Photochemical and Photoorientational Behavior of Liquid Crystalline Carbosilane Dendrimer with Azobenzene Terminal Groups

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The photochemical and photooptical properties of the first-generation LC dendrimer with terminal azobenzene groups which forms a SmA mesophase in a wide temperature range have been studied. A comparative analysis of its photochemical behavior in a dilute solution and a thin film was carried out. Under the action of UV irradiation, the E/Z photoisomerization of the azobenzene group takes place both in the solution and in the film. This process is found to be photochemically and thermally reversible. The kinetics of the thermal Z/E process is studied, and the activation energy of the process is calculated. The process of the photoinduced orientation of the terminal azobenzene groups in films of the dendrimer upon irradiation with linearly polarized UV light (365 nm) and with the green light of an Ar^+ laser (488 nm) was studied. Under irradiation with linearly polarized UV light, the E/Z isomerization takes place, but photoorientation is not observed. However, in the case of linearly polarized green light exposure (488 nm), a well pronounced linear dichroism is generated. The kinetics of the process was studied, and the photoinduced orientational order parameter was calculated.

I. Introduction

Recent years are characterized by an ever-growing interest in the new photosensitive materials which will be able to change their optical properties under light irradiation. This interest has been generated by new challenging applications of such systems for the design of various photooptical devices and preparation of various materials for data recording and storage. Presently, numerous low-molecular-mass and polymer compounds which are able to experience various photoinduced transformations have been developed.[1−3] In addition, the photoinduced physical processes such as light-induced orientation or diffusion are of special interest.

Quite recently, synthesis and characterization of a new class of compounds such as dendrimers provided the subject of numerous publications.[4] The heavily branched structure of dendrimer molecules manifests itself in a set of unique properties including the specific features of their photophysical[5] and photochemical behavior.[6−9] Dendrimers with photosensitive groups (usually azobenzene fragments) localized within the dendrimer molecule and grafted onto their surface are described. The possible applications of dendrimers with terminal azobenzene groups for holographic data recording were recently demonstrated.[9]

Undoubtedly, the preparation of photoactive dendrimers capable of the development of liquid crystalline (LC) phase presents an evident scientific and practical interest because the low viscosity of the dendrimers allows one to anticipate a fast optical response and the rearrangement of their branched structure under the action of external fields and, in particular, light irradiation. This aspect should be interesting for the development of fast-acting photosensitive materials, which can be easily handled.

Using the procedure for the synthesis of carbosilane LC dendrimers described by some of us previously,[10−12] we have synthesized a new first-generation carbosilane LC dendrimer containing terminal propyloxyazobenzene groups capable of undergoing E/Z photoisomerization (Figure 1a).[13] In this case, the terminal azobenzene fragments perform dual function: on the one hand, a rigid rodlike form of azobenzene moieties is responsible for a development of LC phases, and on the other hand, the presence of the $-N{=}N-$ photochromic group provides its sensitivity to the light.

In this work, we present the results on studying the specific features of photooptical behavior of the photochromic LC dendrimer in solution and in amorphous or LC films. The main attention will be given to the discussion of the pioneering data concerning the light-induced orientation of the azobenzene groups of the dendrimer under the action of linearly polarized light.

II. Experimental Section

The synthesis of the photochromic dendrimer was described in ref 13. GPC analyses were carried out with a KNAUER instrument equipped with a “Waters” (8 × 300 mm) column. Measurements were done using a UV detector, THF as the solvent (1 mL/min, 40 °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 Perkin-Elmer DSC-7 thermal analyzer (scanning rate of 10 K/min). The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope. X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered Cu Kα radiation, $\lambda = 1.54$ Å).

