

STRONG INFLUENCE OF GENERATION NUMBER ON THE KINETICS OF Z/E ISOMERIZATION IN CARBOSILANE DENDRIMERS WITH AZOBENZENE TERMINAL GROUPS

Alexey Bobrovsky, Alexey Pakhomov, Sergey Ponomarenko, Natalia Boiko, Valery Shibaev

Chemistry Department, Moscow State University
Leninskie Gory, Moscow, 119899 Russia

Introduction

Among a wide variety of photosensitive compounds^{1, 2} dendrimers with photoactive groups allocated in different parts of their superbranched molecules are of particular interest.³⁻¹⁰ In spite of a large number of publications devoted to investigation of photophysical and photochemical properties of dendrimer solutions, any influence of a generation number of such compounds on a kinetics of isomerization process was not revealed by now.

In this work we synthesized a number of carbosilane dendrimers of 1, 3 and 5 generations (Gn) with 8, 32, and 128 terminal ethoxyazobenzene (AzoEt) groups in order to evaluate an influence of the dendritic matrix size (generation number) on the photochemical properties of such complex molecules. General structural formulae of the dendrimers studied is shown in **Figure 1**.

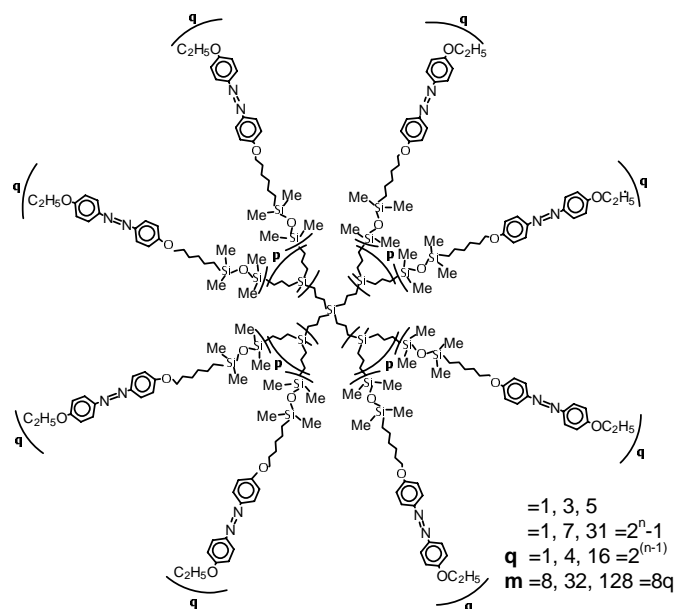


Figure 1. Structure of dendrimers **GnAzoEt**. *n* is a generation number, *m* is a number of terminal groups.

Experimental

Synthesis and characterization. Synthesis of azobenzene-containing carbosilane dendrimers **GnAzoEt** of 1, 3, and 5 generations with 8, 32 and 128 terminal azobenzene groups, respectively, was described in¹⁰.

Photo-optical investigations. Photochemical properties investigations were studied using a special instrument equipped with a DRSh-250 ultra-high pressure mercury lamp. Light with wavelength 365 nm was selected using cut-off filter. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain plane-parallel light beam, quartz lens was used. During forward E/Z and thermal Z/E isomerization processes, the constant temperature of the test samples was maintained using a thermostat. The intensity of light was equal to $1.9 \times 10^{-8} \text{ Es} \times \text{s}^{-1} \times \text{cm}^{-2}$ (as measured actinometrically¹¹). During UV irradiation solutions were stirred using magnetic stirrer. After irradiation absorbance spectra were recorded using Hitachi U-3400 UV-Vis-IR spectrometer.

Results and Discussion

According to preliminary data (polarizing optical microscopy and DSC) all the dendrimers synthesized form crystalline phases (melting points are 94, 84 and 81 °C for **G1AzoEt**, **G3AzoEt** and **G5AzoEt**, respectively). The formation of only crystalline 3D-ordered phases, particularly in the case of fifth generation is rather unexpected experimental fact. As it was shown before in the number of papers, carbosilane dendrimers of high generations (4-5) having similar constitution form rather weakly ordered liquid crystalline columnar structures¹² due to large steric restrictions for the terminal groups packing.

