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Macroscopically Ordered Discotic Columnar Networks

Stefan Disch,[†] **Heino Finkelmann,***[,†] **Helmut Ringsdorf,**[‡] **and Peter Schuhmacher**[‡]

Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany, and Institut für Organische Chemie, Universität Mainz, J. J. Becher Weg 18−20, D-55099 Mainz, Germany

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ABSTRACT: A series of discotic polymer networks varying in the cross-linker concentration is realized. By using a new discotic cross-linker, the columnar mesophase is significantly stabilized compared to discotic networks containing rodlike cross-linkers. Samples with a chemically fixed macroscopic director alignment—so-called monodomains—are prepared by application of an uniaxial mechanical field during the synthesis of the network. The anisotropy of the oriented columnar phase of the monodomains is investigated by applying swelling, X-rays, and thermal expansion measurements. The results are compared to identical but macroscopically isotropic samples which are synthesized in the absence of a mechanical field.

Introduction

Columnar discotic liquid crystals have been established as new materials for rapid charge migration.[1,2] For technical applications a mechanically stable arrangement of the columnar assembly is necessary, preferably involving a macroscopically uniform director alignment. Discotic side-group polymers and in particular main-chain polymers have turned out to be difficult to align because of their high viscosity. Calamitic liquid crystalline (lc) elastomers have been shown to align easily if mechanical fields are applied, as the degree of orientation of the lc phase is strongly coupled to the anisotropy of the network.[3,4] Applying this concept of mechanical orientation, first used for elastomers with calamitic mesogens,[5] to discotic networks offers the possibility of achieving a highly oriented columnar phase. Indeed, the synthesis of a discotic network with a fixed uniform director orientation has been realized recently.[6] Although a highly oriented sample was obtained, the clearing point of the network turned out to be rather low compared to the un-cross-linked discotic polymer. It has been argued that the cross-linkers used—especially the bifunctional rodlike cross-linkers—disturb the columnar packing and destabilize the discotic mesophase. Consequently, the structure of the cross-linker should be adopted to the discotic mesogens to improve the stability of the lc phase.

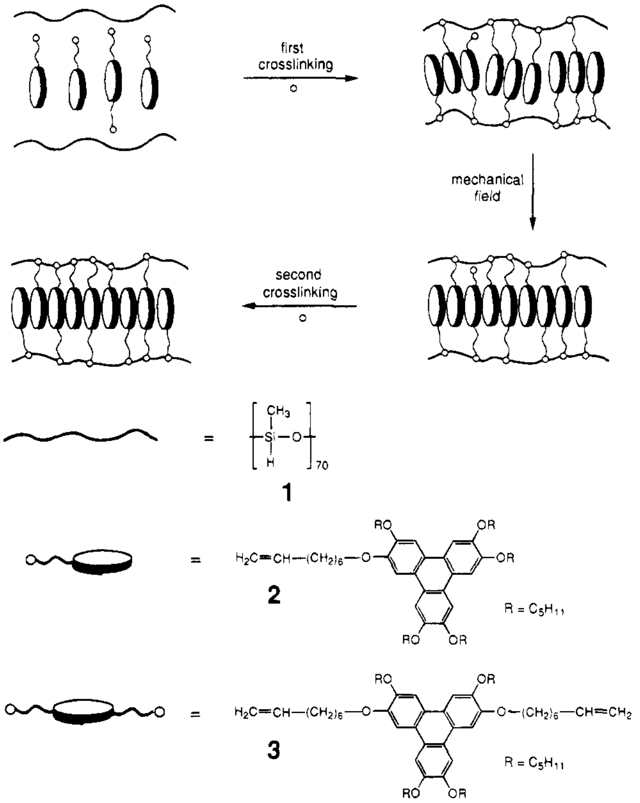
In this paper we present our studies on discotic networks containing a new discotic cross-linker. In the following section the synthesis is described. The characterization and the investigation of the anisotropy of the networks are given in the third section.

