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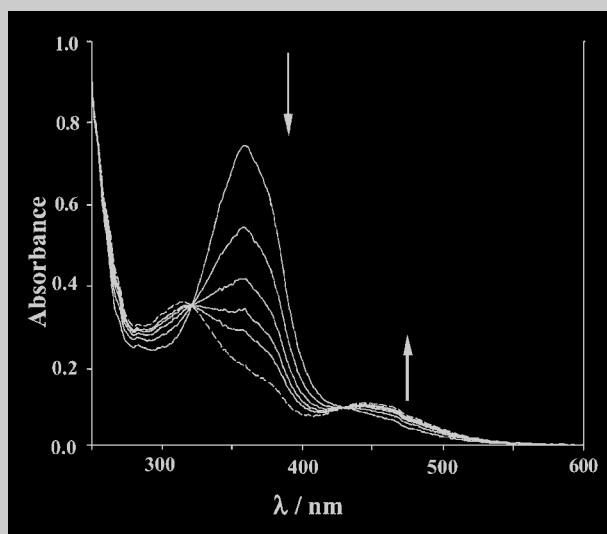
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**Full Paper:** Photo-optical properties of carbosilane dendrimers of the first, third, and fifth generations with terminal azobenzene groups are presented. The dendrimers synthesized display a crystalline phase, which melts into isotropic liquid at 81–91 °C (depending on the generation number). A comparative analysis of the photo-optical behavior of the dendrimers in dilute solutions and films was carried out. It was shown that under the action of UV irradiation (365 nm) an *E/Z* photoinduced isomerization of azobenzene groups takes place in the solutions and amorphous films. This process was found to be thermally reversible: annealing leads to a back *Z/E* isomerization. The processes of photoinduced orientation of terminal azobenzene groups of the dendrimers under the action of polarized UV light (365 nm) were studied.



Changes of absorbance spectra of the dendrimer **G1AzoEt** solution (dichloroethane,  $8.13 \times 10^{-3}$  mg/mL) during UV irradiation (365 nm, intensity  $1.9 \times 10^{-8}$  einstein/(cm<sup>2</sup>·s)). Spectra were recorded each 10 s of irradiation. Dashed line corresponds to the photostationary state ( $\approx 10$  min of irradiation).

## Photochemistry and Photoorientational Phenomena in Carbosilane Dendrimers with Terminal Azobenzene Groups

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**Keywords:** azobenzene terminal groups; dendrimers; photochemistry; *E/Z* photoisomerization; photoorientation phenomena

### Introduction

Recently, photochromism has gained appreciable attention, and now it is an active research area because of its tremendous importance in biological phenomena and potential applications in the fields of linear and nonlinear optics.<sup>[1]</sup> Photochromism, that is a change in the color under light irradiation, is also accompanied by changes in the number of physical characteristics, such as refractive index, dielectric constant, etc. There are numerous photochemical reactions that can lead to photochromism, among which *E/Z* photoisomerization of azobenzene fragments is the well-

known photoreaction. Presently, numerous low molecular mass and polymer compounds which are able to undergo various photochemical irradiation-induced transformations have been synthesized.<sup>[2–7]</sup>

Dendrimers being a distinguished class of superbranched molecules, which are intermediate between polymeric and low-molar-mass compounds, hold a special place among a large number of photochromic compounds. During the last ten years, a lot of reports concerning the study of their photo-physical and photochemical properties have been published.<sup>[8–24]</sup> Special attention has been paid to effects of energy transfer in light-harvesting antenna systems based

on highly conjugated dendrimers.<sup>[8–13]</sup> Dendrimers with photosensitive groups, capable for example for photoisomerizing, are the other interesting class of such compounds.<sup>[14–24]</sup> Depending on the photochromic groups location in the dendritic molecule, one can distinguish at least three main types of such compounds (Scheme 1):

- 1) photosensitive dendrimers with photoactive groups located in the center of the molecule (Scheme 1a);<sup>[14–18]</sup>
- 2) dendrimers with photoactive groups being constituent parts of “branches” of molecules (Scheme 1b);<sup>[18,19]</sup>
- 3) dendrimers with terminal photochromic groups (Scheme 1c).<sup>[14–24]</sup>

At the present time quite a lot of papers concerning study of the properties of all three types of dendrimers have been published. However, most of these papers have been devoted to the investigations of dilute solutions of such compounds and only several papers touched the peculiarities of photochemical behavior of cinnamoyl- and azo-containing dendrimers in films.<sup>[20–24]</sup>

Very recently, photochemical investigation of kinetics of photoorientation processes for a liquid-crystalline (LC) carbosilane dendrimer of the first generation, containing propoxyazobenzene terminal groups, has been reported for the first time by our team.<sup>[23,24]</sup> It was shown that irradiation of the dendrimer film in SmA phase does not lead to photoorientation of azobenzene groups, while the polarized light of Ar-laser (488 nm) irradiation of amorphous films of the dendrimer induces photoorientation of azobenzene chromophores perpendicular to the vector *E* of electric field of incident light and appearance of linear dichroism.<sup>[24]</sup>

In this work, carbosilane dendrimers of 1<sup>st</sup>, 3<sup>rd</sup>, and 5<sup>th</sup> generations with the terminal ethoxyazobenzene groups have been synthesized with a purpose of elucidation of a role of the dendritic matrix size (generation number) in photochemical and photoorientational behavior of such systems.