Study of the photochemical behavior of the dendrimers shows strong spectral changes corresponding to E/Z photoisomerization process during UV irradiation at 365 nm of the solution of **G1AzoEt** in dichloroethane (**Figure 2**).

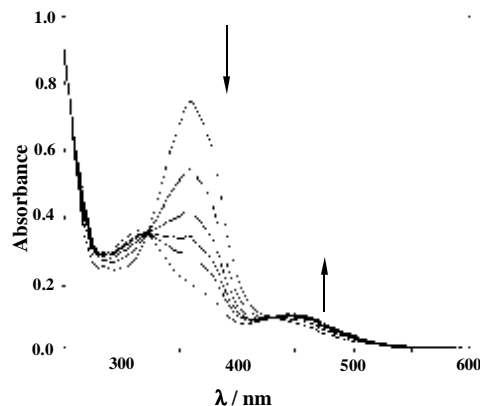


Figure 2. Changes of absorbance spectra of the dendrimer **G1AzoEt** solution (dichloroethane, $8.13 \times 10^{-3} \text{ mg/mL}$) during UV irradiation. Spectra were recorded each 10 s of irradiation. Dashed line corresponds to the photostationary state (~10 min of irradiation).

Namely, the strong decrease of absorption in the region of $\pi-\pi^*$ electron transition ($\lambda_{\text{max}}=359 \text{ nm}$) and its small increase in the region of $n-\pi^*$ transition of azobenzene chromophores occurs. Basically a character of these changes has no differences with those happen in solutions of similar low-molar-mass compounds¹³ or comb-like polymers with the side groups of the similar structure.¹⁴

Analysis of the spectral changes allows to conclude that the solutions of the dendrimers contain about 90% of the azobenzene groups in Z-form and app. 10% – in E-form in a photostationary state after UV irradiation at 365 nm. It is important to note that a position of the maxima of the azobenzene chromophores and the character of the spectral changes during UV irradiation are almost the same for all the dendrimers under study.

The isomerization process is thermally reversible that results from the character of the spectral changes – even at the ambient temperature one can see a complete recovery of the initial shape of the spectra. The peculiar details follow from the study of kinetics of the reverse Z/E isomerization process. **Figure 3** shows the time dependencies of the reduced optical density $(A_{\infty}-A_t) \times (A_{\infty}-A_0)^{-1}$, where A_0 , A_t and A_{∞} are the absorbance at 359 nm at the time $t=0$, current time t and $t \rightarrow \infty$, respectively.

For the first time we observed an interesting and unusual phenomenon: in dichloroethane solutions the rate of Z/E isomerization is significantly higher for the dendrimers of 3 and 5 generations as compared with the first generation dendrimer (**Figure 3**). It means that the dendritic architecture essentially influences on the rate of back isomerization process; thus effect can be called as a "dendritic effect". Let us consider some kinetic peculiarities of the back isomerization process.

The kinetic dependencies for the first generation dendrimer **G1AzoEt** are simply approximated by a monoexponential function (1).

$$(A_{\infty}-A_t)/(A_{\infty}-A_0)=B\exp(-kt), \quad (1)$$

For the dendrimers of 3 and 5 generations an adequate approximation is possible using biexponential function (2) only,

$$(A_{\infty}-A_t)/(A_{\infty}-A_0)=B_1\exp(-k_1t)+B_2\exp(-k_2t), \quad (2)$$

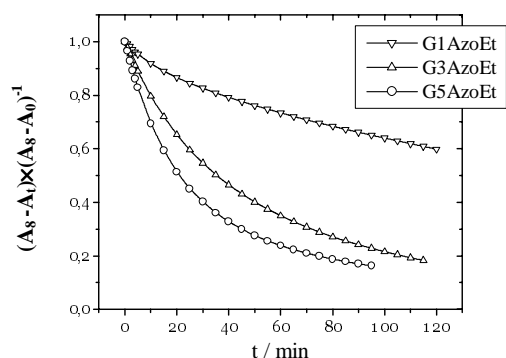


Figure 3. Kinetics of the absorbance growth for solutions of the dendrimers of different generations.

