UV-Photodimerization in Uracil-Substituted Dendrimers for High Density Data Storage

BRIAN LOHSE,[1,2,3] ROBERT VESTBERG,[3] MARIO T. IVANOV,[1,2] SØREN HVILSTED,[4,5] ROLF H. BERG,[1,2] P. S. RAMANUJAM,[1,2] CRAIG J. HAWKER[3]

[1]Polymer Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

[2]Department of Optics and Plasma Research, Risø National Laboratory, DK-4000 Roskilde, Denmark

[3]Department of Chemistry and Materials and Materials Research Laboratory, University of California Santa Barbara, California-93106

[4]Danish Polymer Centre, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

[5]Department of Chemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Received 23 February 2007; accepted 5 May 2007
DOI: 10.1002/pola.22202
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two series of uracil-functionalized dendritic macromolecules based on poly (amidoamine) PAMAM and 2,2-bis(hydroxymethylpropionic acid) bis-MPA backbones were prepared and their photoinduced ($2\pi+2\pi$) cycloaddition reactions upon exposure to UV light at 257 nm examined. Dendrimers up to 4th generation were synthesized and investigated as potential materials for high capacity optical data storage with their dimerization efficiency compared to uracil as a reference compound. This allows the impact of increasing the generation number of the dendrimers, both the number of chromophores, as well as the different steric environments, on the performance of each series of dendrimers to be investigated. The $(uracil)_{12}$-[G-2]-bis-MPA and $(uracil)_8$-[G-1]-PAMAM were observed to have high dimerization efficiency in solution with different behavior being observed for the PAMAM and bis-MPA dendrimers. The dendrimers with the best dimerization efficiency in solution were then examined in the solid state as thin films cast on quartz plates, and their film qualities along with their photodimerization performance studied. High quality films with a transmission response of up to 70% in 55 s. when irradiated at 257 nm with an intensity of 70 mW/cm^2 could be obtained suggesting future use as recording media for optical data storage. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 4401–4412, 2007
Keywords: dendrimers; functionalization of polymers; photochemistry

INTRODUCTION

The continual requirement for higher density storage devices has sparked renewed interest in optical/holographic storage systems and significant effort has been devoted to identifying new types of optical data storage media based on organic materials in order to achieve higher data storage capacity.[1] Previous work has involved the synthesis and evaluation of 1,1′-(α,ω-alkanediyl)bis[pyrimidine] and 1-(ω-bromoalkyl)uracil species[2] as well as di- and oligo-peptides,[3] where information storage was achieved through pho-

Correspondence to: C. J. Hawker (E-mail: hawker@mrl.ucsb.edu)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 45, 4401–4412 (2007)

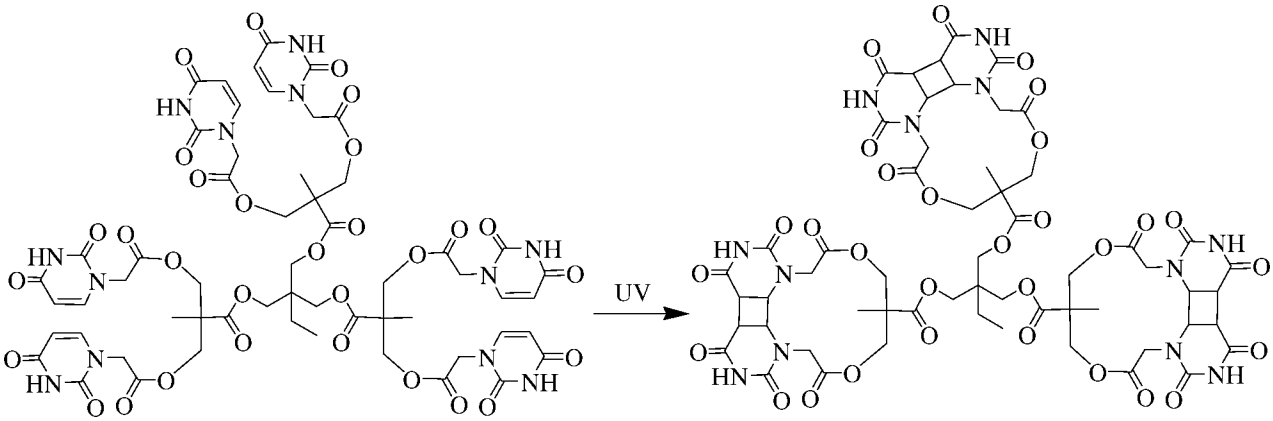


Figure 1. Idealized intramolecular photodimerization process induced by UV-light for a 1st generation uracil bis-MPA dendrimer.

toinduced ($2\pi+2\pi$) cycloaddition reactions on exposure to UV light at 254 nm. The choice of uracil as the chromophore is based on a previous study,[3a] where it was shown that various halogenated pyrimidines, were dehalogenated under irradiation at 254 nm, making the system unsuitable for re-writable systems. In contrast, similar studies showed that uracil derivatives were completely stable under the same conditions.[2] In addition the water solubility of uracil derivatives, coupled with their high dimerization efficiency[4] and ability to record grey levels in thin films leads to a theoretical storage capacity of 1 terabyte[2,5] and strongly suggested the use of uracil as the active component.

In choosing a scaffold for attachment of the uracil moieties, our attention was directed towards dendritic derivatives as they offered a higher density and greater tailorability of the nanoenvironment of the uracil group when compared to traditional alkyl chains or peptide backbones. In addition, dendrimers offer a number of advantages when compared to linear polymers including increased solubility of the uracil derivative[6] and optimal placement of uracil groups for intramolecular chain end coupling as has been shown recently for other dendritic systems.[7] Furthermore, dendrimers offer the potential of efficient intramolecular photodimerization relieving the need for chromophores from other molecular species to be present in the vicinity. A series of uracil-bis-MPA and uracil-PAMAM dendrimers up to 4th generation were therefore prepared and the effect of increasing the generation of the dendrimers on the dimerization efficiency examined. The idealized photodimerization process is shown for the $(uracil)_6$-[G-1]-bis-MPA with 6 chain end uracil groups in Figure 1, and it was reasoned that increasing the generation number would minimize the distance between two uracil chromophores leading to faster photoinduced dimerization.

RESULTS AND DISCUSSION

Representative 2nd generation dendrimeric structures for the uracil substituted bis-MPA series **1–4** and the uracil substituted PAMAM series **5–9** are shown in Figure 2(a,b) respectively and illustrate the highly functionalized, 3-dimensional nature of these chain end functionalized dendrimers. Both series of dendrimers were prepared by a chain end modification strategy, in the case of the PAMAM dendrimers, the terminal, primary amino groups of commercially available PAMAM dendrimers were coupled with the acetyl derivative of uracil to give the desired dendrimers, **5–9**, in high yield (Scheme 1).