Thin films of the dendrimer were prepared by two techniques. In the first one, a small drop of the dendrimer was sandwiched between two quartz plates and annealed at 50 °C; in this case,

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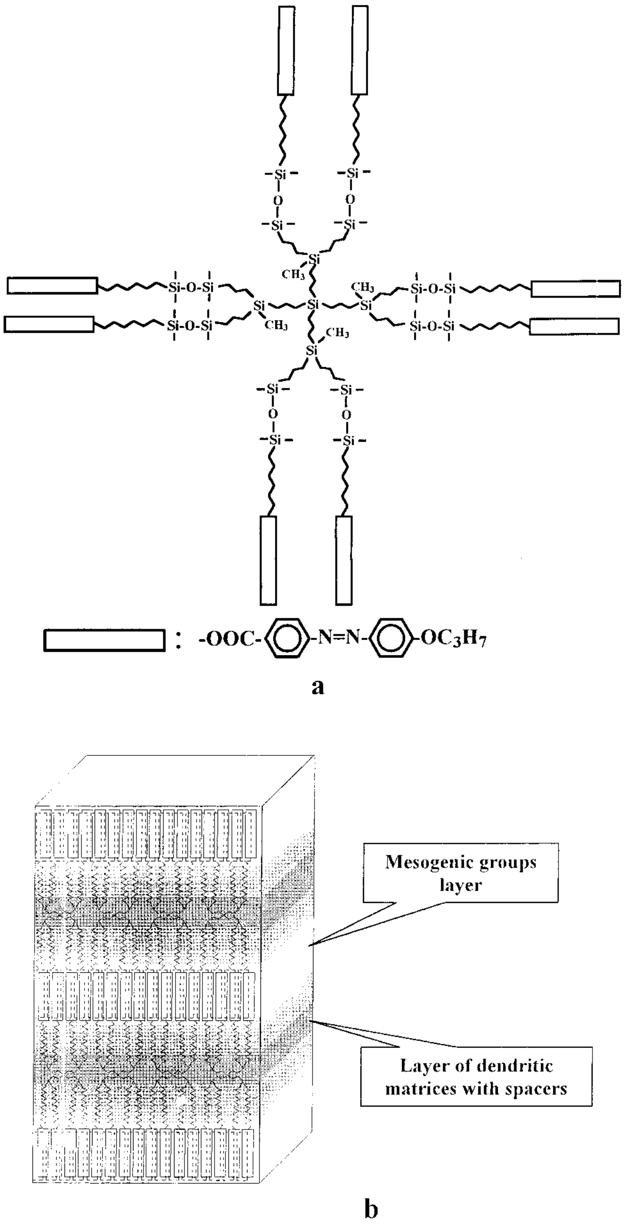


Figure 1. Structural formulas of the dendrimer (a) and scheme of possible packing of dendrimer molecules in SmA phase (b).

thin films having liquid crystalline polydomain texture were prepared. The second type of the films was prepared by the spin-coating technique using chloroform as the solution with a concentration of the dendrimer of about 10 mg/mL; in this case, isotropic transparent films were obtained. The films were dried by annealing at 100 °C during several minutes followed by fast cooling to room temperature in order to prevent SmA phase formation.

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

The photoorientation experiments were performed with the linearly polarized light of an Ar$^+$ laser at 488 nm (Innova 90/4 of Coherent) or, alternatively, with a set of an XBO 150 W lamp, a water IR filter, a metal interference filter (365 nm), and a Glan-Thomson prism as polarizer (the intensity of the light was ∼5.3 mW/cm^2 in this case). The exposure of the samples with the linearly polarized light was carried out in the film normal. The orientational order was studied by polarized UV/visible spectroscopy measuring the angular dependence of the absorbance with a photodiode array spectrometer (XDAP, Polytech). Because the direction of the maximum or minimum is not well-known, spectra are measured with a step-width of 5° each. The detection of dichroism or order parameter respectively is based on the fact that the transition moment of the $\pi\pi^*$ absorbance of the E azobenzene moiety is directed along the long axis of the rodlike moiety.

The linear dichroism was calculated by

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

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

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

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

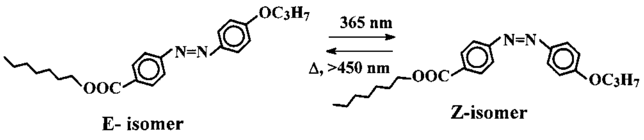
III. Results and Discussion

Phase Behavior. According to the data detected by polarized optical microscopy, DSC, and X-ray analysis, the synthesized dendrimer is characterized by the following phase transitions:

$$\mathrm{G} - 15\ \mathrm{SmX}\ 9\ \mathrm{SmA}\ 51\ \mathrm{I}$$

(temperature in degree Celsius) where SmX is a smectic mesophase with unknown structure. On the basis of the earlier structural studies on carbosilane dendrimers,[10,12] a possible scheme of the packing of the dendrimer molecules in the SmA phase was proposed (Figure 1b). As is shown in Figure 1b, the development of the layered LC order is accompanied by the "deformation" of the dendrimer molecule and the formation of two "segregated" parts composed of alternating layers of aromatic rodlike azobenzene groups and of the dendritic matrixes.[12]

