Chem. Mater. **2001,** *13,* 1447−1452 1447

Articles

First Photosensitive Liquid Crystalline Dendrimer: Synthesis, Phase Behavior, and Photochemical Properties

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Received July 3, 2000. Revised Manuscript Received November 27, 2000

The first photosensitive liquid crystalline (LC) dendrimer with terminal cinnamoyl groups was synthesized. A new approach to the synthesis of photochromic carbosilane LC dendrimers was elaborated. The method consists of synthesis of dendrimer with terminal hydroxyl groups and then coupling of 4-methoxycinnamoyl chloride to it. It was shown that the LC dendrimer of the first generation forms a smectic A (SmA) phase. The photochemical behavior of the dendrimer in dilute solution and in films was studied. The experimental data show that at least two processes, $E-Z$ photoisomerization and [2+2] photocycloaddition leading to the formation of the three-dimensional network, take place.

Introduction

A dendrimers is a macromolecule with a regular tree-like array of branching units. Numerous dendritic structures have been synthesized and studied, including polyamidoamines,[1] polyamides,[2] polyphenyl ethers,[3] and carbosilanes.[4] In recent years, dendrimers with different designed functionalities have become objects of particular academic and practical interest because of their unique superbranched architectures, high densities of peripheral functionalities, symmetrical shapes, and monodispersity. Such compounds have units that are capable of performing specific functions, such as electron-transfer processes (transition metal units[5]), antenna effects (chromophoric groups[6−10]), and photoinduced processes (photoisomerizable groups[11−16]).

Dendrimers containing mesogenic groups show liquid crystalline (LC) mesophase formation.[16−27] However, in the literature, there is no information on photochromic dendrimers forming LC phases, although many photochromic LC polymers have been intensively investigated.[28−30]

The introduction of mesogenic photosensitive groups capable of isomerization into dendrimer molecules is of

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(1) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem*. **1993**, *165*, 193.

(2) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concept, Synthesis, Perspectives*; VCH: Weinheim, Germany, 1996.

(3) Frechet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *Pure Appl. Chem*. **1996**, *A33*, 1399.

(4) Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279 and references therein.

(5) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290.

(6) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354.

(7) Kimura, M.; Shiba, T.; Muto, T.; Hanabusa, K.; Shirai, H. *Macromolecules* **1999**, *32*, 8237.

(8) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.

(9) Gilat, S. L.; Adronov, A.; Frechet, J. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1422.

(10) Schenning, A. P. H.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, 122, 4489.

(11) Weener, J. W.; Meijer, E. W. *Adv. Mater.* **2000**, 12, 741.

(12) Wang, J.; Jia, H.; Zhong, H.; Wu, H.; Li, Yo.; Xu, H.; Li, M.; Wei, Y. *J. Polym. Sci. A: Polym. Chem.* **2000**, 38, 4147.

(13) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4345.

(14) Junge, D. M.; McGrath, D. V. *Chem. Commun.* **1997**, 857.

(15) Nagasaki, T.; Tamagaki, S.; Ogio, K. *Chem. Lett.* **1997**, 717.

(16) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, U.; Ramanujam, P. S.; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 699.

(17) Boiko, N. I.; Zhu, X.; Vinokur, R.; Rebrov, E.; Muzafarov, Az.; Shibaev, V. P. *Ferroelectrics* **2000**, 243, 59.

(18) Ponomarenko, S. A.; Rebrov, E. A.; Boiko, N. I.; Vasilenko, N. G.; Muzafarov, A. M.; Freidzon, Ya. S.; Shibaev, V. P. *Vysokomol. Soedin., Ser. A* **1994**, *36*, 1086; *Polym. Sci., Ser. A* **1994**, *36*, 896.

(19) Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1995**, *117*, 11441.

(20) Ponomarenko, S. A.; Rebrov, E. A.; Bobrovsky, A. Yu.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. *Liq. Cryst.* **1996**, *21*, 1.

(21) Lorenz, K.; Hölter, D.; Stühn, B.; Mülhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8*, 414.

(22) Deschenaux, R.; Serrano, E.; Levelut, A.-M. *Chem. Commun.* **1997**, 1577.

(23) Terunuma, D.; Kato, T.; Nishio, R.; Matsuoka, K.; Kuzuhara, H.; Aoki, Y.; Nohira, H. *Chem. Lett.* **1998**, 59.

(24) Busson, P.; Ihre, H.; Hult, A. *J. Am. Chem. Soc.* **1998**, *120*, 9070.

