Russian Chemical Bulletin, International Edition, Vol. 56, No. 12, pp. 2407—2413, December, 2007

Liquid-crystalline carbosilane dendrimers of different molecular architecture with photochromic mesogenic and aliphatic terminal groups

A. I. Lysachkov,[a] N. I. Boiko,[a]★ E. A. Rebrov,[b] A. M. Muzafarov,[b] and V. P. Shibaev[a]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 0174. E-mail: boiko2@mail.ru
[b]*N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 119333 Moscow, Russian Federation

Second-generation (G-2) liquid-crystalline carbosilane block and statistical dendrimers with aliphatic (decyl) and photochromic (azobenzene-containing) mesogenic terminal groups and a G-2 homo-dendrimer containing the same mesogenic terminal groups were synthesized for the first time. The influence of dendritic architecture on the phase behavior of the dendrimers and on photoinduced *Z*—*E*-isomerization of the azobenzene fragments in mesogenic terminal groups in dendrimer solutions are discussed.

Key words: dendrimer, liquid-crystalline state, smectic mesophase, block codendrimer, statistical codendrimer, photochromic mesogenic groups, photochemistry, isomerization.

Photosensitice polymers with azobenzene groups have been a subject of intensive research for more than two decades. This activity is due to search for novel materials suitable for fast reversible recording and long-term storage of information and for design of optical switches and modulators for opto-electronics and photonics to meet the demands of rapidly growing communication system and information technology industries.

Most advances in the synthesis of and research on photosensitive polymers were made in studies of amorphous and liquid-crystalline (LC) compounds with linear chain topologies.[1—3] Recently, the attention of researchers has been focussed on dendritic systems representing a specific class of spherically symmetric hyperbranched compounds. A number of studies on dendrimers containing photochemically active groups in various structural fragments have been carried out. In particular, dendrimers in which *E*—*Z*-photoisomerizable azobenzene groups are localized only within the dendritic matrix[4—7] or only on the dendrimer "surface"[8—11] have been investigated. It should be noted that most studies were performed using the so-called amorphous or crystalline homodendrimers and that the photochemical properties of codendrimers containing different types of terminal groups was studied fragmentarily.[12,13] Information on photo-active dendrimers capable of forming LC phases is also scarce.[10,11,13,14] But the ability of photochromic LC dendrimers to self-organization makes them of interest from the standpoint of light-assisted control of their molecular and supramolecular structures.

The aim of the present work was to reveal the effect of the molecular architecture of LC dendrimers containing photosensitive mesogenic groups on their phase state and photochemical properties in dilute solutions. We studied second-generation (G-2) carbosilane homo-, block, and statistical dendrimers with mesogenic azobenzene-containing and aliphatic terminal groups (Fig. 1).

The azobenzene fragment has a dual function, namely, its rigid anisometric shape ensures the formation of the LC phase while the chromophore fragment imparts the dendrimer the necessary photosensitivity.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-250 spectrometer in $CDCl_3$ with Me_4Si as the internal reference. GPC analyses and preparative GPC were performed on a Knauer instrument using Waters columns (8S300 mm and 19S300 mm, respectively) filled with Ultrastyragel (pore size 1000 Å), with THF as the eluent. The detectors were a Waters R-410 refractometer and a Knauer UV spectrometer, respectively. The heats of phase transitions were determined by differential scanning calorimetry (DSC) using a Mettler TA-4000 thermal analyzer (scanning rate 10 deg min^{-1}).

Optical studies of textures and determination of phase transition temperatures were carried out with crossed polaroids using a LOMO POLAMR-211 polarization microscope (Russia) equipped with a Mettler FP-800 hot stage. The photochemical properties of the dendrimers were studied using a tailor-made setup including a DRSh-250 ultra-high pressure mercury lamp. Light with $\lambda = 365$ nm was selected using an interference filter; the light intensity was 1.0 mW cm^{-2} (determined using a Laser-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2325—2331, December, 2007.

