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New Insight into the Synthesis of a Novel Azo-Based Optically Active Polyamidoamine Side Chain Dendritic Polyester Architectural Photoswitch

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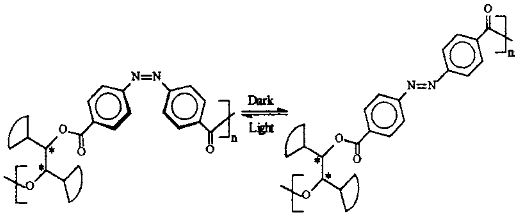
ABSTRACT



Side chain dendritic polyester

A novel chiral polyamidoamine side chain dendritic polyester 4 has been synthesized and found to be a photoresponsive system undergoing reversible *E/Z* photochemical/thermal isomerization of azo units. Thorough characterization (IR,UV–vis, NMR, FAB-MS, elemental analysis, optical rotation, etc.) were performed to ascertain the structures of dendrimers 2, 3, and 4. The intrinsic viscosity of 4 at 36 °C in $CHCl_3$ was found to be 0.48 dl/g.

Chiral dendrimers[1] are of interest for chiral recognition and enantioselective clathration of chiral guest molecules for chemical separations, sensor technology, and asymmetric catalysis. The ability to regulate a chiral dendritic macromolecular structure by light could result in photoresponsive chiral dendritic materials of value. Azobenzene systems undergo efficient and fully reversible photoisomerization [trans(*E*)/cis(*Z*)] reactions to provide versatile photoswitchable systems.[2,3] Side chain dendritic polymers[4,5] have recently been of research interest. In this context, the ability to construct a well-defined side chain dendritic polymeric object possessing azo-based linear photochromic chiral polymeric core axis would be useful.

In continuation of our investigations[2] in the field of photoresponsive dendritic systems, we report a simple, efficient, and novel synthetic approach toward the development of chiral azo-based polyamidoamine side chain dendritic polyester architecture and investigation of its photoresponsive property upon exposure to UV light.

The key dendritic diol for the synthesis of this novel polydendron **4** was synthesized (Scheme 1) by utilizing

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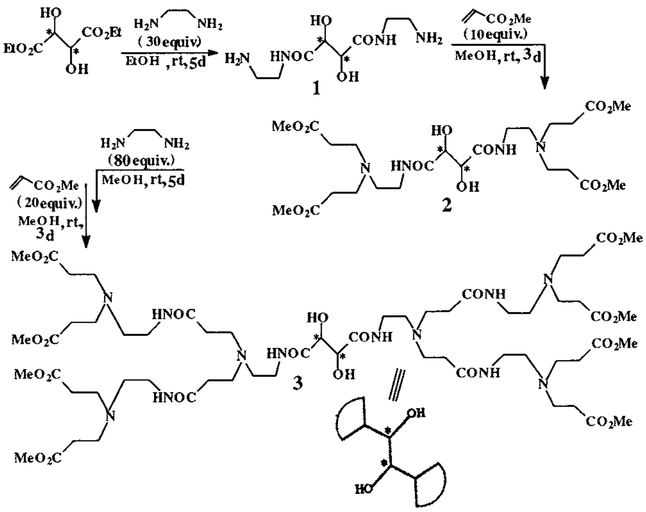
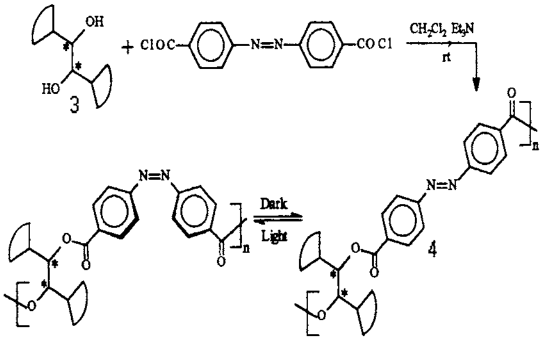
Scheme 1