Let us consider at the beginning a direct process of *E/Z* and a reverse process of *Z/E* isomerisation in solutions of dendrimers, then their photochemical behavior in films, and, finally, peculiarities of the photoorientation processes

of azobenzene groups in the films under the action of polarized light of different wavelengths.

## Experimental Part

### Synthesis and Characterization

Azobenzene-containing carbosilane dendrimers **GnAzoEt** of 1, 3, and 5 generations with 8, 32, and 128 terminal azobenzene groups, respectively, were synthesized via a hydrosilylation reaction in toluene in the presence of Pt-catalyst according to Scheme 2.<sup>[25]</sup> (In the formula **GnAzoEt**, *n* is generation number.) Azobenzene groups were linked to carbosilane dendritic matrices of first to fifth generations through hexamethylene spacers.

Synthesis of initial carbosilane dendrimer matrices with the terminal allyl groups **Gn(All)<sub>m</sub>** was published elsewhere.<sup>[26]</sup>

Azobenzene-containing silane **H-Si-AzoEt** was synthesized by *co*-hydrolysis with dimethylchlorosilane, which was followed by hydrosilylation of 4-ethoxy-4'-hexene-1-yl-azobenzene like it was done before for cyanobiphenyl-containing silane.<sup>[27]</sup>

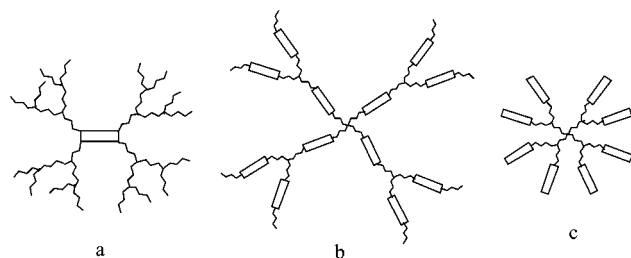
It should be noted that hydrosilylation did not affect the N=N double bond between two benzene rings. It was supported by the <sup>1</sup>H NMR spectroscopy: neither chemical shifts nor integral intensities of the signals from aromatic protons had changed. A 1.5-fold excess of **H-Si-AzoEt** was used to guarantee complete binding of the mesogenic groups to all allyl groups of the dendrimers. Reactions were continued until the allyl groups had disappeared completely. It was controlled by decreasing to zero of the intensities of characteristic proton multiplets in the regions of  $\delta_1 = 4.80$  ppm and  $\delta_2 = 5.74$  ppm due to allyl carbon-carbon double bonds near Si atom in the <sup>1</sup>H NMR spectra. After completion of the reactions, the excess of **H-Si-AzoEt** was removed by the method of column chromatography on silica gel. A high purity of these dendrimers was achieved by preparative HPLC. The structure and purity of all the dendrimers were confirmed by <sup>1</sup>H NMR spectroscopy and GPC analysis. All LC dendrimers synthesized are monodisperse substances with polydispersity equal to 1.01–1.02. Molar masses of the dendrimers were calculated from the GPC results using polystyrene standards. The main molecular characteristics of a novel series of dendrimers are shown below:

#### H-Si-AzoEt

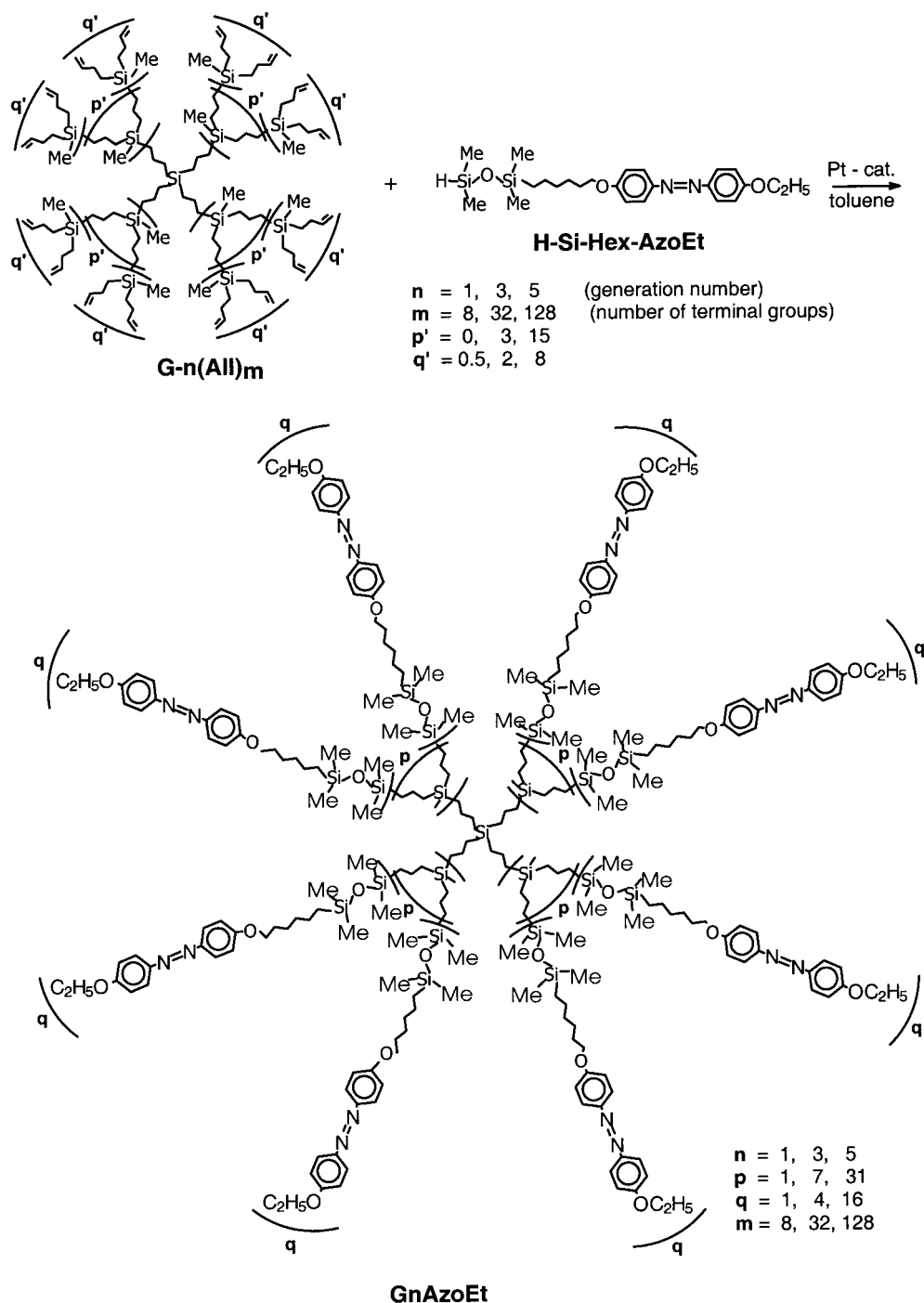
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta = 0.062$  (s, 6H, CH<sub>2</sub>SiCH<sub>3</sub>), 0.159 (d, 6H, CH<sub>3</sub>SiH), 0.5–0.6 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>Si), 1.25–1.45 (m, 14H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.443 (t, 3H, *J* = 7.0 Hz, PhOCH<sub>2</sub>CH<sub>3</sub>), 1.71–1.88 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OPh), 4.024 (t, 2H, *J* = 6.7 Hz, CH<sub>2</sub>CH<sub>2</sub>OPh), 4.106 (q, 2H, *J* = 7.0 Hz, PhOCH<sub>2</sub>CH<sub>3</sub>), 4.680 (m, 2H, (CH<sub>3</sub>)<sub>2</sub>SiH), 6.976 (d, 4H, *J* = 9.2 Hz, Ar–H), 7.853 (d, 8H, *J* = 9.2 Hz, Ar–H).

#### G1AzoEt

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta = -0.072$  (s, 12H, CH<sub>2</sub>SiCH<sub>3</sub>), 0.031 (s, 96H, CH<sub>3</sub>SiOSi), 0.45–0.65 (m, 64H, different CH<sub>2</sub>Si), 1.25–1.45 (m, 72H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.431 (t, 24H,



Scheme 1. Schematic representation of different types of photochromic dendrimers (see explanation in the text).



Scheme 2. Synthesis and general structural formula of azo-containing carbosilane dendrimers.

$J = 6.9$  Hz,  $\text{PhOCH}_2\text{CH}_3$ ), 1.72–1.82 (m, 16H,  $\text{CH}_2\text{-CH}_2\text{CH}_2\text{OPh}$ ), 3.988 (t, 16H,  $J = 6.6$  Hz,  $\text{CH}_2\text{CH}_2\text{OPh}$ ), 4.087 (q, 16H,  $\text{PhOCH}_2\text{CH}_3$ ), 6.957 (d, 32H,  $J = 8.4$  Hz, Ar-H), 7.838 (d, 32H,  $J = 8.8$  Hz, Ar-H).