(25) Ponomarenko, S. A.; Boiko, N. I.; Rebrov E. A.; Muzafarov A. M.; Whitehouse, I. J.; Richardson, R. M.; Shibaev, V. P. *Mol. Cryst. Liq. Cryst.* **1999**, *330*, 1411.

(26) Saez, I. M.; Goodby, J. W. *Liq. Cryst.* **1999**, *26*, 1101.

(27) Baars, M. W. P. L.; Söntjens, S.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, 120, 8199.

(28) Yonetake, K.; Masuko, T.; Morishita, T.; Suzuki, K.; Ueda, M.; Nagahata, R. *Macromolecules* **1999**, *32*, 6578.

(29) *Applied Photochromic Polymer Systems*; McArdle, C. B., Ed.; Blackie & Son Ltd.: New York, 1992.

(30) *Polymers as Electrooptical and Photooptical Active Media*; Shibaev, V. P., Ed.; Springer-Verlag: Berlin, Germany, 1996.

10.1021/cm001116x CCC: $20.00

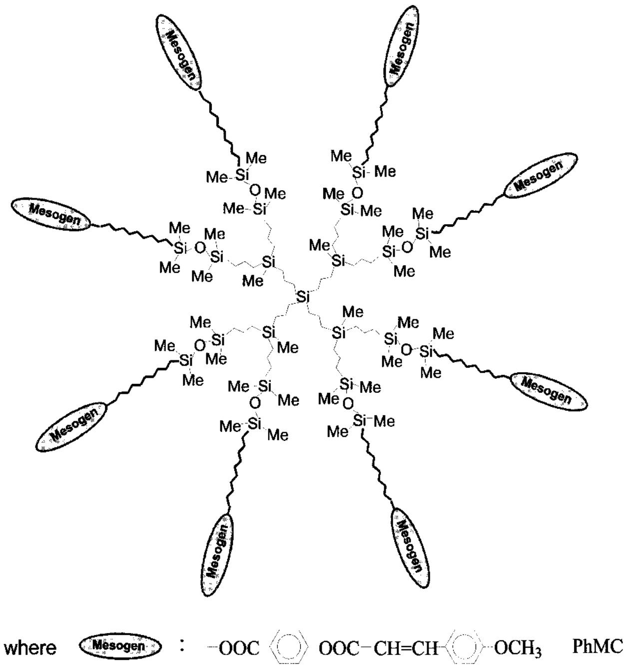

Figure 1. Chemical structure of G-1(10PhMC)$_8$. (G-1 = first generation, 10 = number of methylene groups in spacer, PhMC = cinnamoyl-containing mesogenic group.)

great interest from different points of view. First, the influence of the generation number of the LC dendrimers on the photochemical and photooptical properties of these compounds is not at all clear, when the quantities of photochromic mesogens are increased in a geometric progression and many physicochemical properties (such as free volume, density, and local viscosity of polymer matrix) are drastically changed. In this paper, the synthesis and study of the photochromic LC dendrimer of only the first generation is described, but the synthesis of the next generations is in the progress.

Second, in so far as the LC dendrimers are intermediate in their physical properties between macromolecular compounds and low-molar-mass liquid crystals, photochromic LC dendrimers are of most interest as new potential photooptical media for optical recording. Indeed, the low viscosity inherent to all dendrimers and their rapid response time to an action of external fields can be combined in one and the same material. The combination of these two factors is very important in the creation of new promising photochromic LC materials.

Here, we report the synthesis and investigation of the first LC carbosilane dendrimer of the first generation, which contains terminal photosensitive mesogenic groups that undergo configurational changes in response to light irradiation.

As seen in Figure 1, this dendrimer contains terminal cinnamoyl groups, which can undergo *E*−*Z* photoisomerization and [2+2] photocycloaddition.[31,32]

