

Contents lists available at ScienceDirect

## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

# *Trans–cis* isomerization of arylether dendrimers with azobenzene core and terminal hydroxy groups

### Ji-hye Lee, Daeock Choi\*, Eun Ju Shin\*

Department of Chemistry, Sunchon National University, Suncheon, Jeonnam 540-742, Republic of Korea

#### ARTICLE INFO

#### ABSTRACT

Article history: Received 20 January 2010 Received in revised form 13 May 2010 Accepted 4 June 2010

Keywords: Azobenzene Arylether dendrimer Hydroxy group *Trans-cis* photoisomerization Absorption spectrum Azobenzene-cored arylether dendrimers **2a–2c** with polar hydroxy groups at the periphery have been prepared from hydroboration–oxidation reaction of azobenzene-cored arylether dendrimers **1a–1c** with nonpolar vinyl groups at the periphery. *Trans*  $\rightarrow$  *cis* photoisomerization of central azo group has been investigated by UV–vis spectral changes after photolysis. The results show that dendrimers **1a–1c** and **2a–2c** in methanol/dichloromethane (1/1, v/v) have carried out *trans–cis* isomerization. Reaction rate for *trans*  $\rightarrow$  *cis* photoisomerization of **35**0 nm. On the other hand, the reaction rate of *cis*  $\rightarrow$  *trans* thermal back isomerization for **1a–1c** decrease in higher generation. This result is somewhat different from that for **1a–1c** with nonpolar vinyl groups. Both the reaction rates of *trans*  $\rightarrow$  *cis* photoisomerization and *cis*  $\rightarrow$  *trans* thermal back isomerization for **1a–1c** decrease in higher generation.

© 2010 Elsevier B.V. All rights reserved.

#### 1. Introduction

Recently, dendritic functional molecules [1–18] have received considerable attention in the viewpoint of the potential applications of numerous fields including drug-delivery systems, diagnostic agents, nanoscale catalysts, enzyme mimics, nano-sized molecular electronic device, molecular photoswitch, chemical sensor, display, solar cell, etc. Because of precisely controlled functionality/size/shape and interior void space, dendrimers may play an important role in nanotechnology including the preparation of functional nanomaterials.

Dendrimers including photochromic moiety are especially interesting because those may accomplish the light-controlled specific function. Light-driven simple geometrical change of core molecule or concurrent geometrical changes of many peripheral molecules may result in the large conformational change throughout the dendritic entity [19–22].

Azobenzene is a typical photochromic molecule to show clean reversible isomerization [23–26]. Reversible transformation between more stable *trans*-azobenzene and less stable *cis*-azobenzene can be controlled by UV or visible light irradiation or thermally in the dark. Intense investigation has been carried out for the dendrimer with a photoisomerizable azobenzene unit in the core [27–29] or periphery [30–32].

Dendrimers bearing the polar peripheral groups are especially important for the pharmaceutical, medicinal, and biological applications. For example, one of the strategy for the use of dendrimers as drug-delivery agents is the design of dendrimers having nonpolar interior for solubilizing various hydrophobic organic drug and polar hydrophilic exterior for being susceptible in aqueous solution. The internal cavity of an appropriately designed dendrimer could be used for the entrapment of drugs with the possibility of subsequent controlled release. However, only a few dendrimers with nonpolar interior and polar exterior behaving as unimolecular micelles were reported [33,34].

Recently, we have reported the preparation and isomerization behavior of azobenzene-cored arylether dendrimers with a photoisomerizable azobenzene unit in the core and terminal vinyl groups in the periphery [35,36]. For this azobenzene-cored arylether dendrimers, the introduction of various functional groups by the reaction of terminal vinyl group could allow the easy modification of periphery. Hydroboration–oxidation of terminal vinyl groups may lead to the preparation of azobenzene-cored dendrimer with polar hydroxyl groups in exterior.

Thus, herein we report the synthesis and photochemical/thermal isomerization behavior of azobenzene-cored arylether dendrimers **2a–2c** with polar hydroxyl groups in the periphery in methanol/dichloromethane (1/1, v/v), in comparison with azobenzene-cored arylether dendrimers **1a–1c** with nonpolar vinyl groups in the periphery. Structures of **1a–1c** and **2a–2c** are shown in Fig. 1.

<sup>\*</sup> Corresponding authors. Tel.: +82 61 750 3635; fax: +82 61 750 3508. *E-mail address*: ejs@sunchon.ac.kr (E.J. Shin).