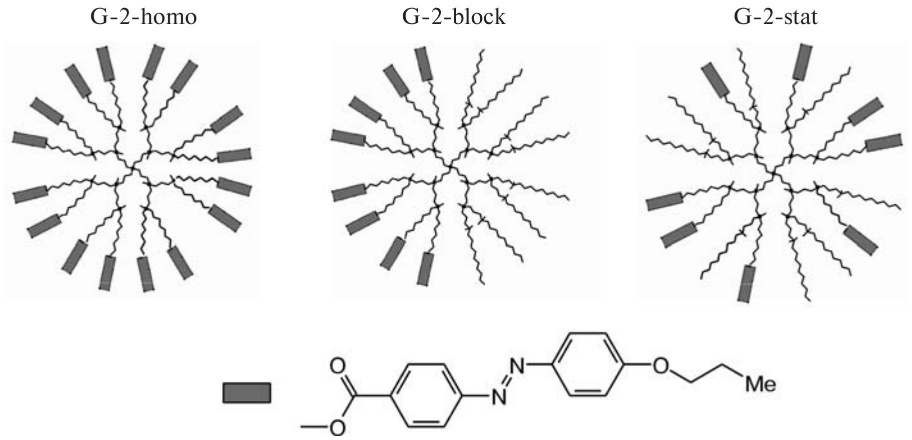


Fig. 1. Schematic view of synthesized photochromic carbosilane LC dendrimers.

Mate-Q (Coherent) intensity meter). Spectral measurements were performed with a Tidas (J&M) UV-Vis spectrometer.

Synthesis of LC dendrimers

G-2-Block dendrimer (Scheme 1). A mixture of compound **1** (0.345 g, $1.04 \cdot 10^{-4}$ mol),[15] $HSiMe_2$Mesogen (0.626 g, $1.25 \cdot 10^{-3}$ mol),[10] and PC072 (3—3.5% platinum complex with cyclovinylmethylsiloxane; ABCR, Germany; 20 μL) in anhydrous toluene (10 mL) was magnetically stirred in a closed vessel at 35 °C for 72 h. Following completion of the reaction, the catalyst was removed by passing the reaction mixture through a column filled with silica gel (with toluene and ethyl acetate as eluents). Final purification was performed by GPC. Yield 490 mg (64%). ^{1}H NMR, δ: –0.08 (s, $Si(CH_3)$); 0.03 (s, O—$Si(CH_3)$); 0.53 (m, Si—CH_2); 0.86 (t, $(CH_2)_3C\underline{H}_3$); 1.05 (t, $O(CH_2)_2C\underline{H}_3$); 1.20—1.45 (m, $CH_2C\underline{H}_2CH_2$, $CH_2C\underline{H}_2CH_3$); 1.80 (m, $OCH_2C\underline{H}_2$); 4.00 (t, $ArOC\underline{H}_2$); 4.30 (t, $COOCH_2$); 7.00—8.20 (m, Ar); the intensity ratio ~5.25 : 6 : 9 : 15 : 15 : 14.5 : 2 : 1 : 1 : 4 is in agreement with calculations.

G-2-Stat dendrimer (Scheme 2). Reaction of G-2 carbosilane dendritic matrix (G-2-$(All)_{16}$) (0.064 g, $3.75 \cdot 10^{-5}$ mol) with $HSiMe_2$Mesogen (0.190 g, $3.77 \cdot 10^{-4}$ mol) and decyldimethylsilane[15] (0.104 g, $5.2 \cdot 10^{-4}$ mol) in the presence of PC072 (15 μL) in anhydrous toluene (7 mL) was conducted, and the product was purified, as described above. Yield 170 mg (62%). ^{1}H NMR exhibits almost the same signals with the same intensity ratio.

G-2-Homo dendrimer (see Scheme 2). Reaction of the carbosilane dendritic matrix G-2-$(All)_{16}$ (0.065 g, $3.81 \cdot 10^{-5}$ mol) with $HSiMe_2$Mesogen (0.459 g, $9.15 \cdot 10^{-4}$ mol) in the presence of PC072 (15 μL) in anhydrous toluene (7 mL) was conducted, and the product was purified, as described above. ^{1}H NMR, δ: –0.09 (s, 36 H, $Si(CH_3)$); 0.02 (s, 192 H, O—$Si(CH_3)$); 0.53 (m, 144 H, Si—CH_2); 1.05 (t, 48 H, $O(CH_2)_2C\underline{H}_3$); 1.20—1.45 (m, 152 H, $CH_2C\underline{H}_2CH_2$); 1.80 (m, 64 H, $OCH_2C\underline{H}_2$); 3.99 (t, 32 H, $ArOC\underline{H}_2$); 4.31 (t, 32 H, $COOCH_2$); 7.00—8.20 (m, 128 H, Ar).

Results and Discussion

The synthesis of the carbosilane block codendrimer containing eight terminal allyl and eight aliphatic decyl groups (compound **1**, see Scheme 1) was reported in detail.[16] The azobenzene-containing mesogenic groups were attached using the hydrosilylation reaction in the presence of the Pt-catalyst PC072.