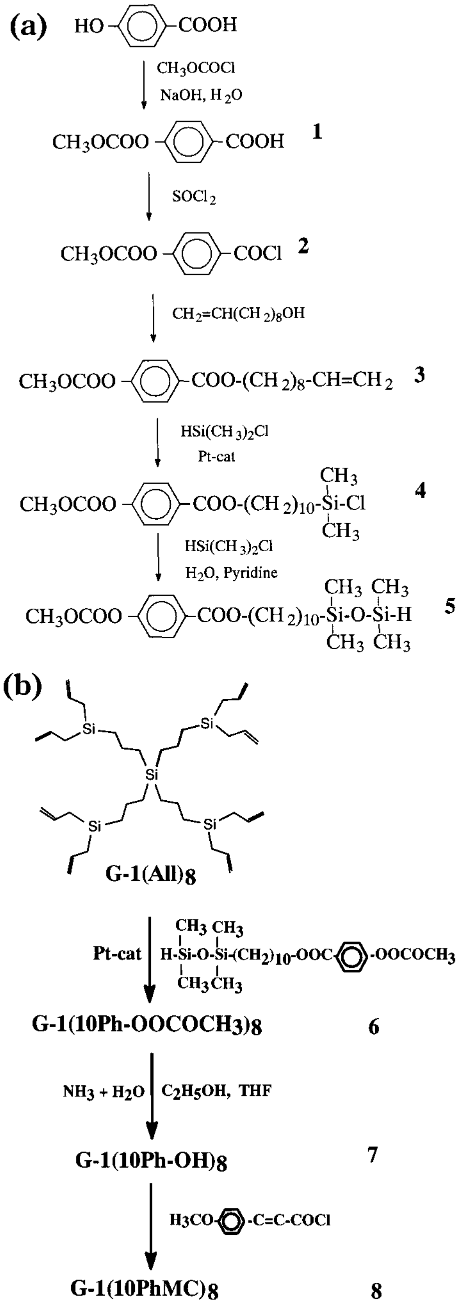

Figure 2. General strategy of the synthesis of carbosilane LC dendrimers: (a) synthesis of fragment with a reactive Si−H terminal group; (b) scheme of synthesis of dendrimers with terminal hydroxyl and cinnamoyl-containing groups.

Experimental Section

Synthesis of Photochromic LC Dendrimer. Methoxycinnamoyl-containing LC dendrimer was prepared according to the techniques that are described below (the scheme of synthesis of the dendrimer is presented in Figure 2).

4-Methoxycarbonyloxybenzoic Acid (1). 4-Methoxycarbonyloxybenzoic acid was prepared by the technique proposed in ref 33. Yield = 70%. Mp = 170 °C. IR (cm^{-1}): 1760 (CO in MeOCOOAr), 1690 (CO in ArCOOH), 1600 (C−C in Ar), 1260 (COC).

4-Methoxycarbonyloxybenzoyl Chloride (2). Thionyl chloride (5 mL) was added slowly to compound **1** (3 g, 15 mmol). To this solution was added a drop of *N*,*N*-dimethylformylamide. The resulting solution was kept at room temperature for 8 h. Then, the excess thionyl chloride was removed by evaporation under reduced pressure. The product was recrystallized from toluene/heptane (1:5). The acid chloride obtained formed colorless needleshaped crystals. Mp = 82 °C. Yield = 3.0 g, 92%.

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[31] *Photochemistry in Organised and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991.

[32] *Einfuhrung in die Photochemie*; Bekker, H. O., Ed.; VEV Deutscher Verlag der Wissenschatten: Berlin, Germany, 1976.

[33] Chin, E.; Goodby, J. W. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 311.

9-Decenyl-4-methoxycarbonyloxybenzoate (3). Compound **2** (5 g, 23 mmol) dissolved in THF (30 mL) was added with stirring to a solution of 9-decene-1-ol (4 mL, 22 mmol) and triethylamine (3.2 mL, 23 mmol) in THF (30 mL) that was cooled by water/ice. The resulting solution was stirred for 6 h without cooling. Then, the solution was filtered and evaporated under reduced pressure. The residue was dissolved in chloroform (200 mL), and the solution was washed with water three times. The resulting solution was dried with sodium sulfate and evaporated in a vacuum. The residue was purified by column chromatography over silica gel using toluene/ethyl acetate (10:1) as the eluent. Yield = 6.1 g of colorless oil, 80%. ^{1}H NMR (250 MHz, C_6D_6) δ (in ppm): 1.20−1.50 (m, 12H), 1.61 (m, 2H), 2.10 (q, 2H), 3.42 (s, 3H), 4.27 (t, 2H), 5.15 (m, 2H), 5.91 (m, 1H), 7.11 (m, 2H), 8.16 (m, 2H). IR (cm^{-1}): 2860 (CH_2), 1760 (CO in MeOCOOAr), 1720 (CO in $ArCOOCH_2$), 1640 (C=C), 1600 (C−C in Ar).