<sup>1386-1425/\$ –</sup> see front matter  $\ensuremath{\mathbb{C}}$  2010 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2010.06.022



Fig. 1. Structures of 1a-1c and 2a-2c.

#### 2. Experimental

#### 2.1. Apparatus

<sup>1</sup>H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in DMSO- $d_6$ . MALDI-TOF Mass Spectra were measured on Applied Biosystem Voyager-DE'STR System 4407 Mass Spectrometer using 2,5-dihydroxybenzoic acid in THF as a matrix. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Photoirradiation was carried out in a Rayonet RPR 100 photochemical reactor equipped with a Southern Ultraviolet 3500 Å lamp using pyrex reaction tube in methanol/dichloromethane (1/1, v/v). Reaction progress of photoisomerization on UV irradiation and reverse thermal isomerization in the dark was monitored by the change of absorption spectra.

#### 2.2. Reagents

All materials used in the present investigation were of analytical reagent grade and purchased from Aldrich Chemical Co. They were used as received.

The preparation of azobenzene-cored arylether dendrimers **1a–1c** of first, second, and third generations with vinyl groups in the periphery has been previously reported [36]. Photoresponsive azobenzene-cored arylether dendrimers **2a–2c** of first, second, and third generations with an azobenzene unit at the core and hydroxy groups at the periphery have been synthesized by hydroboration–oxidation reaction of corresponding **1a–1c** with terminal vinyl groups in the periphery as shown in Fig. 2. Their structures have been identified by <sup>1</sup>H NMR and MALDI-TOF Mass Spectra.

Preparation of azobenzene-cored arylether dendrimers **2a** of first generation with an azobenzene unit at the core and hydroxy groups at the periphery.

To a solution of 1a (0.05 g, 0.074 mmol) in 30 mL dry THF, 2.0 M BH<sub>3</sub>·THF (0.5 mL, 1.0 mmol) was added dropwise via

syringe at -20 °C. After stirring at -20 °C for 12 h, 2 mL of CH<sub>3</sub>OH was added followed by the simultaneous addition of 2 mL of 3 M NaOH aqueous solution and 2 mL of 30% H<sub>2</sub>O<sub>2</sub> aqueous solution. The resulting solution was stirred overnight at -5 °C. The reaction mixture was diluted by ethyl acetate (20 mL), then washed by water and brine and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the reaction mixture was purified by preparative TLC using MeOH/CHCl<sub>3</sub> (1/9, v/v) as eluents to give **2a** as a yellow solid (50 mg, 41%) yield). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.83 (d, 4H, I = 9.0 Hz, -N=N-ArH), 7.18 (d, 4H, J=9.0Hz, -N=N-ArH), 6.60 (d, 4H,  $J=2.1 \text{ Hz}, -O-CH_2-Ar'H), 6.43$  (t, 2H,  $J=2.1 \text{ Hz}, -O-CH_2-Ar'H),$ 5.13 (s, 4H, -O-CH<sub>2</sub>-Ar'-), 4.44 (brs, 4H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 4.03-3.94 (m, 8H, -OCH2CH2CH2CH2OH), 3.45-3.42 (m, 8H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.76-1.69 (m, 8H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.58–1.51 (m, 8H, –OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH) ppm; MALDI-TOF MS m/z 746.89 (C<sub>42</sub>H<sub>54</sub>N<sub>2</sub>O<sub>10</sub> requires 746.38).



Fig. 2. Synthesis of 2a-2c from 1a-1c and *trans-cis* isomerization of 1a-1c and 2a-2c.



Fig. 3. Absorption spectra of 1a-1c (a) and 2a-2c (b) in methanol/dichloromethane (1/1, v/v).

Preparation of azobenzene-cored arylether dendrimers **2b** of second generation with an azobenzene unit at the core and hydroxy groups at the periphery **2b** was synthesized according to the same procedure as in the synthesis of **2a** described above. Yield 26% (35 mg starting from **1b** (0.15 g, 0.11 mmol)); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.83 (d, 4H, J = 8.8 Hz, -N=N–ArH), 7.16 (d, 4H, J = 8.8 Hz, -N=N–ArH), 6.72 (d, 4H, J = 1.9 Hz, -O-CH<sub>2</sub>–Ar'H), 6.63 (brs, 2H, -O-CH<sub>2</sub>–Ar'H), 6.56 (d, 8H, J = 1.9 Hz, -O-CH<sub>2</sub>–Ar'H), 6.41 (brs, 4H, -O-CH<sub>2</sub>–Ar''H), 5.13 (s, 4H, -O-CH<sub>2</sub>–Ar''-), 5.01 (s, 8H, -O-CH<sub>2</sub>–Ar''-), 4.44 (brs, 8H, -O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 4.02–3.93 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 3.45–3.42 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.74–1.68 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.56–1.51 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH) ppm; MALDI-TOF MS m/z 1523.51 (C<sub>86</sub>H<sub>110</sub>N<sub>2</sub>O<sub>22</sub> requires 1522.76).

