Hexagonal Lyotropic Liquid Crystalline Hydrogels: Influence of Uniaxial Stress and pH Value on the Anisotropic Swelling Behavior

Felix Weiss and Heino Finkelmann*

Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Received March 29, 2004; Revised Manuscript Received May 19, 2004

ABSTRACT: A new type of lyotropic liquid crystalline elastomer is described. The elastomer is synthesized by cross-linking a lyotropic epoxide−amine addition polymer that exhibits a hexagonal phase in the binary polymer water mixture. A similar phase behavior is revealed in the water-swollen elastomer. Uniaxial strain of the network causes a macroscopically uniform orientation of the rodlike micelles parallel to the stress axis. Such an oriented sample is characterized by hygroelastic measurements at different temperatures and uniaxial strains monitoring the network dimensions as a function of the water content. Because of the coupling of the lyotropic liquid crystalline phase structure and the network chain conformation, the network swells anisotropically within the hexagonal phase. At the isotropic to hexagonal phase transformation a discontinuous change in length is observed. A partial protonation of the linear polymers dramatically increases the concentration and temperature regime of the hexagonal phase and additionally the solubility in water. Applying this knowledge to the cross-linked system, switching between isotropic and the hexagonal phase is realized by variation of the pH value. The phase transformation becomes apparent in the anisotropic change of dimensions of the network.

Introduction

Liquid crystalline elastomers (LCEs) combine the anisotropy of the liquid crystalline state and rubber elasticity. Because of a coupling of the network chain conformation and the liquid crystalline state of order, a macroscopically uniform orientation of the director can be achieved by mechanical fields.[1] Furthermore, macroscopically oriented samples exhibit an anisotropic change in their dimensions as a function of the state of order.[2] While these properties are well understood experimentally and theoretically for thermotropic liquid crystalline networks, little is known about lyotropic liquid crystalline elastomers.[3]

Löffler et al. realized a lyotropic liquid crystalline elastomer revealing a hexagonal phase H_1 when swollen with water.[4] Actually, a macroscopic orientation of the hexagonal director has been achieved by an uniaxial swelling process of the network in a cylindrical glass tube. This anisotropic swelling process equals an uniaxial strain of the sample parallel to the long axis of the glass tube. A lamellar lyotropic liquid crystalline elastomer has been obtained by Fischer et al. The director of the L_α phase could be macroscopically oriented by uniaxial compression as identified by WAXS and ^{2}H NMR measurements.[5] These experiments have clearly given the first proof of the coupling of the network chain conformation and the lyotropic liquid crystalline state of order similar to that of thermotropic liquid crystalline elastomers. The rodlike micelles of the hexagonal phase are compatible with an overall prolate network chain conformation, while the lamellar phase—built up from disklike micelles—requires an overall oblate chain conformation for a liquid single crystal hydrogel (LSCH).[5]

Fischer et al. investigated the swelling behavior of a macroscopically oriented lamellar elastomer.[6] According to the phase diagram of the corresponding linear polymer, at the phase transformation concentration and at a given temperature a macroscopic anisotropic deformation of the network was observed, and within the lamellar phase anisotropic swelling occurs that reflects the phase symmetry. These experiments were confirmed by Amigo-Melchior[7] and Hickl[8] with different types of lamellar hydrogels. The spontaneous anisotropic deformation of these lamellar hydrogels is about 5% in the direction of the optical or director axis, which is small compared to the spontaneous deformation of thermotropic liquid crystalline elastomers.[9] This indicates that the coupling between the network conformation and the micellar liquid crystalline organization is markedly weaker.

Recently, we reported on the synthesis and phase behavior of linear lyotropic liquid crystalline epoxide−amine addition polymers.[10] These polymers bear functional groups, such as amines and hydroxyl groups, which offer two interesting aspects: The hydroxyl groups are useful for cross-linking reactions to obtain hydrogels. The amine groups, on the other hand, can be easily protonated. This protonation strongly modifies the hydrophilic/hydrophobic balance of the amphiphilic monomer units and effectively alters the lyotropic liquid crystalline phase regime. Both the simple chemistry used in cross-linking these polymers and the pH sensitivity with respect to the liquid crystalline phase behavior make them perfectly suitable for the synthesis of hydrogels. The reversible pH-dependent phase transformation from liquid crystalline to isotropic state could be interesting e.g. for drug delivery systems,[11−14] or an anisotropic mechanical response might be useful for pH sensors or flow control valves.[2,15]

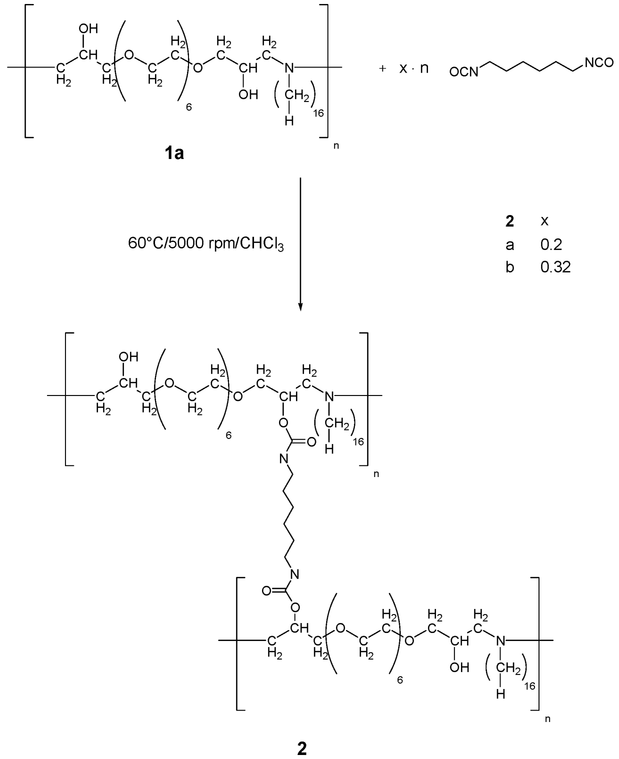
In the first part of this paper, we present detailed hygroelastic measurements of these hydrogels that exhibit a hexagonal structure. Because of the hexagonal geometry, orientation of the director is accessible by an uniaxial mechanical field, and the swelling behavior is investigated by variation of stress. In the second part,

---

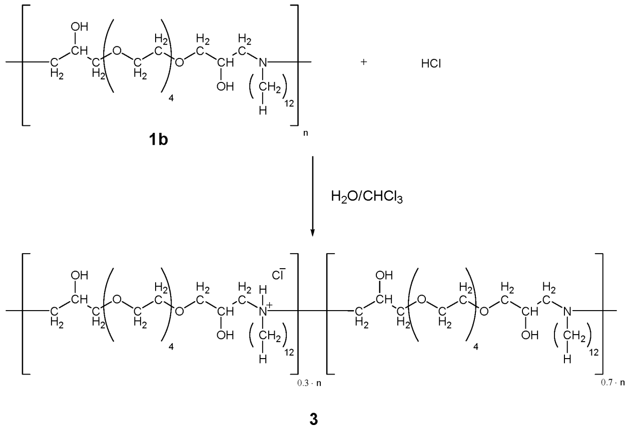
* Corresponding author. E-mail: heino.finkelmann@makro.uni-freiburg.de.