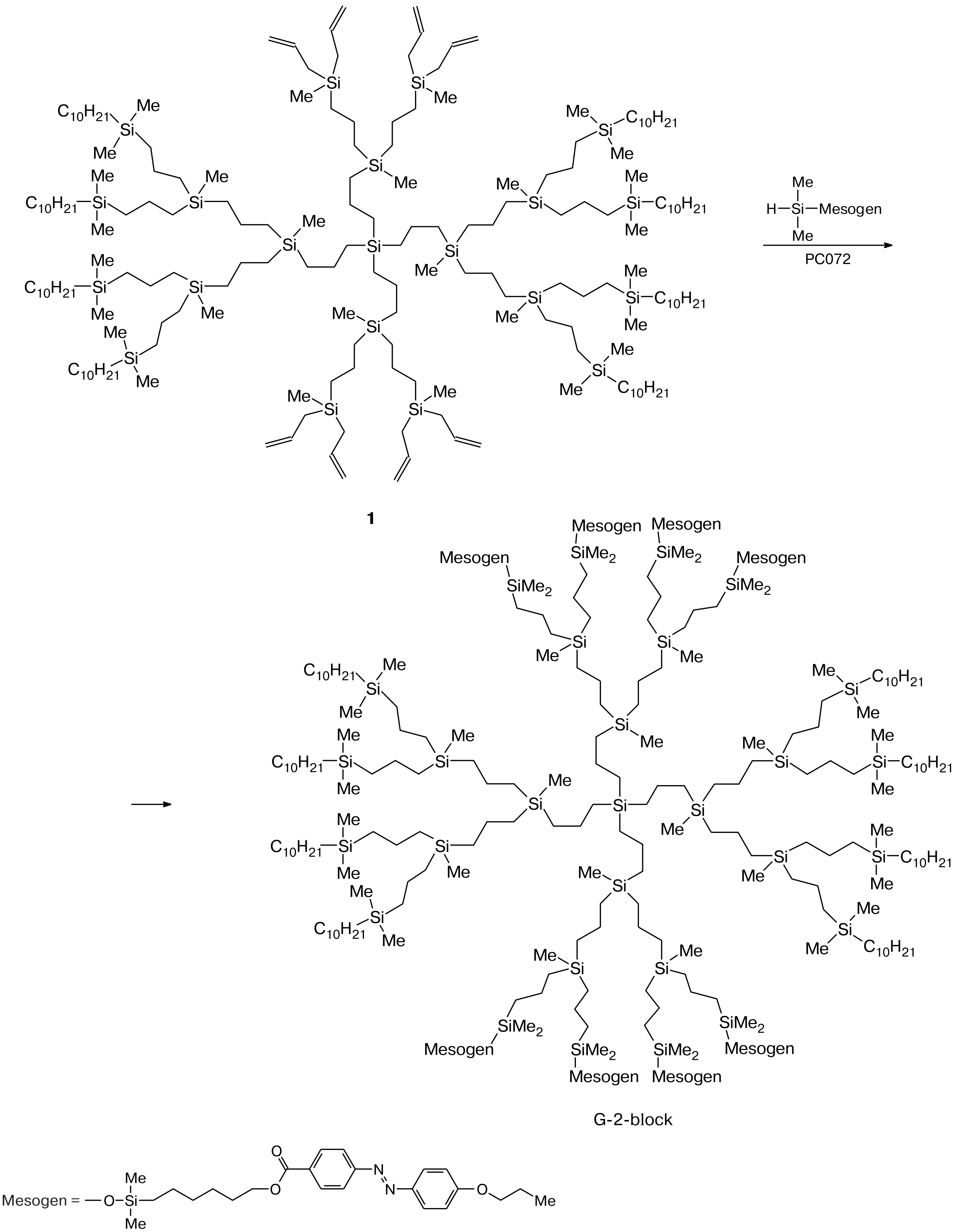
The G-2-homo and G-2-stat dendrimers were synthesized using the procedure proposed by us earlier,[17,18] *viz.*, by hydrosilylation of carbosilane dendritic matrices containing terminal allyl groups with a mesogene-containing fragment (G-2-homo) and a mixture of mesogene-containing and aliphatic fragments (G-2-stat) (see Scheme 2).

In all cases the hydrosilylation reactions were carried out using a 1.5-fold excess of the compounds containing the Si—H bond to ensure complete addition of necessary fragments to the terminal C=C bonds of the dendritic matrices. The course of the reaction was monitored by the disappearance, in the ^{1}H NMR spectra, of the signals at δ 4.9 and 5.8 corresponding to allylic protons of the dendritic matrices. The purity of the dendrimers synthesized was established by GPC and their structures were proved by ^{1}H NMR spectroscopy. The ^{1}H NMR of the G-2-block dendrimer is shown in Fig. 2.

