

DOI: 10.1002/adma.200800776

High-Performance, Nondiffusive Crosslinked Polymers for Holographic Data Storage**

By Anzar Khan, Galen D. Stucky,* and Craig J. Hawker*

Research into the development of new data-storage strategies is fueled by the continuing demand for ultrahigh information capacity, increased data density, smaller form factor, and faster readout rates. Conventional data-storage devices such as magnetic hard-disk drives, optical disks, and semiconductor memories all rely on storing information bit by bit on the surface of a recording medium. However, these two-dimensional storage strategies are rapidly reaching fundamental physical limits, beyond which individual bits become too small to easily write or read and/or are inherently unstable. A promising alternative approach is based on holographic data storage,^[1] in which information is stored three-dimensionally, throughout the volume of a storage medium. This emerging field of volume holography, however, is faced with the challenge of developing suitable storage materials that meet all the stringent requirements, such as high photosensitivity, good storage capacity, dimensional stability, high optical quality, low cost, and efficient manufacturing capabilities, all necessary for commercial viability.^[2]

For commercially viable holographic data-storage systems, a complete page of information is recorded as an optical interference pattern created by two intersecting laser beams within a thick (>200 μm) photosensitive material. The interference pattern of these two coherent writing beams induces a periodic change in the refractive index of the recording material. A variety of photochemical reactions can be utilized to achieve such refractive index modulation. However, very few reactions exhibit quantum yields greater than unity, where one photon of light triggers numerous chemical reactions. This nonlinearity is essential for the high sensitivity and ultrafast recording speeds required for commercial holographic data storage. To achieve this, diffusion-based systems involving photoinduced polymerization reactions are currently the primary area of focus for both

commercial and academic holographic systems.^[3] The practicality of these photopolymer systems is, however, hampered by a number of issues including shrinkage of the recording material, low shelf-life of the storage media due to undesired thermal polymerization of monomers, polymerization inhibition due to oxygen present in the atmosphere, and reduced storage capacity due to necessary pre-exposure steps. Therefore, development of new holographic materials which are photocatalytic in nature but do not suffer from performance issues is critical to the progress of three-dimensional data storage.

In examining other photochemical reactions with quantum yields greater than 1.0, the isomerization of Dewar benzene is noteworthy due to its very high quantum yield (>100 in solution).^[4] Additionally, isomerization of Dewar benzene gives rise to a large change in the electronic structure of the molecule (Fig. 1a) and is therefore anticipated to result in high refractive index modulation upon photoisomerization. These two features, i) nonlinearity of the photochemical reaction and ii) expected high index modulation, represent an opportunity for the development of an information-storage material with fast recording speed and high data-storage capacity. The nondiffusive nature of the isomerization process for the Dewar-benzene-based system ensures high dimensional stability of the recording media, while the high thermal stability of the Dewar benzene reactant may lead to extended shelf-life. Finally, the irreversible isomerization step leads to stability of the recorded hologram, and therefore results in high archival life for the stored data. Seminal work by Dinnocenzo, Robello, Farid, and co-workers has demonstrated the quantum amplification of Dewar benzene photoisomerization and their refractive index modulation.^[5] In situ polymerization resulted in fabrication of millimeter-thick films, necessary for volume holography, which displayed diffraction efficiencies ranging from 5 to 30%. The thickness-normalized sensitivity can be calculated to be 0.00003–0.0004 cm mJ^{-1} .^[5b] However, the commercial viability demands significantly higher diffraction efficiencies and material sensitivity. Additionally, the material suffers the occurrence of dark reactions (continued photochemical reaction after the writing source is turned off), which undermines the stability of the recorded images.^[5c] Here, we report crosslinked polymers whose performance is based on nondiffusive, quantum-amplified photoisomerization of Dewar benzene derivatives, which exhibit remarkable information-storage properties including excellent photosensitivity, high diffraction efficiencies, high data-storage capacity, good dimensional stability, and significant shelf- and archival-lifetimes.