Scheme 2



diethyl-L-tartrate as the core unit, according to our previously reported similar divergent synthetic strategy.[2] The synthesis of chiral azo-based **4** (Scheme 2) was achieved by a simple and efficient solution polymerization of the corresponding chiral dendritic diol **3** with azobenzene dicarboxylic acid chloride[6] in the presence of Et_3N; the product was isolated in moderate yield (65−70%). The yielded chiral polydendron **4** was soluble in many common organic solvents including $CHCl_3$, CH_2Cl_2, and THF. The unequivocal characterizations of **2**, **3**, and **4** have been achieved using IR, UV−vis, NMR (^1H, ^{13}C), and FAB-MS (for **3**) spectroscopies, as well as elemental analysis for **4**.[7] Tartaric acid core is especially appealing for the design of dendrimers as well as chiral side chain dendritic polyester because of its easy availability from the chiral pool and renewable resources, biocompatibility, low toxicity, and C_2-symmetric as well as natural polyfunctionality. In addition, intrinsic chirality may be introduced into the dendrimers and in polydendron using tartaric acid functionality. The low value of intrinsic viscosity of **4** as determined in $CHCl_3$ at 36 °C using the equation derived by Raju et al.[8] could possibly be attributed to the presence of a dendritic side group and the low degree of polymerization due to the sterically hindered dendritic diol comonomer. TGA of **4** reveals its moderate thermal stability and the onset degradation temperature is up to 156 °C under argon at 10 °C/min. Preliminary investigation of the optical rotation of these described systems demonstrates that the specific rotation value of these dendrimers **2** and **3** decreases with increasing generation number, in agreement with the observations made in the literature,[9] but increases again in the polydendron **4** ascribing a number of chiral dendritic repeating units within the main chain. Further study toward the effect of chiral units on the macromolecular asymmetry in **4** will be disclosed in due course.

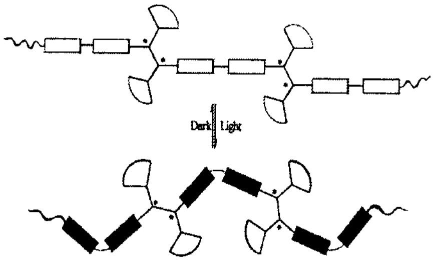


Figure 1. Proposed structural representation of **4** in solution during irradiation

Chiral polydendron **4** exhibits photoresponsive behavior on irradiation by UV light. Azobenzene units, placed in the main chain of **4**, allow propagation of their photochromic isomerization via the chiral tartarate units along the polymeric core. These, in turn, should lead to possible concomitant reorientation of the dendritic segments as proposed in Figure 1. Photoirradiation of this dark incubated acetonitrile solution (1.7 mg/mL) with 332 nm UV light resulted in the marked isomerization of the azo unit from the extended *E*-form to the more compact *Z*-form (Figure 1) as seen by a gradual decrease in absorbance at 332 nm and a concomitant increase in absorbances at 275 and 452 nm with time (Figures 2 and 3, assuming initially the compound is 100% *E*) before reaching the photostationary state. A plot of ln *A* vs time (inset of Figure 3) afforded actually two slopes, similar to that of our previously reported azo-based side chain dendritic polyester, and the determined first-order rate constants [$k_x = 7.63 \times 10^{-2}$ min^{-1} (0−12 min), $t_{1/2} = 9.08$ min; $k_y = 1.98 \times 10^{-3}$ min^{-1} (13−22 min), $t_{1/2} = 350$ min] suggest the effective decrease of first-order rate constant as isomerization advances. Furthermore, the lower value of k_y compared to k_x probably attributes to the gradual increase of sterically congested structural environment originated from the gradual increase of the percentage of more compact

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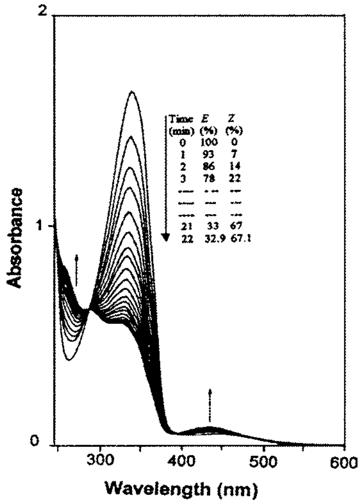

Figure 2. UV−vis absorption spectral change of acetonitrile solution of **4** [1 min interval, 0−22 min, λ_{ex} = 332 nm, 25 °C, *E* to *Z* isomerization].

Z-content of azo units and the presence of bulky dendritic side groups. This solution of **4** was then subjected to thermal back isomerization (*Z* to *E*), monitored at 332 nm (Figures 4 and 5), at three different temperatures (25, 35, and 45 °C) in the dark, and the first-order rate constants and activation energies (Table 1) were determined.