10.1021/ma0493877 CCC: $27.50

Scheme 1. Synthesis of the Elastomers 2a and 2b by the Addition Reaction of HMDI and the Free Hydroxyl Groups of 1a



Scheme 2. Partial Protonation of 1b with of 30 mol % of HCl by Addition of an Aqueous HCl Solution To Give 3



the effect of protonation of the polymers on the phase behavior of the binary polymer water systems as well as the anisotropic pH-dependent swelling of a corresponding elastomer is investigated.

Experimental Section

The elastomers **2a** and **2b** were obtained by reaction of hexamethylene diisocyanate (HMDI) and the free hydroxyl groups of **1a** (Scheme 1). A solution of polymer **1a** ($\overline{M}_n$ = 45 000 g/mol[10]) according to 1 mmol of repeating units in 1 mL of chloroform was prepared. 0.2 mmol (10 mol % per OH group) and 0.32 mmol (16% per OH group) of HMDI in chloroform to yield **2a** and **2b**, respectively, were dissolved in 0.5 mL of chloroform. The polymer and the cross-linker solutions were cooled in an ice bath and injected into a Teflon-coated hollow cylinder. In a centrifuge the linear polymers were cross-linked at 60 °C and 5000 rpm overnight. The obtained network was carefully dried first at room temperature and under normal pressure, and the drying was completed under vacuum at 60 °C.

For the preparation of the partly protonated polymer **3**, **1b** ($\overline{M}_n$ = 30 000 g/mol[10]) was dissolved in chloroform. 30 mol % of HCl with respect to the number of repeating units in an aqueous 1 N solution p.a. was added. Chloroform was evaporated under reduced pressure, and the aqueous polymer solution was freeze-dried.

^{1}H NMR ($CDCl_3$) δ [ppm]: 4.01 (m, $CHOH$), 3.62 (m, $-[CH_2CH_2O]_n-$), 3.49 (m, $CHOHCH_2O$), 2.79 (m, NCH_2), 1.55 (NCH_2CH_2), 1.23 (alkyl-CH_2), 0.86 ($-CH_3$).

To estimate the efficiency of the cross-linking reaction, the isotropic swelling was determined with chloroform at room temperature under a reflection microscope (Will Strübin). After swelling, the dimensions were measured, and the swelling coefficients λ_z in length and λ_x in width were calculated by dividing the dimensions of the swollen state by the initial dimensions. As the dry elastomer had a thickness of just ~300 μm, λ_y was not determined. However, for isotropic swelling λ_y equals λ_x. The swelling parameter was determined according to eq 1:

$$q = \lambda_z \lambda_x^2 \tag{1}$$

WAXS measurements were performed using a Cu X-ray tube coupled with a graphite monochromator and a 0.5 mm collimator (Cu Kα: λ = 1.5418 Å). The elastomer samples were investigated at the swelling equilibrium at room temperature. The samples were kept in water after deformation and investigated after 1 h equilibration time. The intensity of the scattered X-ray beam was detected by an image plate system. With the higher order reflexes at small scattering angles, the lyotropic mesophase are identified. In this way the lattice constants and distance of the centers of adjacent layers are determined.

The macroscopic dimensions of the hydrogel depending on the water concentration are measured with the method of hygroelastic. The method allows the monitoring of the change of dimension of hydrogels during the swelling process by precisely controlling the water content of the sample. The measurements are carried out in a computer-controlled apparatus,[6] which uses a hygrostat. This hygrostat operates by the isopiestic principle. At a given temperature T_2 the sample is equilibrated with the water partial vapor pressure of a nitrogen gas flow. The water partial vapor pressure is alternated by saturating nitrogen with water at a temperature T_1, where $T_1 < T_2$.

Water is absorbed by the hydrogel depending on the water vapor pressure. This change of the polymer concentration can be measured in situ with a microbalance (Sartorius MP4040). Dimensions of the samples are determined by a CCD camera.

The phase diagram of the polymer−water system was generated by the use of polarizing light microscopy POM (Leitz-Ortholux II Poll-BK microscope, Mettler FP 80/82 hotstage). Different polymer−water mixtures were prepared using an analytical balance and Teflon capsules on a vibrating mill. For cooling, a nitrogen flow cooled by liquid nitrogen was channeled around the sample. In this way phases down to 0 °C were investigated. Initial information on the phase behavior was obtained by a contact preparation at different temperatures. The maximal clearing temperature of the mesophase was observed in this way. Lyotropic phases were ascertained by typical textures.

Proton elastic measurements were carried out time dependently. The elastomer is kept under stress by a load and put into a beaker filled with 100 mL of deionized water covered by a PE lid. The temperature is kept constant by a Heidolph MR 3001 K hotstage and a Heidolph EKT 3001 controller unit. The setup is equipped with a buret filled with HCl solution. After addition of HCl solution, the length and width of the elastomer are measured using a CCD camera in defined intervals controlled by a computer program.