Synthesis

In order to obtain lc elastomers with a chemically fixed permanent director alignment, a two-step cross-linking process can be applied.[5] This approach turned out to be successful not only for calamitic elastomers but also for discotic systems.[6]

The key point of the two-step cross-linking process is to use two cross-linkers with different reactive groups: One of the cross-linkers contains two olefinic groups; the other possesses an olefinic group and a methacryloyl group. The latter was shown to react more slowly in the addition reaction than the olefinic group.[5] After the first, fast cross-linking step has taken place, the elastomer is mechanically strained, and this strain induces a macroscopic alignment of the liquid crystalline phase. The second, slow cross-linking process chemically locks-in the network anisotropy, and thus a permanent director alignment can be achieved.

Scheme 1. Reaction Scheme and Chemical Structures of the Compounds Used for the Synthesis



In this study the two-step cross-linking concept is modified and discotic networks with fixed anisotropy are obtained by using just one cross-linker. In Scheme 1, the network formation and the structure of the compounds are shown. The mesogen **2** and the cross-linker **3** are added to poly[oxy(methylsilylene)] (**1**) in a solution of toluene. In an intermediate state of cross-linking, the swollen network is strained: The cross-linking

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[†] Universität Freiburg.

[‡] Universität Mainz.

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Table 1. Stress during Synthesis (σ), Cross-Linker Concentration (c), Glass Transition Temperature (T_g), Discotic–Isotropic Phase Transformation Temperature (T_{di}), Change of the Isobaric Specific Heat (ΔC_p) at the Glass Transition, and Discotic–Isotropic Phase Transformation Enthalpy (ΔH_{di}) of the Discotic Networks (T_{di} and T_g Determined by Extrapolation of the Results from DSC Measurements at Heating Rates of 9, 16, 25, and 36 K min^{-1} to Zero Heating Rate

sample	σ/(N mm^{-2})	c	T_g/K	T_{di}/K	ΔC_p/ (J g^{-1} K^{-1})	ΔH_{di}/ (J g^{-1})
PD5	0	5	223	379	0.2	5.0
PD7.5	0	7.5	224	367	0.2	4.6
MD7.5	0.113	7.5	223	367	0.2	3.9
PD10	0	10	228	351	0.2	1.4
MD10	0.017	10	229	349	0.2	1.7

Table 2. Swelling Coefficients in the Direction of the Stress ($\alpha_\perp$) and Perpendicular to the Stress Axis ($\alpha_\perp$), the Ratio $\alpha_\perp/\alpha_\parallel$, and the Degree of Swelling (q) of the Discotic Networks

sample	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\perp/\alpha_\parallel$	q
PD5	1.5	1.6	1.1	3.8
PD7.5	1.5	1.6	1.1	3.8
MD7.5	1.1	1.8	1.5	3.6
PD10	1.5	1.5	1.0	3.4
MD10	1.3	1.6	1.2	3.3

reaction has to be propagated so far that the swollen network is mechanically stable, but a sufficient amount of unreacted cross-linking groups must remain. The cross-linking reaction is completed in the loaded state which leads to a chemically fixed anisotropy of the network. Due to this fixed network anisotropy, the sample dimension in the direction of the stress does not decrease when the external mechanical field is released.

Five networks with cross-linker concentrations of 5, 7.5, and 10% and different loads applied during the synthesis were prepared. The cross-linker concentration is given by the molar ratio of cross-linker molecules and silylene units in the polymer. Two networks with 7.5 and 10% cross-linkers were mechanically strained during the synthesis so that samples with fixed anisotropy, so-called monodomains, could be obtained. The applied stresses are listed in Table 1 where a network with a cross-linker concentration c is labeled PDc when no stress was applied (polydomain) and MDc if a monodomain network was prepared. The monodomain samples are optically transparent, which is a first indication for a high orientation of the lc phase.

