

The peculiarities of the photoorientation processes in azobenzene-containing liquid crystalline *homo*- and *co*-dendrimers



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ABSTRACT

For the first time the influence of molecular structure and generation number of photochromic LC *homo*- and *co*-dendrimers with azobenzene terminal groups on the photoorientation processes induced by polarized light was studied. It is shown that liquid crystalline smectic or columnar phase formation enables to stabilize photoinduced alignment even at temperatures above the glass transition. Unusual dependence of values of photoinduced dichroism on the generation number was found. For the dendrimers of low generation (1st–3rd) an increase in generation number leads to a decrease in photoinduced dichroism, whereas for the dendrimers of 4th and 5th generation very high values of dichroism were found. These values are comparable with the dichroism for the well-studied before azobenzene-containing side chain polymers. Possible explanations of the observed peculiarities based on the spectral data, difference in phase behavior and aggregation phenomena are suggested. Possibilities of the optical image photorecording on the films of the photochromic LC-dendrimers were demonstrated.

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1. Introduction

The development of new types of “smart” materials and investigations of their properties are the most challenging fields of modern science. One of the most promising substances designed in order to obtain smart materials are dendrimers, high-molecular mass compounds having superbranched molecular structure pre-determining their unique physico–chemical properties [1]. Introduction of photochromic moieties into the central core, dendrimer matrix or as terminal groups enables to create a huge variety of new photoresponsive materials which can be used for regulated drug delivery, development of new types of biosensors, optoelectronics, etc [1–8].

Among different type of stimuli-responsive systems liquid crystalline (LC) dendrimers attract a great attention since their first synthesis in early 90th [9,10]. A special interest present photosensitive LC-dendrimers because they combine symmetrical dendritic molecular architecture, tendency to self-organization and formation of different mesophases with unique photoresponsive properties provided by photochromic moieties [11–18]. This

combination of functionalities enables to realize photoregulation of LC-order, orientation and, thus, optical properties of dendrimers.

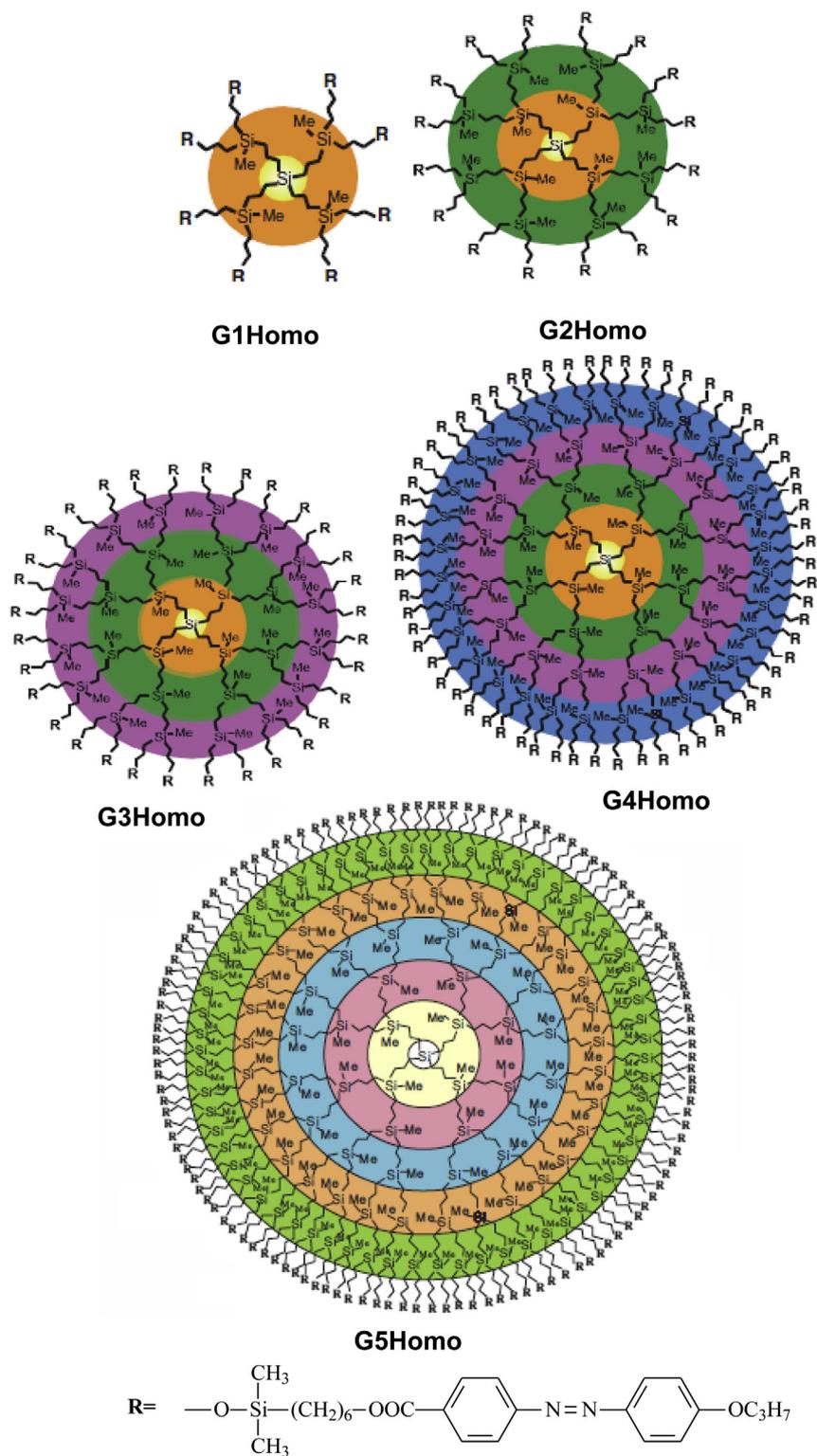
Despite a large number of papers devoted to the synthesis and investigations of light-responsive dendrimers only a few papers describe photochromic self-organized LC dendrimers [18–27].