#### G3AzoEt

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 MHz):  $\delta = -0.072$  (s, 84H,  $\text{CH}_2\text{SiCH}_3$ ), 0.027 (s, 384H,  $\text{CH}_3\text{SiOSi}$ ), 0.4–0.7 (m, 304H, different

$\text{CH}_2\text{Si}$ ), 1.2–1.5 (m, 408H,  $\text{CH}_2\text{CH}_2\text{-CH}_2$  and  $\text{PhOCH}_2\text{CH}_3$ ), 1.68–1.83 (m, 64H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{-OPh}$ ), 3.95 (t, 64H,  $\text{CH}_2\text{CH}_2\text{OPh}$ ), 4.06 (q, 64H,  $\text{PhOCH}_2\text{CH}_3$ ), 6.93 (d, 128H,  $J = 8.4$  Hz, Ar-H), 7.82 (d, 128H,  $J = 8.8$  Hz, Ar-H).

#### G5AzoEt

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 MHz):  $\delta = -0.073$  (s, 372H,  $\text{CH}_2\text{SiCH}_3$ ), 0.019 (s, 1536H,  $\text{CH}_3\text{SiOSi}$ ), 0.4–0.7 (m, 1264H, different

$\text{CH}_2\text{Si}$ ), 1.2–1.5 (m, 1272H,  $\text{CH}_2\text{CH}_2\text{-CH}_2$  and  $\text{PhO-CH}_2\text{CH}_3$ ), 1.65–1.83 (m, 256H,  $\text{CH}_2\text{CH}_2\text{-CH}_2\text{OPh}$ ), 3.91 (t, 256H,  $\text{CH}_2\text{CH}_2\text{OPh}$ ), 4.03 (q, 256H,  $\text{PhOCH}_2\text{CH}_3$ ), 6.90 (d, 512H,  $J=6.9$  Hz, Ar-H), 7.80 (d, 512H,  $J=8.8$  Hz, Ar-H).

#### Physico-Chemical Investigations

GPC analyses were carried out with a KNAUER instrument equipped with a "Waters" ( $8 \times 300$  mm) column. Measurements were made by using a UV detector, THF as solvent (1 mL/min,  $40^\circ\text{C}$ ), a column of  $10^3$  Å, and a calibration plot constructed with polystyrene standards. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of  $10^\circ\text{C}/\text{min}$ . Sample weights were typically chosen between 12 and 25 mg. The polarizing microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarizing microscope.

#### Film Preparation

Thin films of dendrimers were prepared by two techniques. In the first technique small amount of dendrimer was sandwiched between two flat quartz plates and annealed at  $80^\circ\text{C}$ ; in this case crystalline thin film having polydomain texture was obtained. The second type of the films was prepared by spin-coating technique (chloroform solution, concentration of dendrimers was about 10 mg/mL); in this case isotropic, transparent films were obtained. The films were dried by annealing at  $100^\circ\text{C}$  during several minutes followed by the fast cooling to room temperature in order to prevent crystalline phase formation.

#### Photo-Optical Studies

The nonpolarized UV irradiation was performed with a set of a XBO 150 W lamp, water IR filter and metal interference filters (313 and 365 nm). The power density of the incident light was  $\approx 15$  mW/cm<sup>2</sup> for both wavelengths. After irradiation, absorbance spectra were recorded using Lambda 2 (Perkin-Elmer) UV/visible spectrometer.

The photoorientation experiments were performed with the linearly polarized beam of an Ar<sup>+</sup> laser at 488 nm (Innova 90/4 of Coherent) or with a set of a XBO 150 W lamp, water IR filter, a metal interference filter (365 nm) and polarizer (intensity of the light in this case was  $\approx 5.3$  mW/cm<sup>2</sup>). The orientational order was studied using polarized UV/visible spectroscopy, because the transition moment of the *E*-isomer of azobenzene moiety is directed along the long axis of this group. For this purpose, the angular dependence of the absorbance was measured using a photodiode array UV/visible spectrometer (XDAP, Polytech) with a step-width of  $5^\circ$ .

The degree of order (order parameter) determined by spectroscopic method was calculated by

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$$

where  $A_{\parallel}$  is the absorbance at the preferred direction;  $A_{\perp}$  is the absorbance perpendicular to this direction.

## Results and Discussion

#### Phase Behavior

According to preliminary investigations (polarizing optical microscopy and DSC) the dendrimers of all three generations form crystalline phases only. Formation of crystalline 3D-ordered phases even in the case of the dendrimer of fifth generation **G5AzoEt** was rather unexpected experimental fact: as it was shown before in a number of papers, dendrimers of high generations form usually weakly ordered columnar structures.<sup>[25]</sup> (A structure of the phases formed by the dendrimers **G1AzoEt**, **G3AzoEt**, and **G5AzoEt** will be described with more details in our further publications.<sup>[28]</sup> In this paper, we pay attention to dilute solutions and amorphous films of the dendrimers.)