[*] Prof. G. D. Stucky, Prof. C. J. Hawker, Dr. A. Khan
Departments of Materials, Chemistry and Biochemistry
Materials Research Laboratory, and
Mitsubishi Chemical Center for Advanced Materials
University of California
Santa Barbara, CA 93106-9510 (USA)
E-mail: hawker@mrl.ucsb.edu; stucky@chem.ucsb.edu

[**] Financial support from MC-CAM and the central facilities of the UCSB Materials Research Laboratory (NSF Grant DMR05-20415) are gratefully acknowledged. The optical holography setup and the scattering measurement setup were constructed by Dr. Alexander Mikhailovsky, Department of Chemistry and Biochemistry, University of California, Santa Barbara. Supporting Information is available online from Wiley InterScience or from the author.

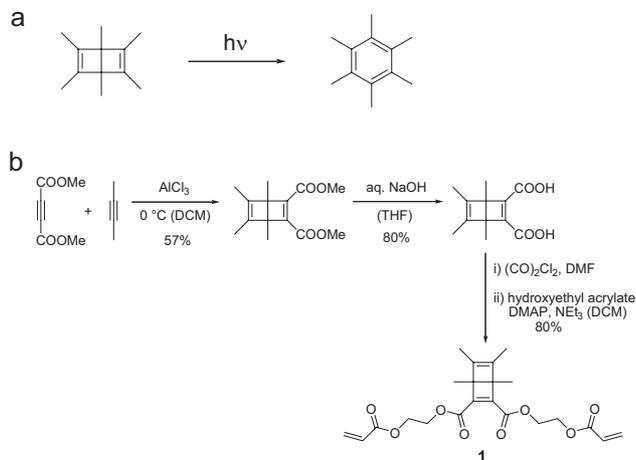


Figure 1. a) Photoisomerization of hexamethyl Dewar benzene to hexamethyl benzene. b) Synthesis of the Dewar benzene derivative **1**.

In designing a high-performance data-storage system, the following aspects of structure/processing–property relationship of the photoactive Dewar benzene monomer have been studied in detail. i) The electronic structure of the photoactive Dewar benzene nucleus: holographic disks with two electronically different Dewar benzene derivatives, having all electron-donor and two electron-acceptor substituents attached directly to the photoactive Dewar benzene core, have been prepared. It is observed that materials containing electron-deficient Dewar benzene derivatives exhibit higher sensitivity as compared to materials that contain electron-rich Dewar benzene derivatives (see Supporting Information). Presumably, this is due to more efficient triplet energy transfer from the sensitizer to the electron-deficient Dewar benzene nucleus. Moreover, the material does not suffer from any unwanted dark reaction. ii) The chemical structure of the photoactive Dewar benzene monomer: novel Dewar benzene derivatives having two crosslinkable side chains have been synthesized, allowing for thick-film fabrication with high loading (~70 wt %) of the photoactive Dewar benzene reactant. iii) The processing method for obtaining high-quality thick films: a mild and facile fabrication process is developed, in which no/negligible thermal isomerization of Dewar benzene occurs, and hence the total storage capacity remains intact until the writing process.

The target Dewar benzene derivative, **1**, was selected based on its synthetic accessibility, substitution with two electron-withdrawing groups, and the ability to undergo efficient crosslinking. The synthesis of **1** involves the initial reaction of dimethyl acetylenedicarboxylate with the in situ generated aluminum complex of tetramethyl cyclobutadiene, resulting in the formation of the Dewar benzene dimethylester. Hydrolysis under basic conditions gives the corresponding dicarboxylic acid in good yield. This was then converted to the diacid chloride, and coupled with 2-hydroxyethyl acrylate to afford the desired Dewar benzene derivative, **1** (see Supporting Information).