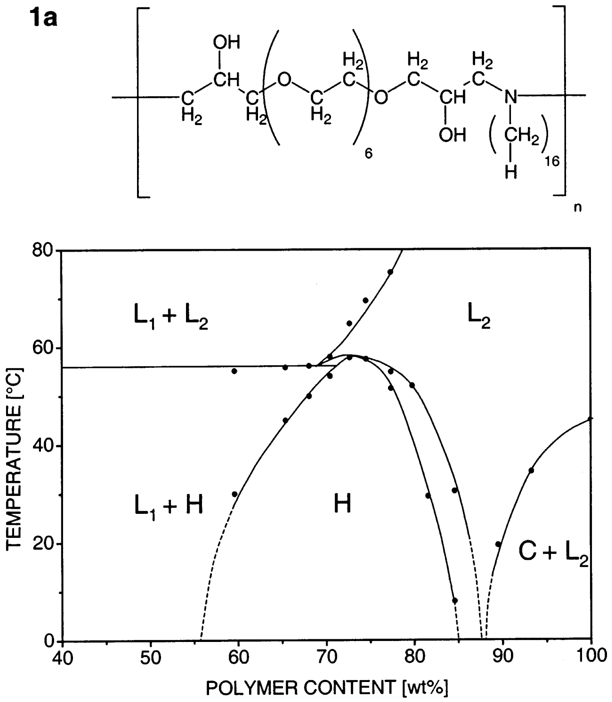


Figure 1. Structure of **1a** and phase diagram of the binary polymer–water mixture. L_1 and L_2 designate isotropic solutions, H is the hexagonal phase, and C refers to the crystalline polymer.[10]

Results and Discussion

The elastomers are synthesized from linear, amphiphilic epoxide–amine addition polymers that we recently investigated with respect to their lyotropic liquid crystalline phase behavior.[10] These linear polymers exhibit a new "head-type" geometry, where the hydrophilic head of the amphiphilic unit is formed by hydrophilic main-chain segments. The hydrophobic units are directly linked to the main chain as side groups without flexible spacer. By changing the length of the hydrophilic main chain and the hydrophobic side chain units, a systematic variation of the phase behavior is feasible. Within this series of lyotropic liquid crystalline polymers we chose polymer **1a,** which is obtained from hexaethylene glycol diglycidyl ether and hexadecylamine. As shown in Figure 1, **1a** exhibits a lyotropic hexagonal phase in binary polymer/water mixtures in the region of 60–80 wt % polymer, which is stable up to 58 °C at about 75% polymer in water.

Weakly cross-linked networks were synthesized by the reaction of hexamethylene diisocyanate (HMDI) with the free hydroxyl groups of **1a** as shown in Scheme 1. The cross-linking densities were modified by changing the concentration of HMDI in order to vary the degree of swelling of the networks with water. The cross-linking process was carried out by means of a spin-casting technique. By using chloroform as the solvent for the reaction mixture, the formation of aggregates of the amphiphilic polymer is suppressed. The reaction conditions in the isotropic, nonassociating solvent ensures the formation of networks having a statistical, random distribution of the cross-links and an overall isotropic network chain conformation. After cross-linking, the elastomers are carefully deswollen and the cross-linking densities characterized by swelling experiments in chloroform. The isotropic swelling confirms the formation of isotropic network of **2a** (cross-linked with 16 mol % HMDI) and **2b** (cross-linked with 10 mol % HMDI). The swelling parameters are $q = 13.3$ for **2a** and $q = 21.9$ for **2b**, which directly reflects the higher cross-linking density of **2a**. Additionally, the elastic moduli of the dry networks are determined by stress/strain measurements as shown in Figure 2.

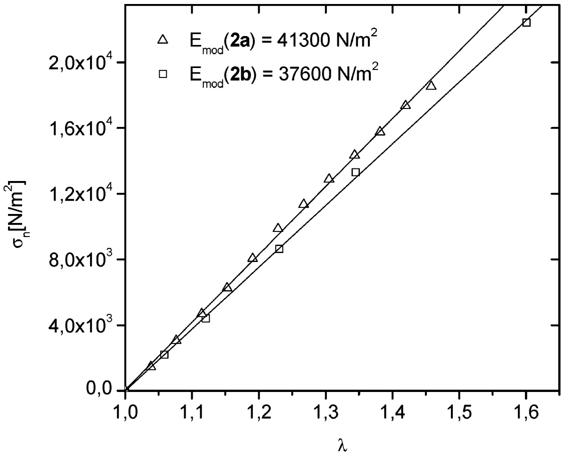


Figure 2. Determination of the elastic moduli of **2a** and **2b** by means of stress–strain measurements at 20 °C.

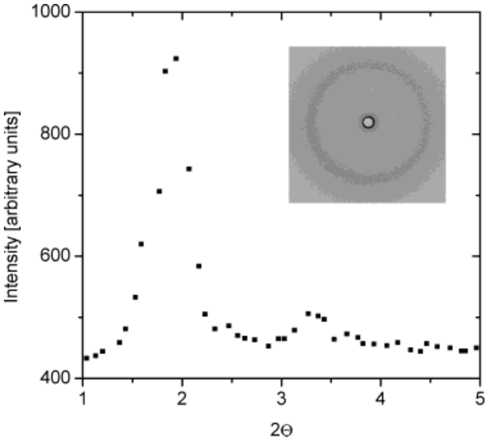


Figure 3. Two-dimensional X-ray pattern of **2a** in the hexagonal state at room temperature (20 °C) and intensity distribution along 2θ. Analyzed peaks are marked by arrows.

Nominal stress σ_n, defined as force per unit unstrained cross-section area of the sample, is plotted vs the strain λ. The elastic modulus is given by gradient of the slope.[16] The higher cross-linking density of **2a** becomes apparent in the modulus of $E_{mod} = 4.1 \times 10^5$ N/m^2 compared to the modulus $E_{mod} = 3.8 \times 10^5$ N/m^2 for **2b**. These moduli are of the same order of magnitude than the moduli of conventional thermotropic nematic side chain LCEs in the isotropic state (about 10^5 N/m^2[17]).

To examine whether the lyotropic hexagonal phase of the linear polymer **1a** is affected by the cross-linking process with HMDI, both elastomers **2a** and **2b** are swollen with water at room temperature and analyzed with respect to the liquid crystalline state of order. According to the phase diagram of **1a** (Figure 1), swelling equilibrium is expected to occur in the hexagonal phase, limited either due to the change of the elastic free energy upon dilatation or due to the phase borderline of the miscibility gap that directly contacts the hexagonal phase regime. Figure 3 shows a WAXS diffraction pattern of **2a** under swelling equilibrium. It displays reflexes corresponding to layer spacings of 46.3