#### Photochemical Behavior of Dilute Solutions of Photosensitive Dendrimers

Let us consider photochemical behavior of dilute solutions of the dendrimers. As one can see from Figure 1, strong spectral changes corresponding to *E/Z* photoisomerization process take place during UV irradiation at 365 nm of the solution of **G1AzoEt** in dichloroethane. Namely, a strong decrease of the absorption in the region of  $\pi\text{-}\pi^*$  electron transition ( $\lambda_{\text{max}} = 359$  nm) and its small increase in the

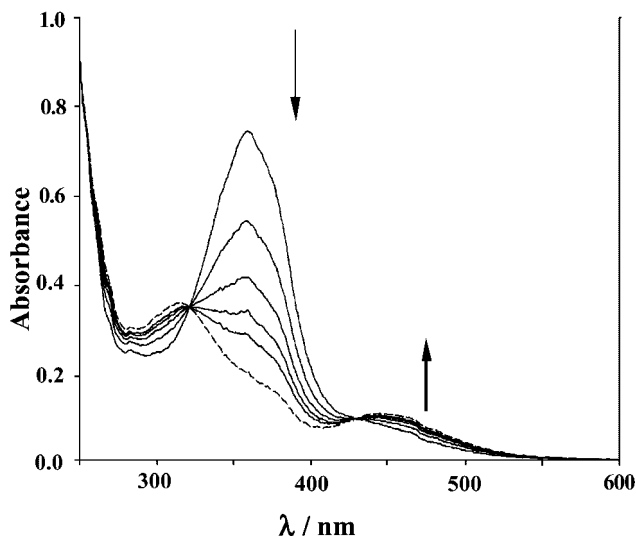


Figure 1. Changes of absorbance spectra of the dendrimer **G1AzoEt** solution (dichloroethane,  $8.13 \times 10^{-3}$  mg/mL) during UV irradiation (365 nm, intensity  $1.9 \times 10^{-8}$  einstein/(cm<sup>2</sup> · s)). Spectra were recorded each 10 s of irradiation. Dashed line corresponds to the photostationary state ( $\approx 10$  min of irradiation).

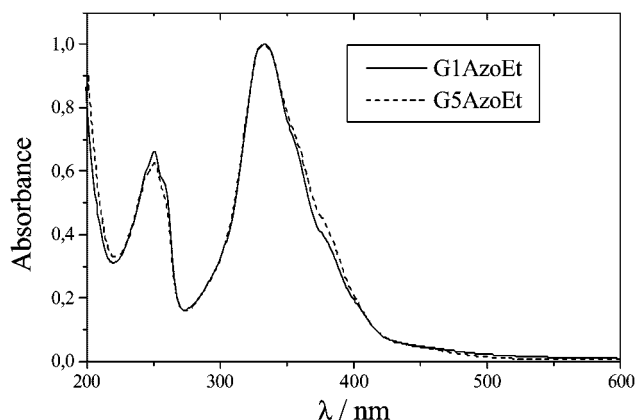


Figure 2. Normalized spectra of spin-coated films of dendrimers **G1AzoEt** and **G5AzoEt**.

region of  $n-\pi^*$  transition of azobenzene chromophores occurs. Basically character of these changes has no differences with those happening in solutions of similar low-molar-mass compounds<sup>[29–31]</sup> or comb-like polymers with

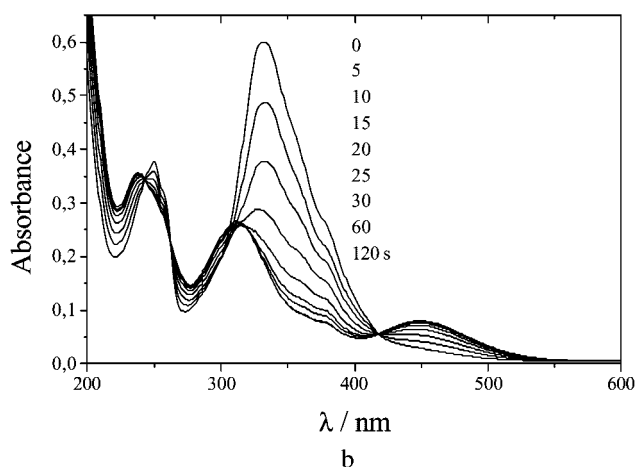
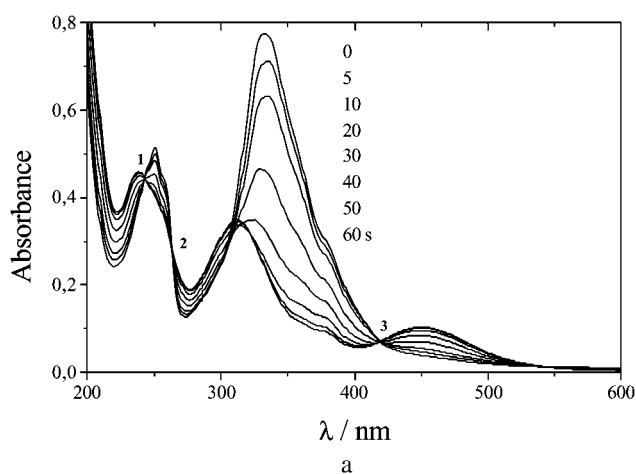


Figure 3. Spectral changes during UV irradiation (365 nm) of spin-coated films of dendrimer **G1AzoEt** (a) and **G5AzoEt** (b). 1–3 correspond to the isosbestic points.

the side groups of the similar structure.<sup>[32]</sup> Analysis of spectral changes allows to conclude that solutions of the dendrimers in a photostationary state after UV irradiation at 365 nm contain about 90% of azobenzene groups in *Z*-form and approximately 10% in *E*-form. It is important to note that position of the maxima of azobenzene chromophores and character of the spectral changes during UV irradiation are almost the same for all the dendrimers independent on generation number.