For a viable holographic system, in addition to the photosensitive Dewar benzene **1**, a photosensitizer and a matrix crosslinker are required. For recording a wavelength of 407 nm, high-throughput optimization of both the structure and the relative percentage of these components led to the selection of divinylbenzene (**2**) as crosslinker, and isopropyl-9*H*-thioxanthen-9-one (**3**) as the photosensitizer (Fig. 2a). The selection of **3** (1 wt %) was important, and driven by its high solubility in a mixture of **1** (70 wt %), and **2** (29 wt %), allowing for the fabrication of thick films by solventless processing. In addition, a low absorption cross-section at the recording wavelength of 407 nm ensures homogeneous recording throughout the depth of the recording media, while very efficient energy transfer to the Dewar benzene, **1**, via the higher triplet energy of **2**, was observed.^[6]

A major requirement for the fabrication of high-density holographic-storage systems is the necessity for thick films ($\geq 200 \mu\text{m}$) with good optical qualities such as low scattering and low optical density. Traditionally, this is not a trivial requirement for either holographic or other crosslinked polymer-based storage systems.^[7] However, the design of a system based on **1**, **2**, and **3** allows for a thermal, bulk polymerization procedure to be used in association with doctor blading or mold-casting. Facile and inexpensive thermal curing of this photosensitive mixture by free-radical-initiated crosslinking was shown to afford freestanding polymeric films under a solventless processing technique that are transparent and colorless with thicknesses of up to several millimeters. The optical density of a 1 mm thick film prepared by this method is ~0.42 at 407 nm (Fig. 2b), and this low optical density at the recording wavelength is an important characteristic, as strong absorption at the writing wavelength can prevent uniform irradiation throughout the thickness of the film, leading to inhomogeneous hologram recording. This requirement becomes even more critical since volume holography requires film thicknesses of 200 μm and above. Scattering measurements revealed essentially no light-scattering by these films, demonstrating the very high optical quality of crosslinked films of **1**, **2**, and **3**. In order to evaluate the efficiency of these highly crosslinked Dewar benzene films, a single hologram was

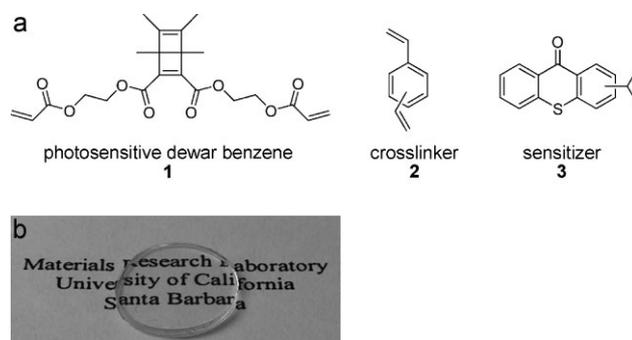


Figure 2. a) Chemical structures of the different holographic media components **1**, **2**, and **3**. b) One millimeter thick optical disk fabricated from these components by azobisisobutyronitrile-initiated free-radical crosslinking.

recorded by illuminating the sample with an interference pattern from two collimated 407 nm laser beams with total optical power density of $\sim 6 \text{ mW cm}^{-2}$ and beam diameter of $\sim 10 \text{ mm}$. Figure 3a shows the growth in diffraction efficiency of the hologram as a function of exposure time. Only 40 s of exposure to the writing beams was sufficient to attain a diffraction efficiency of $\sim 60\%$ with the photosensitivity “*S*” of the material calculated to be 0.08 cm mJ^{-1} . The real-time diffraction efficiency of the hologram was then monitored for 45 h after recording, and no increase in the hologram strength was detected. This high photosensitivity allows for ultrafast recording speeds, and the absence of dark reactions strongly suggests complete consumption of photoactive Dewar benzene reactant in exposed regions of the holographic media, again demonstrating the efficiency of the isomerization reaction. Each hologram was found to have an angular bandwidth of 0.3°