10-Chlorodimethylsilyldecyl-4-methoxycarbonyloxybenzoate (4). This compound was prepared according to the technique described in refs 18 and 20. A solution (20 μL) of platinum divinyltetramethylsiloxane complex in xylene (PC072) was added to a solution of compound **3** (5 g, 15 mmol) and dimethylchlorosilane (5 mL, 46 mmol) in absolute toluene (3 mL). The resulting solution was stirred under argon at room temperature for 48 h. The completion of the reaction was checked by IR and ^{1}H NMR spectroscopy. In the IR spectrum of the reaction products, the disappearance of the band for the stretching vibrations of the terminal carbon−carbon double bonds in the region of 1640 cm^{-1} was observed. Simultaneously, the appearance of the absorption band in the region of 1260 cm^{-1} corresponding to the stretching vibration of the Si−CH_3 bond was detected. The ^{1}H NMR spectrum of compound **4** exhibited no signals due to protons of the terminal carbon−carbon double bond (5.15 and 5.91 ppm). These results verified that the hydrosilylation was complete. Compound **4** was not extracted from the reaction mixture because of its instability.

10-Tetramethyldisiloxyldecyl-4-methoxycarbonyloxybenzoate (5). To the reaction mixture obtained in the previous stage were added 70 mL of dimethylchlorosilane (0.64 mol) and 20 mL of THF. To the resulting solution, cooled by water/ice, a mixture of water (6.2 mL, 0.34 mol), pyridine (45 mL, 0.56 mol), and THF (20 mL) was added slowly with vigorous stirring. The reaction mixture was stirred for 2 h at 20 °C. Then, 300 mL of ether was added to the reaction mixture. The ether layer was separated off and then washed with water three times and dried over sodium sulfate. Then, the solution was evaporated to dryness in a vacuum. The residue was purified by column chromatography over silica gel using toluene/ethyl acetate (20:1) as the eluent. Yield = 4.2 g of colorless oil, 60%. ^{1}H NMR (250 MHz, $CDCl_3$) δ (in ppm): 0.045 (s, 6H), 0.147 (d, 6H), 0.51 (m, 2H), 1.19−1.47 (m, 16H), 1.75 (m, 2H), 3.91 (s, 3H), 4.30 (t, 2H), 4.67 (m, 1H), 7.24 (m, 2H), 8.09 (m, 2H). IR (cm^{-1}): 2100 (SiH), 1760 (CO in COOAr), 1720 (CO in $ArCOOCH_2$), 1600 (C−C in Ar).

G-1(10PhOOCOCH$_3$)$_8$ (6). This compound was prepared according to the technique described in refs 18 and 20. To a solution of compound **4** (1.8 g, 3.8 mmol) and G-1(All)$_8$ (0.223 g, 0.32 mmol) in 2 mL of absolute toluene was added 10 μL PC072. The resulting solution was stirred under argon for 7 days. The extent of the reaction was monitored by GPC analysis. After the reaction was complete, the Pt catalyst was removed by column chromatography over silica gel using ethyl acetate as the eluent. The product was purified by preparative GPC ($M_w/M_n = 1.02$). Yield = 0.8 g of colorless oil, 56%. ^{1}H NMR (250 MHz, $CDCl_3$) δ (in ppm): −0.088 (s, 12H), 0.017 (s, 96H), 0.54 (m, 64H), 1.20−1.46 (m, 136H), 1.74 (m, 16H), 3.91 (s, 24H), 4.29 (t, 16H), 7.24 (m, 16H), 8.07 (m, 16 H). IR (cm^{-1}): 2860 (CH_2), 1760 (CO in MeOCOOAr), 1720 (CO in $ArCOOCH_2$), 1600 (C−C in Ar).

G-1(10Ph−OH)$_8$ (7). A 25% water solution of ammonia (12 mL) was added to a solution of compound **6** (0.424 g, 0.095 mmol) in 40 mL of ethanol/THF (1:1) that was cooled by water/ice. The reaction mixture was then stirred without cooling until it became homogeneous solution (about 2 h.). Then, the solution was poured into water and brought to pH 8 by acetic acid. The resulting emulsion was extracted by ether three times. The combined ether solution was washed with water three times and dried with anhydrous sodium sulfate. Then, the solution was evaporated in a vacuum. Yield = 0.2 g of colorless oil, 53%. ^{1}H NMR (250 MHz, $CDCl_3$) δ (in ppm): −0.089 (s, 12H), 0.012 (s, 96H), 0.55 (m, 64H), 1.20−1.46 (m, 136H), 1.73 (m, 16H), 4.27 (t, 16H), 6.86 (d, 16 H), 7.94 (d, 16H). IR (cm^{-1}): 2920, 2860 (OH, CH_2), 1720 (CO in $ArCOOCH_2$), 1600 (C−C in Ar).