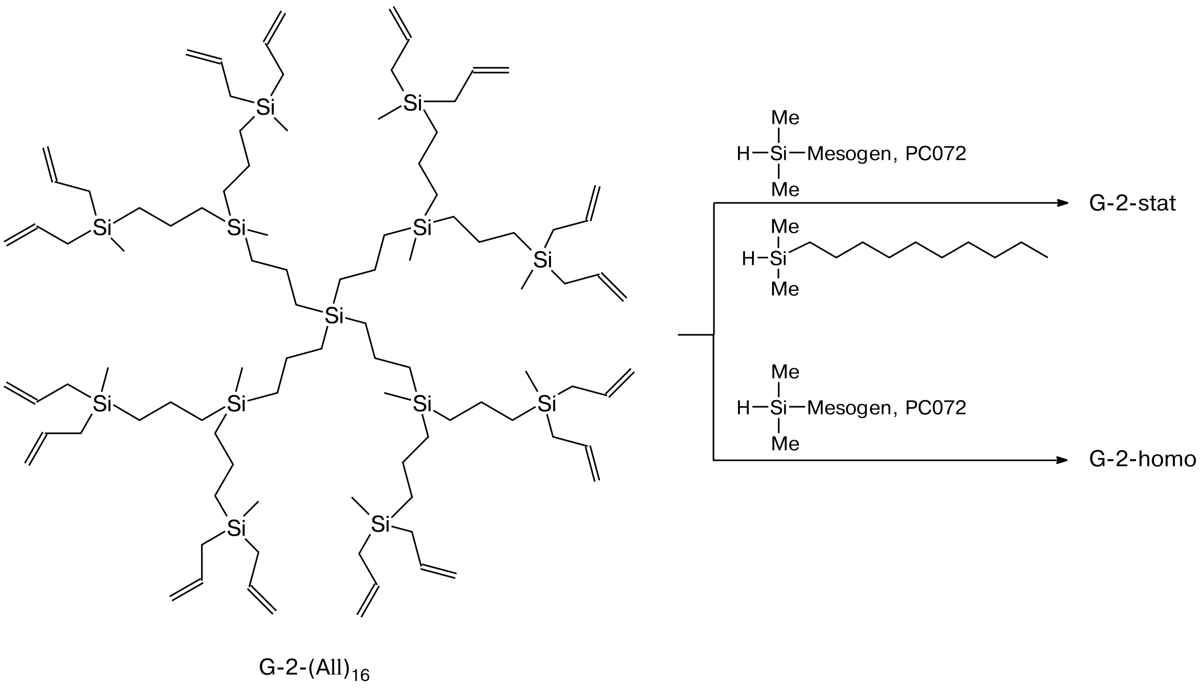
The composition of the G-2-stat dendrimer was determined from the ratio of the integrated intensities of the signals at δ 0.86 and 1.05 in the ^{1}H NMR spectrum corresponding to terminal Me groups of different-type terminal fragments of the dendrimer (Fig. 3). This ratio is ~1 : 1, *i.e.*, the dendrimer contains almost equal amounts of the mesogenic azobenzene-containing terminal fragments and the aliphatic decyl residues.

Phase behavior of LC dendrimers. The phase state of the dendrimers synthesized in this work was studied by DSC and polarization optical microscopy. The DSC curves of the dendrimers show two endothermic peaks. The low-temperature peak can be attributed to the transition from the crystalline phase to the LC mesophase (based on heat of melting of ~7 J g^{-1}, which is in agreement with the published data[18] for carbosilane dendrimers with terminal mesogenic groups). The high-temperature peak cor-