Photochemical Behavior of the Dendrimer in Solution and Smectic Films. Let us consider the photochemical properties of the dendrimer in solution and in films. Figure 2 presents the changes of the absorption spectra of the solution and film of dendrimer under the action of UV irradiation (365 nm). As follows from Figure 2a, in the case of solution irradiation, it leads to marked spectral changes: one may observe a dramatic decrease in the optical density in the spectral region corresponding to the $\pi-\pi^*$ transition with the maximum at 360 nm, whereas in the region of the $n-\pi^*$ transition (∼450 nm), a slight increase in absorbance is observed. The above changes and the presence of isobestic points suggest the occurrence of a single UV-light-induced E−Z isomerization of azobenzene groups:[14]



In the case of the film, prepared by pressing a dendrimer drop between quartz plates (Figure 2b), the absorption maximum of the $\pi-\pi^*$ transition is somewhat shifted to shorter wavelengths. As is shown for LC side chain azobenzene-containing polymers,[15−19] this behavior is caused by the aggregation of azobenzene chromophores because of $\pi-\pi$ stacking. This head-to-head aggregation is always promoted by the development of smectic order. Upon UV irradiation, the spectral changes are

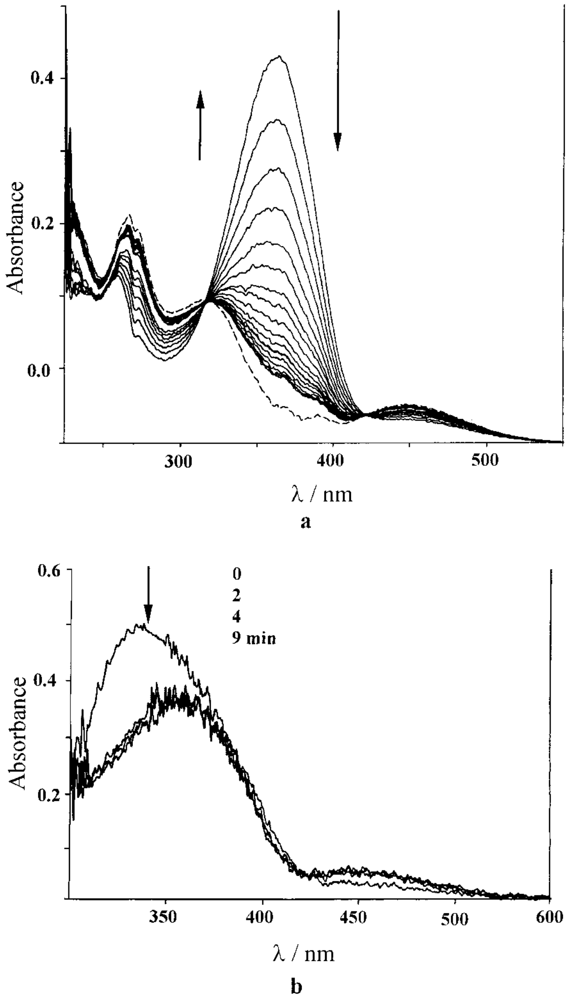


Figure 2. Spectral changes for solution (a) and LC film (b) of the dendrimer during UV irradiation (365 nm). In the case of a, spectra were recorded each 10 s of irradiation. The dashed line corresponds to a photostationary state. $T = 25$ °C. (b) Irradiation time is shown in the figure, $T = 25$ °C.

quite similar compared to that found in solution. Initially, the maximum is shifted to 360 nm destroying the aggregates at the beginning of irradiation process. However, in solution, a steady state with a very large amount of the E isomer is established under these irradiation conditions, whereas only a part of the groups can undergo isomerization in the film establishing a steady state with a much higher content of E isomers.