G-1(10PhMC)$_8$ (8). The compound **7** (0.2 g, 0.049 mmol) and triethylamine (0.13 mL, 0,9 mmol) were dissolved in dry THF (5 mL). 4-Methyoxycinnamoyl chloride (0.16 g, 0.8 mmol) dissolved in dry THF (5 mL) was added to the resulting solution cooled by water/ice. The resulting mixture was stirred for an additional 24 h without cooling. Then, the solution was filtered and evaporated under reduced pressure. The residue was dissolved in chloroform (100 mL), and the solution was washed with water three times. The resulting solution was dried with anhydrous sodium sulfate and evaporated in a vacuum. After repeated boiling in methanol, the target cinnamoyl-containing dendrimer was obtained as a colorless viscous oil. Yield = 87%. ^{1}H NMR (250 MHz, $CDCl_3$) δ (in ppm): −0.085 (s, 12H), 0.20 (s, 96H), 0.54 (m, 64H), 1.18−1.49 (m, 136H), 1.75(m, 16H), 3.85 (s, 24H), 4.30 (t, 16H, $J = 6.7$ Hz), 6.47 (d, 8H, $J = 15.9$ Hz), 6.93 (d, 16H, $J = 8.5$ Hz), 7.23 (d, 16H, $J = 8.5$ Hz), 7.53 (d, 16H, $J = 8.5$ Hz), 7.83 (d, 8H, $J = 15.9$ Hz), 8.08 (d, 16 H, $J = 8.5$ Hz). IR (cm^{-1}): 2860 (CH_2), 1721 (CO in ArCOO), 1632 (C=C), 1600 (C−C in Ar). GPC analysis: $M_n = 5680$ ($M_{theor} = 5264.5$), $M_w/M_n = 1.03$. Elemental analyses (%): calcd C (65.71), Si (11.20), H (8.50); found C (64.97), Si (10.67), H (8.17)

Physicochemical Methods of Investigation. IR spectra were recorded on a Bruker IFS-88 spectrophotometer using KBr pellets.

^{1}H NMR spectra of samples in $CDCl_3$ solution were recorded using a Bruker WP-250 spectrometer.

GPC analysis was performed in THF (1 mL min^{-1}, 20 °C) on a Knauer setup equipped with an Ultrastyragel 8 × 300 mm column (Waters) having a pore size of 10^3 Å; the detector was a UV spectrometer from Knauer. A calibration plot was constructed with polystyrene standards. A Waters 19 × 300 mm column filled with Ultrastyragel 10^3 Å was used for preparative GPC.

Phase transitions in the photochromic dendrimer were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 K/min. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. Absorbance spectra of the dendrimer solutions and films were recorded with a Hitachi U-3400 UV−vis−IR spectrometer equipped with a Mettler FP-80 hot stage.

Photochemical Investigations. Photochemical investigations were performed using a special instrument[34] equipped with a DRSh-250 ultra-high-pressure mercury lamp. Using the filter, light with a maximum wavelength of 313 nm was selected. To prevent heating of the samples due to IR irradiation of the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensities of UV irradiation were determined actinometrically[35] and were equal to 1.0×10^{-9} einstein s^{-1} cm^{-2} ($\lambda_{ir} = 313$ nm).

The photochemical properties of the dendrimer were studied by illuminating thin films obtained by casting of the dendrimer solution in dichloroethane, followed by evaporation at 60 °C. Immediately after irradiation, absorbance or transmittance spectra were recorded using a Hitachi U-3400 UV−vis−IR spectrometer.

Results and Discussion

Synthesis. Carbosilane LC dendrimers were usually synthesized using the hydrosilylation reaction between

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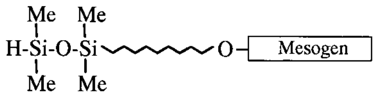
(34) Bobrovsky, A. Yu.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1998**, *25*, 393.

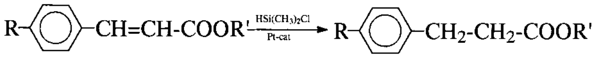
(35) Kurien, K. C. *J. Chem. Soc. B* **1971**, *75*, 2081.

a carbosilane matrix and a mesogen-containing fragment with a Si−H terminal group.



$$H\text{-}Si(Me)_2\text{-}O\text{-}Si(Me)_2\text{-}(CH_2)_n\text{-}O\text{-}\boxed{\text{Mesogen}}$$

This approach to the synthesis of such dendrimers earlier elaborated by us allowed for the successful synthesis of a number of different LC dendrimers.[20,25] Such a synthetic pathway has one restriction: the mesogenic groups should be “indifferent" to the hydrosilylation reaction. However, the cinnamoyl group contains a carbon−carbon double bond that is modified by $HSi(CH_3)_2Cl$ in the presence of Pt catalyst, which changes cinnamoyl-containing mesomorphous monomer during the hydrosilylation reaction.



