Dendronized macromonomers for three-dimensional data storage†

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Received (in Cambridge, UK) 17th September 2008, Accepted 25th November 2008
First published as an Advance Article on the web 11th December 2008
DOI: 10.1039/b816298k

A series of dendritic macromonomers have been synthesized and utilized as the photoactive component in holographic storage systems leading to high performance, low shrinkage materials.

A continuing trend in information storage is the desire for greater storage capacity, a feature that demands the development of both new storage techniques as well as new materials. One of the most promising approaches for achieving high density data storage is based on volume holography which allows data to be stored in 3 dimensions. This significant increase in capacity is in direct contrast to the fundamental size limitations found in traditional 2-D systems such as magnetic hard disk drives.[1] In volume holography, information is stored in the form of optical interference patterns throughout the volume of a photosensitive material. This is accomplished by intersecting two coherent laser beams with the first, called the object beam, containing the information to be stored. The second, called the reference beam, is used to retrieve the stored information. When the object beam and the reference beam intersect in the storage medium, they cause a change in the chemical or physical properties of the material which results in refractive index modulation. By shifting the angular position of the storage media, multiple interference patterns (holograms) can be recorded within the same volume, enabling high density information storage.‡

While promising, this 3-D volumetric storage strategy has limited commercial implementation due to a variety of material challenges. An ideal storage media must meet numerous stringent requirements including high photosensitivity, high storage capacity, non-volatile read-out, dimensional stability, millimetre thickness, and low-cost.[2] Photopolymer systems[3] fulfill many of these requirements and are promising candidates for three-dimensional data storage applications. Typically they consist of a mixture of monomer and photoinitiator dissolved in a thick, crosslinked network (Fig. 1). Upon holographic exposure, a polymerization reaction initiates in the bright regions of the holographic media leading to consumption of the monomer in the bright regions and generation of a concentration gradient with associated diffusion of the monomers from the dark regions. This monomer diffusion results in a permanent compositional and density change in the recording material and creates a refractive index modulation. However an intrinsic problem with the photopolymer system is the writing induced shrinkage of the recording material due to the monomer diffusion and the formation of new covalent

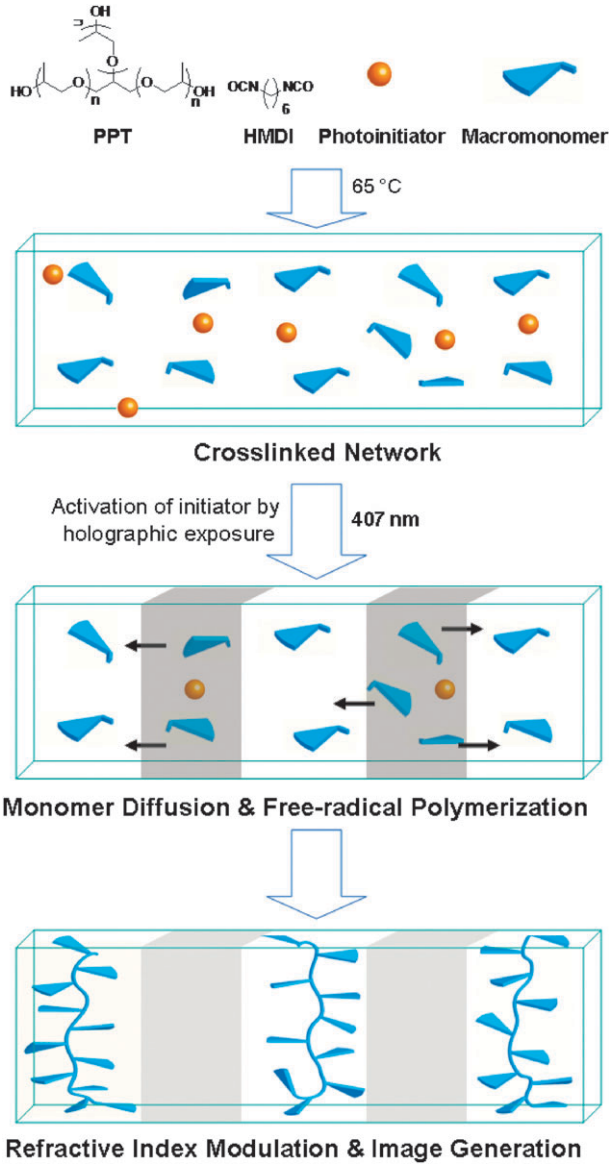

Fig. 1 Schematic representation of refractive index modulation and hologram formation due to the photopolymerization of dendronized monomers dispersed within a thick, crosslinked film.