For the bis-MPA dendrimers, a divergent growth approach[8,9] starting from 2,2-bis(hydroxymethyl)butan-1-ol gave the hydroxyl-terminated dendrimers in excellent yield, which could then be quantitatively esterified with uracil 1-acetic acid using DCC coupling[10a] in dry DMF (Scheme 2). The reaction was monitored by TLC and purification of the lower generation derivatives could be accomplished by flash chromatography; however, due to the increased polarity of higher generation dendrimers a multi-step precipitation strategy was found to be effective and afforded high yields of essentially monodisperse uracil-bis-MPA dendrimers (Fig. 3).[10b]

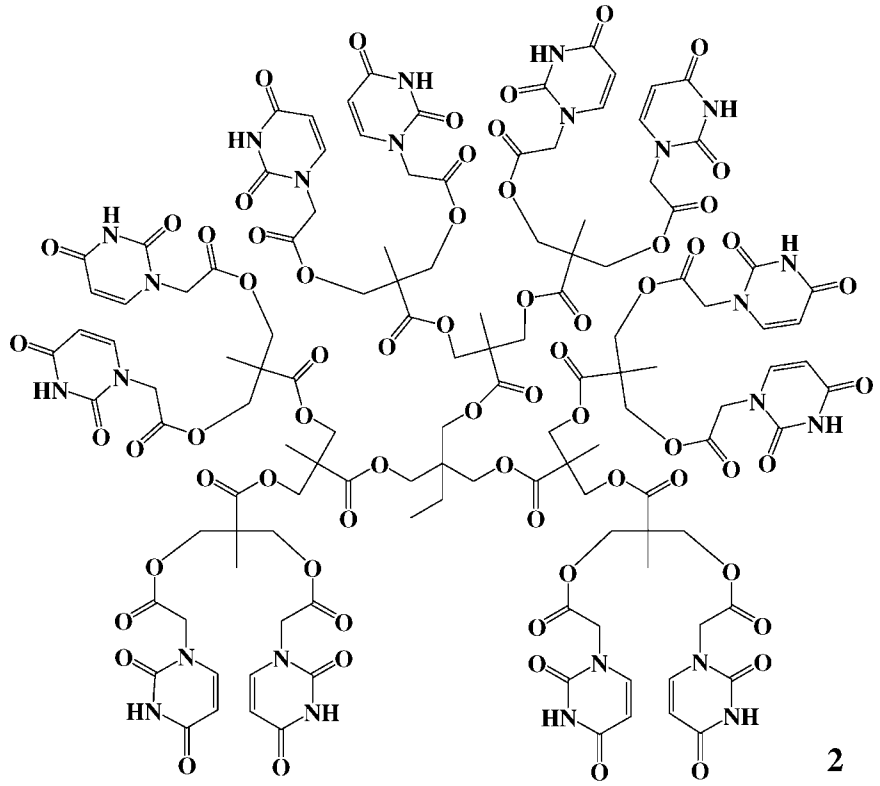


Figure 2. (a) Uracil-bis-MPA 2nd generation dendrimer, $(uracil)_{12}$-[G-2]-bis-MPA, **2**. (b) Uracil-PAMAM 2nd generation dendrimer, $(uracil)_{16}$-[G-2]-PAMAM, **6**.

To demonstrate the effectiveness of these synthetic strategies and the high level of purity for the uracil derivatives, these materials were fully characterized by ^{1}H, ^{13}C NMR spectroscopy, and GPC chromatography. In each case essentially complete functionalization of the chain end groups by uracil units was observed in addition to the expected low polydispersities and increasing molecular size with generation number for each dendrimer series (Fig. 4).

The effect of both generation number and the nature of the dendritic repeat units on the efficiency of the photochemical uracil-uracil dimerization reaction for the two series of functionalized dendrimers, **1**–**4** and **5**–**9**, were then studied in aqueous solution using an experimental set-up similar to that described previously.[3a] The concentration of the dendrimer solution was varied to provide an absorbance of approximately 1.0 and the sample was measured before irradiation and after each irradiation period (i.e. 15, 30, and 60 min). The decrease in absorbance at 260 nm is an indication of the dimerization efficiency as the starting uracil moieties show a strong peak at $\sim$ 260 nm due to the pyrimidine ring while for the dimer, reaction of the 5,6-double bond gives rise to a cyclobutane unit, which leads to a significant decrease in absorption.

Initial examination of uracil as a reference compound showed a slow decrease in the absorbance at 260 nm [Fig. 5(a)] and after 60 min of irradiation a significant peak is still observed. In direct contrast, irradiation of the second generation, bis-MPA dendrimer, $(uracil)_{12}$-[G-2], **2**, leads to a rapid coupling of uracil units and high dimerization efficiency [Fig. 5(b)].

These initial results clearly show a significant dendritic effect leading to an acceleration of the uracil dimerization reaction. To further confirm these results and develop accurate structure/property relationships for both series of dendrimer, absorption measurements of the uracil-bis-MPA and uracil-PAMAM species synthesized in this work, before irradiation and after 15, 30, and 60 min of irradiation in solution (H_2O) were undertaken and are shown in Figure 6(a,b), respectively.

To understand the structure/property relationships for both series of dendrimers, it is instructive to examine the change in absorption values (λ_{max}) or dimerization efficiency for both series of dendrimers with generation number