The specific feature of the photochemical behavior of the photochromic dendrimer is that the LC order of the films is violated because of irradiation, and the LC phase of the dendrimer is transformed into an isotropic state. This process is related to the fact that the Z isomer has a bent shape and in this way a low anisometry. Violation of the LC order is likely to be accompanied by a concomitant breakdown of H aggregates: as follows from Figure 2b, upon irradiation, the wavelength maximum is shifted to 360 nm which is characteristic for the isolated, nonaggregated isomer.

The sensitivity of such aggregates formed by azobenzene groups to the phase state of dendrimer is proved by the different spectra of film in LC phase and in isotropic melt (Figure 3).

Hence, upon irradiation of LC films of the photosensitive dendrimer, one may observe the occurrence of several processes such as E/Z photoisomerization, breakdown of aggregates, and isothermic phase SmA−I transition.

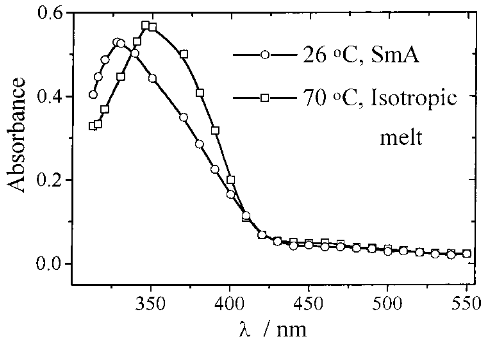


Figure 3. Spectra of the dendrimer film in the SmA phase and isotropic melt.

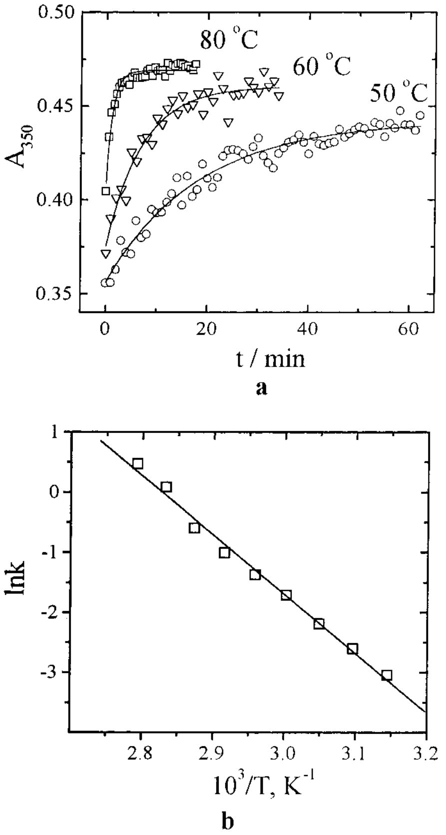


Figure 4. (a) Absorbance growth during annealing of LC film of dendrimer at different temperatures and (b) Arrhenius plot for temperature dependence of rate constant of thermal Z/E process.

Kinetics of Thermal Z/E Isomerization and I−SmA Transition in the Dendrimer Films. In the case of films and solutions of the dendrimer, the process of E−Z isomerization is photochemically and thermally reversible; that is, under the action of visible light and annealing, back Z−E isomerization takes place. The kinetics of the thermal back isomerization was studied in the LC state and in the isotropic melt, i.e., at different temperatures. To this end, the film of the dendrimer was irradiated with UV light for 20 min and annealed at different temperatures. The increase in the optical density at the wavelength corresponding to the maximum of $\pi-\pi^*$ absorbance was measured (Figure 4). Figure 4a shows the temperature dependence of the Z/E isomerization rate. To calculate the rate constant of this process, the values of $(A_\infty - A_t)/(A_\infty - A_0)$ were plotted versus the time, where A_0 is the initial optical density and A_t and A_∞ stand for the values of optical density at the time t and at the steady state, respectively.