This work deals with the study of the photooptical properties and photoorientation phenomena in films of dendrimers of different generation with azobenzene-containing terminal groups. Synthesis and detailed investigations of the phase behavior of these substances were published earlier [26,27]. Constitution of dendrimers is presented in Schemes 1 and 2. Dendrimers with different generation number, from 1st to 5th (Scheme 1), and *co*-dendrimers with azobenzene and aliphatic terminal groups were studied (Scheme 2). All dendrimers studied in this work consist of carbosilane dendritic matrix and terminal azobenzene moieties. *Homo*-dendrimers **G1Homo–G5Homo** consist of different number of terminal groups varying from 8 to 128. *Co*-dendrimers have different molecular architecture: **G2Stat** has statistical distribution of terminal alkyl and chromophore units (with ratio 1:1), whereas in **G2Block** all chromophores and alkyl chains are separated as in block-copolymers.

A choice of azobenzene chromophores is explained as follows. Azobenzene derivatives are the most convenient type of chromophores undergoing reversible E–Z photoisomerization accompanied by significant changes in their molecular anisometry (rod-like

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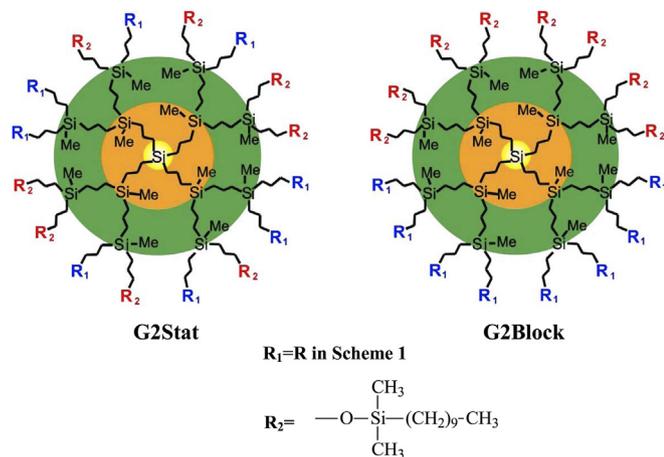
E-mail address: bbrvsky@yahoo.com (A. Bobrovsky).



Scheme 1. Structure of azobenzene-containing LC homo-dendrimers of different generations.

E-form transforms to bent-like Z-isomer). In LC-media such structural changes enable to realize isothermal phase transitions [28–34], LC-director rotation [28,29], nonlinear optical effects [28], photomobility [28,35], and many other interesting phenomena which is also promising for the different applications. It is noteworthy, that polarized light action induces in films of polymeric

and, in some cases, in low-molar-mass azobenzene derivatives photoorientation processes [28,29]. These phenomena are associated with the repetitive processes of E–Z–E isomerization accompanied by rotational diffusion of chromophores in direction perpendicular to the polarization plane of light (or electric field vector). The photoorientation effects allow one to effectively



Scheme 2. Structure of azobenzene-containing LC co-dendrimers of 2nd generation (concentration of the terminal groups R_1 and R_2 is equal).

regulate optical properties of films, such as birefringence and dichroism that makes azobenzene-containing substances very promising for different applications in photonics [28].

Table 1 summarizes phase transitions temperatures of all investigated dendrimers. Homo-dendrimers of 1–4th generations form only smectic mesophase and low-temperature crystalline phase, whereas dendrimer of 5th generation is characterized by the columnar phase. Details of the mesophases structure of dendrimers are described earlier [2,26,27].

The main goal of the present work is the study of light-induced phenomena in LC photochromic dendrimers in order to elucidate the influence of molecular structure (generation number, molecular architecture of co-dendrimers) on photooptical properties of these substances. It is very important to point out that the difference in the mesophase types of homodendrimers of the first–fourth generation (G1-Homo–G4-Homo) forming layered smectic structure and the homodendrimer of the fifth generation (G5-Homo) forming the columnar structure had to predetermine their different behavior with respect to the light illumination. This suggestion was clearly evidenced in the framework of our experimental work (see below). A special attention is paid to the investigation of photo-orientation processes in spin-coated films of photochromic LC-dendrimers induced by polarized visible light.

2. Experimental

2.1. Synthesis and phase behavior

Synthesis of photochromic LC-dendrimers was described earlier [26,27]. The phase transition temperatures of the monomers and

Table 1
Phase behavior of photochromic LC dendrimers (Cr—crystalline phase, SmA—smectic A phase, Col_{rec}—rectangular columnar phase, G—glassy state.)