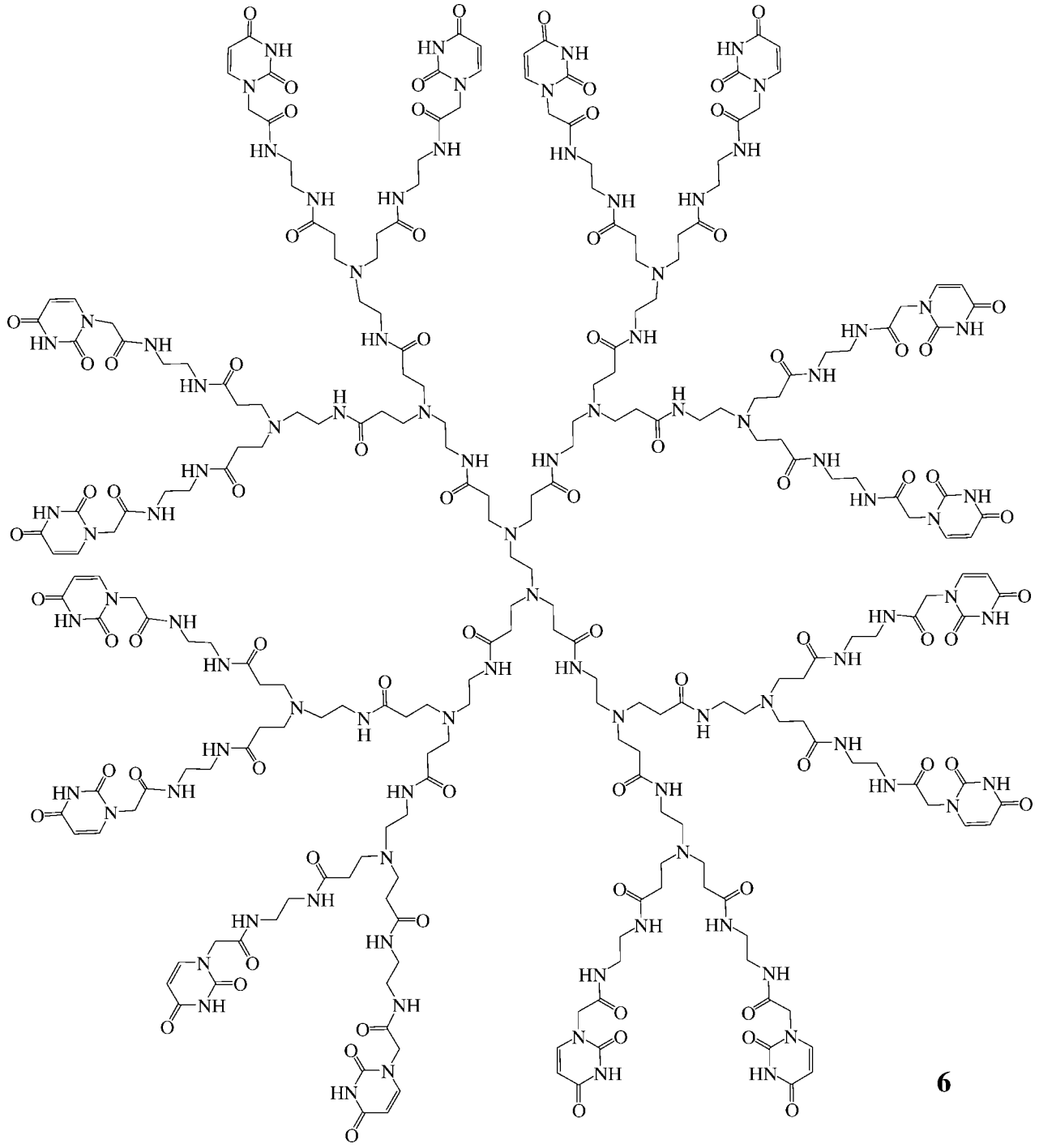
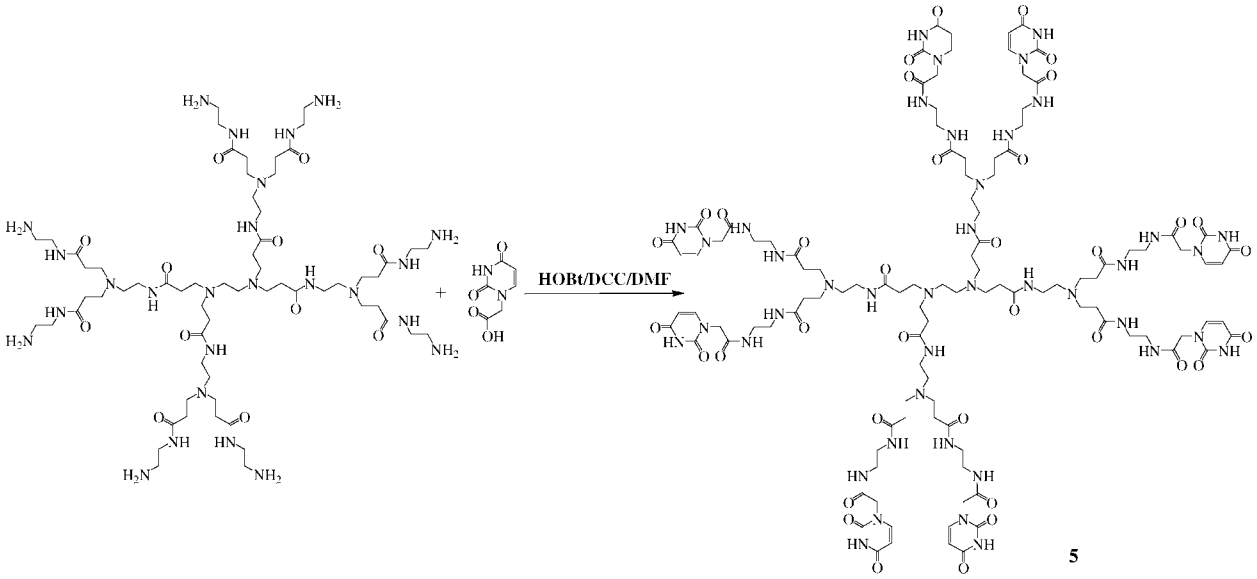
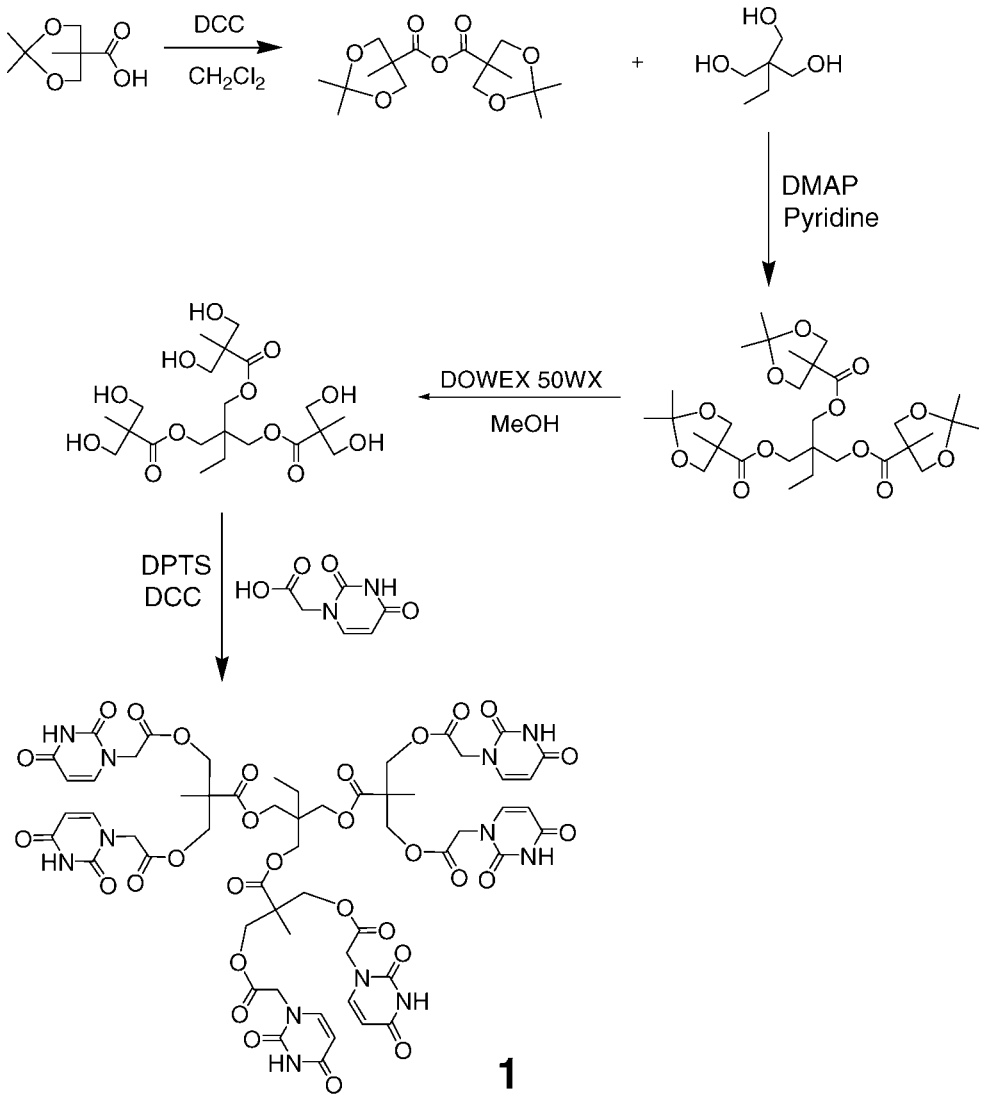


Figure 2. (Continued)

(Fig. 7). Because of the different core functionality (3 for bis-MPA and 4 for PAMAM dendrimers) the results are normalized with respect to the number of uracils per dendrimer/generation. In both cases, a high, maximum dimerization efficiency of greater than 80% was observed for lower generation dendrimers with 8 and 12 uracil units for the uracil-PAMAM and uracil-bis-MPA dendrimers species respectively. As the generation number for the uracil-PAMAM series increased the dimerization efficiency decreased slightly to ca. 70–75% and remained relatively constant and significantly greater than monomer uracil. In direct contrast, a sharp decrease



Scheme 1. General synthetic strategy for uracil chain end functionalized dendrimers, $(uracil)_8$-[G-1]-PAMAM, **5** as shown.