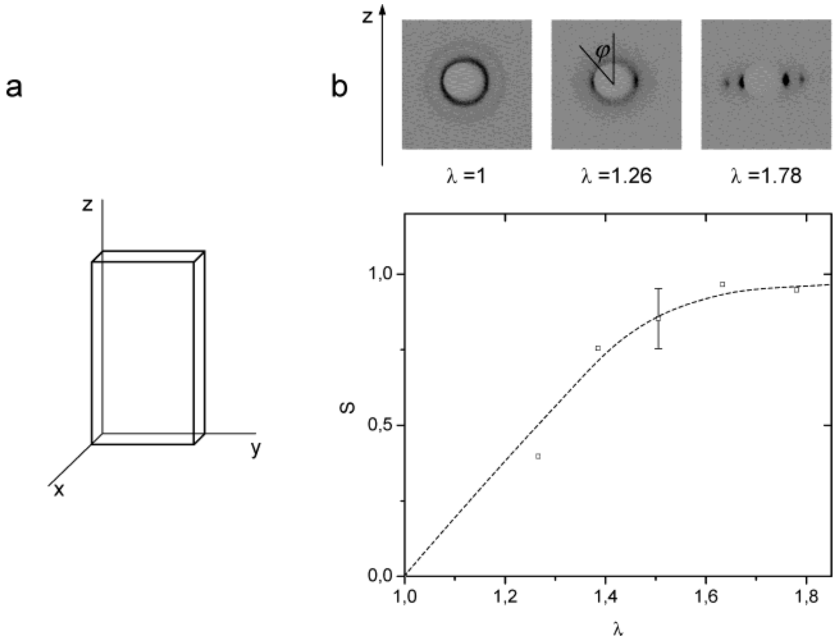


Figure 4. (a) Nomenclature of the network dimensions x, y, and z. (b) Order parameter S (calculated according to eq 2) as a function of strain λ for **2a** at room temperature (20 °C) and swelling equilibrium (error bar represents the experimental error; dash-point line is a guide for the eye) corresponding to the two-dimensional X-ray patterns for different strains in z-direction as shown above.

and 26.7 Å according to the ratio of $1:1/3^{1/2}$. This is a clear proof for the lyotropic hexagonal state of order of the networks. The values of the spacings are comparable to those of the corresponding linear polymer/water system at a concentration, where the maximal clearing temperature is observed.[10] The constant azimuthal scattering intensity at fixed scattering angle indicates that the hexagonal phase is macroscopically nonordered (polydomain).

Whether the polydomain of **2a** can be converted into a macroscopically uniformly aligned monodomain is determined by applying a mechanical field in analogy to thermotropic nematic elastomers. According to the phase symmetry of the hexagonal phase, uniaxial strain causes alignment of the hexagonally ordered rodlike micellar aggregates parallel to the uniaxial stress/strain axis.[4] The orientation process of **2a** is analyzed by X-ray measurements as a function of uniaxial elongation at the equilibrium state of swelling with water. The results are summarized in Figure 4. The polydomain network is elongated in the z-direction (Figure 4a), the X-ray beam enters the sample in the x-direction, and an overall uniform orientation of the micelles should be observed in the z-direction. Without deformation ($\lambda = 1$), the nonoriented polydomain sample reveals a constant azimuthal scattering intensity of the first-order reflex (Figure 4b, also see Figure 3). With increasing strain, equatorial maxima are formed, indicating the orientation of the micellar aggregates in the z-direction. To quantify the orientation process, we determined the overall orientational order parameter S of the hexagonal network from the azimuthal intensity distribution $I(\varphi)$ of the first-order reflex by

$$S = \frac{\int_0^{\pi/2} I(\varphi)\,\dfrac{3\cos^2\varphi - 1}{2}\,\sin\varphi\,\mathrm{d}\varphi}{\left(-\dfrac{1}{2}\right)\int_0^{\pi/2} I(\varphi)\,\sin\varphi\,\mathrm{d}\varphi} \qquad (2)$$

that is based on a model of a set of regularly spaced and infinitely long rods.[18] In Figure 4b, S is shown as a function of λ. At $\lambda = 1$ the polydomain sample is characterized by $S = 0$. With increasing λ the orientation process proceeds, and for $\lambda > 1.5$ it can be assumed that S remains constant at about $S = 0.9$. In the region $1 < \lambda < 1.5$ the reorientation of the rodlike micellar aggregates toward a monodomain occurs, while for $\lambda > 1.5$ the order parameter S reflects the intrinsic orientational long-range order of about 0.9 of the hexagonal monodomain. It has to be noted that these results resemble that of the orientation process for a polydomain sample of a thermotropic nematic elastomer. As discussed below, the condition $\lambda > 1.5$ for obtaining a hexagonal monodomain is of particular interest. For nematic elastomers this elongation reflects the anisotropy of the main-chain conformation induced by the nematic order.

The X-ray investigations have proven that by uniaxial mechanical deformation of the original polydomain network a highly ordered hexagonal monodomain of the hydrogel is obtained. It is possible to measure the macroscopic dimensions of the monodomain network as a function of the concentration of water (hygroelastic measurements) and the changes of dimensions of the network analyzed at the isotropic-to-hexagonal phase transformation. These measurements directly provide information about the coupling between the lyotropic hexagonal phase structure and the overall network chain conformation.

For a hydrogel that exhibits a hexagonal phase, the expected hygroelastic behavior is schematically shown in Figure 5. In the isotropic state L_2 at low concentrations of water in the network, essentially isotropic swelling is expected with equal dilatation perpendicular ($\lambda_{x,\,y}$) and parallel (λ_z) to the z-direction, where a slight mechanical field is applied. The dimensions of dilatation λ_x, λ_y, and λ_z are given by the cubic root of the relative volume. Assuming an ideal binary mixture, the volume of the system is given by the sum of the volume of water and polymer

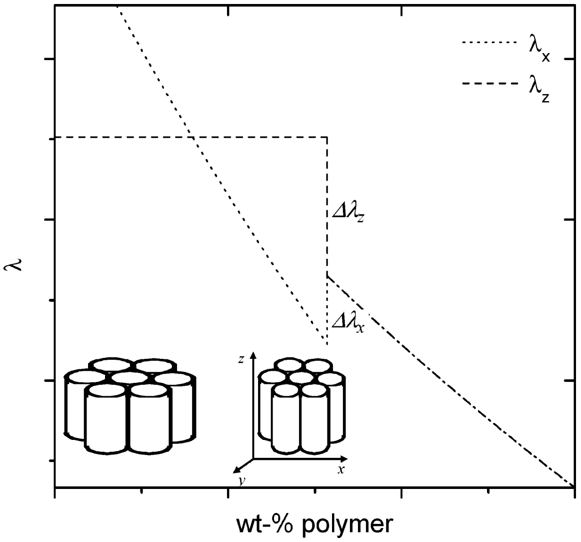


Figure 5. Schematic plot of the expected hygroelastic curve of a hexagonal sample with the relative swelling coefficients parallel (λ_z) and perpendicular (λ_x) to the hexagonal director. Sketch of the swelling of hexagonally ordered rods perpendicular to the long axis within the hexagonal phase.