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† Electronic supplementary information (ESI) available: 19 pages of experimental data. See DOI: 10.1039/b816298k

bonds during polymerization. This dimensional instability has a detrimental effect on the retrieval of the data from stored holograms (hologram position shifts from the original position) and hence severely limits the commercial viability of the photopolymer system for volume holographic applications.[2,4] This issue becomes even more critical for high capacity storage systems as holograms recorded in thicker films are more sensitive to dimensional changes than those recorded in thin films.[4] To overcome these limitations, new monomers need to be developed that have low viscosities for efficient diffusion, do not lead to appreciable shrinkage on polymerization and possess a high refractive index.

Here, we demonstrate that the use of highly branched dendritic macromonomers can address many of these issues and allow writing induced shrinkage to be successfully reduced to negligible values. A critical feature of dendritic macromonomers is their inherent large volume to functional group ratio where the influence of the single focal point unit decreases with increasing generation number. In addition, the highly branched molecular architecture maintains a low viscosity[5] and consequently high mobility in the initial crosslinked matrix. Finally, the incorporation of numerous high refractive index moieties at the chain ends increases the average refractive index of the macromonomer and leads to enhanced data storage capacity. The use of novel dendritic macromonomers therefore permits development of a low shrinkage photopolymer based holographic material without sacrificing the sensitivity or the storage capacity of the recording media. The modular nature of dendrimer chemistry and the precise control over the generation number, nature of chain ends, focal point, and repeat units also allows a direct structure–property relationship to be developed for these materials.[6,7]

Benzyl ether based dendrimers were selected for initial investigations due to their ease of synthesis, relatively high refractive index, increased solubility and unique hydroxyl group at the focal point. The dendritic acrylate monomers **2**, **3**, and **4** were synthesized convergently from 4-bromobenzylbromide and 3,5-dihydroxybenzyl alcohol in 2, 4, and 6 steps with overall yields of 70–80%, respectively, followed by facile functionalization by reaction with acryloyl chloride (Fig. 2).†[8]

In order to fabricate millimetre thick transparent optical films suitable for holographic recording; monomers **1**, **2**, **3**, or **4** (3 wt%) were individually mixed with polyurethane based matrix precursors hexamethylenediisocyanate (19.48 wt%), polypropylene-triol (M_n = 1000) (77.2 wt%), and dioctyltin dilaurate (0.02 wt%) with 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirine) (0.3 wt%) added as a photoinitiator. Initial orthogonal reaction between the triol and diisocyanate derivatives afforded crosslinked thick films of high optical quality with no observed phase separation of the unreacted dendritic macromonomer or photoinitiator. Illumination of these crosslinked thick films with an interference pattern from two collimated 407 nm laser beams (total optical power density of ~6 mW cm^{-2} and beam diameter of ~5 mm) initiates the photopolymerization and associated diffusion of unreacted dendritic macromonomers **1**, **2**, **3**, or **4** to generate a refractive index modulation. The high sensitivity of this system allows at least 60 holograms to be individually recorded in each holographic disc and from these data, the storage capacity ($M/\#$)†[9] of holographic systems containing **1**, **2**, **3**, or **4** was calculated to be 8, 8, 10, and 6, respectively (Table 1). Fig. 3 shows angular selectivity response of the 60 holograms recorded by utilizing monomer **3** as the photoactive component in the holographic disks (see also Fig. S1 in the ESI†).

Volume shrinkage due to holographic recording was then calculated according to the method reported by Dhar and co-workers.†[10] For the control system containing the tribromo acrylate monomer **1** a volume shrinkage of 0.23% was observed after recording of 60 holograms in a standard 0.5 mm disk format (see ESI†). Use of the first generation dendritic monomer **2** led to materials with the same storage capacity as **1** (Table 1—similar refractive index (RI) of the monomers **1** (RI = 1.614) and **2** (RI = 1.616)),†[11] while

Table 1 Holographic properties of the data storage systems containing monomer **1**, **2**, **3**, or **4**

Monomer	Storage capacity ($M/\#$)	Sensitivity/ cm mJ^{-1}	Volume shrinkage (%)	Refractive index
1	8	0.20	0.23	1.614
2	8	0.37	0.10	1.616
3	10	0.46	0.04	1.647
4	6	0.05	0.03	1.663

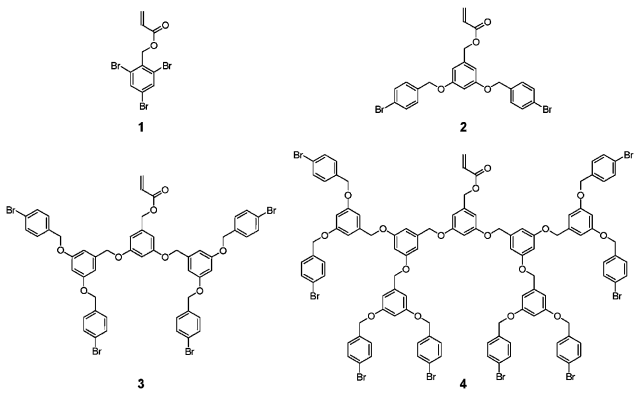

Fig. 2 Chemical structures of the dendritic monomers examined for holographic storage.