That is why we have worked out a new protection−deprotection technique for the synthesis of photosensitive carbosilane LC dendrimers. The method consists of the synthesis of dendrimer with terminal hydroxyl groups and then the coupling of 4-methoxycinnamoyl chloride to it. The synthetic route of the cinnamoyl-containing LC dendrimer preparation is shown in Figure 2.

The hydroxyl group of 4-hydroxybenzoic acid was protected by chloroformate in a water solution of sodium hydroxide. Then, 9-decen-1-ol was coupled to the acid chloride **2** of the protected acid **1**. The obtained compound **3** underwent hydrosilylation with dimethylchlorosilane in the presence of a platinum catalyst. The completion of the reaction was checked by the disappearance of the signals due to the protons of the terminal carbon−carbon double bond in the ^{1}HNMR spectra. Cohydrolysis of compound **4** and a 40% molar excess of dimethylchlorosilane gave the compound **5** containing a terminal reactive −SiH group. The ^{1}HNMR spectrum of this compound displays a multiplet signal for the protons at the silicon atoms in the region of 4.67 ppm and a doublet signal for the methyl protons at Si−H in the region of 0.15 ppm.

Compound **5** was linked to the carbosilane matrix **G1-(All)$_8$** with terminal vinyl groups using a hydrosilylation reaction in the presence of catalyst to give compound **6**. The bands and proton signals corresponding to the allylic double bonds of the initial dendritic matrix are absent in the IR and ^{1}HNMR spectra of compound **6**. The protection group was removed in ethanol/THF by addition of a water solution of ammonia to give compound **7**, which contains terminal phenol groups (the IR spectrum of this compound shows absorption band in the region 2920 cm^{-1}). The target dendrimer **8** was prepared by the eserification reaction of compound **7**, using a 15% molar excess of methoxycinnamoyl chloride. The excess of methoxycinnamic acid, which forms from the acid chloride after extraction (see the Experimental Section) was removed from the target dendrimer by prolonged washing with boiling methanol. The purity of the final dendrimer obtained was established by GPC. The GPC trace of the dendrimer with methoxycinnamoyl groups had a symmetric peak after final purification (Figure 3). The molecular mass distribution (M_w/M_n) of the LC dendrimer was 1.03, confirming the monodispersity of the compound synthesized. Note that the molecular weight of the target dendrimer calculated from the polystyrene standards diverts from theoretical molecular weight calculated from the structural formula (see the Experimental Section). These results are in agreement with the literature data for similar systems.[36,37] It is well-known that dendrimers have less hydrodynamic volume than their linear analogues because of the compact architecture of the latter.[2]

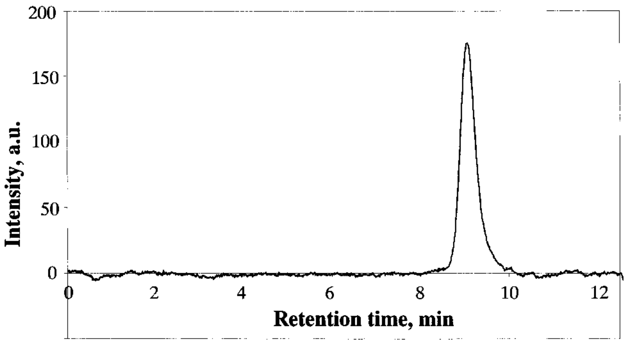


Figure 3. GPC chromatogram of dendrimer G-1(10PhMC)$_8$.

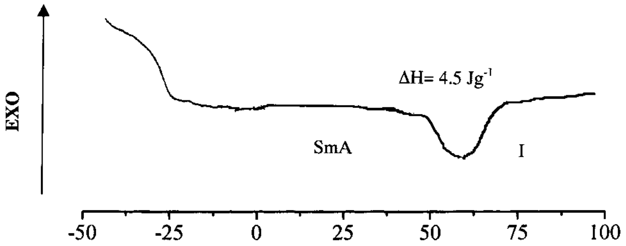


Figure 4. DSC curve for the LC dendrimer with terminal cinnamoyl-containing mesogenic group.

Phase Behavior. According to the data obtained by polarizing optical microscopy, the LC dendrimer is characterized by fan-shaped or homeotropic textures, depending on the conditions of the sample preparation. Examination of the DSC data (Figure 4) shows that the dendrimer is able to form a mesophase in a wide temperature range, which is transformed into an isotropic melt at $T_{cl} = 58$ °C (glass transition temperature $T_g = -28$ °C). The corresponding X-ray pattern obtained at room temperature shows a diffuse halo at a wide scattering angle ($D_{dif} = 4.6$ Å) and two intensive small-angle X-ray reflections corresponding to the interlayer distances $d_{001} = 44$ Å and $d_{002} = 22$ Å. These results imply the existence of an orthogonal disordered smectic A mesophase for the synthesized dendrimer.