Dendrimer	Phase transitions/°C
<i>Homodendrimers</i>	
G1Homo	Cr 13 SmA 66 I
G2Homo	Cr 8 SmA 62 I
G3Homo	Cr 3 SmA 58 I
G4Homo	Cr 3 SmA 59 I
G5Homo	G-22 Col _{rec} 62 I
<i>Co-dendrimers</i>	
G2Stat	Cr ₁ –17 Cr ₂ 2 I
G2Block	Cr 12 SmA 40 I

polymers were detected by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min). The polarizing optical microscope investigations were performed using LOMO P-112 polarizing microscope equipped by Mettler TA-400 heating stage. Detailed X-ray investigations were performed earlier and described elsewhere [27].

2.2. Photo-optical investigations

Thin films of the dendrimers for photo-optical experiments were obtained by spin-coating technique using solutions of different concentration in chloroform (~20 mg/mL). In order to completely remove any traces of chloroform the spin-coated films were kept at room temperature during one day. Thickness of the films was in the range of 100–200 nm.

Photochemical investigations were performed using an optical set up equipped with KLM-473/h-150 diode laser (473 nm, ~2 W/cm²). Spectral measurements were performed using Unicam UV-500 UV-Vis spectrophotometer. The linearly polarized spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with rotating polarizer (Glan–Taylor prism controlled by computer program). All irradiation experiments were performed at room temperature. For heating of the irradiated samples Mettler TA-400 heating stage was used.

The dichroism values, D , of the polymer films were calculated from the spectra using the following eq (1):

$$D = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + A_{\perp}) \quad (1)$$

where A_{\parallel} and A_{\perp} are the absorbance parallel and perpendicular to the preferred azobenzene chromophore orientation direction, respectively.

3. Results and discussion

3.1. Spectral properties and aggregation phenomena in homo-dendrimers films

In order to obtain the information about the local arrangement of chromophores in LC-films it is worthy of attention a comparison

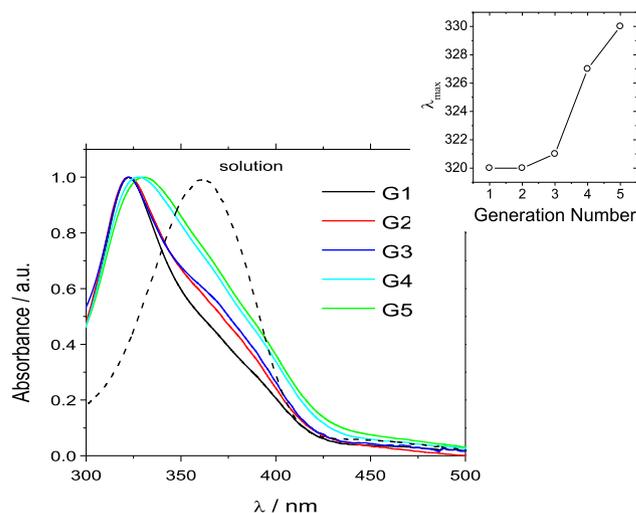


Fig. 1. Normalized absorbance spectra of spin-coated dendrimers films. Dashed line corresponds to absorbance of dendrimers solutions in dichloroethane. Insert shows wavelength of $\pi\text{--}\pi^*$ electronic transition maxima on generation number (error in λ_{max} determination is ± 1 nm).

of the electronic absorbance spectra of all dendrimer films. First of all, it should be noticed, that absorbance maximum corresponding to $\pi-\pi^*$ electronic transition of azobenzene chromophore for all dendrimer films is shifted to the shorter wavelength ($\lambda_{\max} \sim 320-330$ nm) in comparison with the dilute solution of dendrimers in dichloroethane ($\lambda_{\max} = 362$ nm) (Fig. 1). This shift is caused by well-known aggregation phenomena and formation of so-called H-aggregates with antiparallel packing of chromophores (Scheme 3a) [36–38]. In addition, a comparison of the absorbance spectra reveals noticeable differences in position of absorbance maximum; for dendrimers of the 4th and 5th generation position of maximum is noticeably shifted to longer wavelength (see inset in Fig. 1). Absorbance spectra for dendrimer of the first three generations have the same position of maximum, but, nevertheless, consist of “shoulder” coinciding with the $\pi-\pi^*$ electronic transition peak of dendrimers solution (Fig. 1, dashed line). Relative intensity of this “shoulder” increases with the generation number growth. Such spectral difference could be explained by geometrical constraints provided by carbosilane dendrimers matrix increasing with the generation number and preventing antiparallel layered packing of azobenzene chromophores in H-aggregates (Scheme 3b). As was already shown in our papers [2,27], for dendrimers of low generations the mesogen groups are easily adopt a layered ordering due to the flexibility of dendritic matrix and relatively small numbers of terminal groups. Apparently, the influence of matrix strongly increases with growth of generation number (the 4th and, especially the 5th generation). A comparison of the possible local arrangement and packing of the mesogenic groups for low and high generations of homodendrimers is shown in Scheme 3. One can clearly imagine the steric hindrances existing for the formation of layered structures of photochromic fragments in the high generations of homodendrimers. Namely these structural features determine the difference in photooptical behavior of homodendrimers of the low and high generation, which considered below.

