



Synthesis of photoresponsive polyamidoamine (PAMAM) dendritic architecture

Samaresh Ghosh and Ajit K. Banthia*

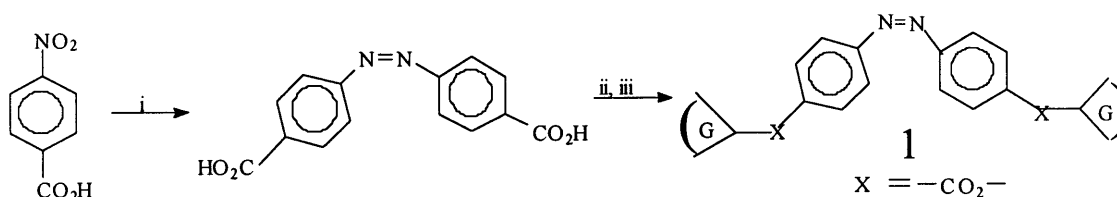
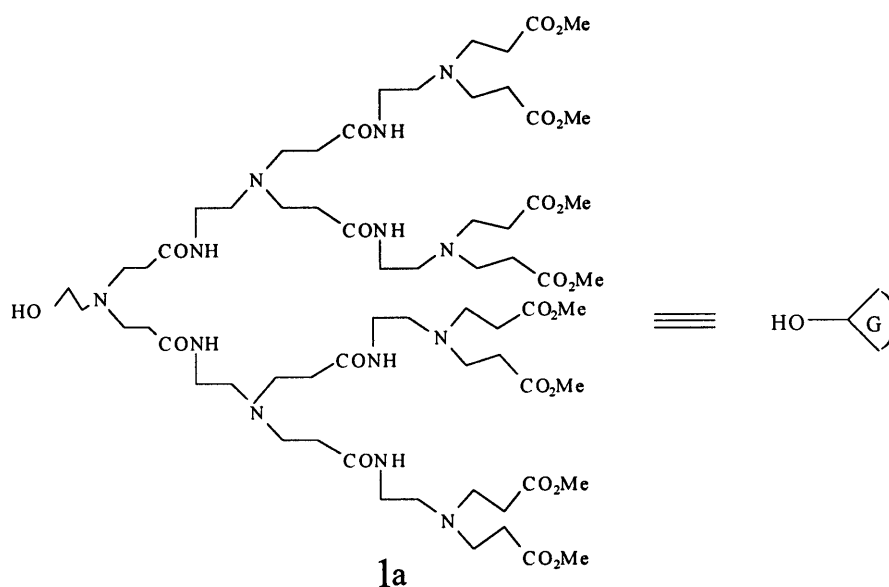
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

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Abstract—Polyamidoamine (PAMAM) dendrimer **1** with an azobenzene central linker has been synthesized and found to undergo reversible *trans/cis* isomerization upon exposure to UV-light. © 2001 Published by Elsevier Science Ltd.

Recently the preparation of dendritic macromolecules has received a great deal of attention particularly with respect to the synthesis of dendrimers with precisely placed groups within the dendrimer interior or at the

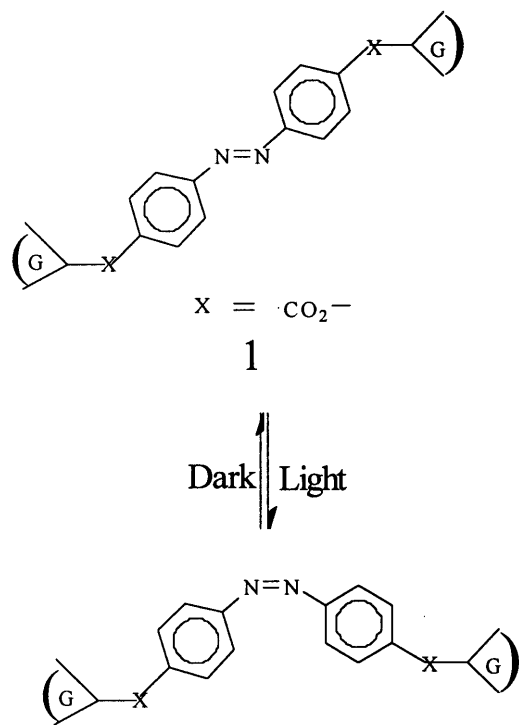
periphery.¹ Novel dendrimers with electroactive, photoactive, and recognition elements at the core, within the branches, or at the periphery of the dendritic structure have recently been reported² as potential functional



Scheme 1. (i) Glucose, NaOH, (ii) PCl₅, 1,2-dichloroethane, (iii) **1a**, CH₂Cl₂, Et₃N.