Scheme 1


1
Me
H—Si—Mesogen
Me
PC072
G-2-block
Mesogen = —O—Si— (Me)(Me)
C10H21
SiMe2
Mesogen

Scheme 2



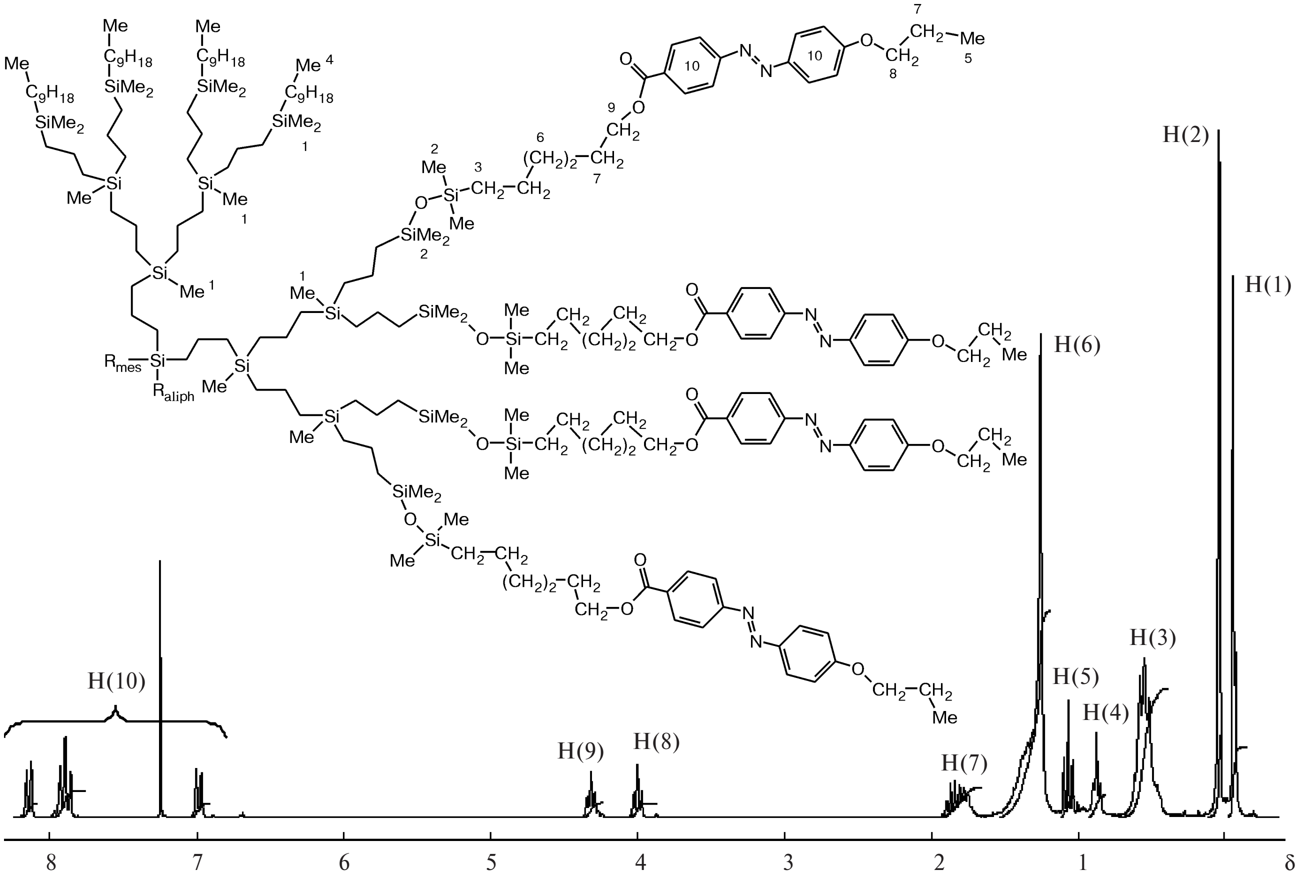


Fig. 2. ^{1}H NMR spectrum of G-2-block dendrimer (R_{mes} and R_{aliph} are the branches of the dendritic molecule with mesogenic azobenzene-containing and decyl terminal groups, respectively).

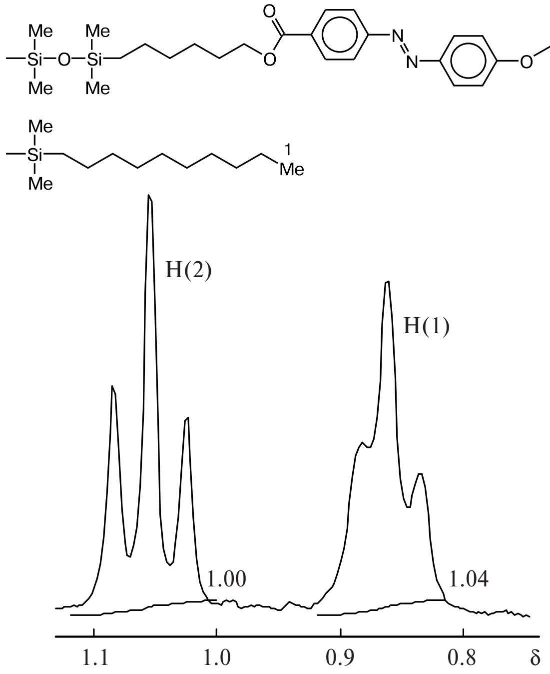


Fig. 3. Determination of composition of G-2-stat codendrimer by ^{1}H NMR spectroscopy.