The faster rate of reverse isomerization process in the first step (0−77 min) probably suggests the relaxation of the highly strained environment arisen from the higher content of more compact *Z*-form as well as the dendritic side groups in the irradiated polydendron **4**. The second step (77−212 min) probably implies the further relaxation of strained environment still possessing significant fraction of the *Z*-form as well as the increase of secondary interactions in **4**.

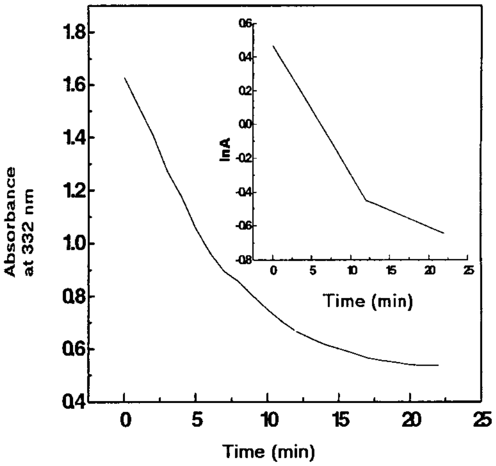

Figure 3. Plot of absorbance change at 332 nm vs time under irradiation for the data in Figure 2. Inset is the first-order rate constant plot of ln *A* vs time].

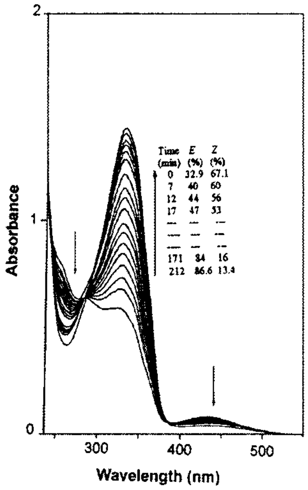

Figure 4. UV−vis absorption spectral change of irradiated acetonitrile solution of **4** [0−212 min, kept in dark at 25 °C, *Z* to *E* isomerization].

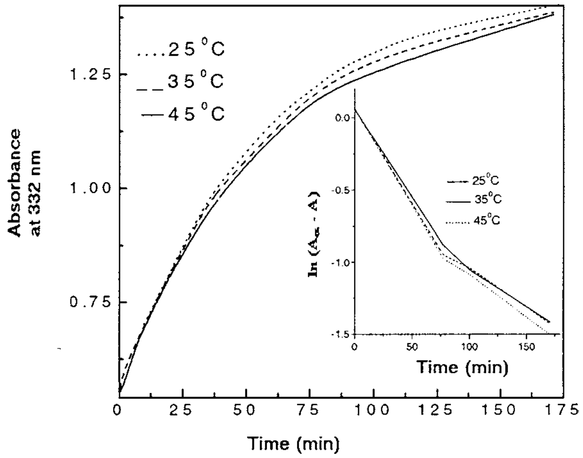

Figure 5. Plot of absorbance change at 332 nm vs time for the sample **4** kept in the dark at 25, 35, and 45 °C, 0−212 min. Inset is the first order rate constant plot of ln(A_{α} − *A*) vs time].

Table 1. Rates and Activation Energies for Thermal *Z* to *E* Isomerization in **4**

temp (°C)	rate constants (min^{-1})	$t_{1/2}$ (min)	E_{act} (kcal/mol)
	0−77 min		
25	1.22×10^{-2}	56.8	
35	1.30×10^{-2}	53.02	0.95
45	1.34×10^{-2}	51.71	
	77−212 min		
25	5.06×10^{-3}	136.9	
35	5.48×10^{-3}	126.45	1.42
45	5.92×10^{-3}	117.06	

Furthermore, the presence of two isobestic points (at 295 and 395 nm) during reversible isomerization processes clearly indicated the effective and reversible conversion of the azo unit. It also indicated that the isomerization was not accompanied by degradation, which would have resulted in a shift at 295 and/or 395 nm.

We have thus successfully developed for the first time a strategy to prepare chiral tartaric acid centered hybrid polyamidoamine dendrimers **2** and **3** and azo-based chiral side chain dendritic polyester **4**, which were characterized thoroughly. We anticipate that the photoswitchable side chain dendritic polyester of this type having the chiral conduit between the azo units in the main chain of the polymer would be most welcome in the field of stimuli-responsive transport process as well as recognition of small chiral guest molecules. Further studies toward the stimuli-responsive chiral clathration abilities of **4** and the synthesis of other azo-based chiral side chain dendritic polymers by incorporating polyamidoamine dendritic diol **3** in random/block fashion are under progress in our laboratory.

Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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