Keywords: polyamidoamine; dendrimer; photoresponsive.

* Corresponding author.



Scheme 2.

materials. It is well-known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction, and thereby find their extensive use for the construction of photoswitchable devices.^{3,4} However, the dendritic macromolecules, with precisely placed azo units within their structural interior, represent an intriguing scaffold for photoresponsive materials.^{3–6} Therefore, more predictable control of well-defined photoinduced configurational as well as constitutional changes in the dendritic system should be possible, allowing reversible alteration of function.

The polyamidoamine (PAMAM) family of starburst dendrimers (SBDs)⁷ is a novel class of macromolecules which possess a definite molecular composition and constitution. In this context, a challenging target is the construction of well-defined PAMAM dendrimers possessing photochromic azobenzene core units so that there is efficient photoinduced *trans/cis* isomerization of the photochromic moiety in the dendritic structure.

Therefore, we report herein the divergent construction of the novel polyamidoamine (PAMAM) dendrimer (G2.5) **1** possessing an azobenzene core unit. To our knowledge this is the first photoresponsive PAMAM dendrimer displaying photoinduced configurational changes in the dendritic structure reported so far.

Our strategy for the divergent synthesis of the ester-terminated PAMAM dendritic wedge **1a** involves the Michael reaction of ethanolamine with methyl acrylate followed by exhaustive amidation of the resulting esters with a large excess of ethylenediamine to afford the next generation dendrimer with reactive amine groups.

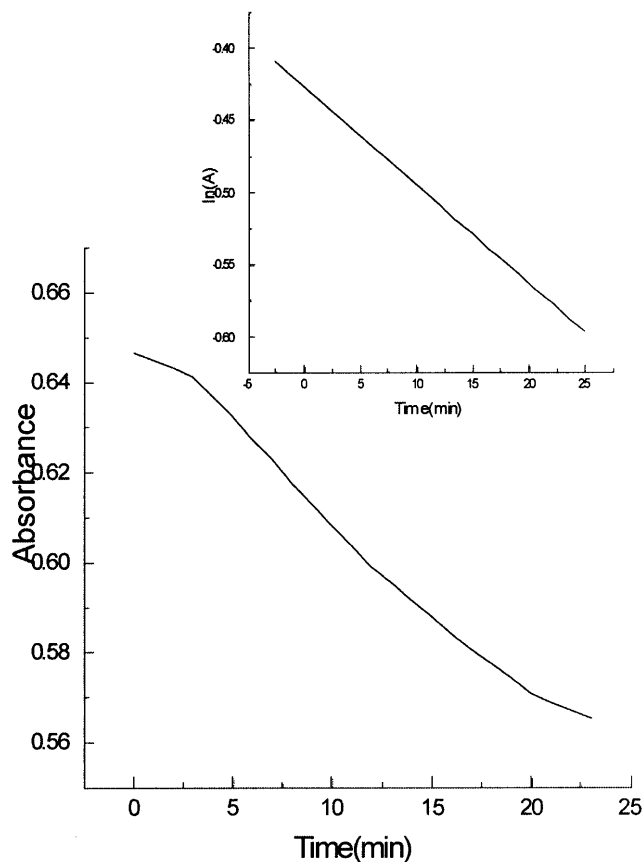


Figure 1. Plot of absorbance versus time under irradiation. Conditions (330 nm, 1 min intervals; 3.3×10^{-7} M in CHCl_3 ; 27°C). Inset: first order rate constant plot of $\ln A$ versus time.