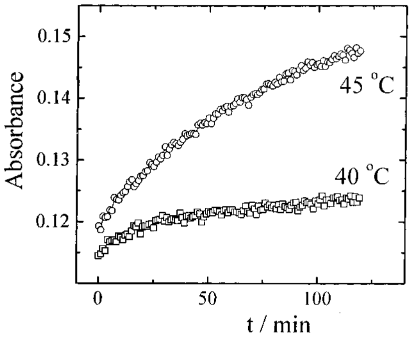


Figure 5. Absorbance growth at wavelength 600 nm during the annealing of the isotropic film at different temperatures. Before annealing, the film was irradiated for 20 min by UV light.

TABLE 1: Values of Half-Life Period and Rate Constants for Back Z/E Isomerization Process at Different Temperatures

T, °C	$t_{1/2}$, min	k_1, min^{-1}
50	9.37	0.074
60	3.85	0.18
70	1.93	0.36
80	0.37	1.87

The dependencies can be approximated by the following biexponential function:

$$(A_\infty - A_t)/(A_\infty - A_0) = B_1 \exp(-k_1 t) + B_2 \exp(-k_2 t) \quad (1)$$

where k_1 and k_2 are the rate constants of fast and slow processes, respectively, and B_1 and B_2 stand for the relative contributions of the fast and the slow process to the kinetics of the isomerization, respectively. Taking into account that, in our case $B_1 \gg B_2$, a detailed analysis of the rate constants of the slow process is beyond the scope of this work.

It is well-known that the kinetics of the isomerization processes in viscous (for example, polymeric) media does not often obey a classic kinetic law.[20] This is assigned to the different structures of cages which involve reacting molecules. However, in our case, this deviation is not so large, and we analyzed the contribution of only the fast process. So, Table 1 presents the rate constants of the fast process. As is well seen, the Z/E isomerization rate strongly depends on the temperature.

To calculate the activation energy of the thermal Z/E isomerization, the rate constants are plotted against the reciprocal temperature (Figure 4b). E_A is calculated from the slope of this plot, and it is found to be about 19.5 kcal/mol. The value of the activation energy is typical for azobenzene derivatives.[21]

The kinetics of the transition of the irradiated and in this way amorphized dendrimer film from its isotropic state to a film with smectic domains was analyzed. For this purpose, the optical density is measured at 600 nm (Figure 5) during the annealing procedure.

The dendrimer molecules do not absorb in this spectral region; the increase in optical density at this wavelength is exclusively related to the development of SmA domains. This process is accompanied by the appearance of light scattering.

Analysis of the kinetic dependencies through eq 1 allows one to estimate the rate constants of the I−SmA phase transition; the calculated values are summarized in Table 2. Similar to the Z/E isomerization, the as-calculated rate constants strongly depend on the temperature, but the corresponding values are somewhat lower. In this case, the activation energy is about 33 kcal/mol, and this is 1.5 times higher than that of Z/E isomerization. This difference in the values of rate constants and activation energy is likely to be related to the fact that, in the case of the irradiated film, the rate of isothermic I−SmA phase transition is controlled by the two processes: first, thermally induced Z/E isomerization and, second, the development of domains with smectic order. Both processes proceed almost simultaneously and provide the contribution to the irradiation-induced transition of dendrimer to initial state which is characterized by SmA order with a 100% content of E isomeric form of the azobenzene terminal groups.

TABLE 2: Values of Half-Life Period and Rate Constants for Phase Transition I−SmA for Amorphous Films of the Dendrimer at Different Temperatures[a]

T, °C	$t_{1/2}$, min	k_1, min^{-1}
40	43.3	0.016
45	36.5	0.019
50	15.8	0.044

[a] In order to obtain amorphous films, UV light irradiation at room temperature was performed.

Photochemical Behavior of Spin-Coated Films of the Dendrimer. Using the spin-coating technique, thin isotropic, optically transparent films were prepared with a thickness of less than 1 μm. Even though the glass transition temperature of the dendrimer is low, the development of the smectic phase takes several days at room temperature. This process is accompanied by a loss in transparency and the development of a focal conics texture which is typical for SmA mesophase. In this case, the kinetic hindrances provide a unique possibility to study the specific features of E/Z photoisomerization and photoorientation of the amorphized film of dendrimer. Let us consider photochemical behavior of these films.