Preparation of azobenzene-cored arylether dendrimers 2c of third generation with an azobenzene unit at the core and hydroxy groups at the periphery **2c** was synthesized according to the same procedure as in the synthesis of 2a described above. Yield 22% (35 mg starting from **1c** (0.15 g, 0.054 mmol)); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.81 (d, 4H, J = 8.9 Hz, -N=N-ArH), 7.16 (d, 4H, J = 8.9 Hz, -N=N-ArH), 6.74 (brs, 4H, -O-CH<sub>2</sub>-Ar'H), 6.70 (d, 8H, J=1.8 Hz,  $-O-CH_2-Ar''H$ ) 6.65 (brs, 2H,  $-O-CH_2-Ar'H$ ), 6.62 (t, 4H, J=1.8 Hz,  $-O-CH_2-Ar''H)$ , 6.61 (d, 16H, J=1.9 Hz,  $-O-CH_2-Ar'''H)$ , 6.40 (t, 8H, I = 1.9 Hz,  $-O-CH_2-Ar'''H)$  5.13 (s, 4H,  $-O-CH_2-Ar'-$ ), 5.03 (s, 8H, -O-CH<sub>2</sub>-Ar"-), 4.99 (s, 16H, -O-CH<sub>2</sub>-Ar"'-) 4.44 (brs, 16H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 3.95-3.92 (m, 32H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 3.45-3.39 (m, 32H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.73-1.67 (m, 32H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.55-1.51 (m, 32H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH) ppm; MALDI-TOF MS *m*/*z* 3075.81 (C<sub>174</sub>H<sub>222</sub>N<sub>2</sub>O<sub>46</sub> requires 3075.51).

#### 3. Results and discussion

#### 3.1. Absorption spectra

The absorption spectra of *trans*-azobenzene-cored arylether dendrimers **1a–1c** and **2a–2c** in methanol/dichloromethane (1/1, v/v) are shown in Fig. 3. Their absorption maxima are similar regardless of dendrimer generation and appear around 277–282, 358 nm for *trans* isomers *trans* **1a–1c** and *trans* **2a–2c**, around 282, 319, 444 nm for *cis* **1a–1c**, and around 259, 275, 320, 440 nm for *cis* **2a–2c** (Table 1). While the intensities at 358 nm absorption band of azobenzene moiety are similar for all six *trans* dendrimers, the absorbance at 277–282 nm absorption band of aryl ether dendrimers **1a** and **2a** to third generation dendrimers **1c** and **2c**. In *cis* isomers, broad long-wavelength band at 440–444 nm appears.

#### 3.2. Trans $\rightarrow$ cis photochemical isomerization

The absorption spectral changes of **1a–1c** and **2a–2c** in methanol/dichloromethane (1/1, v/v) on irradiation at 350 nm were measured by 5 s interval for monitoring  $trans \rightarrow cis$  photoisomerization of azobenzene moiety. On 350 nm irradiation, intensities of absorption bands at 358 nm of dendrimers remarkably decrease and new band at 440–445 nm appears, as azobenzene moiety at the core of dendrimers **1a–1c** and **2a–2c** converts photochemically from *trans* to *cis* form. Fig. 4 shows *trans–cis* isomerization of **1c** and **2c**.

The absorption spectral changes of azobenzene-cored arylether dendrimers **1a–1c** containing vinyl peripheral groups in methanol/dichloromethane (1/1, v/v) upon irradiation of 350 nm are shown in Fig. 5.

As azobenzene moiety at the core of dendrimers *trans* **1a–1c** converts photochemically from *trans* to *cis* form on 350 nm irradiation, intensity of absorption band at 358 nm of dendrimers remarkably decreases with appearing new band at 444 nm.