Scheme 2. Synthetic strategy for the preparation of uracil-bis-MPA dendrimers such as $(uracil)_6$-[G-1]-bis-MPA, **1**.

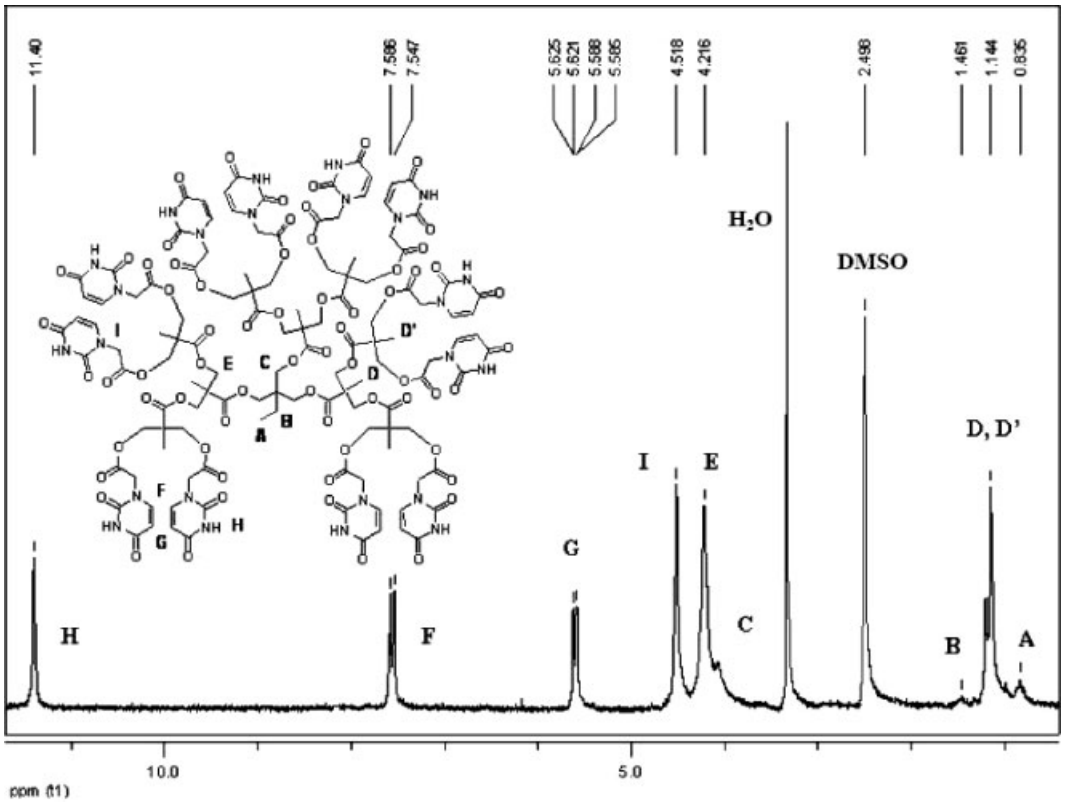


Figure 3. ^{1}H NMR spectrum of the 2nd generation uracil dendrimer, $(uracil)_{12}$-[G-2]-bis-MPA, **2**.

in performance for the bis-MPA derivatives was observed and at generation 4 with 48 chain end uracil groups, a lower dimerization efficiency (20%) than uracil itself was observed. The significant decrease in photodimerization efficiency in the case of the bis-MPA dendrimers is believed to be due to the structural rigidity of the bis-MPA repeat units which does not allow sufficient conformational mobility at higher generations for efficient intramolecular dimerization of the chain end uracil groups. For the uracil-PAMAM dendrimers, the repeat unit is larger and more flexible, which allows the uracil units to adopt the appropriate conformation for dimerization. In addition, the presence of H-bonding amide and amino groups throughout the internal structure of the PAMAM dendrimer, which are absent in the bis-MPA case, may lead to preferential stabilization and packing of the uracil end group.

To discount agglomeration or significant intermolecular reaction/crosslinking as a cause of this strikingly different behavior, dynamic light scattering measurements of all samples showed essentially the same hydrodynamic diameters before and after reaction which suggests that the photodimerization reaction was primarily intra-molecular in both cases. The solid-state behavior of compounds showing high dimerization efficiency (>75%); uracil-bis-MPA derivatives, **1**, **2** and uracil-PAMAM dendrimers **5–7** was then examined in terms of their application as a recording medium for optical data storage.

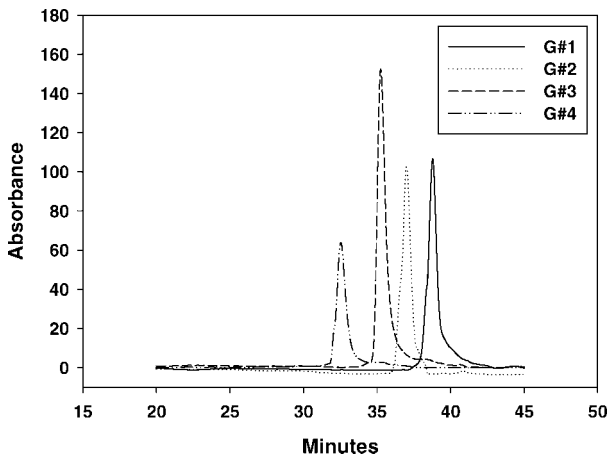


Figure 4. Overlay of GPC chromatographs for the $G = 1$ to $G = 4$ series of uracil-bis-MPA dendrimers, **1–4**.

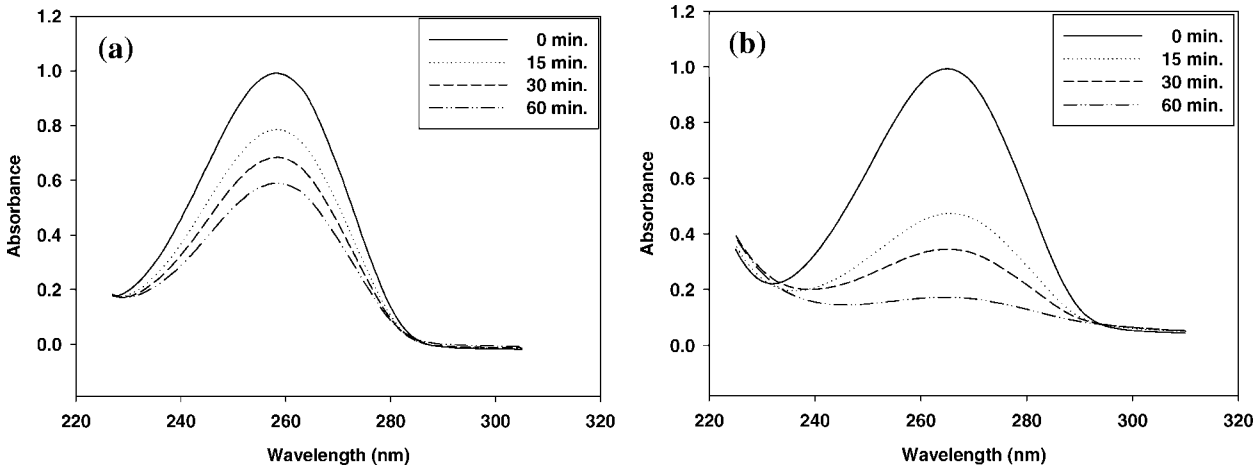


Figure 5. Change in UV spectra on irradiation for (a) uracil in water and (b) $(uracil)_{12}$-[G-2]-bis-MPA, **2** in water at $t = 0$, 15, 30, and 60 min.