Figure 6 presents the corresponding spectra for such amorphized film of dendrimer upon irradiation with UV (Figure 6a) and subsequent visible light exposure (Figure 6b). In the case of the spin-coated film, the UV irradiation leads to better pronounced spectral changes as compared with those that are seen for the LC sample (compare Figures 2b and 6a). This evidence implies that, in the amorphous film, the conversion of E/Z photoisomerization is much higher than that in the ordered film. In this case, LC order markedly prevents the photoisomerization process. As compared with the solution, the maximum of $\pi-\pi^*$ transition of the azobenzene chromophore is shifted to the shorter wavelengths (see Figures 2a and 6a). Let us also note that for the smectic and amorphized films the absorption maxima almost coincide at 326 nm. These facts suggest that, both in the amorphous and in LC films, aggregation takes place. The absence of isosbestic points and shift of the maximum of the $\pi-\pi^*$ transition to 360 nm during the first seconds of UV irradiation indicate the breakdown of these aggregates in the course of the E/Z photoisomerization.

As in the case of the LC film, the process of E/Z isomerization is thermally and photochemically reversible. Irradiation with visible light leads to an increase in the absorption in the spectral region of the $\pi-\pi^*$ transition, but as compared with fresh film, its maximum is slightly shifted to a longer wavelength region (Figure 6a). This behavior is related to the fact that the development of aggregates requires a certain time; in the case studied, the initial profile of the corresponding spectra is restored within several minutes.

Photoorientational Phenomena in Spin-Coated Films of the Dendrimer. Photoinduced orientation of azobenzene groups in polymeric materials under polarized light is a well-known process.[17,22] In the present work, the peculiarities of photoorientation of the terminal azobenzene groups of the carbosilane dendrimer have been studied for the first time. The irradiation

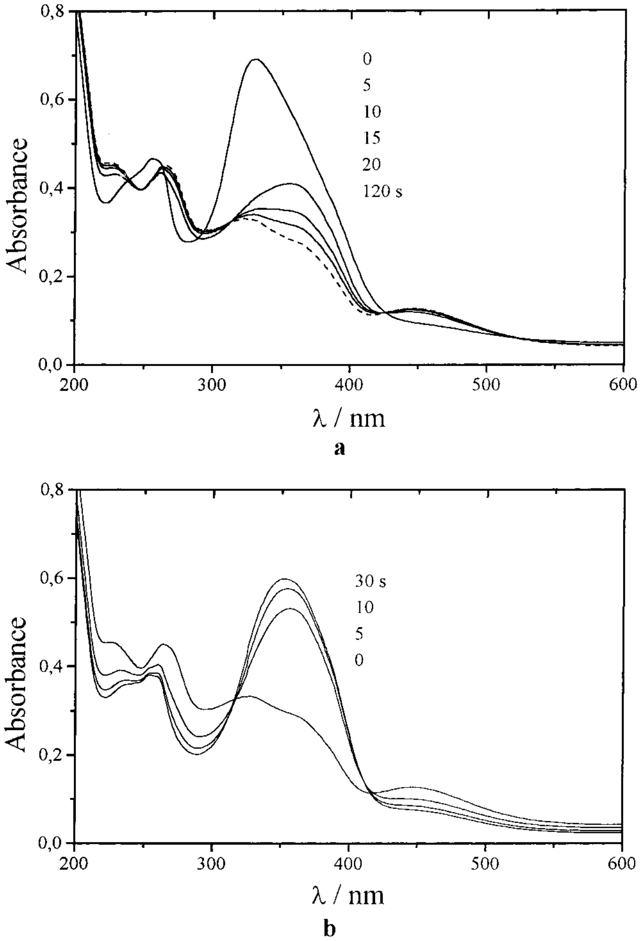


Figure 6. Spectral changes during UV irradiation (a, 365 nm) and visible light irradiation (b, 436 nm) of spin-coated amorphous dendrimer film.