In methanol/dichloromethane (1/1, v/v), absorption spectrum of **1a** is not changed any more after 120s irradiation. It is supposed that *trans* **1a** converts completely to the *cis* isomer in 120s. It takes 120s up to reach to the photostationary state in *trans*  $\rightarrow$  *cis* conversion of **1b** and **1c**, too.

Absorption spectral changes of **2a–2c**, azobenzene-cored arylether dendrimers containing hydroxy peripheral groups, with irradiation time (0–120 s, 5 s interval) on irradiation at 350 nm in methanol/dichloromethane (1/1, v/v) are shown in Fig. 6.

*Trans*  $\rightarrow$  *cis* photoisomerization reactions of azobenzene-cored arylether dendrimers **2a–2c** reach to the photostationary state when irradiated for ~100 s at 350 nm in methanol/dichloromethane (1/1, v/v). Absorption band intensity at 358 nm remarkably decreases with appearing new band at 440 nm, as *trans* **2a–2c** converts from *cis* **2a–2c** on 350 nm irradiation,

#### Table 1

Absorption maxima  $\lambda_a^{trans}$  and  $\lambda_a^{cis}$ , and rate constants  $k_{t \rightarrow c}$  and  $k_{c \rightarrow t}$  for trans  $\rightarrow cis$  photoisomerization and  $cis \rightarrow trans$  thermal back isomerization of **1a–1c** and **2a–2c** in methanol/dichloromethane (1/1, v/v).

Compound $\lambda_a^{trans}$ , nm	$\lambda_a^{cis}$ , nm	$k_{t \to c}$ , s <sup>-1</sup>	$k_{c ightarrow t}$ , $\mathrm{h}^{-1}$
1a         283,357           1b         282,358           1c         282,359           2a         277,358           2b         277,358           2c         277,358	283, 319, 445 282, 318, 444 282, 319, 444 259, 275, 320, 440 259, 275, 320, 440	$\begin{array}{c} 3.2\times10^{-2}\\ 2.5\times10^{-2}\\ 2.6\times10^{-2}\\ 2.3\times10^{-2}\\ 2.5\times10^{-2}\\ 2.5\times10^{-2}$	$\begin{array}{c} 2.7\times10^{-2}\\ 2.9\times10^{-2}\\ 1.9\times10^{-2}\\ 2.7\times1\times10^{-2}\\ 2.9\times10^{-2}\\ 2.9\times10^{-2}\\ 2.1\times10^{-2}\\ 2.1\times10^{-$



Fig. 4. Trans-cis isomerization of 1c and 2c.

Regardless of peripheral groups, all six azobenzene-cored dendrimers carried out very fast *trans*  $\rightarrow$  *cis* photoisomerization on irradiation of 350 nm and reached to the photostationay state within 120 s. *Trans*  $\rightarrow$  *cis* photoisomerization rates  $k_{t \rightarrow c}$  were calculated from the absorbance changes with irradiation time *t* using the following equation.

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = k_{t \to c} t$$

where  $A_0$ ,  $A_t$ , and  $A_\infty$  represent absorbances before irradiation, at irradiation time *t*, and at the photostationary state gained after the prolonged irradiation, respectively.

Plots of  $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$  vs. *t* for **1a–1c** and **2a–2c** in methanol/dichloromethane (1/1, v/v) give the values of  $k_{t\to c}$  from

their slopes. As shown in Table 1, *trans*  $\rightarrow$  *cis* photochemical isomerization rates ( $k_{t\rightarrow c}$ ) of **1a–1c**, which are dendrimers bearing terminal vinyl groups, are similar to those of **2a–2c**, which are dendrimers bearing terminal hydroxy groups.

The initial reaction rate of  $trans \rightarrow cis$  photochemical isomerization  $(k_{t\rightarrow c})$  in methanol/dichloromethane (1/1, v/v) decreases slightly with increasing the dendrimer generation for **1a–1c** (**1a**  $(3.2 \times 10^{-2} \text{ s}^{-1}) >$ **1b**  $(2.5 \times 10^{-2} \text{ s}^{-1}) \approx$ **1c**  $(2.6 \times 10^{-2} \text{ s}^{-1}))$ , but increases with increasing the dendrimer generation for **2a–2c** (**2a**  $(2.3 \times 10^{-2} \text{ s}^{-1}) \approx$ **2b**  $(2.5 \times 10^{-2} \text{ s}^{-1}) <$ **2c**  $(3.2 \times 10^{-2} \text{ s}^{-1}))$ .