(full-width measured at half-maximum) determined at 632.8 nm (Fig. 3b). In addition, the presence of well-defined nulls indicates that the refractive index grating is stored throughout the depth of the recording medium, and coupled with the above results demonstrates the high performance of these materials (Fig. 3c). After recording the holograms, the films diffracted ambient light and thus a number of colors could be seen macroscopically (see Supporting Information), indicating that a refractive index grating of high strength has been stored in the depth of the recording material. The ability to prepare dimensionally stable, crosslinked thick films of the Dewar benzene derivative **1** also permits storage of multiple holograms at the same spatial position within the thickness of the material (angular multiplexing). Figure 4a shows ten angularly multiplexed holograms of roughly equal strength recorded by rotating the sample in 2° increments. The recording time for each hologram was 6 s, and the performance value that characterizes the capacity of these materials, defined by the dynamic range ($M/\#$), can be calculated from this data by summing the square root of the diffraction efficiency of each hologram. The $M/\#$ determined for this material was 2.5. However, it should be noted that due to limited rotation (experimental constraint), the total storage capacity was not exhausted; hence the calculated $M/\#$ value of 2.5 represents a lower limit for storage capacity in the present recording material. This is graphically represented in Figure 4b, which shows an almost linear relationship between $M/\#$ and the exposure energy, with no indication of a plateau. The sharp, highly symmetrical, and narrow bandwidth of the angular selectivity curves further indicates the high resolution that can be achieved by an isomerization-based Dewar benzene holographic system. In comparison to a state-of-the-art, diffusion-based photopolymer system for holographic storage from InPhase Systems^[3c] (utilizing styrene as monomer in a crosslinked epoxy-mercaptan matrix), the performance of the Dewar benzene-based material is found to exceed that of photopolymers (45% diffraction efficiency after exposure of 120 s, $M/\# = 1$) under identical conditions (see Supporting Information). To further demonstrate the practicality of the present holographic system, shelf- and archival-life of the recording media were studied. Figure 5a shows the storage capacity of the material ($M/\#$) as a function of time between the initial formulation and the holographic exposure. The material exhibits no reduction in the dynamic range over a period of several months at room temperature, indicating significant shelf-life and stability of the Dewar benzene system (cf. $\sim 80\%$ reduction in the storage capacity for the photopolymer system is observed after 16 days^[3b]). In order to investigate the archival life of the recorded data, the shape of the angular selectivity curve of the hologram was also examined. Figure 5b shows the angular selectivity curve of a hologram immediately following recording, while 5c shows the angular selectivity curve of the same sample after several weeks of storage at room temperature. The shape of the angular selectivity curves remained intact, demonstrating good archival life of the stored data.