$$\lambda_{\mathrm{iso}} = \left(\frac{V}{V_0}\right)^{1/3} = \left(1 + \frac{m_1}{m_2/\rho_2}\right)^{1/3} = \left(1 + \left(\frac{1}{c_2} - 1\right)\rho_2\right)^{1/3} \quad (3)$$

where m_1, m_2 and ρ_1, ρ_2 denote the masses and densities of water and polymer. The mass fraction of the polymer is indicated by c_2. At the isotropic-to-hexagonal phase transformation, a spontaneous uniaxial elongation is expected in the z-direction due to the formation of rodlike, ordered micelles in the z-direction. Uniaxiality of the deformation of the swollen network is given by

$$(1 - \Delta\lambda_x)^2(1 + \Delta\lambda_z) = 1 \quad (4)$$

Within the hexagonal phase it can be assumed that the micelles do not grow in length with increasing water concentration, which is revealed by a constant λ_z. Under these conditions an increase in volume is only given by a swelling of the micelles in the x,y-plane. If a continuous change of volume is assumed, as given by eq 3, without discontinuity at the isotropic-to-hexagonal phase transformation, λ_x and λ_y are given by

$$\lambda_x = \lambda_y = \left(\frac{1 + \left(\frac{1}{c_2} - 1\right)\rho_2}{\lambda_z}\right)^{1/2} \quad (5)$$

To evaluate the assumptions shown in Figure 5, hygroelastic experiments were performed with the hexagonal elastomer **2b** at 18 °C. To ensure that the network spontaneously forms a monodomain when swollen with water above the isotropic-to-hexagonal phase transformation, a constant load of 8.6 kN/m^2 was applied in the z-direction. For the dry network this load causes an elongation of about $\lambda_z = 1.2$, which should be sufficient to induce the monodomain state in the swollen network (see also Figure 4). The hygroelastic measurements are equilibrium measurements for defined water contents of the sample.

The experimental results are displayed in Figure 6, where the swelling deformation in width λ_x perpendicular and in length λ_z parallel to the stress axis are normalized to the dimensions of the dry network. Interestingly, in the isotropic L$_2$ phase (100−86 wt % polymer) a nonisotropic swelling is observed. The swelling behavior and elongation parallel to the stress axis is lower than perpendicular to the stress axis ($\lambda_z < \lambda_{x,y}$). A plausible explanation for this behavior might be given by the formation of micellar aggregates that are formed by adding small quantities of water to the dry network. Because of the external field, these aggregates are slightly ordered toward the strain axis, which affects the swelling behavior, as discussed below for the hexagonal phase.

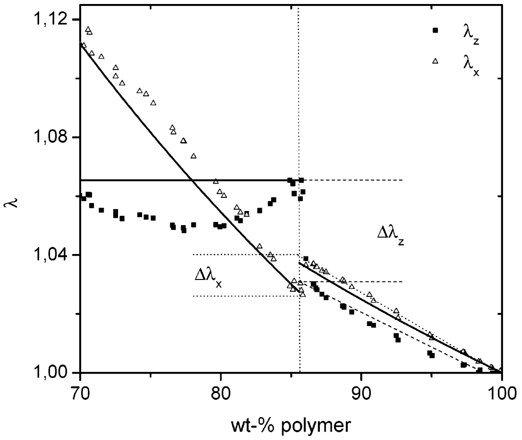


Figure 6. Relative swelling coefficients of **2b** parallel (λ_z) and perpendicular (λ_x) to the stress axis at 18 °C in dependence of polymer concentration (solid lines illustrate expected swelling from the model; vertical dash-point line indicates the phase transformation concentration).

At the isotropic-to-hexagonal phase transformation, a spontaneous elongation of $\Delta\lambda_z = 0.035$ occurs. Simultaneously, the network shortens in the perpendicular directions by $\Delta\lambda_x = 0.014$, which fits with eq 3. Similar to thermotropic nematic elastomers, the elongation can be explained by the spontaneous alignment of rodlike objects with their long axis parallel to the z-axis. It has to be noted that the spontaneous elongation of the network is only 3.5%, which is far below the spontaneous deformation of thermotropic nematic elastomers (up to 400%).[2] This clearly indicates that the micellar organization—even with the high-order parameter of $S > 0.9$ for this hexagonal phase—only weakly couples to the network conformation. The second important result that has to be noted relates to the director orientation of the polydomain sample. As shown before (Figure 4), a monodomain hexagonal phase was only observed for $\lambda > 1.5$. This deformation greatly exceeds the spontaneous deformation of $\Delta\lambda_z = 0.035$ at the isotropic-to-hexagonal phase transformation. Whether the large deformation that is needed to obtain the mono-/polydomain transition is due to the intrinsic properties of the lyotropic hexagonal phase or to nonequilibrium conditions of the orientation experiment (Figure 4) has yet to be clarified. Such nonequilibrium situations are observed for smectic elastomers, where the long-range positional order of the smectic layers prevents the polymer backbone in obtaining the equilibrium conformation.[19]

As expected, below the phase transformation concentration and within the hexagonal phase anisotropic swelling is observed. With increasing water content the network swells nearly two-dimensionally in the x,y-direction as given by eq 5. In the z-direction—which of

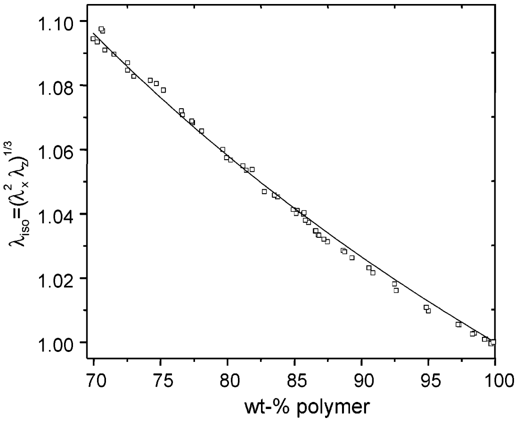


Figure 7. Isotropic swelling coefficient λ_{iso} of **2b** at 18 °C as a function of polymer concentration and theoretical fit (solid line) according to eq 3.

course is also reflected in the other dimensions—a clear decrease in the length is found, reaching a minimum in the region of 75 wt % polymer. Thereafter λ_z increases toward a lower network concentration. This behavior strongly deviates from the ideal picture of the hexagonal phase as indicated in Figure 6 with the solid lines. An explanation may be found from the phase diagram of the corresponding polymer **1a** (see Figure 1). For the linear polymer the maximal phase transformation temperature is at 77.5 wt % polymer. In the hygroelastic experiment, which is performed at constant temperature, this concentration refers to the lowest reduced temperature $T/T_{i,hexagonal}$ of the hexagonal phase. It should be noted that within this experiment the hexagonal phase exhibits the most stable state of order and also the most stable state of the micellar aggregates. With respect to the concentrations near the hexagonal—isotropic phase boundaries this is obviously directly reflected in the minimum of λ_z.