3.2. Spectral properties and aggregation phenomena in co-dendrimer films

Molecular architecture of the studied co-dendrimers of low generation has extreme influence on the aggregation phenomenon. Thus, significant aggregation takes place in block co-dendrimers, spectra of homo- and block co-dendrimers are almost coincide, but the aggregates almost completely disappear in statistical co-

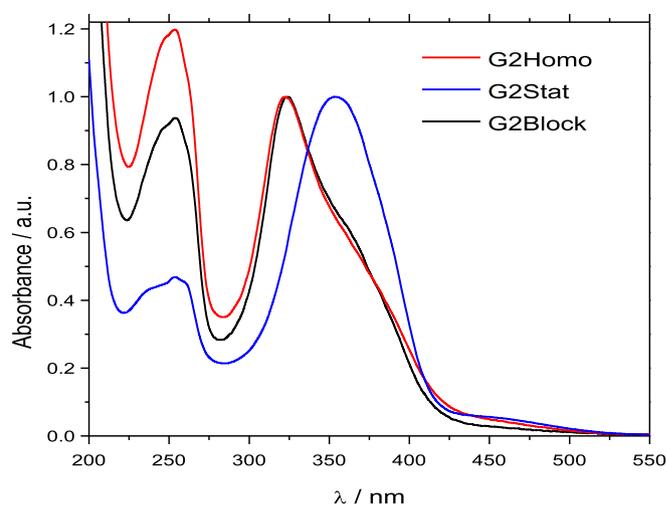


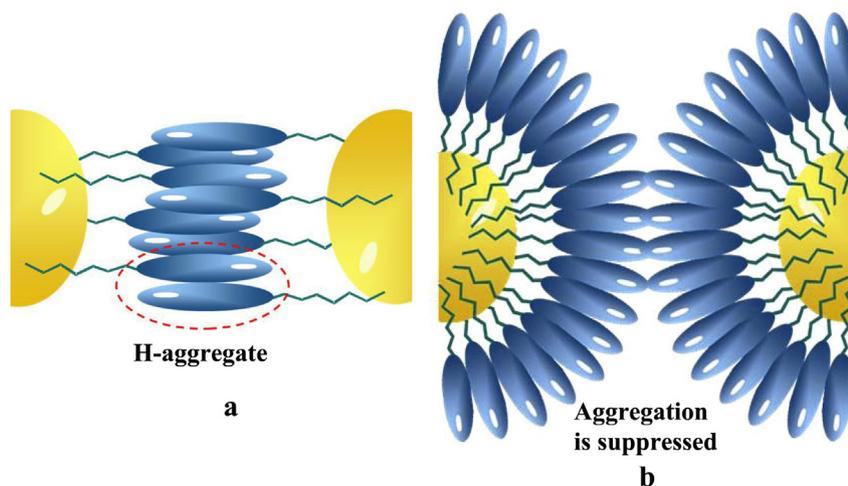
Fig. 2. Comparison of normalized absorbance spectra of spin-coated films of homo- and co-dendrimers of the second generation.

dendrimers (Fig. 2). In other words, a “dilution” of azobenzene chromophores by aliphatic fragments in statistical co-dendrimers completely suppresses the aggregation process.

3.3. Photoorientation process in homo-dendrimers films induced by polarized light

Preliminary investigation of photooptical properties of azobenzene dendrimers have revealed that UV-light action leads to efficient E–Z isomerization of photochromes, whereas polarized UV-light induces only small optical anisotropy (with dichroism values $D \sim 0.2$) decreasing under prolonged irradiation [2,22,23]. This effect is explained by a high concentration of Z-isomer disturbing LC-order in the films. Taking into account this fact, for the photoorientation study we have used the blue polarized light (473 nm) instead UV-light.

Irradiation of dendrimers films by the polarized blue light results in an appearance of the anisotropy in absorbance spectra. After the polarized light action the azobenzene chromophores are oriented in direction perpendicular to the polarization plane that



Scheme 3. Models showing possible chromophores local arrangement for dendrimers of low (a) and high generations (b).