Repetition of this two-step procedure ultimately leads to the targeted PAMAM dendritic wedge **1a** with one hydroxyl group at the focal point. Photoresponsive dendrimer **1** was synthesized from azobenzene dicarboxylic acid⁸ by coupling with dendritic wedge **1a** (Scheme 1). The dendrimer **1**, which was honey colored and gummy in nature, was isolated in 60–70% yield. The dendrimer obtained is very soluble in halogenated organic solvents like chloroform, dichloromethane etc. The dendritic wedge **1a** as well as the dendrimer **1** have been characterized by means of IR and NMR spectroscopy.^{9,10}

We have established the photoresponsive behavior of the azobenzene containing dendrimer **1** to be essentially identical to that of small molecule azobenzenes. However, the dark incubation of a chloroform solution (3.3×10^{-7} M) of dendrimer **1** served to maximize the absorption at 329 nm corresponding to the *trans* azobenzene chromophore. On irradiation of this dark incubated solution with 330 nm UV light, obtained from a high pressure xenon lamp coupled with a monochromator, the energetically preferred ground state *trans*-form goes to the *cis*-form via a photochemical isomerization process (Scheme 2), as evidenced by a gradual decrease in absorbance at 329 nm with time (Fig. 1) [assuming initially the compound is 100% *trans*].

The first order rate constant for this process ($k = 0.00684 \text{ min}^{-1}$; $t_{1/2} = 101 \text{ min}$) as determined from the inset of Fig. 1, is similar in magnitude to that of other azobenzenes.¹¹ We have thus demonstrated the photochromic property is due to the isomerism of the azobenzene moiety of dendrimer **1** on irradiation of 330 nm UV light. We anticipate that photoswitchable dendrimers of this type will have applications in transport systems based on the reversible perturbation of their ability to encapsulate small molecules. Further studies in our laboratory are in progress.

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9. Selected data for dendritic wedge (**1a**): IR (KBr): 3375, 1732(s), 1644 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ : 6.2 (bs, 6H, all $-\text{CONH}-$), 4.30(bs, 1H, $-\text{OH}$), 3.66 (s, 26H, $-\text{CO}_2\text{CH}_3$, $\text{HO}-\text{CH}_2-$), 3.29–3.27 (m, 12H, $-\text{CONH}-\text{CH}_2-$), 2.85–2.33 (m, 70H, all other $-\text{CH}_2-$); ^{13}C NMR (50 MHz, CDCl_3) δ : 177.1 (NC=O; out), 174.1 (NC=O; in), 172.3 (C=O), 56.8, 56.1, 52.2, 51.2, 50.2, 49.9, 49.2, 45.1, 42.4, 37.7, 36.9, 32.5, 32. Anal. calcd for $\text{C}_{64}\text{H}_{115}\text{N}_{13}\text{O}_{23}$: C, 53.58; H, 8.07; N, 12.69; found: C, 51.68; H, 7.79; N, 10.92.
10. Selected data for dendrimer (**1**): IR (KBr): 3315, 1722, 1632 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 8.21 (d, 4H, $J = 9 \text{ Hz}$), 8.0 (d, 4H, $J = 9 \text{ Hz}$), 6.21 (bs, 12H, $-\text{CONH}-$), 3.68 (s, 52H), 3.11 (q, 24H), 2.81–2.39 (m, 140H); ^{13}C NMR (50 MHz, CDCl_3) δ : 173.0 (broad and unresolved, $-\text{CONH}-$, $-\text{COOCH}_3$, $-\text{COOCH}_2-$), 152.4 (ArC), 129.0 (ArC), 124.6 (ArCH), 121.5 (ArCH), 79.3, 75.1, 55.9, 53.0, 50.1, 49.0, 47.2, 46.5, 39.8, 36.9, 35.0, 32.5, 29.9. Anal. calcd for $\text{C}_{142}\text{H}_{236}\text{N}_{28}\text{O}_{48}$: C, 54.95; H, 7.66; N, 12.63; found: C, 52.79; H, 7.14; N, 11.21.
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