The reaction rate of  $trans \rightarrow cis$  photochemical isomerization of **1c** is slowest among **1a–1c** because of its bulkiness. Meanwhile, probably, the enhancement of intramolecular hydrogen bonding in *cis* isomer of higher generation for **2a–2c** bearing terminal



**Fig. 5.** Absorption spectral changes of **1a** (a), **1b** (b), and **1c** (c) in methanol/dichloromethane (1/1, v/v) with irradiation time (0-120 s, 5 s interval) on irradiation at 350 nm.

hydroxyl groups in methanol/dichloromethane (1/1, v/v) leads to faster *trans*  $\rightarrow$  *cis* photoisomerization in higher generation. Generation dependency of *trans*  $\rightarrow$  *cis* photochemical isomerization rate  $(k_{t\rightarrow c})$  is significantly altered by different exterior groups (hydroxy or vinyl groups) in dendrimer structure.

#### 3.3. Cis $\rightarrow$ trans thermal isomerization

Thermal reversion reactions of azobenzene-cored dendrimers **1a–1c** and **2a–2c** are slow at room temperature and monitored by absorption spectral changes in methanol/dichloromethane (1/1, v/v) during the incubation in the dark. As the solutions of **1a–1c** and **2a–2c** were kept in the dark after irradiated at 350 nm for 3 min, slow thermal back reversion from *cis* form to *trans* form in methanol/dichloromethane (1/1, v/v) occurs. During the dark incubation, absorption band intensity at 358 nm of dendrimers



**Fig. 6.** Absorption spectral changes of **2a** (a), **2b** (b), and **2c** (c) in methanol/dichloromethane (1/1, v/v) with irradiation time (0-120 s, 5 s interval) on irradiation at 350 nm.

increases remarkably while absorbance at 440–445 nm decreases. It indicates that azobenzene moiety at the core of dendrimers **1a–1c** and **2a–2c** reverts thermally from *cis* to *trans* form.

Absorption spectral changes of 1a-1c in methanol/dichloromethane (1/1, v/v) with dark incubation time (0-75 h) after 350 nm irradiation for 3 min are shown in Fig. 7.

During the dark incubation of dendrimers 1a-1c, absorption band intensity at 358 nm increases remarkably, while absorbance at 445 nm decreases. For 1a-1c, dark incubation time of 72–75 h is required for recovery to the original spectra of corresponding *trans* isomers in methanol/dichloromethane (1/1, v/v).

Absorption spectral changes of 2a-2c in methanol/ dichloromethane (1/1, v/v) with dark incubation time (0–75 h) after 350 nm irradiation for 3 min are shown in Fig. 8.

Similarly, during the dark incubation of dendrimers **2a–2c**, absorption band intensity at 358 nm increases remarkably, while



**Fig. 7.** Absorption spectral changes of **1a** (a), **1b** (b), and **1c** (c) in methanol/dichloromethane (1/1, v/v) with dark incubation time (0-75 h) after 350 nm irradiation for 3 min.

absorbance at 440 nm decreases. Isomerization reactions from *cis* **2a–2c** to corresponding *trans* isomers are completed after the dark incubation of 72–74 h in methanol/dichloromethane (1/1, v/v). The reaction time (72–75 h) of *cis*  $\rightarrow$  *trans* thermal isomerization for **1a–1c** and **2a–2c** is independent of both the dendrimer generation and the exterior groups (hydroxy or vinyl groups).

However, as shown in Fig. 8(b) and (c), absorption spectra of **2b** and **2c** are not completely recovered to the original spectra of corresponding *trans* isomers even after dark incubation of 75 h. Hydrogen bonding between adjacent terminal hydroxyl groups in folded geometry of *cis* isomers for **2b** and especially **2c** may inhibit the formation of unfolded and fully stretched geometry of *trans* isomers, even if central azo group isomerizes during the dark incubation. *Trans* **2c** obtained after 75 h dark incubation of *cis* **2c** shows very structured absorption spectra, apart from the original spectra of *trans* **2c** obtained after



**Fig. 8.** Absorption spectral changes of **2a** (a), **2b** (b), and **2c** (c) in methanol/dichloromethane (1/1, v/v) with dark incubation time (0-75 h) after 350 nm irradiation for 3 min.

75 h dark incubation of *cis* **2c** has twisted geometry, as shown in Fig. 4.