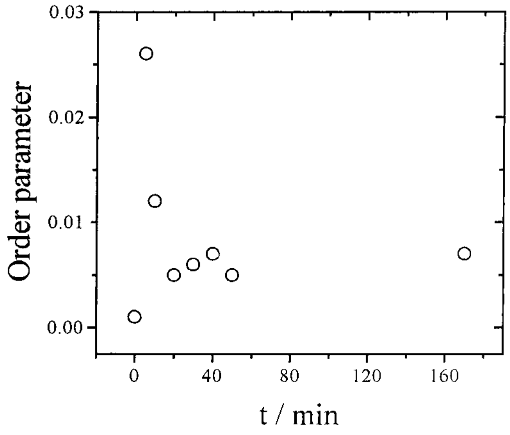


Figure 7. Change of order parameter during polarized UV light (365 nm) irradiation calculated at 332 nm.

with linearly polarized UV light (365 nm) results in an angular dependent E/Z photoisomerization, but the photoorientation process was not practically observed. As follows from Figure 7, a weak optical anisotropy is generated during the first minutes of the polarized UV irradiation. In this time, an orientational order is induced, but upon further irradiation, the order decreases almost to zero. The high amount of Z isomers which is formed under this condition prevents the development of a photoinduced order.

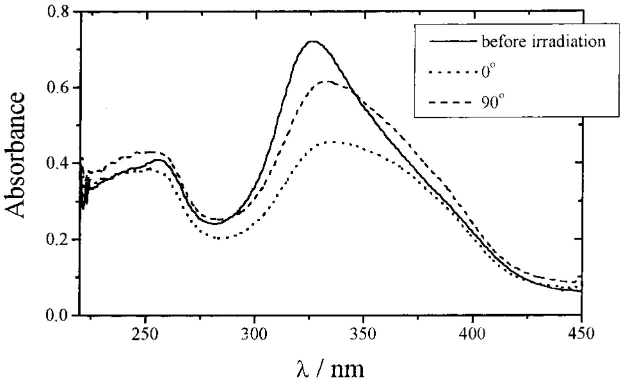


Figure 8. Linear dichroic spectra measured for the spin coated film of the dendrimer before irradiation and after irradiation by Ar$^+$ laser (100 mW/cm^2) during 60 min. In the last case, spectra were recorded along and perpendicular electric vector.

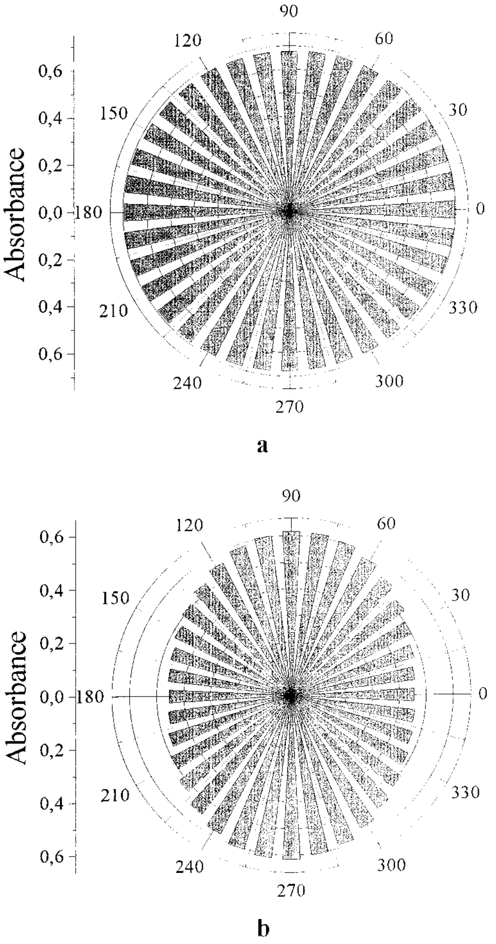
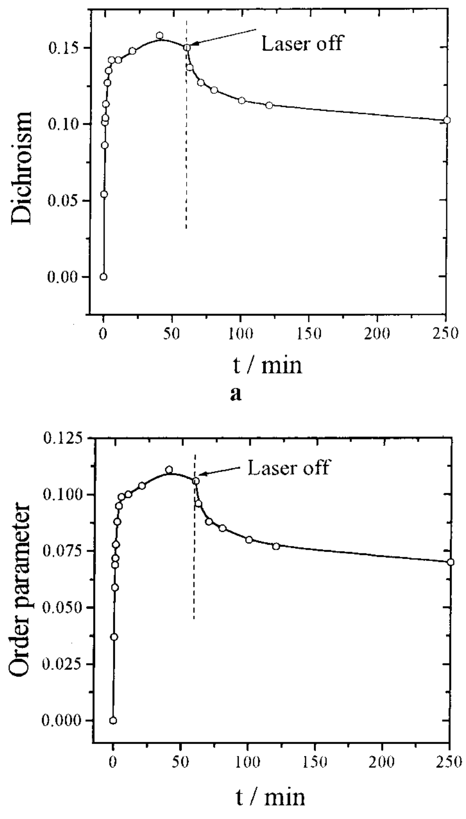