Characterization

Thermal Analysis by Differential Scanning Calorimetry. The results of the thermal characterization of the networks by DSC are given in Table 1. The results show that the clearing points of the networks with a cross-linker concentration of 10% are 49 K higher than the clearing point of the network containing the same concentration of calamitic cross-linkers.[6] The discotic mesophase is more stable if the structure of the cross-linker is adopted to the shape of the discotic mesogen. However, even for the networks containing discotic cross-linkers consistent with the discotic mesophase, a strong decrease of T_{di} with increasing cross-linker concentration has to be noted. The clearing point is depressed by almost 30 K when the cross-linker concentration is increased from 5 to 10%. Additionally, the enthalpy of the discotic–isotropic phase transformation decreases drastically with increasing cross-linker concentration. This demonstrates that the discotic mesophase is highly sensitive to structural constraints such as the presence of a cross-linker or the modification of the alkyl chains attached to the rigid disks. The decreased phase stability of lc elastomers compared to that of the analogous linear polymer is due to the thermodynamic mixing effect with the cross-linker which has a lower discotic–isotropic transformation temperature than the linear polymer.[7] It has been shown for discotic polymers that the discotic phase is destabilized when the alkyl chain region of the discotic mesogen is disturbed by a longer spacer.[8] As the cross-linker contains two longer spacers of eight carbon atoms, a higher cross-linker concentration causes a larger decrease of the phase stability. An additional reason for the depression of the stability of the discotic mesophase is the orientational order of the mesogenic units in the vicinity of the cross-links. Because most of the cross-linkers react in the isotropic swollen state, they remain isotropically distributed even when the network becomes liquid crystalline. The isotropically ordered cross-links prevent a high orientation of the mesogens in their vicinity, even for samples with macroscopic director alignment, and generate defects in the lc phase. A high density of defects will destabilize the phase. It was recently found that an isotropic distribution of the cross-links decreases the phase stability of nematic elastomers.[9] Brand and Kawasaki proposed a theoretical model which takes into account the influence of the state of order of the cross-links on the stability of the lc phase.[10] The orientational distribution of the cross-links has to be considered also for discotic networks. A broad distribution will also cause the observed decrease of the stability of the columnar phase.

While both the orientation and the concentration of the cross-links influence the phase behavior of discotic networks, the macroscopic director orientation of the columns in the network has no effect on the stability of the discotic mesophase. This is shown in Table 1 where monodomains and polydomains synthesized with the same cross-linker concentration exhibit the same discotic–isotropic transformation temperature and the same phase transformation enthalpy within the experimental error.

To analyze the anisotropy of the network, swelling measurements, X-ray experiments, and measurements of the thermal expansion were performed.

Swelling Experiments. Both the degree of cross-linking and the anisotropy of a network can be investigated by swelling experiments in toluene. The swelling coefficient can be defined as the ratio of the dimension of the network in the swollen and in the unswollen state. For anisotropic networks, the swelling coefficient $\alpha_\parallel$ in the direction of the stress is less than the coefficient $\alpha_\perp$ perpendicular to the stress axis. The ratio $\alpha_\perp/\alpha_\parallel$ is a measure of the anisotropy of the network. For isotropic networks the swelling coefficients are identical. The degree of swelling $q = \alpha_\parallel\alpha_\perp^2$ is related to the average molar mass of the strands of the network and thus is a function of the cross-linking density.[11] In Table 2, the results of the swelling experiments are given. The data show that the networks prepared without load during the synthesis swell isotropically in toluene, whereas the swelling of the monodomain samples is highly anisotropic. These results are evidence of the anisotropic network structure induced by the two-step cross-linking process.

X-ray Experiments. The X-ray patterns of the networks MD7.5, PD7.5, MD10, and PD10 at room temperature are displayed in Figure 1. The incident