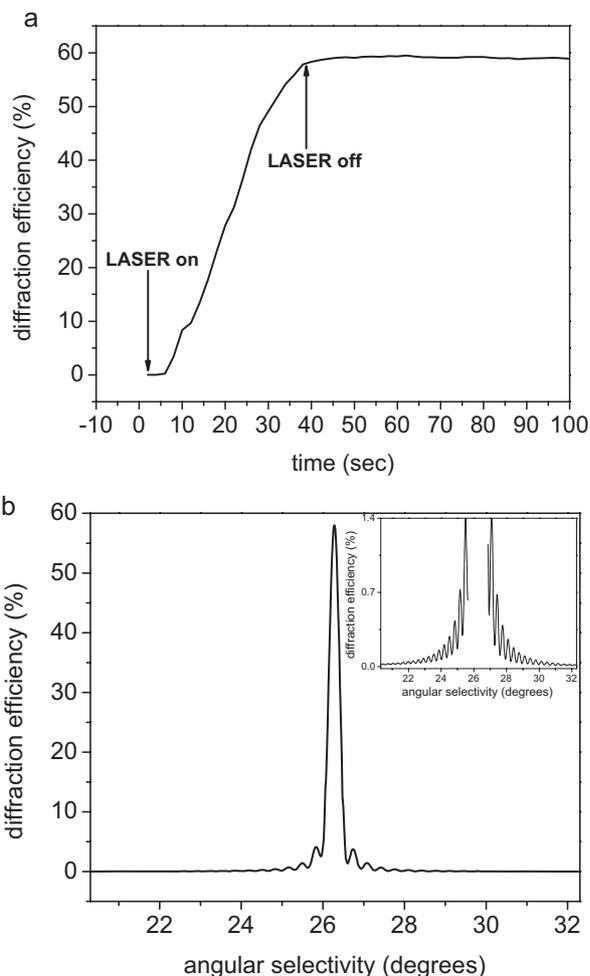


Figure 3. Real-time diffraction efficiency and angular selectivity response of a plane-wave single hologram. a) Growth in first-order diffraction efficiency of a hologram recorded in a 0.5 mm thick film as a function of exposure time. The first-order diffraction efficiency of 58% corresponds to a refractive index modulation (Δn) of 3.5×10^{-4} . b) Diffraction efficiency of the hologram as a function of rotation angle. c) Well-defined fringes accompanying the hologram.

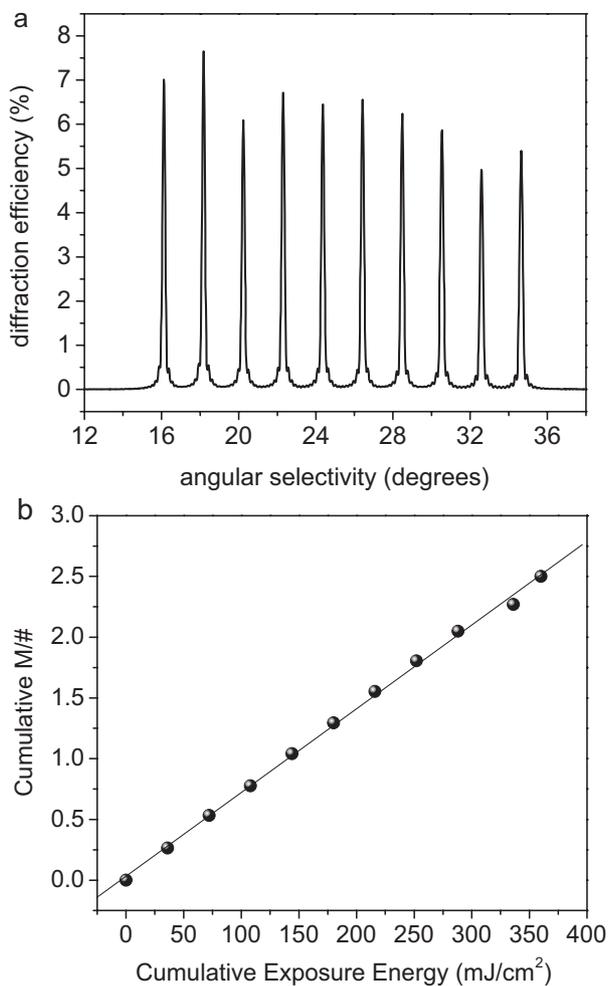


Figure 4. Angular multiplexing: a) Ten holograms were recorded in a 0.5 mm thick film. The gratings were recorded at different angles while the angle between the recording beams was kept constant. The diffraction efficiency as a function of rotation angle was measured subsequently using laser at 632.8 nm. b) Cumulative exposure energy as a function of cumulative M/#. The data points were collected from Figure 4a. Note that the dynamic range of the sample has not reached maximum at the end of exposure.

In the present system, holograms were recorded by irradiation at 407 nm and read-out was performed at 632.8 nm. Ideally, a single light source is desired for recording and reading the information. Hence, new strategies are required to achieve this nonvolatile read-out. One way to realize the nondestructive read-out is by utilizing a sensitizer that can only be excited to its triplet state by using a combination of two laser beams. Therefore, reading the data by utilizing only one laser beam will be insufficient to erase the recorded information. Research in our laboratory is now focused on achieving this nonvolatile read-out in the presented holographic system.