Figure 9. Polar diagrams for the dendrimer obtained before (a) and after (b) irradiation with Ar$^+$ laser (100 mW/cm^2) during 60 min. The temperature is 22 °C. Polar diagrams were plotted for $\lambda = 332$ nm.

A quite different behavior is observed when the film of dendrimer is irradiated with an Ar$^+$ laser (488 nm): a well-pronounced linear dichroism is developed (Figures 8 and 9). In this case, maximum values of dichroism and order parameter S are about $D = 0.16$ and $S = 0.11$, respectively. This is rather low as compared, for example, with the azobenzene-containing comb-shaped polymers having glass transitions above the room temperature.[19] This evidence implies that the degree of photoorientation of azobenzene groups is rather low, so, the photoinduced parameter is much lower than the order parameter of the aligned SmA mesophase.

Once irradiation is ceased, the values of linear dichroism tend to decrease (Figure 10). This behavior should be associated with



a

b

Figure 10. Change of the linear dichroism (a) and order parameter (b) during Ar^+ laser irradiation (100 mW/cm^2) calculated at 332 nm.

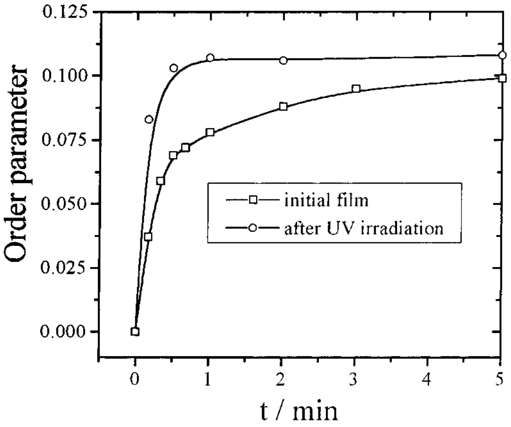


Figure 11. Change of the order parameter during Ar^+ laser irradiation (100 mW/cm^2) calculated at 332 nm for the film nonirradiated and irradiated previously by UV light (365 nm, 2 min).

the relatively low viscosity of the dendrimer even at room temperature. Upon the prolonged annealing (several hours), the dichroism is decreased to zero.

The irradiation of film of dendrimer in the SmA phase with linearly polarized visible light does not lead to the appearance of linear dichroism at room temperature. The smectic order prevents completely the photoorientation process of the azobenzene groups.[19]

We also have studied the influence of photochemical pretreatment of the dendrimer film by UV irradiation on the kinetics of the photoorientation process caused by visible light (488 nm). The UV irradiation results in a high content of azobenzene groups in its Z form causing a breakdown of the aggregates which hinder the light-induced orientation process. The subsequent Ar^+ laser exposure establishes immediately the related steady state, in which the photoorientation takes place. As follows from Figure 11, the limiting values of the photoinduced order parameter almost coincide with those of non-UV irradiated film. This finding is in contrast to other, stronger aggregated samples below the glass transition temperature and at lower power density of the laser. In addition, the rate of photoorientation is much higher in the case without pretreatment.

IV. Conclusion

Hence, in this work, the kinetics of E/Z and Z/E isomerization of terminal azobenzene groups of the first-generation carbosilane LC dendrimer was studied. UV irradiation leads to the breakdown of smectic order and to the transition of the sample to an isotropic melt. The irradiation with linearly polarized visible light causes a photoorientation of terminal azobenzene groups; however, the photoinduced anisotropy is rather small. Further work in this direction will be focused on a comparative analysis of the kinetic features of photoisomerization and photoorientation for dendrimers of various generations and higher glass transition temperatures.

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