Photodimerization Processes in the Dendrimer Films

The absorption spectrum of an $(uracil)_8$-[G-1]-PAMAM, **6**, film before and after irradiation, for 210 min at 257 nm is shown in Figure 8 with an isosbestic point being identified at 286 nm. It should be noted that the long irradiation time is due to the very low power of the UV laser used in this experiment <0.5 mW/cm^2.

Tomlinson and coworkers[11] have developed a theory for the dynamics of photodimerization processes in films of arbitrary thickness. Using their model and matching the experimentally obtained transmission makes it possible to obtain with the simulated transmission a value for the absorption cross-section as a function of time. In the Experimental Section, the preparation of films for transmission measurements is discussed. The thickness of the film was 2.5 μm.

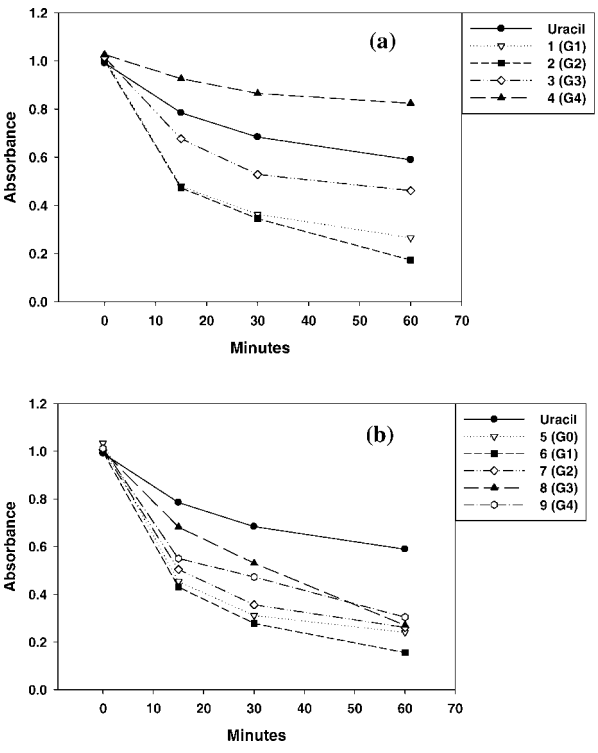


Figure 6. Decrease in absorption at 260 nm upon irradiation in aqueous solution for (a) uracil and uracil-bis-MPA dendrimers, **1–4**, and (b) uracil and uracil-PAMAM dendrimers, **5–9**. The lines between points are added to help the reader.

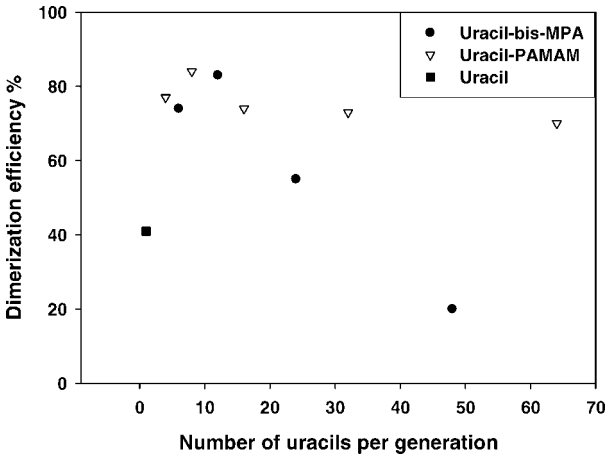


Figure 7. The dimerization efficiency and its dependency of the number of uracil groups per generation/dendrimer for uracil-bis-MPA **1–4** and uracil-PAMAM **5–9** dendrimers in aqueous solution.

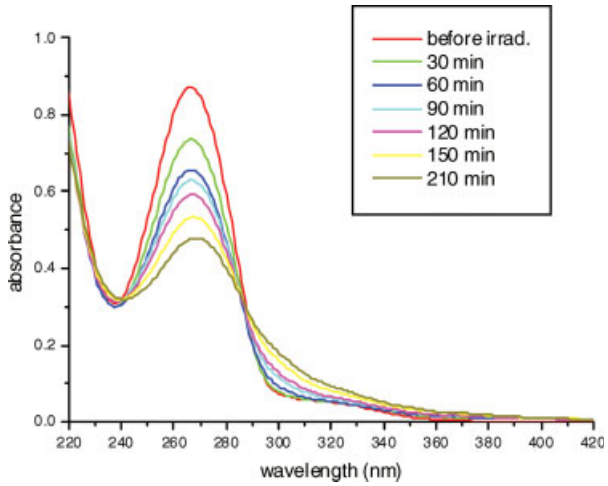


Figure 8. Absorption spectrum of an $(uracil)_8$-[G-1]-PAMAM, **6**, film before and after irradiated at 257 nm, with a low intensity power source (<0.5 mW/cm^2), an isosbestic point is observed at 286 nm.

A laser beam from a frequency doubled argon ion laser at 257 nm, with an intensity of 70 mW/cm^2 was sent through the film, and the transmission through the film was monitored by means of a power-meter. The power-meter was connected to a pc for real-time measurements. From the initial absorption and final transmission, it is possible to simulate the transmission through the film as a function of time, as outlined previously.[2] The simulated transmission curve is shown as the line connecting dots in Figure 9, which allows the absorption cross-section to be calculated as 1.7×10^{-18} cm^2. The small mismatch between the theory and experiment is attributed to a distribution in the quantum efficiency for dimerization and the random arrangement of dendrimer molecule in the matrix which will vary from location to location, resulting in a range of quantum efficiencies. The obtained cross-section compares favorably with those estimated (10^{-17} to 10^{-18} cm^2) by Tomlinson et al.[11a] for different chromophores.

Holographic Grating Recording

As the demands for digital storage capacity in a variety of applications increases, alternative technologies are being examined with the exploitation of holographic strategies holding significant promise. Using a thick holographic storage medium and making use of multiplexing techniques, it has been proposed that terabyte storage is possible. However, one of the main challenges to the successful implementation of this technology has been a lack of suitable materials. The high efficiency achieved with these dendritic uracil derivatives prompted thick films of dendrimers to be evaluated as recording holographic gratings at UV wavelengths. The experimental set-up has been described in detail previously[2] and involves a diffraction grating inscribed in a dendrimer film through interference of two laser beams derived from the same laser source. The grating is read-out with a 3 mW laser operating at 405 nm, which is outside the absorption band of uracil. The interbeam angle between the interfering beams is 6° corresponding to a grating period of 2.5 μm and a diffraction efficiency of approximately 0.7% was achieved within 5 s (Fig. 10).

As reported earlier,[2] it was found that this recording process gives rise to a patterned surface relief in the thin film. In order to confirm the presence of the surface relief, the irradiated area was scanned with an atomic force microscope (Fig. 11). The maximum height of the surface relief obtained here is 165 nm, and it should be noted that the surface relief height does not change with the film thickness, but with the laser power applied onto the film. The surface relief arises because of the change in the dimensions of the film on dimerization.