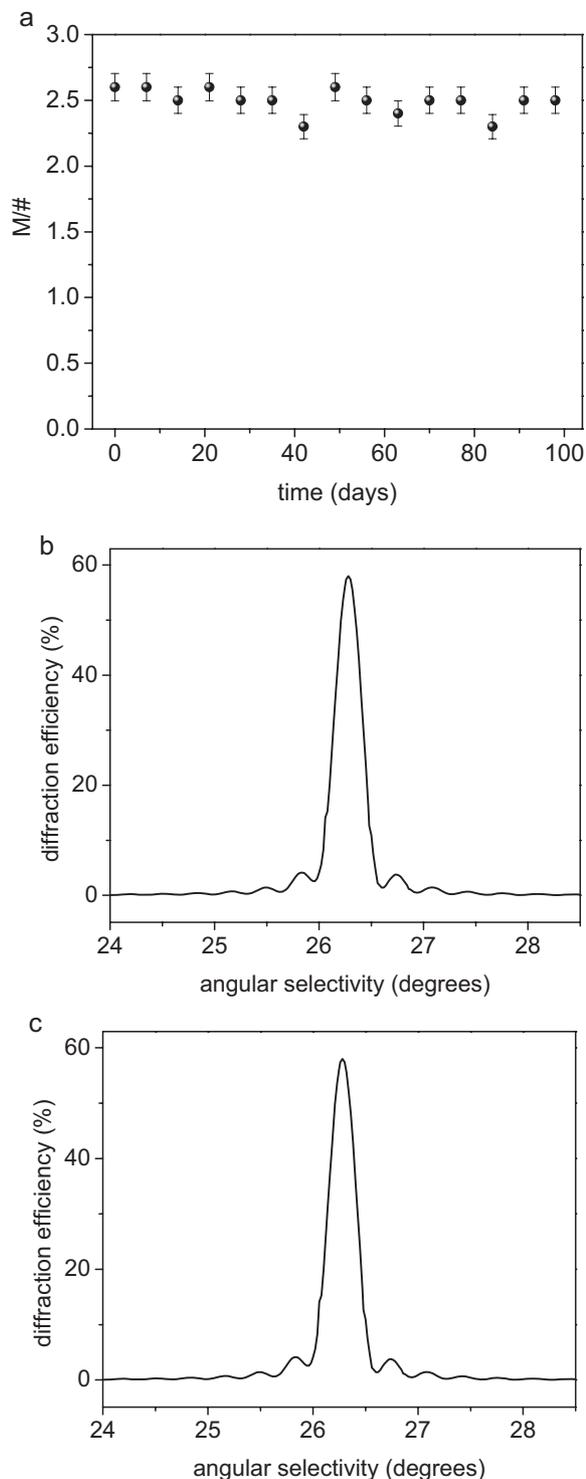


Figure 5. Shelf- and archival-life of the holographic media. a) Storage capacity (M/#) of the material plotted as a function of the time between formulation and the holographic exposure. Various samples were prepared at the same time ($t = 0$), and kept at room temperature until exposure time. b) Angular selectivity curve of a hologram after recording and c) 30 days after recording.

In conclusion, an efficient and solventless processing technique is reported for the fabrication of millimeter-thick, high-quality optical films for holographic storage based on a nondiffusion strategy. Incorporation of crosslinkable Dewar benzene derivatives allow for thick films that display no light scattering and low absorption cross-section at recording wavelength to be prepared. By exploiting the quantum amplification of the photoinduced isomerization of the Dewar benzene groups within the network, high-performance holographic films that have excellent shelf- and archival-life qualities can be obtained. By utilizing 1 mm thick films of the described recording medium, diffraction efficiencies of up to 100%, and M/λ of higher than 6 can be achieved. These results represent a significant advance in the field of three-dimensional data-storage systems, and suggest that Dewar benzene systems are attractive candidates for write-once disk-based holographic memory devices.