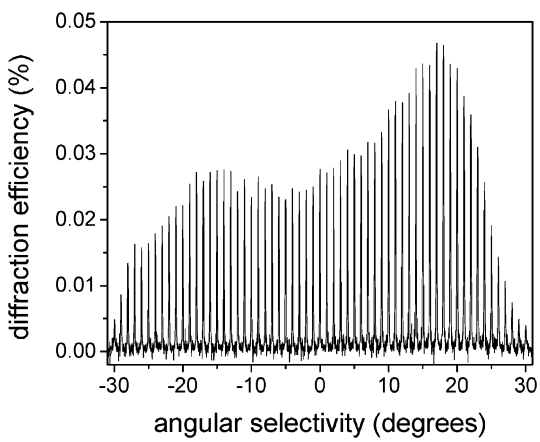

Fig. 3 Angular selectivity curves of the 60 holograms recorded in 0.5 mm thick holographic disc containing second generation based monomer **3**.

volume shrinkage was reduced to 0.1%. To further understand the relationship between generation number and volume shrinkage, the second generation dendritic macromonomer **3** having 4 chain end bromophenyl groups was synthesized and utilized as the photoactive component in a series of holographic discs. The experimental results reveal that the increased refractive index (1.647) of **3** leads to an increased storage capacity ($M/\#$ = 10) and the higher generation number per molecular weight resulted in a further reduction in volume shrinkage to 0.04%. Significantly, the high solubility of **3** allowed thick, photosensitive (0.46 cm mJ^{-1}) systems to be prepared and demonstrated the effect of increasing generation number and branched structure on the performance of dendritic macromonomers as holographic storage components. Further increasing the generation number gives the third generation derivative, **4**, which was found to exhibit poor solubility in the original matrix components. As a result, the oligomeric matrix precursor polypropylene-triol (M_n = 1000) was replaced with a mixture of polycarbonatediol (M_n = 800) and trimethylolpropane (9 : 1) (referred to as polycarbonate matrix henceforth), which allowed for fabrication of thick films suitable for holographic recording. Utilization of monomer **4** resulted in an additional decrease in the volume shrinkage to 0.03% and displayed a similar storage capacity to **1** and **2**. However the sensitivity was reduced (Table 1), presumably due to the unfavorable nature of the polycarbonate matrix.[12] This is confirmed by utilizing monomers **1**, **2**, and **3** in the polycarbonate matrix which led to a decrease in the sensitivity and storage capacity of all the storage systems.†

In conclusion, we have demonstrated the synergistic effect that dendritic branching has on the performance of photopolymerizable materials for holographic storage. Careful design of the molecular structure of the dendritic macromonomers allowed the second generation, poly(benzyl ether) **3** to be identified as the optimal structure for this material set. Negligible volume shrinkage, high $M/\#$, as well as excellent photosensitivity was observed. Significantly, the minimal volume shrinkage assures high fidelity for data recovery, while the high $M/\#$ imparts elevated storage capacity to the recording material with good photosensitivity allowing for rapid recording speed. The general approach of exploiting the unique structural features of functionalized dendritic macromonomers for shrinkage reduction presented here will also be useful for materials used in optical devices that require high dimensional stability such as holographic optical elements (HOEs), gradient refractive index (GRIN) materials, optical circuits, and optical waveguides. These results also demonstrate a further advantage of the dendritic architecture in the design of materials with improved properties,[13] in this case significant reduction in volume shrinkage for a photopolymer system without sacrificing the photosensitivity of the storage medium.

Financial support from MC-CAM and the central facilities of the UCSB Materials Research Laboratory (NSF Grant DMR05-20415) is gratefully acknowledged. A. D. would like to thank the Berg, Nielsens legat, Aage Corrits legat, Otto Mønsteds fund and the Danish Research Council for Technology and Production Sciences (through the framework program "Design and Processing of Polymers for Microfluidic Applications", grant 26-04-0074) for financial support.

Notes and references

‡ *Hologram recording*: 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, 404 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. The resulting beams passed through spatial filters and collimating lenses, which produced beams with a diameter of ~5 mm. The angle between the recording beams was 37.4°. Optical power density in a single recording beam was ~6 mW cm.

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