To check the experimental accuracy, the volume degree of swelling q is calculated by eq 1 with the experimental date of Figure 6. The cubic root of q resembles a pseudo-isotropic swelling parameter and will be denoted λ_{iso}. Figure 7 shows the calculated data of λ_{iso} as a function of the polymer concentration. The solid line represents the ideal binary system as calculated from eq 3 with $\rho_2 = 0.74 \pm 0.01$ g/cm^3 ($\rho_1 = 1$ g/cm^3). The agreement of the data over the whole concentration range is remarkable. This reveals uniaxiality of the deformation and shows that the elastomer follows incompressibility. However, within the experimental accuracy, the isotropic-to-hexagonal phase transformation cannot be unambiguously identified.

Another presentation of the experimental data from Figure 6 allows an interpretation of the network anisotropy in analogy to thermoelastic measurements.[9] Introducing the reduced swelling coefficients $\epsilon_z = \lambda_z/\lambda_{iso}$ and $\epsilon_x = \lambda_x/\lambda_{iso}$ the relation between ϵ and the water content of the network directly indicates the deviation from the original network conformation in the dry state, as shown in Figure 8. Over the whole concentration range swelling obeys incompressibility given by

$$\epsilon_z = 1/\epsilon_x^{\,2} \tag{6}$$

As discussed above, in the L_2 phase a slight anisotropy is observed, which might be attributed to small, oriented aggregates.

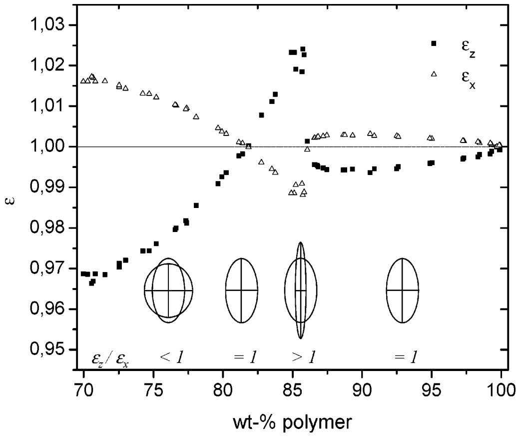


Figure 8. Reduced swelling coefficients ϵ_z and ϵ_x of **2b** and sketches of the deviation from the initial network chain conformations at 18 °C by means of ϵ_z/ϵ_x.

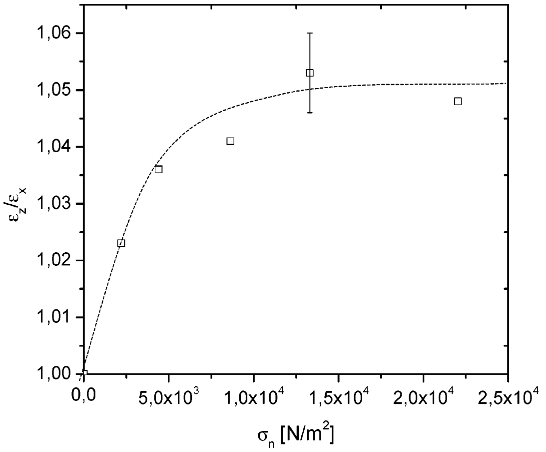


Figure 9. Influence of nominal stress on the maximal network deformation ϵ_z/ϵ_x of **2b** at the phase transition at 18 °C (error bar represents the experimental error; dash-point line is a guide for the eye).

If the hydrophilic part of these aggregates form discontinuous rodlike clusters, preferential swelling perpendicular to the long axis (and the direction of the mechanical field) can be assumed, and the network changes toward a less prolate conformation. Note that the original dry state of the network exhibits an slight prolate chain conformation due to the applied mechanical field in the z-direction. At the isotropic-to-hexagonal phase transformation $\epsilon_z > 1$ while $\epsilon_x < 1$, indicating the additional and spontaneous prolate deformation of the network due to the macroscopic orientation of rodlike aggregates. With increasing water content, swelling perpendicular to the director of the hexagonal phase acts like a biaxial deformation in the x,y-plane and deforms the network toward an overall oblate conformation. Interestingly, at about 82 wt % polymer, the state of the original dry sample is obtained. The change in the slope of ϵ_z and ϵ_x as a function of the concentration within the hexagonal phase in the region of 75 wt % polymer coincides with the minimum in Figure 6, as discussed above.

To identify whether the discontinuous change in the dimensions of the network depends on the initial load of the samples, the ratio of ϵ_z/ϵ_xhas been measured as a function of the initial load of the samples. The results are shown in Figure 9 and resemble the X-ray experiments on the orientation of the hexagonal phase (Figure 4).

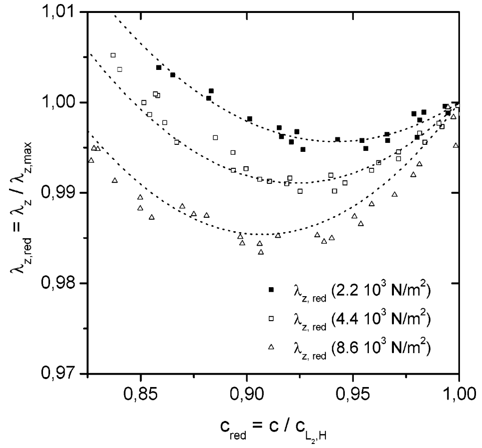


Figure 10. Stress-dependent, reduced swelling coefficients $\lambda_{z,red}$ within the hexagonal phase at 18 °C as a function of the reduced concentration (dash-point lines are second polynomial fit functions).