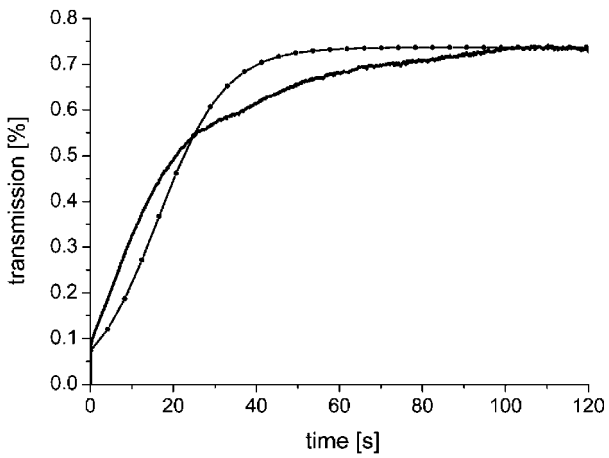


Figure 9. Transmission through a thin film of an $(uracil)_8$-[G-1]-PAMAM, **6**, film as a function of time. The solid curve is the experimental measurement, while the line joining dots is the simulated curve.

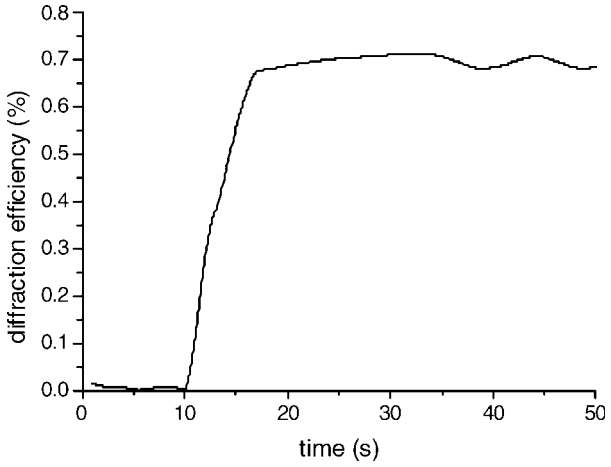


Figure 10. Thin film diffraction efficiency of an $(uracil)_{16}$-[G-2]-PAMAM, **7**, film as a function of time. The grating is recorded at 257 nm and read-out at 405 nm. The recording laser beam is turned on at t = 10 s.

CONCLUSION

We have presented new, high density optical data storage media based on well-defined dendrimers as scaffolds and photoreactive uracil groups at the chain ends of the dendrimers. The monodispersity of these materials coupled with the ability to accurately vary the number and environment of the chain end uracil groups permitted a structure/property relationship to be developed for two series of uracil-functionalized dendritic macromolecules based on poly(amidoamine) PAMAM and 2,2-bis(hydroxymethylpropionic acid) bis-MPA backbones. The $(uracil)_{12}$-[G-2]-bis-MPA, **2**, and $(uracil)_8$-[G-1]-PAMAM, **6**, derivatives were observed to have high dimerization efficiency in solution with no increase in efficiency at higher generations with significant decreases being observed for bis-MPA dendrimers. High dimerization efficiency was also observed in the solid state with a transmission response of up to 70% in 5 s being obtained which suggests future use as recording media for optical data storage.

EXPERIMENTAL SECTION

NMR spectra were recorded on a Bruker 200 MHz apparatus. Irradiation of the compounds in solution was performed using a Spectroline® UV-lamp, model ENF-260C/ FE (CM-10), and recorded on a Shimadzu UV-1700 spectrophotometer. The irradiation of the films were done using a frequency doubled argon laser at 257 nm with a blue GaN laser (405 nm) used for reading out holographic gratings written at 257 nm. MALDI-TOF mass spectra were recorded on a Bruker Reflex IV, using the following method: Reflectron MALDI-TOF with pulsed ion extraction (PIE^{TM}), positive ion analysis, where the sample was either applied pure, mixed with the matrix reagent 2,5-dihydroxybenzoic acid (10 mg/mL MeOH)). TLC was done in the solvent system ethyl acetate/ hexane (3/1 v/v) ratio, using ALUGRAM® SIL G/UV_{254} 0.20 mm silica gel 60. GPC was performed using a Waters 2690, Separation Module equipped with Waters 2410 Refractive Index Detector and Autosampler. All molecular weights are relative to polystyrene standards. The GPC was equipped with four Ultrastyragel linear mixed-bed columns (HR 0.5, HR 2, HR 4, and HR 5). DMF with 0.1% LiBr was used as the eluent at constant flow rate of 1.0 mL/min, at 30 °C. The concentrations of all the samples analyzed were 10 mg/mL.

Preparation of Films

A quartz plate was cleaned thoroughly using a Piranha solution, (warm mixture of H_2SO_4 and H_2O_2) (warning! can be explosive) and approximately 1.0 mg of dendrimer was dissolved in a 1% solution of (3-(methylamino)propyl)-trimethoxysilane (MAP), in Milli-Q water (1 mL). Then the mixture was filtered through a 0.22 μm filter, Millex®-GS, and applied directly onto

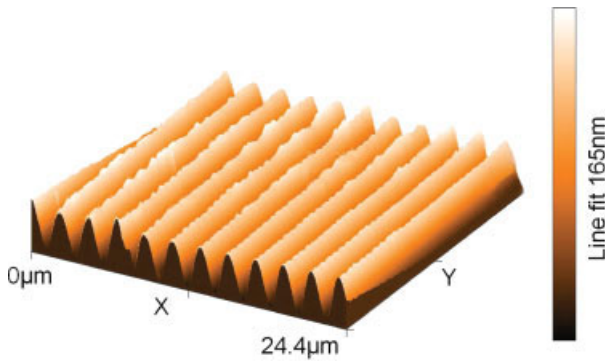


Figure 11. Atomic force microscope scan of the diffraction grating recorded in a film (24 × 24.4 μm^2) of $(uracil)_{16}$-[G-2]-PAMAM, **7**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the cleaned quartz plate, and finally inserted into an oven for 1 h at 100 °C. After baking the mixture in the oven, a hard and transparent film was obtained, the film was stable at room temperature, under and after testing of the film, and no changes in the film quality was observed.

General Synthesis of Uracil-bis-MPA-TMP Dendrimers—$(Uracil)_{12}$-[G-2]-bis MPA, 2

The bis-MPA dendrimers, generations 1–4,[8–10] and the uracil-1-acetic acid were prepared according to literature.[3a] For each generation the coupling procedure was as described below for the 2nd generation derivative, **2**. To a solution of $(HO)_{12}$-[G-2]-TMP, (1.00 g, 0.85 mmol) dissolved in a minimum amount of dry DMF (5 mL) was added uracil-1-acetic acid (2.60 g, 15.2 mmol), dissolved in a minimum amount of dry DMF (10 mL), followed by DCC (4.20 g, 20.3 mmol) and DPTS (0.60 g, 2.04 mmol). The reaction mixture was then stirred under nitrogen at rt. overnight. The reaction mixture was filtered, and the DMF was reduced in volume to ca. 5 mL and this solution precipitated into diethyl ether, giving a pale yellow powder. The powder was then again dissolved in a minimum of DMF and precipitated in water to give the desired $(Uracil)_{12}$-[G-2]-bis MPA, **2**, as a white powder in 85% yield; ^{1}H NMR (DMSO-d_6) δ: 0.95 (t, 3H, J = 14.0 Hz), 1.14 (s, 18H), 1.30 (s, 9H), 1.56 (dd, 2H, J = 28 Hz), 3.63 (dd, 24H, J = 40 Hz), 4.14 (s, 6H), 4.30 (dd, 12H, J = 38 Hz), 4.15 (s, 24H), 5.53 (dd, 12H, J = 8 Hz, J = 2 Hz), 7.65 (d, 12H, J = 8 Hz), 11.20 (broad, 12H, NH); ^{13}C NMR (DMSO-d_6) δ: 7.89, 17.28, 18.24, 23.96, 26.03, 42.65, 47.90, 51.64, 65.07, 65.74, 66.08, 173.83, 175.82, 170.70, 161.27, 151.47, 146.60, 101.22, 49.15. *m/z* (MALDI-TOF MS) [Found: 3043.64 $(C_{123}H_{134}N_{24}O_{66} + K)^+$ calculated 3043.60]. GPC: PDI = 1.10.