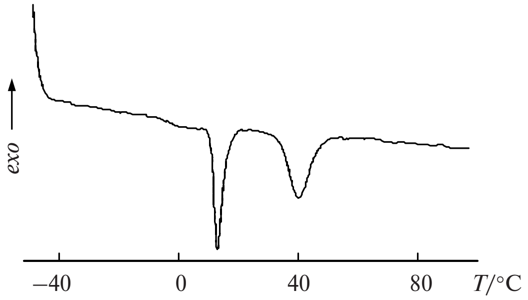


Fig. 4. DSC curve for G-2-block codendrimer.

responds to transition from the LC phase to the isotropic state. As an example, Fig. 4 shows the DSC curve for the G-2-block dendrimer.

The formation of the LC phase was also confirmed by polarization optical microscopy; the dendrimer was characterized by a fan-shaped texture typical of smectic A (SmA) mesophase.

Thus, irrespective of the molecular architecture the three dendrimers (G-2-homo, G-2-stat, and G-2-block) are characterized by the formation of the same set of phases, namely, the crystalline phase and the LC phase SmA. However, the phase transition temperatures strongly depend on the composition and pattern of organization of terminal groups on the surface of the dendritic matrix (Table 1).

First of all, it should be noted that all the dendrimers synthesized are monodisperse individual compounds. The G-2-block and G-2-stat codendrimers are characterized by a considerable decrease in the temperature interval of existence of the LC mesophase and by a decrease in the isotropization temperature compared to the G-2-homo homodendrimer (see Table 1). This seems to be due to a decrease in the content of mesogenic groups responsible for the formation of LC ordering in these dendrimers. Although the G-2-stat and G-2-block codendrimers have the same compositions, the clearing point of the former is lower than that of the latter. Apparently, this is a consequence of different conformational distortions in the packing of the terminal fragments on the surface of the dendritic molecules. One can assume the formation of a more defect smectic phase in the case of the G-2-stat codendrimer with statistically arranged different-type terminal fragments compared to the G-2-block codendrimer where the molecular topology predetermines a more perfect packing of mesogenic groups. This leads to a lower clearing point and to a decrease in the temperature interval of the existence of the mesophase for the G-2-stat codendrimer.

Table 1. Phase behavior and polydispersity indices of dendrimers according to polarization optical microscopy, DSC, and GPC data

Dendrimer	Phase behavior*	M_w/M_n (GPC)
G-2-homo	Cr 8 SmA 62 I	1.02
G-2-block	Cr 12 SmA 40 I	1.05
G-2-stat	Cr −9 SmA −2 I	1.03

* Cr stands for crystalline phase, SmA stands for liquid-crystalline smectic A mesophase, and I stands for isotropic melt; the temperatures are given in °C.

Photo-optical properties of LC dendrimers. Irradiation of dendrimer solutions (λ = 365 nm) produces significant changes in their absorption spectra. Figure 5 shows that an increase in the irradiation time causes a considerable decrease in the optical density in the spectral region cor-

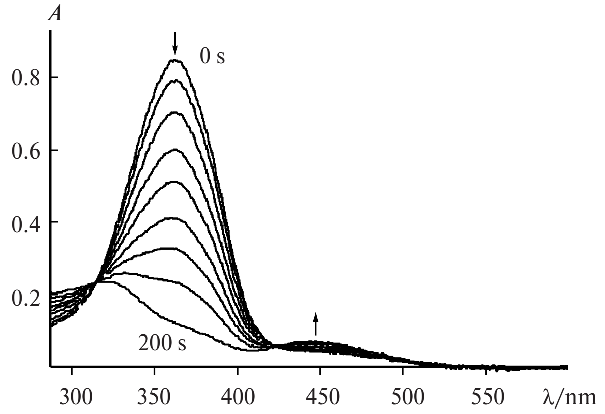
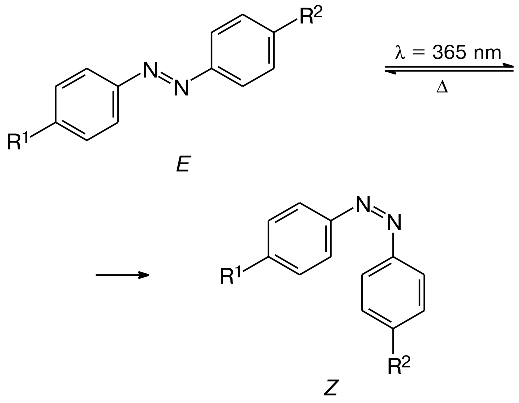


Fig. 5. Changes in absorption spectra of a solution of G-2-block codendrimer in dichloroethane upon irradiation at 365 nm (time scale: 0—200 s).

responding to the π—π* electronic transition of the azobenzene chromophore. A slight increase in absorption is observed in the region of n—π* electronic transition (~450 nm). These changes, as well as the isosbestic points, indicate the occurrence of only one process, namely, *E*—*Z*-isomerization of azobenzene groups[19] (Scheme 3) upon UV irradiation.