The isomerization process is thermally reversible; that results from the character of the spectral changes – even at ambient temperature one can see a complete recovery of the initial shape of the spectra of the dendrimers. Kinetics of this process will be considered in our separate paper.<sup>[33]</sup>

### Photochemical Properties of Photosensitive Dendrimers in Films

Prolonged irradiation of the crystalline films of the dendrimers leads to only small spectral changes. 3D-order in the azobenzene groups strongly affects on *E/Z* photoisomerization process,<sup>[34]</sup> and complicated spectral and kinetic

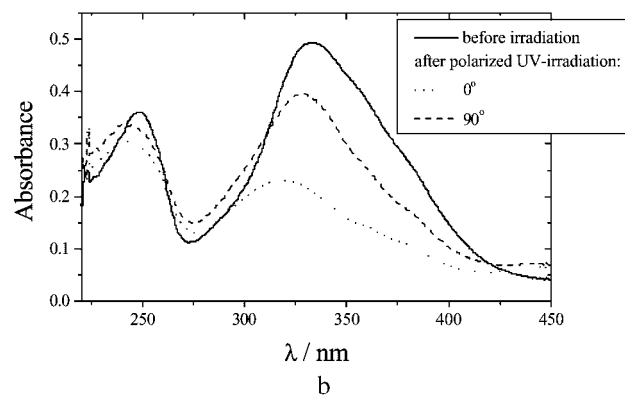
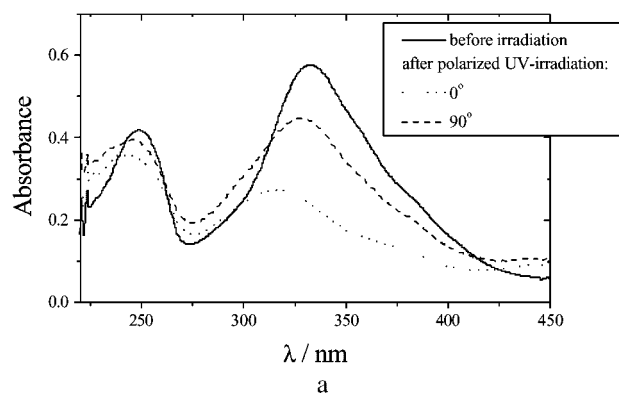


Figure 4. Linear dichroic spectra measured for spin-coated films of **G1AzoEt** (a) and **G5AzoEt** (b) before irradiation and after polarized UV light irradiation during 140 s (a) and 90 s (b); in the last cases spectra were recorded along and perpendicular electric vector of light.