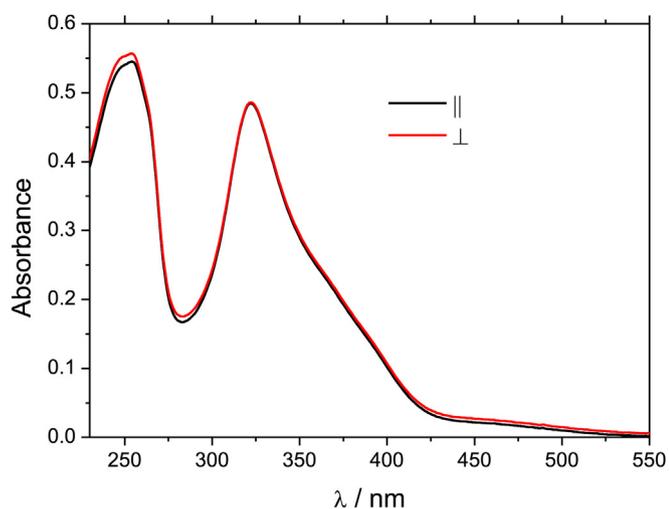
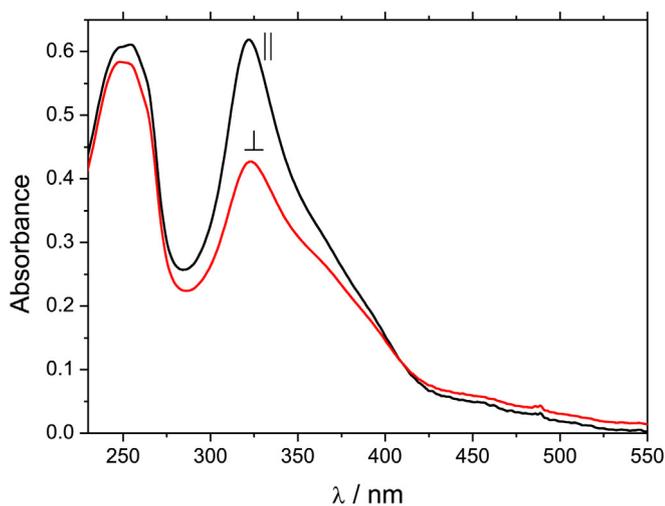
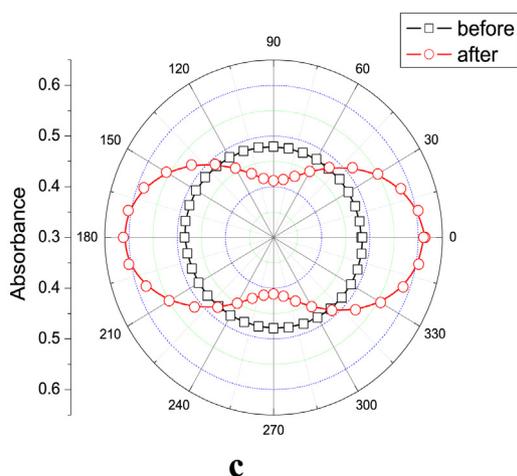
**a****b****c**

Fig. 3. (a) Polarized absorbance spectra of **G2Homo** film before (a) and after 140 min of polarized blue light (473 nm) irradiation (b). (c) Polar plot of absorbance at 323 nm.

leads to growth of significant absorbance anisotropy (Figs. 3 and 4). Using eq (1) dichroism values were calculated and comparative study of kinetics of dichroism growth for all dendrimers was performed (Fig. 5).

It should be pointed out that in order to establish the exact mechanism of photoorientation phenomena in smectic or columnar mesophases it is necessary to perform detailed X-rays investigations of films exposed to an irradiation. Nevertheless, we may assume that polarized light induces rotation diffusion of chromophores and photoinduced melting of the mesophase followed by “recrystallization” and formation of LC-domains with chromophores predominately oriented perpendicular to the polarization plane (Scheme 4). The domain growth model recently developed for nematic azobenzene-containing LC-polymer [39,40] could be applied in future in order to explain the observed peculiarities.

For dendrimers of low generations (1st–3rd) an increase in generation number results in strong decrease in photoorientation efficiency (Fig. 5). This effect could be explained by partial disruption of the smectic mesophase layered structure by the carbosilane matrix that is supported by decreasing of isotropization enthalpies measured by DSC [27].

Nevertheless, dendrimers of the 4th and 5th generations show highest values of photoinduced dichroism. Maximal value of dichroism was observed in films of the **G5Homo**. Possible explanation of this peculiarity can be connected with the strong

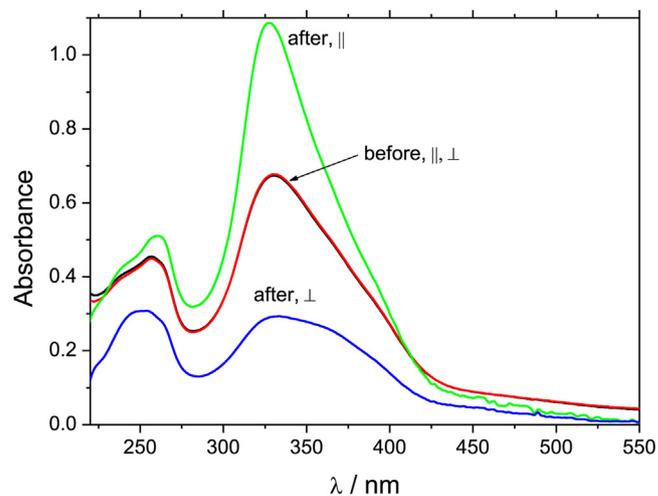
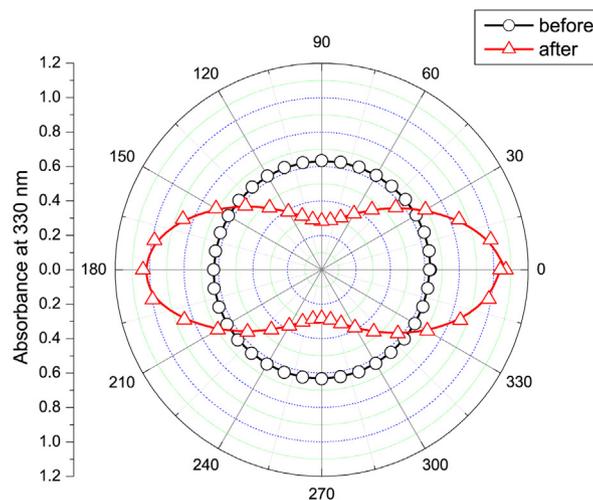
**a****b**

Fig. 4. (a) Polarized absorbance spectra of **G5Homo** before and after 100 min of laser irradiation. (b) Polar plot of absorbance at 330 nm.