Scheme 3



The reverse reaction (*Z*—*E*-isomerization) occurs both upon irradiation at λ ~450 nm and upon heating. To study the kinetics of the thermal process, the dendrimer solutions were irradiated at 365 nm until photostationary state and then the kinetics of an increase in the optical density at the wavelength corresponding to maximum of electronic π—π*-transition of azobenzene groups (362 nm) were measured at different temperatures.

The rate of the reverse isomerization strongly depends on temperature. To calculate the rate constants (k) for reverse isomerization of all dendrimers at different temperatures, the parameters $(A_t - A_\infty)/(A_0 - A_\infty)$ were plotted *vs*. time; here A_0, A_t, and A_∞ denote the absorption at $t = 0$, at instant t, and in the stationary state, respectively (Fig. 6).

The plots are correctly approximated by a monoexponential function

$$(A_t - A_\infty)/(A_0 - A_\infty) = e^{-kt}. \qquad (1)$$

The calculated rate constants for *Z*—*E*-isomerization are listed in Table 2.

Table 2. Rate constants for *Z*—*E*-isomerization of azobenzene groups in the dendrimers synthesized (for solutions in dichloroethane)

Dendrimer	$k \cdot 10^3/\mathrm{s}^{-1}$ at different T/°C		
	52	60	65
G-2-homo	0.76	1.7	2.9
G-2-block	0.75	1.6	3.2
G-2-stat	0.88	1.7	2.6

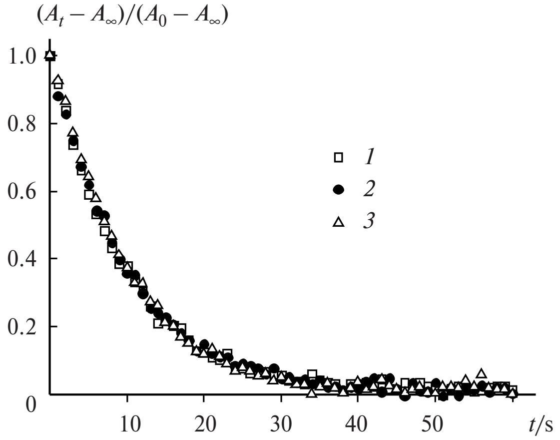


Fig. 6. Kinetic curves for *Z*—*E*-isomerization of azobenzene groups in G-2-homo (*1*), G-2-block (*2*), and G-2-stat (*3*) dendrimers at 60 °C.

The results obtained show that the rate constants for *Z*—*E*-isomerization of azobenzene groups in the three dendrimers at the same temperature are similar within the limits of measuring error, which indicates that the molecular structures of the dendrimers do not influence the kinetics of *Z*—*E*-isomerization of terminal azobenzene groups in the dendrimer solutions.

Constructing temperature dependences of the rate constants for back transfer in the coordinates of the Arrhenius equation (Fig. 7) made it possible to estimate the activation energy for thermal *Z*—*E*-isomerization of azobenzene groups. The activation energies for the three dendrimers are also similar, being nearly 90 kJ (mole of mesogenic groups)$^{-1}$, which is in reasonable agreement with the value determined for low-molecular-weight azobenzene-containing analogs.[20]

Thus, we synthesized three photochromic carbosilane LC dendrimers of different molecular topology, namely, the homo, block, and statistical dendrimers, for the first time and studied their phase behavior and photo-optical properties.

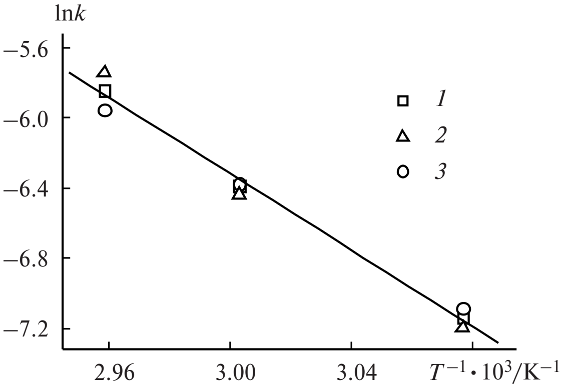


Fig. 7. Temperature dependence of logarithm of rate constant for *Z*—*E*-isomerization of azobenzene groups in G-2-homo (*1*), G-2-block (*2*), and G-2-stat (*3*) dendrimers.