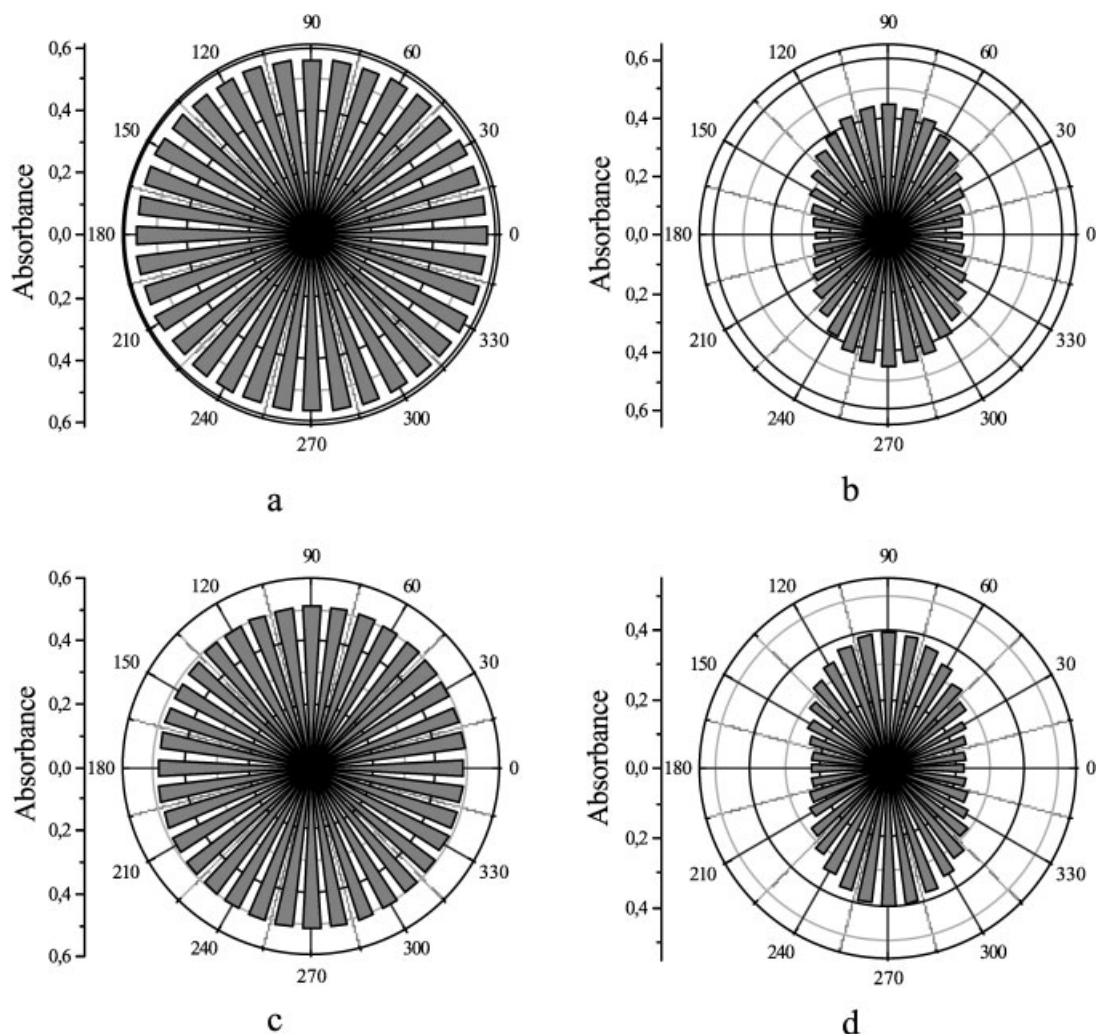


Figure 5. Polar diagrams for dendrimers **G1AzoEt** (a, b) and **G5AzoEt** (c, d) obtained before (a, c) and after irradiation (b, d) with polarized UV light during 140 s (b) and 90 s (d); temperature is 22 °C. Polar diagrams were plotted for  $\lambda = 328$  nm.

features of photo-optical behavior of crystalline films will be considered in our next publication.<sup>[28]</sup>

Totally different situation occurs under irradiation of amorphous films of the dendrimers, obtained by spin-coating technique. Usage of this method allowed to make optically transparent amorphous films of the dendrimers, which were stable during several days under ambient conditions (however, prolonged annealing leads to crystallization). It is interesting to note that, first of all, the spectra of the amorphous films of the dendrimers of different generations are actually identical (Figure 2). Maximum of  $\pi$ - $\pi^*$  electronic transition of azobenzene chromophores is strongly dislocated as compared to the solutions in short wavelength region of the spectrum ( $\lambda_{\text{max}} = 332$  nm) that testify formation of H-aggregates, in which azobenzene groups are antiparallel arranged.<sup>[35–37]</sup> Therefore, overlapping of azobenzene terminal groups of neighboring

molecules of the dendrimers is realized in the amorphous films. Slight difference, however, is observed in the spectral region near 380 nm: optical density of the film of **G5AzoEt** is slightly higher; that can be attributed to some lower extent of aggregation of azobenzene groups in the case of the dendrimer of fifth generation (absorption in this region corresponds to either non-aggregated chromophores or J-aggregates with parallel arrangement of azobenzene chromophores<sup>[37]</sup>). In other words, the extent of overlapping of the terminal groups in the dendrimer **G5AzoEt** and content of H-aggregates are still slightly lower than those in the dendrimer of the first generation.

UV irradiation of the amorphous films of the dendrimers leads to existence of two processes simultaneously – *E/Z* photoisomerization and disappearance of H-aggregates, connected with the first one (Figure 3). The first processes appear as decrease of the absorption in the region of  $\pi$ - $\pi^*$

electronic transition of azobenzene chromophores and in increase of the optical density in the region of  $n\text{-}\pi^*$  electronic transition. The additional process of disappearance of the aggregates appears as absence of the isosbestic point in the region of the spectra near 300 nm, while the other isosbestic points at 243 (1), 264 (2), and 421 nm (3) can be clearly seen (Figure 3). As in the case of the solutions of the dendrimers, isomerization process is thermally reversible.

Therefore, it is possible to note that UV irradiation leads to significant spectral changes in the films of the dendrimers that is connected first of all with the *E/Z* photoisomerization of azobenzene groups; character of the photochemical transformations being practically independent on the generation number.