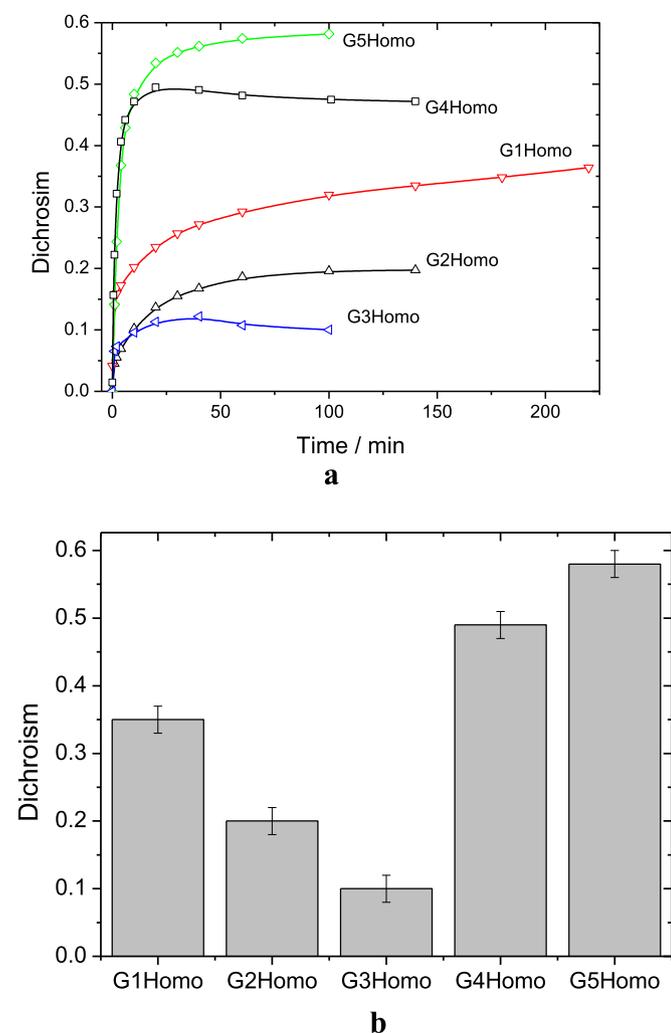


Fig. 5. Comparison of dichroism growth kinetics (a) and its maximal value (b) for dendrimers of the different generations.

suppression of aggregation phenomena in the dendrimers of 4th and 5th generations discussed above. It is noteworthy that mechanism of chromophores photoorientation in films of dendrimer **G5Homo** forming columnar phase is rather complicated. There are at least two possibilities of photoinduced ordering schematically shown in Scheme 4b. In all cases according to spectral observations chromophores are aligned perpendicular to the polarization plane of incident light. However, one possibility is the orientation of columns in direction perpendicular to the polarization of light (shown by blue arrow (in web version)), whereas another possibility is the alignment of columns along the polarization vector.

Kinetics curves presented in Fig. 5a show the noticeable difference in kinetics of dichroism growth for *homo*-dendrimers of the different generations. For the dendrimers **G3Homo**, **G4Homo** after ~25 min irradiation slight decrease in dichroism takes place which is accompanied by decrease in polarized absorbance components (Fig. 6c). Fast increase in dichroism at the first stage followed by the slow decrease under prolonged irradiation is explained by the homeotropic orientation of chromophores during irradiation (along the normal to film plane). This effect was also observed earlier for smectogenic side-chain azobenzene polymers [41–44]. Photoinduced homeotropic alignment did not find for dendrimer **G5Homo** forming columnar mesophase (Fig. 6d) as well for the smectic dendrimers of lower generations (1st, 2nd) (Fig. 6a, b).

3.4. Photoorientation process in co-dendrimer films induced by polarized light

The *co*-dendrimers molecular architecture plays crucial role in the photoorientation process. For statistical *co*-dendrimer this process does not take place at all (Fig. 7a). This effect is most probably associated with the difference in phase behavior of dendrimers. As discussed in Introduction section temperature range of mesophase for statistical *co*-dendrimers located far below room-temperature and irradiation of samples is performed in isotropic non-glassy state. Thus, we may assume that polarized light action could also induce the photoorientation process, but due to the low viscosity of dendrimer film at room temperature and absence of the mesophase this induced uniaxial order can not be preserved.