With increasing stress an increase in the swelling anisotropy is observed, and for $\sigma_n >$ about 10^4 N/m^2 (a deformation of $\lambda_z \approx 1.25$ of the initial, dry sample) additional increases of the load does not noticeably enhance the swelling anisotropy. We cannot identify within experimental error whether a monodomain sample is still influenced by increasing external mechanical field as expected from measurements on thermotropic nematic elastomers.[20]

The polydomain/monodomain transition is also clearly identified, when we analyze the reduced length $\lambda_{z,red}$ as a function of the reduced concentration c_{red} for different stresses. $\lambda_{z,red}$ is obtained by dividing λ_z with the maximal value at the phase transition $\lambda_{z,max}$ and c_{red} is related to the concentration at the isotropic-to-hexagonal phase transformation $c_{L_2,H}$ by $c_{red} = c/c_{L_2,H}$. An increase in stress leads to a lowering of the minima, and for $\sigma > 8.6 \times 10^3$ N/m^2 all curves are identical within experimental error. Furthermore, at low polymer concentrations λ_z remains below 1 as expected for a two-dimensional swelling perpendicular to the director of the hexagonal phase. As discussed above, the minimum in the curves can be related to an increase in the order parameter (or decrease of defects) due to the lowest reduced temperature.

Finally, it has to be noted that the hydrophobic cross-linker HMDI, which has a concentration of 10% within the network, modifies the phase behavior of the network **2b** compared to the linear polymer **1a.** From temperature-dependent hygroelastic measurements the phase transformation temperature can be sensitively determined as a function of the water concentration. Measurements in the range of 16−22 °C are indicated in the original phase diagram of the linear polymer in Figure 11. In agreement with experiments on elastomer systems described in the literature,[4,6,21] the cross-linking reaction with HMDI causes a destabilization of the mesophase. The concentration boundary of the hexagonal phase at the water-rich side is limited either by the swelling equilibrium due to the cross-linking density or by the miscibility gap that contacts the hexagonal phase.

The hygroelastic measurements reveal that the lyotropic liquid crystalline state couples to the network conformation and causes spontaneous, anisotropic change of dimensions at the isotropic-to-hexagonal phase transformation of the hydrogels. With the experiments described above, the isotropic-to-hexagonal phase transformation is obtained by variation of the water concentration within the elastomer. On the other hand, as already mentioned, the chemical constitution of the linear polymer **1a** and the elastomers **2** offers the possibility to modify the hydrophilic/hydrophobic balance by protonation of the tertiary amino group of the monomer units. This has already been described in the literature for low molar mass surfactants,[22] where the lyotropic liquid crystalline phase regime is effectively altered by pH variation. It is straightforward to analyze whether such a pH variation also effects the phase regime of the linear polymer **1a** and whether an isotropic, swollen network can be transformed into the hexagonal phase by pH variation of the coexisting solution.

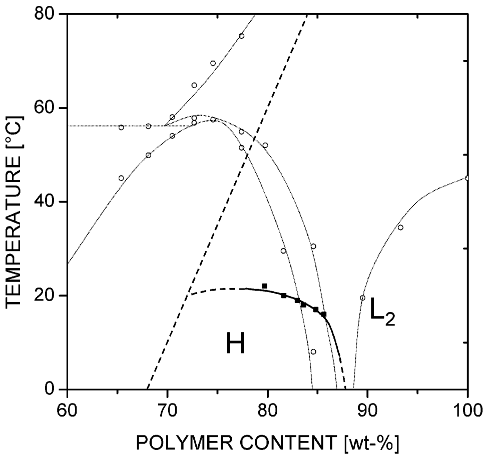


Figure 11. Phase diagram of the binary mixture of **2b** and water (full symbols) compared to the corresponding linear polymer. L$_2$ designates the isotropic state, and H is the hexagonal state.

To investigate the influence of the pH on the hexagonal phase regime, concentration gradients of polymer **1b** and different citric acid buffer solutions in the range of pH = 6−2 were prepared. By varying the temperature, the maximal clearing temperature $T_{hex,i}$ of the hexagonal phase can be determined. The results are shown in Figure 12a, where $T_{hex,i}$ is plotted vs the pH of the buffer solution. Starting from a maximal clearing temperature of 15 °C, $T_{hex,i}$ increases up to about 30 °C at pH = 2. As expected, the hexagonal phase becomes noticeably stabilized by protonation. For these contact experiments with buffer solutions it has to be noted that the ionic strength of the solution also affects the phase behavior, which has not been considered here. To get more detailed evidence for the influence of protonation on the lyotropic liquid crystalline phase behavior, the phase diagram of the partial protonated polymer **3** (see Experimental Section) is analyzed. In Figure 12 the phase diagrams of **3** and the non-**1b** with water are compared. As qualitatively identified from the contact preparation, the remarkable change in the phase behavior with protonation is obvious. Two aspects should be noted. First, **3** does not exhibit a miscibility gap within the investigated temperature and concentration region. The solubility is strongly enhanced due to the conversion of tertiary amino groups into the corresponding quaternary ammonium compound. Second, the phase regime of the hexagonal phase is nearly only broadened toward low polymer concentration and higher temperatures. An explanation for this behavior might be given by an increase of the statistical segment length (or rigidity) of the polymer chains with increasing

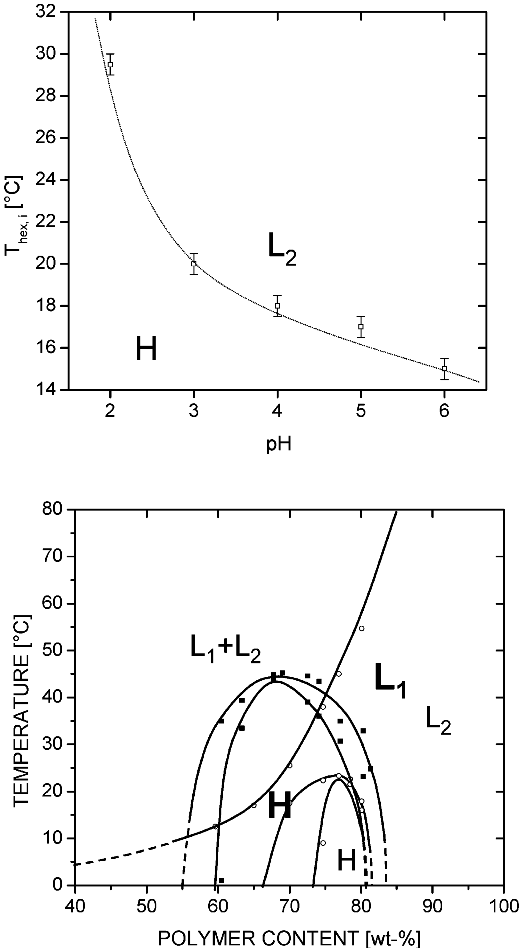


Figure 12. Maximal clearing temperatures of the hexagonal phase of polymer **1b** and citric acid buffer solutions as a function of pH value (top) and phase diagrams of **1b** (dash-point lines) and the partially protonated polymer **3** (bottom). L_1 and L_2 designate isotropic solutions, and H is the hexagonal phase. Bold notation refers to the protonated species.

charge density along the backbone, which has been investigated in detail for rodlike amphiphilic polyelectrolytes.[23] The results clearly show that an isotropic-to-hexagonal phase transformation can be induced by pH variation, if a swollen, nonprotonated network is composed of a protonated network within the hexagonal phase regime.