Using the same procedure, the first generation derivative afforded $(uracil)_6$-[G-1]-bis-MPA, **1**, as a white solid in 91% yield; ^{1}H NMR (DMSO-d_6) δ: 0.95 (t, 3H, J = 15.2 Hz), 1.16 (s, 9H), 1.56 (dd, 2H, J = 22.4 Hz), 3.60 (d, 6H, J = 11.2 Hz), 3.69 (d, 6H, J = 11.2 Hz), 4.10 (s, 12H), 5.53 (dd, 6H, J = 8 Hz, J = 2 Hz), 7.65 (d, 6H, J = 8 Hz), 11.20 (broad, 6H, NH); ^{13}C-NMR (DMSO-d_6) δ: 8.36, 17.88, 24.63, 43.07, 52.33, 65.09, 66.04, 176.70, 170.70, 161.27, 151.47, 146.60, 101.22, 49.15. *m/z* (MALDI-TOF MS) [Found: 1434.27 $(C_{57}H_{62}N_{12}O_{30} + K)^+$ calculated 1434.40]. GPC: PDI = 1.03.

Using the same procedure, the third generation derivative afforded $(uracil)_{24}$-[G-3]-bis-MPA, **3**, as a white solid in 90% yield; ^{1}H NMR (DMSO-d_6) δ: 1.00 (t, 3H, J = 14.4 Hz), 1.15 (s, 36H), 1.30 (s, 18H), 1.34 (s, 9H), 1.60 (dd, 2H, J = 28.0 Hz), 3.66 (dd, 48H, J = 40 Hz), 4.19–4.34 (m, 42H), 4.15 (s, 48H), 5.53 (dd, 24H, J = 8 Hz, J = 2 Hz), 7.65 (d, 24H, J = 8 Hz), 11.20 (broad, 24H, NH); ^{13}C NMR (DMSO-d_6) δ: 8.14, 17.37, 18.18, 18.37, 26.53, 42.83, 47.91, 51.74, 65.83, 66.13, 67.00, 173.49, 173.77, 175.90, 170.70, 161.27, 151.47, 146.60, 101.22, 49.15. *m/z* (MALDI-TOF MS) [Found: 6224.45 $(C_{255}H_{278}N_{48}O_{138} + H)^+$ calculated 6224.19]. GPC: PDI = 1.01.

Using the same procedure, the fourth generation derivative afforded $(uracil)_{48}$-[G-4]-bis-MPA, **4**, as a white solid in 87% yield; ^{1}H NMR (DMSO-d_6) δ: 1.00 (t, 3H, J = 10.4 Hz), 1.15 (s, 72H), 1.31 (s, 36H), 1.33 (s, 18H), 1.38 (s, 18H) 3.59–3.69 (m, 96H), 4.24–4.37 (m, 90H), 4.15 (s, 96H), 5.53 (dd, 96H, J = 8 Hz, J = 2 Hz), 7.65 (d, 96H, J = 8 Hz), 11.20 (broad, 96H, NH); ^{13}C NMR (DMSO-d_6) δ: 8.24, 17.34, 18.17, 18.23, 18.33, 25.88, 42.83, 42.71, 47.76, 47.90, 48.01, 51.61, 65.29, 65.74, 65.98, 66.79, 66.95, 173.17, 173.25, 173.68, 175.81, 170.70, 161.27, 151.47, 146.60, 101.22, 49.15. *m/z* (MALDI-TOF MS) [Found: 12,700.01 $(C_{519}H_{566}N_{96}O_{282} + K)^+$ calculated 12,699.63]. GPC: PDI = 1.03.

General Synthesis of Uracil-PAMAM Dendrimers; $(uracil)_{16}$-[G-2]-PAMAM, 7

To a solution of the 2nd generation PAMAM (555 mg, 1.71×10^{-4} mmol) dissolved in a minimum amount of dry DMF (5 mL) was added uracil-1-acetic acid (0.70 g, 4.1×10^{-3} mmol) dissolved in a minimum amount of dry DMF (5 mL) followed by HOBt (737 mg, 5.46×10^{-4} mmol) and DCC (1.13 g, 5.46×10^{-4} mmol). The reaction mixture was then stirred under argon at rt. overnight, followed by filtration and removal of the DMF by distillation. The yellow residue was then dissolved in a minimum of methanol and precipitated in diethyl ether, giving a white yellowish powder. This procedure was repeated (2×) to give $(uracil)_{16}$-[G-2]-PAMAM, **7**, as a white solid in 92% yield; ^{1}H NMR (DMSO-d_6) δ: 10.30 (broad, 16H, NH), 7.55 (d, 16H, J = 8 Hz), 5.55 (dd, 16H, J = 8

Hz, J = 2 Hz), 4.05 (s, 32H), 8.01 (16H, NH), 3.12 (64H), 8.25 (28H, NH), 2.25 (56H), 2.71 (56H), 2.62 (24H), 3.30 (24H), 2.48 (4H); ^{13}C NMR (DMSO-d_6) δ: 164.38, 151.54, 143.30, 101.23, 49.32, 167.54, 42.35, 43.5, 171.61, 54.2, 42.8, 170.07, 33.79, 47.97, 50.0. *m/z* (MALDI-TOF MS) [Found: 5691.20 ($C_{238}H_{352}N_{90}O_{76}$ + H)$^+$ calculated 5690.90]. GPC: PDI = 1.07.

Using the same procedure, the zero generation derivative afforded (uracil)$_4$-[G-0]-PAMAM, **5**, as a white solid in 94% yield; ^{1}H NMR (DMSO-d_6) δ: 10.30 (broad, 4H, NH), 7.55 (d, 4H, J = 8 Hz), 5.55 (dd, 4H, J = 8 Hz, J = 2 Hz), 4.05 (s, 8H), 8.01 (4H, NH), 3.12 (16H), 8.25 (4H, NH), 2.25 (8H), 2.71 (8H), 2.48 (4H); ^{13}C NMR (DMSO-d_6) δ: 164.38, 151.54, 143.30, 101.23, 49.20, 167.54, 42.35, 43.5, 170.07, 33.79, 47.97, 50.0. *m/z* (MALDI-TOF MS) [Found: 1160.30 ($C_{46}H_{64}N_{18}O_{16}$ + K)$^+$ calculated 1164.11]. GPC: PDI = 1.04.

Using the same procedure, the first generation derivative afforded (uracil)$_8$-[G-1]-PAMAM, **6**, as a white solid in 94% yield; ^{1}H NMR (DMSO-d_6) δ: 10.30 (broad, 8H, NH), 7.55 (d, 8H, J = 8 Hz), 5.55 (dd, 8H, J = 8 Hz, J = 2 Hz), 4.05 (s, 16H), 8.01 (8H, NH), 3.12 (32H), 8.25 (12H, NH), 2.25 (24H), 2.71 (24H), 2.62 (8H), 3.30 (8H), 2.48 (4H); ^{13}C NMR (DMSO-d_6) δ: 164.38, 151.54, 143.30, 101.23, 49.32, 167.54, 42.35, 43.5, 171.61, 54.2, 42.8, 170.07, 33.79, 47.97, 50.0. *m/z* (MALDI-TOF MS) [Found: 2647.70 ($C_{110}H_{160}N_{42}O_{36}$ + H)$^+$ calculated 2647.72]. GPC: PDI = 1.04.