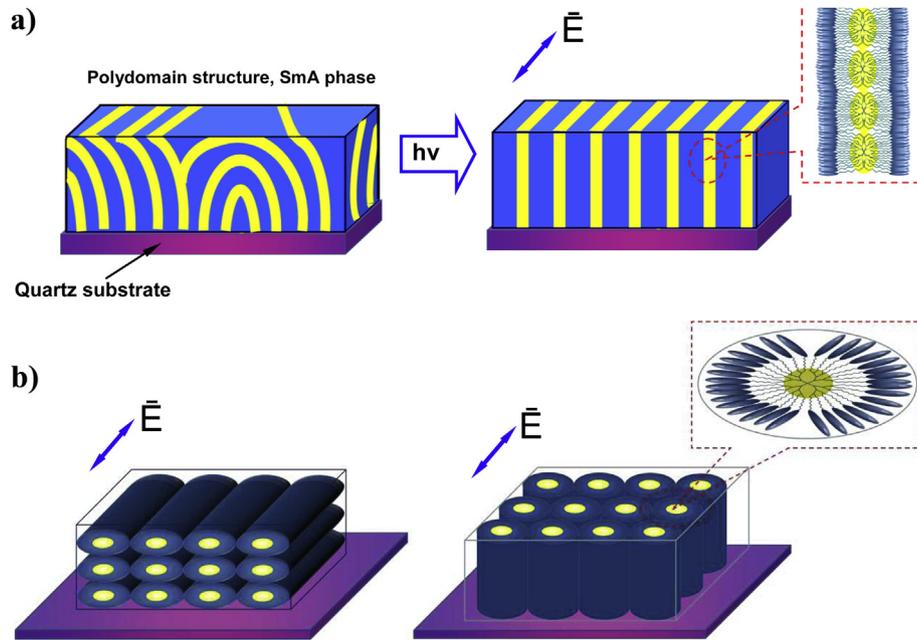
Fig. 7b demonstrates kinetic curves of dichroism growth for *homo*-dendrimer and block *co*-dendrimer. For block *co*-dendrimer the rate of dichroism growth is much higher, whereas maximal values of dichroism is twice less than for *homo*-dendrimer (Fig. 7b). The presence of aliphatic nonmesogenic units decreases an ability to uniaxial order photoinduction.

3.5. Photooptical recording on dendrimers films

Dichroism values obtained for dendrimers **G4Homo** and **G5Homo** are comparable with the dichroism for the well-studied before azobenzene-containing side chain polymers [29,45]. High values of photoinduced dichroism enable to record the birefringent images visible between crossed polarizers. Fig. 8 shows polarizing optical micrograph showing spin-coated film of **G5homo** irradiated by 473 nm laser through the mask during 40 min. Brightest areas in the image correspond to the irradiated zones with high photoinduced order, whereas gray zones are the birefringent regions having polydomain columnar supramolecular structure. It is noteworthy, that the recorded images are stable in time at room temperature at least for several months. Such thermostability is rather unusual, especially taking into account the fact that glass and melting transition temperature of all dendrimers are lower than room temperature (Table 1). An ultimate stability of photoinduced orientation is caused by the formation of LC-phase in films. A complete disappearance of photoinduced dichroism was found only at temperatures corresponding to the isotropic phase of films.

4. Conclusions

For the first time, the peculiarities of photoorientation processes in series of photochromic LC-dendrimers and LC codendrimers of different structure and generation number are investigated. It is shown that liquid crystalline phase formation plays a crucial role in photoorientation processes and predetermines the ultimate stability of photoinduced order. The dichroism growth kinetics in LC dendrimers is studied and an influence of generation number on the photoinduced dichroism is revealed. Higher degree of LC-order in dendrimer of the 1st and 5th generations results in the larger values of photoinduced dichroism. H-aggregation of photochromic groups partially prohibits the photoorientation process decreasing the achievable values of dichroism. It is also found that increase in generation number of homodendrimers reduces aggregation tendency, thus, the highest values of photoinduced dichroism are found for dendrimers of 4th and 5th generations. LC homodendrimer of the fifth generation is used for the spin-coated film preparation and an image recording by laser illumination. Obtained results allow one to consider photochromic LC dendrimers as promising materials for applications in optics, optoelectronics and photonics.



Scheme 4. Idealized hypothetical scheme of photoorientation process in smectic LC-dendrimers of low generations (a), and two possible photoinduced orientations of columns in irradiated films of G5Homo (b). (\vec{E} – electric field vector of polarized light).