Computer modeling has shown that the length of a terminal mesogenic group with a spacer in the trans conformation is about 33 Å. This is quite a bit smaller than the interlayer distance d_{001}. Thus, we suggest a one-layer packing with overlapping mesogenic groups in the SmA phase (Figure 5)

Photochemical Properties. The photochemical behavior of the photochromic dendrimer was studied in dilute solutions and in the LC phase (thin films). Figure

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(36) Balagurusami, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.

(37) Ponomarenko, S. A.; Rebrov, E. A.; Boiko, N. I.; Muzafarov, Az. M.; Shibaev, V. P. *Polym. Sci., Ser. A* **1998**, *40*, 763.

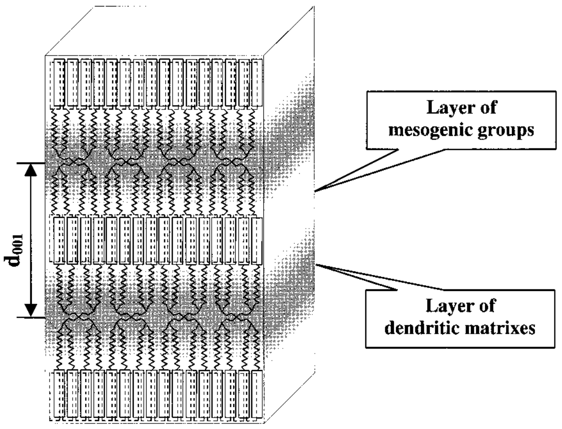


Figure 5. Scheme of packing of LC dendrimer of generation 1 in the smectic A mesophase.

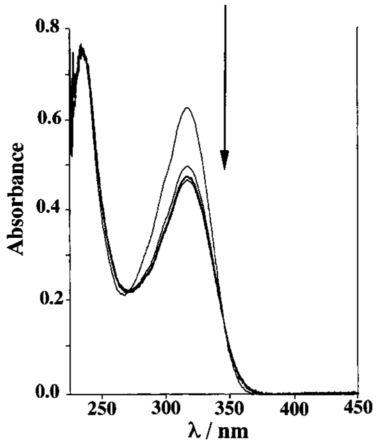
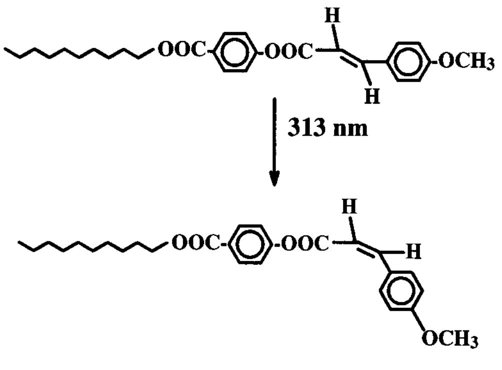


Figure 6. Absorbance spectra changes during UV irradiation of dendrimer solution in dichloroethane. Spectra were recorded each 5 min of irradiation.

6 shows the spectra corresponding to the dilute solutions of the dendrimer in dichlorethane ($c = 1.36 \times 10^{-2}$ mg/mL) during UV irradiation ($\lambda_{ir} = 313$ nm). As follows from the Figure 6, the optical density of the peak, corresponding to the $\pi-\pi^*$ and $n-\pi^*$ electronic transitions of the cinnamoyl chromophore, is decreased as a result of light irradiation (shown by the arrow in the figure), and an isosbestic point at 280 nm is established in the initial step of irradiation. According to the results presented in the literature,[38] the above-mentioned changes in the electronic spectra of this class of photochromic compounds are associated with the occurrence of the $E-Z$ isomerization of cinnamoyl groups.



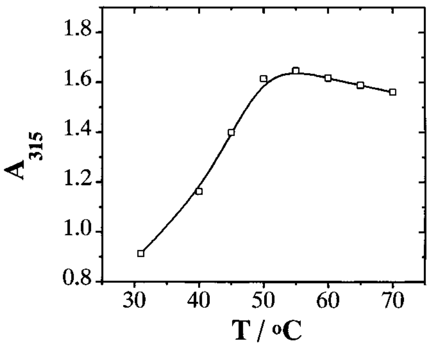


Figure 7. Temperature dependence of absorbance for the film of dendrimer.

