10	900	2280	2760	3240
-9	920	2340	2840	3340
-8	960	2380	2920	3440
-7	980	2440	3000	3540
-6	1020	2500	3100	3660
-5	1040	2560	3200	3800
-4	1080	2640	3300	3940
-3	1120	2720	3420	4100
-2	1160	2800	3540	4260
-1	1200	2880	3680	4440
0	1260	2980	3840	4620
1	1300	3080	4000	4840
2	1360	3200	4160	5060
3	1420	3320	4340	5300
4	1480	3440	4560	5560
5	1560	3580	4760	5840
6	1640	3740	5000	6160
7	1720	3900	5260	6500
8	1800	4080	5520	6860
9	1900	4260	5820	7260
10	2020	4480	6140	7680
11	2120	4700	6500	8160
12	2260	4940	6880	8680
13	2380	5200	7300	9240
14	2540	5480	7740	9860

15	2700	5800	8240	10520
16	2860	6140	8780	11260
17	3060	6500	9360	12060
18	3280	6900	10000	12960
19	3500	7340	10700	13940
20	3760	7800	11460	15000
21	4020	8320	12300	16200
22	4320	8900	13240	17500
23	4660	9520	14260	18960
24	5020	10200	15380	20560
25	5440	10940	16600	22340
26	5880	11760	17980	24320
27	6580	12680	20120	27460
28	7400	14080	22600	31100
29	8620	15680	26340	36700
30	10100	18100	30840	43520

Monomer Conversion in the holographic disc;

A holographic disk containing the photoactive monomer was exposed to blue light for 5 minutes at each side (note that this is a blanket exposure and not a holographic exposure). The optical power of the light source was 10 mW/cm^2. After the exposure, the sample was immersed in THF to extract the unreacted monomer, and then the concentration of the monomer in the THF solution was measured by using liquid chromatography. The conversion was calculated from the concentration change before and after the light exposure. The concentration of the monomer in the holographic disk before the light exposure was also measured as a reference.

Monomer	Monomer conversion (%)
1	99
2	68
3	46
4	45

References.

(1) K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc. Perkin Trans. 1*, 1991, 1059

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