 $Cis \rightarrow trans$  reverse thermal isomerization rates  $(k_{c\rightarrow t})$  were calculated from the absorbance changes with dark incubation time t using the following equation.

$$\ln \frac{A_{\infty} - A_0}{A_{\infty} - A_t} = k_{c \to t} t$$

where  $A_0$ ,  $A_t$ , and  $A_\infty$  represent absorbances just after 350 nm irradiation for 3 min, at dark incubation time t, and at the stationary state gained after the prolonged dark incubation, respectively.

The values of  $k_{c\rightarrow t}$  for **1a–1c** and **2a–2c** are evaluated from the slopes of the plots of  $\ln[(A_{\infty} - A_0)/(A_{\infty} - A_t)]$  *vs.* dark incubation time *t* and are summarized in Table 1.

As shown in Table 1, the initial reaction rate of  $cis \rightarrow trans$  thermal isomerization ( $k_{c\rightarrow t}$ ) is slow in higher generation dendrimers **1c** 

 $(1a (2.7 \times 10^{-2} h^{-1}) \approx 1b (2.9 \times 10^{-2} h^{-1}) > 1c (1.9 \times 10^{-2} h^{-1}))$  and **2c**  $(2a (2.7 \times 10^{-2} h^{-1}) \approx 2b (2.9 \times 10^{-2} h^{-1}) > 2c (2.4 \times 10^{-} h^{-1})).$ 

The enhancement of bulkiness in higher generation leads to slower  $cis \rightarrow trans$  thermal isomerization.  $Cis \rightarrow trans$  thermal isomerization rate is affected by the generation of azobenzene-cored dendrimers, but not much altered with exterior group of dendrimer.  $Cis \rightarrow trans$  thermal isomerization rate of **1a–1c** bearing terminal vinyl groups in methanol/dichloromethane (1/1, v/v) is similar to that of **2a-2c** bearing terminal hydroxy groups.

#### 4. Conclusions

Photoresponsive arylether dendrimers **2a–2c** with azobenzene unit at the core and hydroxyl groups at the periphery were prepared from arylether dendrimers **1a–1c** with azobenzene unit at the core and vinyl groups at the periphery. Comparative study of reversible *trans-cis* isomerization between dendrimers containing polar exterior groups and dendrimers containing nonpolar exterior groups was accomplished. Both the reaction rate for *trans*  $\rightarrow$  *cis* photoisomerization  $(k_{t\rightarrow c})$  and the reaction rate of  $cis \rightarrow trans$  thermal back isomerization  $(k_{c \to t})$  of dendrimers **1a-1c** containing nonpolar exterior groups in methanol/dichloromethane (1/1, v/v) decrease with increasing generation. This result is somewhat different from that for 2a-2c. For dendrimers 2a-2c containing polar exterior groups, the reaction rate of *trans*  $\rightarrow$  *cis* photoisomerization ( $k_{t \rightarrow c}$ ) increases in higher generation, but the reaction rate of  $cis \rightarrow trans$ thermal back isomerization  $(k_{c \rightarrow t})$  decreases in higher generation. The reaction rates of  $trans \rightarrow cis$  photochemical isomerization and  $cis \rightarrow trans$  thermal isomerization for azobenzene-cored arylether dendrimers are affected by both the generation and the exterior group. It is noteworthy that trans 2c obtained after 75 h dark incubation of cis 2c shows very structured absorption spectra, apart from original spectra of *trans* **2c**. For **2c**, hydrogen bonding between adjacent terminal hydroxyl groups in cis isomer of folded geometry may inhibit the formation of unfolded and fully stretched geometry of *trans* isomers. It is plausible that twisted *trans* **2c** is formed from the  $cis \rightarrow trans$  thermal isomerization of central azo group.

#### Acknowledgements

This work is financially supported by the Ministry of Education, Science and Technology (MEST), the Ministry of Knowledge Economy (MKE) through the fostering project of the Industrial-Academic Cooperation Centered University and by the Ministry of Knowledge Economy (MKE) through the project of GTFAM Regional Innovation Center (RIC).