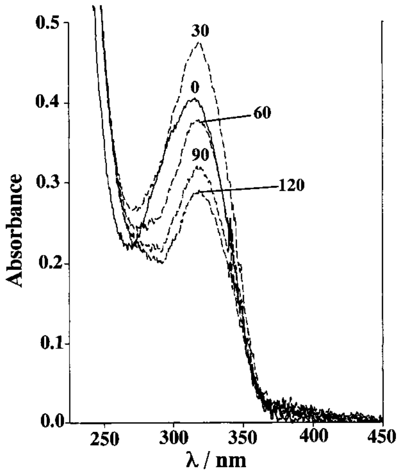


Figure 8. Absorbance spectra changes during UV irradiation of dendrimer film. Irradiation time (in minutes) is shown in the figure. Temperature of the sample is 25 °C.

As shown in our previous paper,[39] LC dendrimer molecules in dilute solutions can be considered as spherical particles (see Figure 1). In this case, there is a small probability of [2+2] photocycloaddition because of the large distance between the cinnamoyl groups of the carbosilane dendrimer of the first generation, since such a process is controlled topochemically.[32] Therefore, only one process, $E-Z$ photoisomerization of the carbon–carbon double bond, is observed in the dilute solution of the dendrimer.

In the case of the LC dendrimer film, the situation is more complicated. As already noted, the spontaneous occurrence of homeotropic orientation of the mesogenic groups (perpendicular to the support) is observed in the thin films obtained by the slow evaporation of a solution of the LC dendrimer in dichloroethane or by the spin-coating method. The occurrence of this homeotropic orientation is confirmed by polarizing optical microscopy and by the character of the temperature dependence of the optical density maximum A_{315} (Figure 7). Increasing temperature leads to an increase in A_{315}, which, perhaps, is due to the decrease in orientational order of the mesogenic groups and the transition to an isotropic liquid at 58 °C.

As seen in Figures 8 and 9, during the first minutes of the UV irradiation of the homeotropically oriented films, a rapid growth in optical density is observed,

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(38) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981**, *14*, 95.

(39) Lezov, A. V.; Mel'nikov, A. B.; Polushina, G. E.; Ponomarenko, S. A.; Boiko, N. I.; Kossmehl, E.; Rymtsev, E. I.; Shibaev, V. P. *Doklady Phys. Chem.* **1998**, *362*, 338.

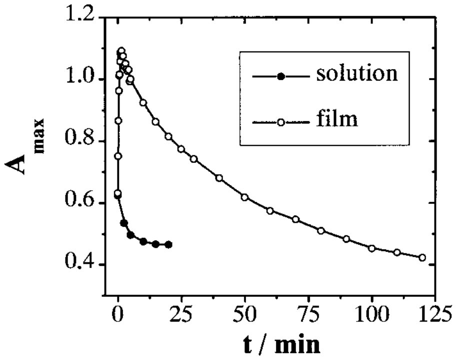

Figure 9. Optical density changes during UV irradiation of dendrimer solution in dichloroethane ($c = 1.36 \times 10^{-2}$ mg/mL) and film at 25 °C.

which is associated with the destruction of the homeotropic orientation of the mesogenic groups. An isothermal photoinduced transition SmA−I is probably also observed in this system. The optical density of the films decreases upon further irradiation (in this case, the decrease amplitude is much larger than in the case of the dilute solution), the isosbestic point is lost, and the dendrimer films become insoluble in organic solvents. It is obvious that a strongly cross-linked structure has been formed. The experimental data show that at least two processes, namely, *E*−*Z* photoisomerization and [2+2] photocycloaddition, take place in the dendrimer films.

To summarize, in this work, a new approach to the synthesis of photochromic carbosilane LC dendrimers was elaborated. A LC dendrimer of the first generation with terminal cinnamoyl groups was successfully synthesized. The structure and purity of this LC dendrimer were confirmed by ^{1}H NMR and GPC methods. It was shown that the LC dendrimer synthesized in this work exhibits photochromic properties. Such a dendrimer, under UV irradiation, can undergo *E*−*Z* isomerization of the cinnamoyl groups and [2+2] photocycloaddition leading to the formation of a three-dimensional network. The two above-mentioned processes lead to a disordering effect and an isothermal photoinduced SmA−I phase transition.

Acknowledgment. This research was supported by the Russian Foundation of Fundamental Research (Grants 99-03-33495 and 00-03-33141), International Soros Science Educational Program (Grant a99-1495), Russian Research Program “Universities of Russia” (Grants 991721 and 5178), and INTAS (Grant 9900365) and partially by the ESF “RESPOMAT” Program.

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