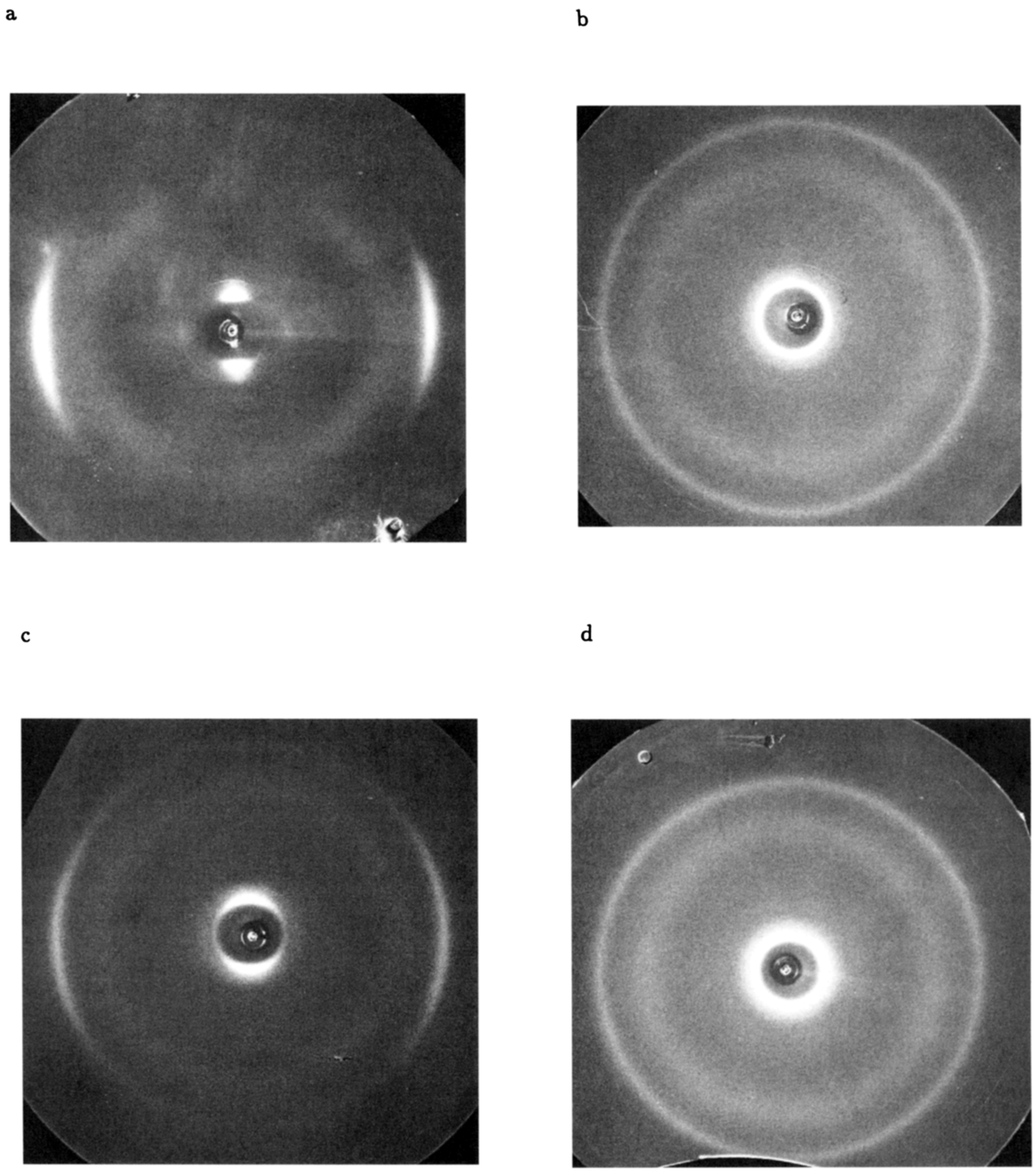

Figure 1. X-ray patterns of discotic networks at room temperature: (a) MD7.5; (b) PD7.5; (c) MD10; (d) PD10.

beam is perpendicular to the stress direction and to the surface of the film. The wide-angle reflections can be attributed to the intracolumnar disk spacing, and the ordering of the columns (intercolumnar disk spacing) generates the small-angle reflections.[12] The spacings corresponding to the reflections are not influenced by the orientation of the discotic mesophase. The polydomain samples show a homogeneous azimuthal distribution of the intensities which indicates an isotropic director distribution. For the monodomain networks the azimuthal distribution of the intensities is characterized by the occurrence of sharp maxima. The locations of the maxima—the wide-angle reflections in the direction of the stress and the small-angle reflections perpendicular to it—prove that the columns are macroscopically aligned parallel to the axis of the applied stress. The azimuthal distribution of the intensities is narrower for MD7.5 than for MD10, showing a higher order of the discotic phase of MD7.5. During the synthesis, a higher stress was applied for MD7.5 than for MD10, leading to a higher anisotropy of the discotic phase. This result is in good agreement with the data from the swelling measurements. Assuming that the cross-linker has no influence on the phase structure of the columnar phase, the lattice should be rectangular, in analogy to the corresponding linear polymer.[8]