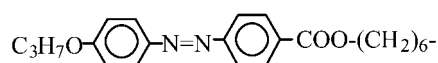
### Photoorientation Phenomena in Azobenzene-Containing Dendrimers

Under irradiation of the amorphous films of the dendrimers **G1AzoEt** and **G5AzoEt** by polarized UV light, the process of photoorientation of azobenzene groups in the direction perpendicular to the direction of vector *E* of incident light is observed (Figure 4–6). It follows directly from the linear

dichroism appearance in the films after UV irradiation (Figure 4, 5). It is well-known that a process of photoorientation in similar systems is induced by a photoselection phenomenon, i.e. selective photoexcitation of chromophores, the transitional moment of which directed parallel to the vector *E* of incident light.<sup>[2,3]</sup> Nevertheless, we revealed the following unusual, on our opinion, phenomenon in the processes of photoorientation in such systems.

First of all, kinetics of the process, the values of linear dichroism and of the order parameter do not depend on the generation number of the dendrimers. It points out that a local surrounding of azobenzene groups in amorphous films of the dendrimers is practically similar independently on the generation number (it is confirmed also by the spectra of the films (Figure 2)).

The second feature is absence of the photoorientation processes under irradiation of the films by polarizing light of Ar-laser (488 nm). This is a very unexpected effect, especially if one takes into account that irradiation of comb-shaped polymers with side azobenzene groups of similar structure usually is accompanied by their reorientation.<sup>[2]</sup> Moreover, for the dendrimer of the first generation with propyloxybenzoate terminal groups studied earlier a vice versa effect was observed:<sup>[16]</sup> irradiation with polarized UV light has not actually led to a photoorientation, while irradiation with Ar-laser was accompanied with appearing of photoorientation with an order parameter commensurable to those obtained for the dendrimers **G1AzoEt** and **G5AzoEt**. Such difference in behavior is apparently in direct connection with the difference in the structure of the substituents of azobenzene fragments. For the dendrimers under consideration, there are two alkoxy-substituents in *para*-position, and for the dendrimer described in the paper,<sup>[24]</sup> one of the substituent is a carboxy group being an electron-acceptor:



In this case, *E*-isomer has a noticeable longitudinal dipole moment that apparently leads to such substantial difference in photoorientational behavior of the dendrimers.

The third feature is connected with unusual change of the order parameter of azobenzene groups under irradiation with polarized UV light (Figure 6): at the beginning one can see an increase of the order parameter, then its maximal value is achieved (about 0.2), and finally, although it looks strange on a first glance, the order parameter decreases almost to zero. Analogous behavior was observed recently<sup>[38]</sup> for polyacrylic homopolymers with azobenzene groups of the similar structure. Most likely, this effect is connected with increase of the contents of *Z*-isomer during UV irradiation. As far as *Z*-isomer has very low anisotropy, increase of its concentration leads to full degeneration of the orientational order of the system under prolonged action of UV light.

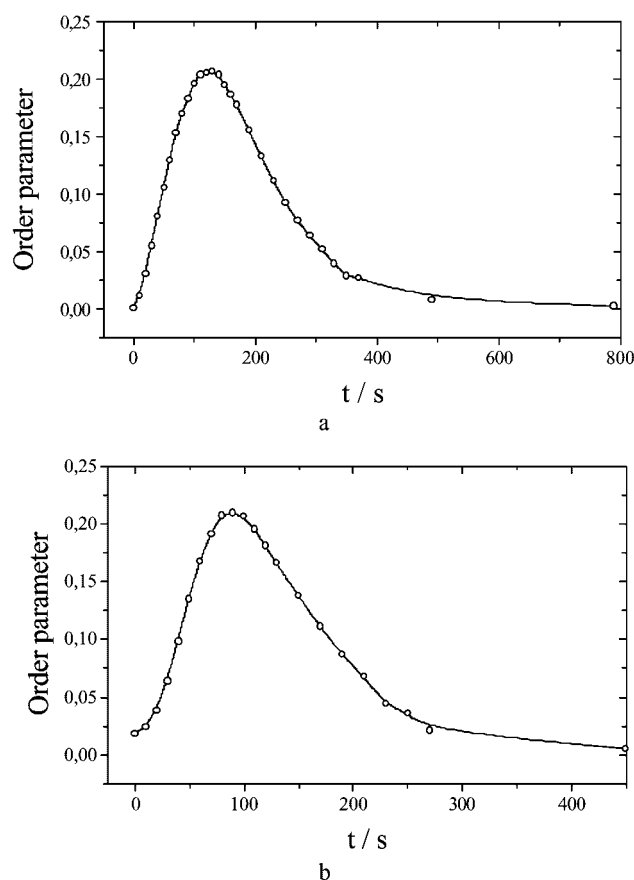


Figure 6. Change of order parameter calculated at 328 nm for dendrimers **G1AzoEt** (a) and **G5AzoEt** (b) during polarized UV light irradiation.



## Conclusion

In this work the photo-optical behavior of solutions and films of carbosilane dendrimers of different generations with azobenzene groups has been studied. It was shown that the generation number of the dendrimers does not have a significant influence on the kinetics of the photoorientation process and the values of the photoinduced order parameter.

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