Using the same procedure, the third generation derivative afforded (uracil)$_{32}$-[G-3]-PAMAM, **8**, as a white solid in 90% yield; ^{1}H NMR (DMSO-d_6) δ: 10.30 (broad, 32H, NH), 7.55 (d, 32H, J = 8 Hz), 5.55 (dd, 32H, J = 8 Hz, J = 2 Hz), 4.05 (s, 64H), 8.01 (32H, NH), 3.12 (128H), 8.25 (60H, NH), 2.25 (120H), 2.71 (120H), 2.62 (56H), 3.30 (56H), 2.48 (4H); ^{13}C NMR (DMSO-d_6) δ: 164.38, 151.54, 143.30, 101.23, 49.32, 167.54, 42.35, 43.5, 170.07, 33.79, 47.97, 54.2, 42.8, 50.0. *m/z* (MALDI-TOF MS) [Found: 11,932.13 ($C_{494}H_{736}N_{186}O_{156}$ + DHB)$^+$ calculated 11,930.29]. GPC: PDI = 1.07.

Using the same procedure, the fourth generation derivative afforded (uracil)$_{64}$-[G-4]-PAMAM, **9**, as a white solid in 85% yield; ^{1}H NMR (DMSO-d_6) δ: 10.30 (broad, 64H, NH), 7.55 (d, 64H, J = 8 Hz), 5.55 (dd, 64H, J = 8 Hz, J = 2 Hz), 4.05 (s, 128H), 8.01 (64H, NH), 3.12 (256H), 8.25 (124H, NH), 2.25 (8H), 2.71 (8H), 2.48 (4H); ^{13}C NMR (DMSO-d_6) δ: 164.38, 151.54, 143.30, 101.23, 167.54, 42.35, 43.5, 170.07, 33.79, 47.97, 50.0. *m/z* (MALDI-TOF MS) [Found: 24,065.41 ($C_{1070}H_{1568}N_{314}O_{316}$ + DHB)$^+$ calculated 24,039.84]. GPC: PDI = 1.05.

We thank the Danish Technical Research Council (STVF) and the National Science Foundation under the MRSEC program (UCSB MRL, DMR-0520415) for financial support. The authors wish to thank Dr. Krystyna R. Brzezinska from MRL at UCSB for her help with MALDI-TOF and GPC analysis.

REFERENCES AND NOTES

1. (a) Berg, R. H.; Hvilsted, S.; Ramanujam, P. S. Nature 1996, 383, 505–508; (b) Rasmussen, P. H.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. J Am Chem Soc 1999, 121, 4738–4743; (c) Gabor, D. Nature 1948, 161, 777–778; (d) Gabor, D. Science 1972, 177, 299–313; (e) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. Macromolecules 1992, 25, 2268–2273; (f) Meerholz, K.; Volodin, B. L.; Sandalphon; Kippelen, B.; Peyghambarian, N. Nature 1994, 371, 497–500; (g) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. Chem Eur J 1998, 4, 699–706.
2. Lohse, B.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. Chem Mater 2006, 18, 4808–4816.
3. (a) Lohse, B.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. J Pep Sci 2005, 11, 499–505; (b) Lohse, B.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. J Photochem Photobiol A 2007, submitted for publication.
4. Lohse, B.; Berg, R. H.; Hvilsted, S.; Ramanujam, P. S. Jpn J Appl Phys 2006, 45, 488–492.
5. Ramanujam, P. S.; Berg, R. H. Appl Phys Lett 2004, 85, 1665–1667.
6. (a) Hawker, C. J.; Fréchet, J. M. J. J Am Chem Soc 1990, 112, 7638–7647; (b) Hawker, C. J.; Wooley, K. L. Science 2005, 309, 1200–1204.
7. (a) Lemcoff, N. G.; Spurlin, T. A.; Gewirth, A. A.; Zimmerman, S. C.; Beil, J. B.; Elmer, S. L.; Vandeveer, H. G. J Am Chem Soc 2004, 126, 11420–11421; (b) Elmer, S. L.; Zimmerman, S. C. J Org Chem 2004, 69, 7363–7366; (c) Beil, J. B.; Lemcoff, N. G.; Zimmerman, S. C. J Am Chem Soc 2004, 126, 13576–13577; (d) Taranekar, P.; Park, J.-Y.; Patton, D.; Fulghum, T.; Ramon, G. J.; Advincula, R. Adv Mater 2006, 18, 2461–2465; (e) Adeli, M.; Haag, R. J Polym Sci Part A: Polym Chem 2006, 44, 5740–5749; (f) Shabat, D. J Polym Sci Part A: Polym Chem 2006, 44, 1569–1578; (g) Dvornic, P. R. J Polym Sci Part A: Polym Chem 2006, 44, 2755–2773; (h) Kim, C. J.; Song, E. S.; Kim, H. J.; Park, C.; Kim, J. K.; Kim, Y. C.; Yu, J. W.; Kim, C. J Polym Sci Part A: Polym Chem 2006, 44, 5855–5862; (i) Steffensen, M. B.; Hollink, E.; Kuschel, F.; Bauer, M.; Simanek, E. E. J Polym Sci Part A: Polym Chem 2006, 44, 3411–3433.

8. (a) Ihre, H.; Hult, A. J Am Chem Soc 1996, 118, 6388–6395; (b) Malkoch, M.; Malmström, E.; Hult, A. Macromolecules 2002, 35, 8307–8314; (c) Malkoch, M.; Claesson, H.; Löwenhielm, P.; Malmström E.; Hult A. J Polym Sci Part A: Polym Chem 2004, 42, 1758–1767; (d) Hietala, S.; Nyström, A.; Tenhu, H.; Hult, A. J Polym Sci Part A: Polym Chem 2006, 44, 3674–3683; (e) Vestberg, R.; Nilsson, C.; Lopes, C.; Lind, P.; Eliasson, B.; Malmström, E. J Polym Sci Part A: Polym Chem 2005, 43 1177–1187.
9. (a) Ihre, H.; Hult, A.; Fréchet, J. M. J.; Gitsov, I. Macromolecules 1998, 31, 4061–4068; (b) Wu, P.; Malkoch, M.; Hunt, J. N.; Vestberg, R.; Kaltgrad, E.; Finn, M. G.; Fokin, V. V.; Sharpless, K. B.; Hawker, C. J. Chem Commun 2005, 5775–5777.
10. (a) Moore, J. S.; Stupp, S. I. Macromolecules 1990, 23, 65–77; (b) Other recent examples of uracil containing polymers—Tang, H.; Radosz, M.; Shen, Y. J Polym Sci Part A: Polym Chem 2006, 44, 6607–6615; (c) Lutz, J. F.; Thünemann, A. F.; Nehring, R. J Polym Sci Part A: Polym Chem 2005, 43, 4805–4818.
11. (a) Tomlinson, W. J.; Chandross, E. A.; Fork, L.; Pryde, C. A.; Lamola, A. A. Appl Opt 1972, 11, 533–548; (b) Tomlinson, W. J. Appl Opt 1972, 11, 823–831; (c) Tomlinson, W. J. Appl Opt 1976, 15, 821–826.