Thermal Expansion of Discotic Networks. The anisotropy of a lc elastomer can be quantitatively analyzed by measuring the thermal expansion. According to previous experiments on networks containing rodlike mesogens, a change of the order parameter of an anisotropic lc network is reflected in a change of the

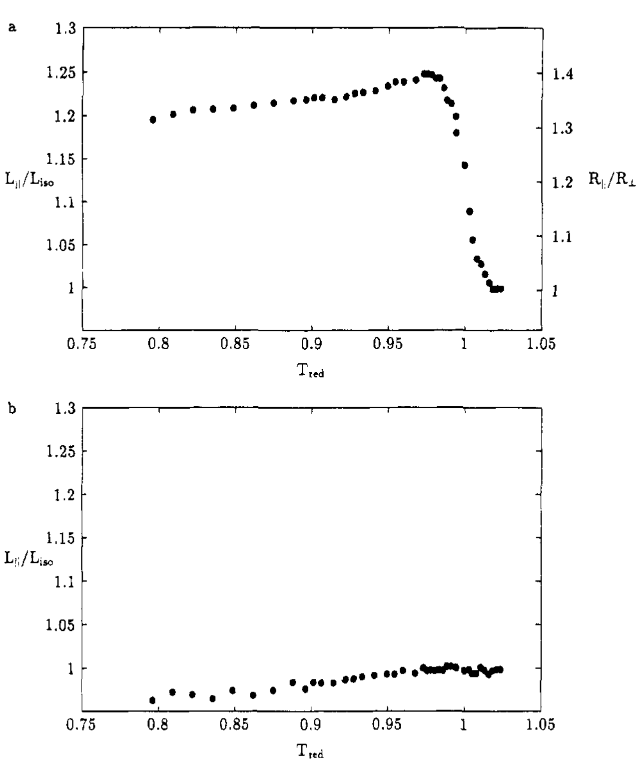

Figure 2. Thermal expansion of discotic networks: (a) MD7.5; (b) PD7.5.

macroscopic dimensions of the network.[9,13] Thus, a change of the state of order of a monodomain elastomer can be directly followed by measuring the sample dimensions as a function of temperature. For anisotropic lc elastomers, a jump of the length at the transformation from the liquid crystalline to the isotropic phase is expected. From the change of the length at the phase transformation, the ratio of the radii of gyration parallel and perpendicular to the stress axis $R_{\|}/R_{\perp}$ in the lc phase can be easily calculated on the basis of the affine network model.[14,15]

$$\frac{L_{\|}}{L_{\mathrm{iso}}} = \frac{R_{\|}}{R_{\mathrm{iso}}} = \left(\frac{R_{\|}}{R_{\perp}}\right)^{2/3} \qquad (1)$$

$L_{\|}$ is the dimension of the elastomer in the direction of the stress axis at a given temperature, and L_{iso} is the dimension in the isotropic phase in the same direction. The radius of gyration in the isotropic state, R_{iso}, characterizes a spherical conformation of the polymer backbone. In a lc phase, the polymer backbone conformation deviates from the spherical shape: For $R_{\|} > R_{\perp}$, the conformation is prolate and for $R_{\|} < R_{\perp}$ oblate. A discotic network based on a side-group polymer is expected to orient the columns in the direction of the stress if the columnar phase becomes aligned. This could be verified for our system by the X-ray results. The oriented liquid crystalline phase forces the polymer backbone into a conformation which is consistent with the columnar phase symmetry. This should lead, in analogy to nematic elastomers, to a prolate backbone conformation. At the discotic–isotropic phase transformation, the polymer backbone changes its conformation to a spherical one. The change in the backbone conformation must be reflected in a macroscopic change of the dimensions of the elastomer.