Figure 4 presents the values of B_1 and B_2 and the rate constants of Z-E isomerization process. As can be seen from the values in **Figure 4** the maximal rate of this process occurs in the case of the fifth generation dendrimer. The back isomerization process is about 6 times (!) faster for the dendrimer of the fifth generation and 4 times faster for the dendrimer of the third generation, then that for the first generation dendrimer. It means that the influence of dendritic architecture could be found even at rather low generation dendrimers. Oversimplifying, one can say that in the case of the dendrimers of generations 3 and 5 one part of the azobenzene groups transforms from Z to E isomer with a fast velocity (constant k_1), and the other part – with significantly lower one (constant k_2). (For more precise description of the kinetics of this process one should take into account a continuous distribution of the rate constants.^{15, 16} However, in our case a character of this distribution is not known a priori, therefore we used the biexponential approach.) It should be noted, however, that a contribution of the fast process is higher in the case of the dendrimer of the fifth generation as compared with the dendrimer G3AzoEt.

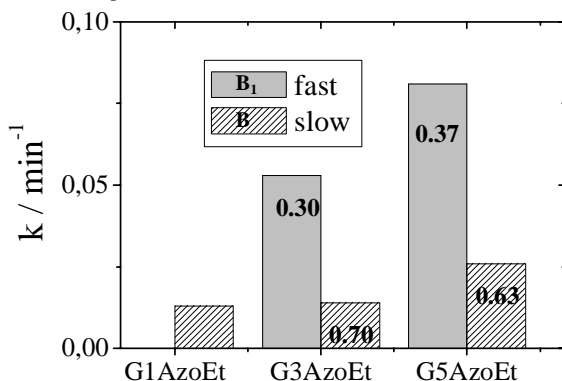


Figure 4. Values of rate constants for thermal Z/E isomerization process (slow and fast) of dendrimers of different generations and model compound in dichloroethane at 30 °C. Values of B_1 and B_2 are also presented in Figure.

In the number of papers^{15, 16} concerning the study of the kinetics of E/Z and Z/E isomerization processes in polymeric films it was shown that a presence of a certain free volume is a necessary condition for such isomerization processes.

In regard to our case the unusual behavior of the dendrimers of the high generations was observed in the dilute solutions where interactions between different dendritic molecules are unlikely. One of the possible reasons of the strong acceleration of the Z/E isomerization process could be explained by a high local concentration of the terminal azobenzene groups in the dendrimers of third and fifth generations. In fact, increasing the generation number gives rise to increase the number of terminal groups in the dendritic molecule by a geometrical progression law ($m = 2^{n+2}$, see structure of the dendritic molecule), while the surface of the dendritic molecule increase only squared to its' radius ($S = \pi r^2$).¹⁷ As a result, a surface area per one terminal group on the curvature formed by the dendrimer's radii decreased almost exponentially from generation 1 to generation five¹⁸ that means an increase of a sterical hindrance between the terminal groups. E/Z photoisomerization leading to the formation of the bent-

shaped Z-isomeric terminal azobenzene groups should strengthen the "sterical interactions" as compared to the linear E-isomers. Therefore, increased sterical hindrance between Z-isomeric azobenzene groups linked to the carbosilane dendrimers of high generations could destabilize Z-form and dramatically accelerate their back transformation to E-form. Search for the detailed explanation of the phenomenon observed is in progress.

To sum up, thus this work revealed the strong dependence of the rate of back thermal Z/E isomerization process in solution of the photochromic carbosilane dendrimers on the generation number. To the best of our knowledge, such "dendritic effect" was observed for the first time. The next works in this direction will be devoted to the influence of a solvent nature on the kinetics of direct E/Z and inverse Z/E isomerization. Preliminary results showed that similar dependences were observed and for the solutions of these dendrimers in tetrahydrofuran, however, in the case of toluene, such difference in the kinetics is small. One can suggest that the most important for the "dendritic effect" appearance is thermodynamic quality of the solvent with respect to the dendritic matrix (swelling or squeezing): "good" solvent makes dendritic core more swelled that increase molecular radius and consequently decrease the sterical hindrance between the terminal groups. In the other case, "bad" solvent squeezed the dendritic core that lead to smaller radius of the dendritic molecule and, as a result, to stronger interactions between the terminal azobenzene groups that allow "to see" such "dendritic effect".

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