#### References

- [1] R.W.J. Scott, O.M. Wilson, R.M. Crooks, J. Phys. Chem. B 109 (2005) 692-704.
- [2] D.V. McGrath, Mol. Pharm. 2 (2005) 253-263.
- [3] A.-M. Caminade, J.-P. Majoral, Acc. Chem. Res. 37 (2004) 341-348.
- J.M.J. Fréchet, J. Polym. Sci. A 41 (2003) 3713-3725. [4]
- [5] G.R. Newkome, C.N. Moorefield, F. Vögtle, Dendrimers and Dendrons-Concepts, Synthesis Applications, Wiley-VCH, New York, 2001. S.M. Grayson, J.M.J. Fréchet, Chem. Rev. 101 (2001) 3819-3867.
- M.W.P.L. Baars, E.W. Meijer, Top. Curr. Chem. 210 (2000) 131-182. [7] 181 D.K. Smith, F. Diederich, Top. Curr. Chem. 210 (2000) 183-227.
- A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665-1688. [9]
- [10] G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689-1746. [11] O.A. Matthews, A.N. Shipway, J.F. Stoddart, Prog. Polym. Sci. 23 (1998) 1-56.
- [12] F. Zeng, S.C. Zimmerman, Chem. Rev. 97 (1997) 1681-1712.
- [13] J.M.J. Fréchet, Science 263 (1994) 1710-1715.
- D.A. Tomalia, Adv. Mater. 6 (1994) 529-539.
- [15] D.A. Tomalia, A.M. Naylor, W.A. Goddard III, Angew. Chem., Int. Ed. Engl. 29 (1990) 138-175.
- [16] Y.-S. Shon, D. Choi, Chem. Lett (2006) 644-645.
- O.M. Wilson, M.R. Knecht, J.C. Garcia-Martinez, R.M. Crooks, J. Am. Chem. Soc. [17] 128 (2006) 4510-4511.
- [18] S.-y. Lim, D. Choi, E.J. Shin, Bull. Korean Chem. Soc. 29 (2008) 1353-1358.
- [19] A. Momotake, T.J. Arai, Photochem. Photobiol. C: Photochem. Rev. 5 (2004)
- [20] S. Hecht, J.M.J. Fréchet, Angew. Chem., Int. Ed. Engl. 40 (2001) 74-91.
- [21] Y.-J. Mo, D.-L. Jiang, M. Uyemura, T. Aida, T. Kitagawa, J. Am. Chem. Soc. 127 (2005) 10020-10027.
- [22] T. Hasobe, P.V. Kamat, M.A. Absalom, Y. Kashiwagi, J. Sly, M.J. Crossley, K. Hosomizu, H. Imahori, S. Fukuzumi, J. Phys. Chem. B 108 (2004) 12865-12872.
- [23] S. Shinkai, O. Manabe, Top. Curr. Chem. 121 (1984) 67-104.
- [24] G.S. Kumar, D.C. Neckers, Chem. Rev. 89 (1989) 1915-1925.
- [25] R. Cimiraglia, H.-J. Hofmann, Chem. Phys. Lett. 217 (1994) 430-435.
- [26] Z. Sekkat, J. Wood, W. Knoll, J. Phys. Chem. 99 (1995) 17226-17234.
- [27] A. Momotake, T. Arai, Tetrahedron Lett. 45 (2004) 4131-4134.
- [28] D.-L. Jiang, T. Aida, Nature 388 (1997) 454-456.
- [29] D.M. Junge, D.V. McGrath, Chem. Commun. (1997) 857-858.
- [30] A. Archut, F. Vögtle, L. De Cola, G.C. Azzellini, V. Balzani, P.S. Ramanujam, R.H. Berg, Chem. Eur. J. 4 (1998) 699-706.
- [31] A. Archut, G.C. Azzellini, V. Balzani, L. De Cola, F. Vögtle, J. Am. Chem. Soc. 120 (1998) 12187-12191.
- [32] K.-Y. Kay, K.-J. Han, Y.-J. Yu, Y.D. Park, Tetrahedron Lett. 43 (2002) 5053-5056.
- [33] C.J. Hawker, K.L. Wooley, J.M.J. Fréchet, J. Chem. Soc. Perkin Trans. 1 (1993) 1287-1297.
- [34] H. Tatewaki, N. Baden, A. Momotake, T. Arai, M. Terazima, J. Phys. Chem. B 108 (2004) 12783-12789.
- [35] D. Choi, J.-h. Lee, K.-h. Shin, E.J. Shin, Bull. Korean Chem. Soc. 28 (2007) 983-989.
- [36] J.-H. Lee, D. Choi, J.E. Park, E.J. Shin, Bull. Korean Chem. Soc. 29 (2008) 761-766.