The thermal expansion measurements were performed on the networks with a cross-linker concentration of 7.5%. The results are shown in Figure 2, where $L_{\|}/L_{\mathrm{iso}}$ and $R_{\|}/R_{\perp}$ obtained from eq 1 are plotted against the reduced temperature T_{red} ($T_{\mathrm{red}} = T/T_{\mathrm{di}}$). The thermal expansion curve of the monodomain in Figure 2a can be subdivided in two regions. In the first region, the length increases continuously as a function of temperature up to the maximum at $T/T_{\mathrm{red}} = 0.97$. At higher temperatures, a second region can be discerned where the dimension decreases rapidly with temperature. The first part can be attributed to the isobaric thermal expansion of the network. From the slope of the straight line, obtained by linear regression of the data points up to the maximum in Figure 2a, the specific isobaric expansion coefficient in the direction of the stress can be calculated to be $(6 \pm 2) \times 10^{-4}$ K^{-1}. For the polydomain in Figure 2b, the length increases continuously with temperature over the whole temperature range. Linear regression of all data points gives an specific isobaric expansion coefficient of the same magnitude ($(4 \pm 2) \times 10^{-4}$ K^{-1}). In contrast to the monodomain, the thermal expansion of the polydomain in Figure 2b does not show a decrease near the phase transformation. Such a behavior is expected for a network with a macroscopically average, isotropic director distribution. For both samples, at temperatures well below the discotic–isotropic transformation temperature, the change of the length with temperature is dominated by the thermal expansion and does not reflect a change of the state of order of the network. Consequently, eq 1 cannot be applied in this temperature region. The observed behavior is due to the high viscosity of the columnar phase: A temperature increase should cause a decrease of the state of order of the network. But on experimental accessible time scales, the entire system, in particular the polymer backbone, cannot change its arrangement because of the high viscosity. Thus, a change of the state of columnar order does not result in a change of the macroscopic dimensions of the network. It has to be noted that the thermal expansion measurements below the discotic–isotropic transformation temperature are not carried out under thermal equilibrium conditions.

If the temperature is increased, the viscosity of the columnar phase decreases drastically just below the phase transformation. At temperatures above $T/T_{\mathrm{red}} = 0.97$, the monodomain MD7.5 in Figure 2a can be considered to be in the equilibrium state. Under this condition, a change of the macroscopic dimensions is directly reflected in a change of the state of order, and thus eq 1 is a valid relation. In Figure 2a the monodomain MD7.5 shows a jump of the dimension parallel to the oriented columns at the discotic–isotropic phase transformation in agreement with the theoretical model discussed above. According to eq 1, the anisotropy of the network in the lc state can be calculated from the extent of the jump: MD7.5 changes its length by 25% which corresponds to $R_{\|}/R_{\perp} = 1.40$ in the discotic mesophase at $T/T_{\mathrm{red}} = 0.97$. This result proves both the prolate backbone conformation and the high anisotropy of the discotic phase. Analogous measurements on oriented calamitic nematic networks showed an anisotropy of the same magnitude.[9,13]

The thermal expansion data given in Figure 2 were obtained upon heating. If the monodomain is kept in the isotropic state for a long time, the sample does not relax back to its original length when it is cooled into the discotic mesophase since the thermal degradation of the network starts to affect the anisotropy. The following observations can prove that the anisotropy is chemically fixed and that the incomplete relaxation is caused by thermal degradation: First, if the monodomain sample is heated up into the isotropic state for a short time and then cooled into the columnar phase, the network retains its anisotropy and relaxes fully back to the original length. Second, after swelling the monodomain networks in toluene they regain their original anisotropic dimensions when toluene is removed.