To verify such an experiment, elastomer **1b** is brought into the swelling equilibrium with water at 40 °C. Additionally a load is applied, which is sufficient to obtain a monodomain when the network enters a hexagonal phase. By addition of a defined amount of aqueous hydrochloric acid, the reduced values ϵ_z parallel and ϵ_x perpendicular to the stress axis are monitored as a function of time, as shown in Figure 13. After addition of HCl, due to the diffusion of the acid the elastomer is continuously protonated and swells according to the different stages of protonation. Actually, at about 15 min an anisotropic swelling is observed that indicates the phase transformation from the isotropic into the hexagonal state of the network. As directly deducible from the hygroelastic measurements, ϵ_z increases while ϵ_x decreases within the biphasic region. It should be noted that the anisotropy of swelling markedly exceeds the anisotropy observed for the nonprotonated network. Obviously, the coupling between the more rigid protonated system and the hexagonal phase is more effective than that of the nonprotonated network. With increasing time and due to the preferential swelling of the network perpendicular to the director of the hexagonal phase, the anisotropy of swelling decreases. Further investigations are in progress to quantify these results with measurements in the equilibrium state of swelling.

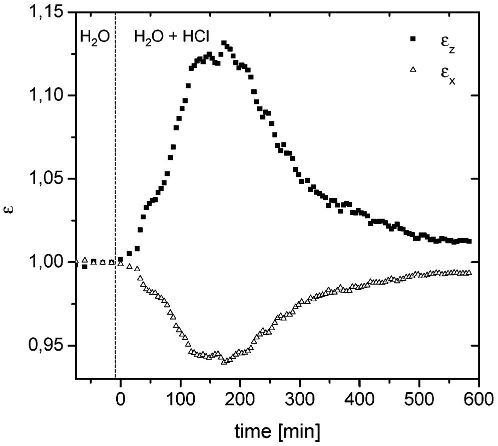


Figure 13. Time-dependent proton elastic measurement of the reduced swelling coefficients ϵ_z and ϵ_x of **2a** in water after addition of an aqueous HCl solution.

Conclusions

The synthesis and characterization of a new kind of lyotropic liquid crystalline elastomer are described, which is obtained by a cross-linking reaction of a linear epoxide−amine addition polymer with HMDI. The network exhibits similar phase behavior as the corresponding linear polymers, and in the equilibrium state of swelling, a lyotropic hexagonal phase exists. Uniaxial deformation of the swollen hydrogel causes an overall uniform director orientation of the hexagonal phase. Such an oriented elastomer shows anisotropic swelling as a function of the water content. The coupling between the lyotropic phase structure and the network chain conformation becomes apparent in an anisotropic deformation at the isotropic-to-hexagonal phase transformation and the anisotropic swelling within the mesophase. Stress-dependent measurements indicate that the magnitude of anisotropy is given by the initial deformation of the isotropic network, which determines the orientational order of the director. By varying the pH value of the coexisting aqueous solution the hydrophilic/lipophilic balance HLB of the network can be easily modified. Protonation causes stabilization of the hexagonal phase regime with respect to temperature and concentration without modifying the polymorphism. This enables an isotropic-to-hexagonal phase transformation that can be induced by pH variation and which can be identified in an anisotropic swelling of the network.

Acknowledgment. Financial support from Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 428) and Fonds der Chemischen Industrie is gratefully acknowledged. The authors thank Jens Stephan for participation in this research as part of his undergraduate studies.

References and Notes

(1) Wang, X. J.; Warner, M. *J. Phys. A: Math. Gen.* **1987**, *20*, 713.

(2) Wermter, H.; Finkelmann, H. *e-Polym.* **2001**.
(3) Warner, M.; Terentjev, E. *Liquid Crystal Elastomers*; Calendron Press: Oxford, 2003.
(4) Löffler, R.; Finkelmann, H. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 321.
(5) Fischer, P.; Schmidt, C.; Finkelmann, H. *Macromol. Rapid Commun.* **1994**, *16*, 435.
(6) Fischer, P.; Finkelmann, H. *Prog. Colloid Polym. Sci.* **1998**, *111*, 127.
(7) Amigo-Melchior, A.; Finkelmann, H. *Polym. Adv. Technol.* **2002**, *13*, 363.
(8) Hickl, M.; Finkelmann, H. PhD thesis, Universität Freiburg, 2003.
(9) Küpfer, J.; Finkelmann, H. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 717.
(10) Weiss, F.; Finkelmann, H. *Colloid Polym. Sci.* **2003**, *281*, 1007.
(11) Yatvin, M.; Kreutz, W.; Horwitz, B.; Shinitzky, M. *Science* **1980**, *210*, 1253.
(12) Thomas, J.; Tirrell, D. *Acc. Chem. Res.* **1992**, *25*, 336.
(13) Seki, K.; Tirrell, D. *Macromolecules* **1984**, *17*, 1692.
(14) Martin, T.; Prochazka, K.; Munk, P.; Webber, S. *Macromolecules* **1996**, *29*, 6071.
(15) Arndt, K.; Kuckling, D.; Richter, A. *Polym. Adv. Technol.* **2000**, *11*, 496.
(16) Treloar, J. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1975.
(17) Greve, A.; Finkelmann, H. *Macromol. Chem. Phys.* **2001**, *202*, 2926.
(18) Lovell, R.; Mitchell, G. R. *Acta Crystallogr.* **1987**, *A37*, 135.
(19) Nishikawa, E.; Finkelmann, H. *Macromol. Chem. Phys.* **1997**, *198*, 2531.
(20) Kaufhold, W.; Finkelmann, H.; Brand, H. *Makromol. Chem.* **1991**, *192*, 2555.
(21) Kratzat, K. In *Lyotrope Flüssigkristalle*; Stegemeyer, H., Ed.; Steinkopff Verlag: Darmstadt, 1999; p 59.
(22) Wärnheim, T.; Bergenstahl, B.; Henriksson, U.; Malmvik, A.; Nilsson, P. *Colloid Interface Sci.* **1987**, *118*, 233.
(23) Bockstaller, M.; Köhler, W.; Wegner, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **2000**, *33*, 3951.

MA0493877