The authors express their gratitude to T. E. Grokhovskaya for carrying out DSC measurements and to A. Yu. Bobrovsky for discussions of the results obtained in this work.

This work was finacially supported by the Russian Foundation for Basic Research (Project No. 07-03-01089) and the Council on Grants at the President of the Russian Federation (Program of State Support for Leading Scienfic Schools, Grant NSh-5899.2006.3).

References

1. *Applied Photochromic Polymer System*s, Ed. C. B. McArdle, Blackie, Glasgow, 1992, p. 80.
2. *Polymers as Electrooptical and Photooptical Active Media*, Ed. V. P. Shibaev, Springer-Verlag, Berlin, 1966, p. 37.
3. V. P. Shibaev, *Int. J. Polym. Mater.*, 2000, **45**, 533.
4. M. Smet, L.-X. Liao, W. Dehaen, and D. V. McGrath, *Org. Lett.*, 2000, **2**, 511.
5. J. Hellman, M. Hamano, O. Karthaus, K. Ijiro, M. Shimomura, and M. Irie, *Jpn J. Appl. Phys.*, 1998, **37**, L816.
6. O. Karthaus, K. Ijiro, M. Shimomura, J. Hellman, and M. Irie, *Langmuir*, 1996, **12**, 6714.
7. D. M. Junge and D. V. McGrath, *J. Am. Chem. Soc.*, 2000, **122**, 6795.
8. A. Archut, F. Vögtle, L. De Cola, G. C. Azzellini, U. Balzani, P. S. Ramanujam, and R. H. Berg, *Chem. Eur. J.*, 1998, **4**, 699.
9. J. Wang, H. Jia, H. Zhong, H. Wu, Yo. Li, H. Xu, M. Li, and Y. Wei, *J. Polym. Sci., Part A, Polym. Chem.*, 2000, **38**, 4147.
10. A. Yu. Bobrovsky, A. A. Pakhomov, X.-M. Zhu, N. I. Boiko, and V. P. Shibaev, *Vysokomolekulyar. soedineniya, Ser. A*, 2001, **43**, 683 [*Polym. Sci., Ser. A*, 2001, **43**, 431 (Engl. Transl.)].
11. R. Advincula, M. K. Park, and Sh. Wang, *Polym. Mater. Sci. Eng.*, 2001, **84**, 236.
12. J. W. Weener and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 741.
13. R. Alcala, R. Gimenez, L. Oriol, M. Pinol, J. L. Serrano, B. Villacampa, and A. Vinuales, *Chem. Mater.*, 2006, **18**, 5437.
14. N. I. Boiko, X. Zhu, A. Yu. Bobrovsky, and V. P. Shibaev, *Chem. Mater.*, 2001, **13**, 1447.
15. E. A. Rebrov, G. M. Ignatreva, A. I. Lysachkov, N. V. Demchenko, and A. M. Muzafarov, *Vysokomolekulyar. soedineniya, Ser. A*, 2007, **49**, 757 [*Polym. Sci., Ser. A*, 2007, **49**, 483 (Engl. Transl.)].
16. A. M. Muzafarov, O. B. Gorbatsevich, E. A. Rebrov, G. M. Ignatreva, T. B. Chenskaya, V. D. Myakushev, A. F. Bulkin, and V. S. Papkov, *Vysokomolekulyar. soedineniya, Ser. A*, 1993, **35**, 1967 [*Polym. Sci., Ser. A*, 1993, **35**, 1215 (Engl. Transl.)].
17. S. A. Ponomarenko, E. A. Rebrov, A. Yu. Bobrovsky, N. A. Boiko, A. M. Muzafarov, and V. P. Shibaev, *Liq. Cryst.*, 1996, **21**, 1.
18. E. V. Agina, N. I. Boiko, R. M. Richardson, B. I. Ostrovskii, V. P. Shibaev, E. A. Rebrov, and A. M. Muzafarov, *Vysokomolekulyar. soedineniya*, *Ser. A*, 2007, **49**, 639 [*Polym. Sci., Ser. A*, 2007, **49**, 412 (Engl. Transl.)].
19. *Einfuhrung in die Photochemie*, Ed. H. O. Bekker, VEB Deutscher Verlag der Wissenschaften, Berlin, 1976.
20. D. Geiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 15.

Received May 29, 2007;
in revised form October 30, 2007