Conclusion

Macroscopically ordered discotic columnar networks with a high stability of the mesophase can be realized. The columnar phase is stable over a wide temperature range when the structure of the cross-linker is adopted to the discotic mesogen. The conformation of the polymer backbone of monodomain networks is prolate and thus consistent with the symmetry of the oriented columnar phase. The network with the highest achieved orientation possesses a ratio of the radii of gyration $R_\parallel/R_\perp$ of 1.40. The oriented columnar phase of this network should be suitable for one-dimensional charge transport. However, for most technical applications (e.g., photoconducting layers) the columns should be oriented perpendicular to the film surface. This may be realized by compressing a swollen network with cylindrical shape or by applying the same procedure used in this study in the synthesis of discotic main-chain polymers which are known to orient perpendicular to the applied stress direction.[16]

Experimental Part

Synthesis. Monomer. Monomer **2** was synthesized according to the literature.[17] Phase behavior: c 53 D_h 100 i (°C).

Cross-Linker (3). A total of 1 g (1.45 mmol) of 2,7-diacetoxy-3,6,10,11-tetrakis(pentyloxy)triphenylene (obtained by recrystallization of a tetrakis(pentyloxy)triphenylene diacetate isomeric mixture from petrol ether[17] and 0.55 g (2.9 mmol) of bromooctene are dissolved in 10 mL of dry DMF. After addition of 0.33 g (5.8 mmol) of powdered sodium hydroxide, the mixture is heated for 8 h at 70 °C under an argon atmosphere. The crude product can be precipitated by pouring the mixture into water and then filtering it and washing it with methanol. Chromatography on silica gel (CH_2Cl_2/heptane 4/1) and recrystallization from ethanol yields 0.96 g (80.1%) of white crystals. Phase behavior: c 55 D_h 73 i (°C). Anal. Calcd for $C_{54}H_{80}O_6$: C, 78.60; H, 9.77. Found: C, 78.51; H, 9.68. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.82 (s, 6H, Ar-*H*, 5.82 (tdd, 2H, $CH_2CH{=}CH_2$, $J_{cis} = 10.2$ Hz, $J_{trans} = 16.7$ Hz, $J_{tripl.} = 6.7$ Hz), 5.00 (d, 2H, $CH{=}CH_2$, $J_{trans} = 17.0$ Hz), 4.94 (s, 2H $CH{=}CH_2$, $J_{cis} = 10.2$ Hz), 4.22 (t, 12H, OCH_2, $J = 6.6$ Hz), 2.12−1.87 (m, 16H, $OCH_2CH_2 + CH_2CH{=}CH_2$), 1.61−1.35 (m, 28H, $OCH_2CH_2(CH_2)_{2/3}$), 0.97 (t, 12 H, CH_2CH_3, $J = 6.9$ Hz). MS-EI: *m/z* 825.0 [M^+].

Elastomers. The synthesis is described elsewhere.[5,6] For MD10, 47.8 mg (0.8 mmol of SiH groups) of poly[oxy(methylsilylene)] (**1**), 500.0 mg (0.63 mmol) of mesogen (**2**), 70.1 mg (0.085 mmol) of cross-linker (**3**), and 4 μL of Pt catalyst SLM 86005 (Wacker Chemie Burghausen) were dissolved in 1 mL of toluene. The reaction was carried out under centrifugation (4000 rpm) at 65 °C for 3 h. A Teflon film was placed into the centrifuge for better handling of the swollen elastomer. After the swollen elastomer was removed from the centrifuge, it was uniaxially strained by a stress of 0.017 N/mm^2 and annealed for 24 h at room temperature, to complete the cross-linking reaction.

Differential Scanning Calorimetry. DSC measurements were performed with a Perkin-Elmer DSC 7.

Swelling Measurements. The dimensions of the networks in the swollen and the unswollen state were determined with a Leitz Ortholux II microscope.

X-ray Experiments. X-ray experiments were carried out with a Philips PW 1730 and Cu Kα radiation.

Thermal Expansion. The thermal expansion measurements were performed with a home-built apparatus which allowed the sample temperature to be kept constant to 0.1 K. The dimensions of the networks were determined with a cathetometer with an accuracy of 30 μm. The temperature was kept constant for at least 2 h between two measurements. The length of the networks in the stress direction at room temperature was 15.89 mm for MD7.5 and 12.46 mm for PD7.5. In the isotropic state the length in the stress direction, L_{iso}, was 13.27 mm for MD7.5 and 12.92 mm for PD7.5.

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