Experimental

Experimental details and procedures are described in the Supporting Information.

Received: March 19, 2008

Revised: April 29, 2008

- [1] a) D. Gabor, *Nature* **1948**, 161, 777. b) D. Gabor, *Science* **1972**, 177, 299. c) D. Psaltis, F. Mok, *Sci. Am.* **1995**, 70. d) J. F. Heanue, M. C. Bashaw, L. Hesselink, *Science* **1994**, 265, 749. e) D. Psaltis, *Science* **2002**, 298, 1359. f) M. Hackle, L. Kador, D. Kropp, H. W. Schmidt, *Adv. Mater.* **2006**, 19, 227. g) P. H. Rasmussen, P. S. Ramanujam, S. Hvilsted, R. H. Berg, *J. Am. Chem. Soc.* **1999**, 121, 4738. h) L. Hesselink, S. S. Orlov, A. Liu, A. Akella, D. Lande, R. R. Neurgaonkar, *Science* **1998**, 282, 1089. i) R. H. Berg, S. Hvilsted, P. S. Ramanujam, *Nature* **1996**, 383, 505. j) K. Meerholz, B. L. Volodin, B. K. Sandalphon, B. Kippelen, N. Peyghambarian, *Nature* **1994**, 371, 497. k) B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, B. K. Sandalphon, J. Y. Yao, J. F. Wang, H. Rokel, L. Erskine, N. Peyghambarian, *Science* **1998**, 279, 54. l) S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, *Macromolecules* **2002**, 35, 8751. m) B. Lohse, R. Vestberg, T. M. Ivanov, S. Hvilsted, R. H. Berg, P. S. Ramanujam, C. J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, 45, 4401.
- [2] a) G. T. Sincerbox, *Opt. Mater.* **1995**, 4, 370. b) S. J. Zilker, *Chem-PhysChem* **2002**, 3, 333. c) M. Haw, *Nature* **2003**, 422, 556.
- [3] a) L. Dhar, A. Hale, H. E. Katz, M. Schilling, M. G. Schnoes, F. C. Schilling, *Opt. Lett.* **1999**, 24, 487. b) T. J. Trentler, E. J. Boyd, V. L. Colvin, *Chem. Mater.* **2002**, 12, 1431. c) L. Dhar, A. Hale, H. E. Katz, M. L. Schilling, M. L. Schnoes, US Patent 6103454, **2000**.
- [4] a) T. R. Evans, R. W. Wake, M. M. Sifain, *Tetrahedron Lett.* **1973**, 9, 701. b) J. E. Norton, L. P. Olson, K. N. Houk, *J. Am. Chem. Soc.* **2007**, 128, 7835.
- [5] a) J. G. Gillmore, J. D. Neiser, K. A. McManus, Y. Roh, G. W. Dombrowski, T. G. Brown, J. P. Dinnocenzo, S. Farid, D. R. Robello, *Macromolecules* **2005**, 38, 7684. b) J. P. Dinnocenzo, D. R. Robello, S. Y. Farid, M. R. Mis, L. Ferrar, P. S. Aaron, T. G. Brown, US Patent 7022392 B2, **2006**. c) D. R. Robello, S. Y. Farid, P. J. Dinnocenzo, T. G. Brown, *Proc. SPIE.* **2006**, 6117, 611170. F1.
- [6] P. B. Merkel, Y. Roh, P. J. Dinnocenzo, D. R. Robello, S. Farid, *J. Phys. Chem. A* **2007**, 111, 1188.
- [7] M. Beinhoff, L. D. Bozano, J. C. Scott, K. R. Carter, *Macromolecules* **2005**, 38, 4147.