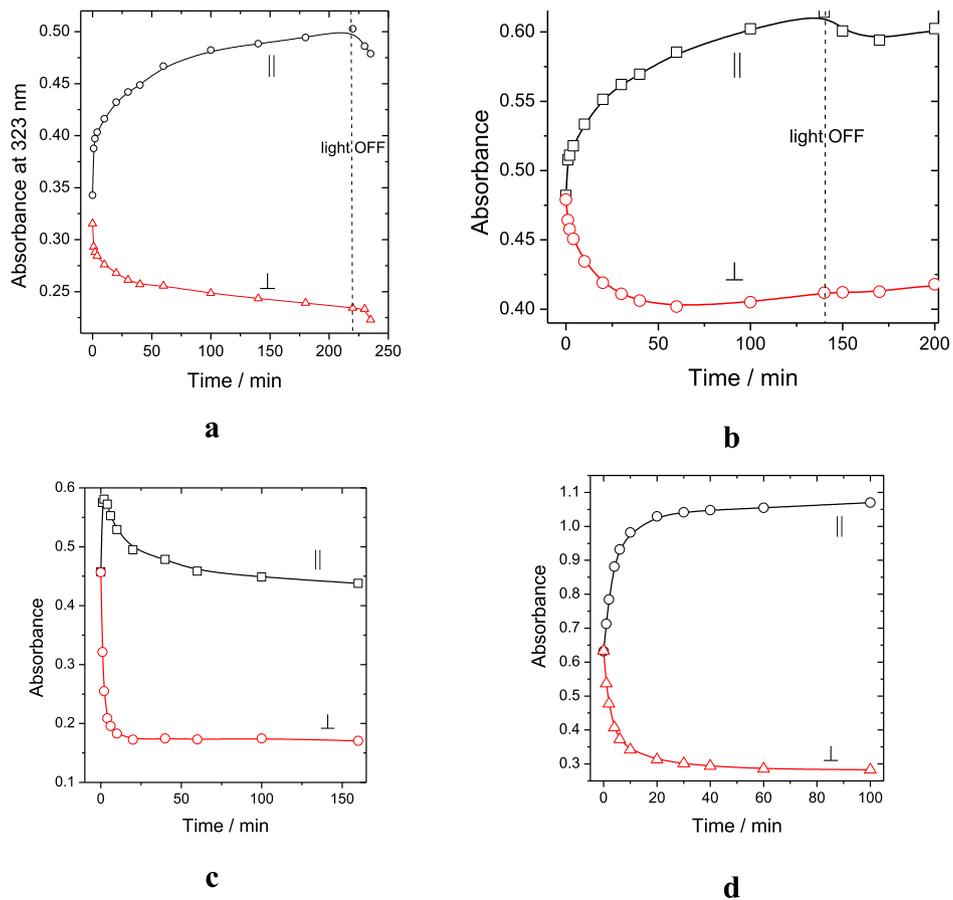


Fig. 6. Changes in polarized absorbance for dendrimers G1Homo (a), G2Homo (b), G4Homo (c) and G5Homo (d) during polarized light irradiation.

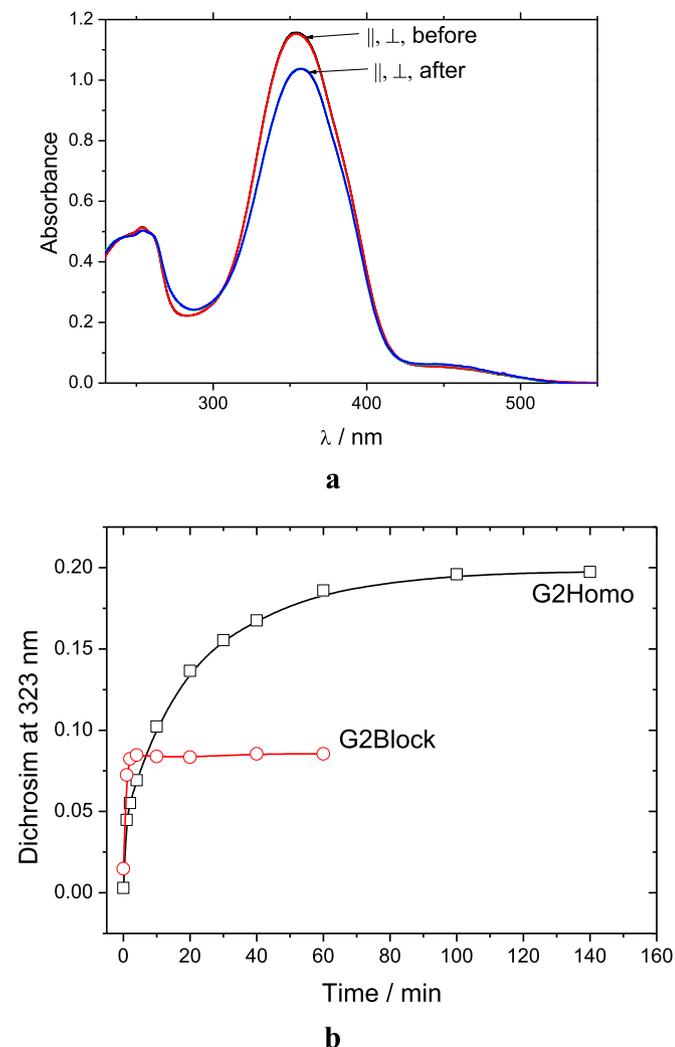


Fig. 7. (a) Polarized absorbance spectra of **G2Stat** film before and after 20 min of laser irradiation and (b) dichroism growth in **G2Block** and **G2Homo** films at room temperature.

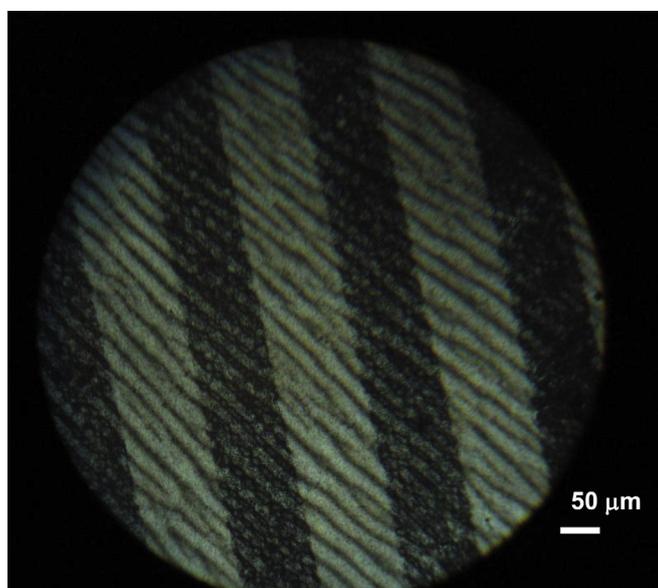


Fig. 8. Polarizing optical micrograph showing spin-coated film of **G5homo** irradiated by 473 nm laser through the mask during 40 min. Bright areas correspond to the irradiated zones. Tilted stripes are caused by the inhomogeneity in film thickness during film preparation by spin-coating.

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