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Structure of polymer networks in liquid crystals studied by ^{13}C NMR

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We report on ^{13}C NMR measurements above and below the clearing temperature of the liquid crystal 4-n-hexyloxyphenyl 4-methoxybenzoate constrained to an oriented, low concentration polymer network. The network is obtained by UV-irradiation of the reactive monomer 1,4-di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene which is in admixture with the liquid crystal. The characterization of orientational order of the mixtures before UV-radiation, and hence before polymerization, reveals the high order of the components at the polymerization temperature. The chosen geometry explains the LC director orientation only by the aligned network. Above the nematic–isotropic transition a strong pretransitional order is detected. Fast molecular translational diffusion averages the order over dimensions smaller than 1 μm. The Landau–de Gennes theory predicts a relation between pretransitional order and the lateral dimension of the LC regions. The experimental data are successfully explained by pore diameters of 35 and 98 nm for concentrations of 20 and 8 mol% of monomer, respectively. The results support the model of nearly cylindrical shaped liquid crystal domains surrounded by thin walls of crosslinked network.

1. Introduction

Polymer networks influence the behaviour of the surrounding liquid crystal. Based on their morphology there are two main types of liquid crystal–polymer composites. One is the polymer dispersed liquid crystal (PDLC) with usually more than 40% of polymer. The liquid crystal forms isolated spheres embedded in a continuous isotropic polymer matrix. The dimensions of the spheres are of the order 1 μm. The orientations of the director field in different domains are independent of each other and vary statistically. These materials have been intensively studied in recent years and are already in use for electronic devices to switch between opaque and transparent states [1, 2].

On the other hand, mixed systems with low polymer concentration, the so-called liquid crystal dispersed polymers (LCDP), can also be prepared [3–5]. By this preparation technique, networks of cross-linked polymers in a liquid crystalline host phase are obtained. Such systems have also found great interest recently because of their promising use in electro-optical devices [6–9]. But they are also of fundamental interest [10–23]. The formation of cross-links promotes an effective attraction between reacting monomers and this effect tends to induce a segregation of network and solvent. This segregation, controlled by the competition between curing and phase separation, occurs on a microscopic scale. The monomers, in most cases diacrylates, are bifunctional molecules, and those with large anisotropies of their shape have liquid crystalline phases. This fact increases the monomer orientational order in the nematic mixture. Systems with micro-separated polymer networks are often called liquid crystalline gels [6]. In most cases the polymerization is induced in the aligned liquid crystalline phase, and this generates an anisotropic polymer network.

The voltage dependence of light transmission of thin cells containing aligned gels depends on the polymer concentration and composition [21]. Two models for those networks are assumed by many authors. The first model describes the network as an irregular mesh of fine fibrils within the LC. SEM (Scanning Electron Microscopy) and X-ray investigations of networks formed from short molecules indicate similar structures [10, 17, 23] consisting of thin parallel fibres of nanometer radius joined further into bundles of submicrometer size. In this way, regions with smaller and with larger liquid crystal domains are formed. The other model, however, assumes that the liquid crystals form

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liquid crystalline channels separated by thin walls [11, 21]. Such structures are also confirmed by results obtained from optical investigations on thin cells filled with different types of reactive monomer [16].

^{2}D NMR investigations of liquid crystals in low concentration networks obtained from short reactive monomers demonstrate the stability of the network and its influence on the LC phase director orientation [14]. Proton NMR relaxation measurements show a relatively large order in the surface layer and a fine distribution of the network [22] which has not yet been quantified. In this paper we report on ^{13}C NMR studies of a liquid crystal with an embedded low-concentration polymer network. The NMR technique is widely used to investigate molecular order in bulk systems [24–26]. The ^{13}C NMR technique needs no special preparation of the materials and allows a high resolution of microscopic details. We have used the NMR technique to characterize the orientational order of the solutions before and after UV-irradiation. The measured line shifts in the spectra allow calculation of the order parameters, of which the magnitude and temperature dependence provide important information about the structure of the network.

2. Experimental
2.1. *Materials*

In our experiment the bifunctional reactive monomer **1** used was laboratory synthesized with the structure shown in figure 1. This monomer is of the same type as that already used by Hikmet [3, 4], but it was synthesized by a different reaction path. Di-esterification of 2-methylhydroquinone with 4-(6-hydroxyhexyloxy)benzoic acid prepared from 4-hydroxybenzoic acid and 6-chlorohexanol was achieved using dicyclohexylcarbodi-imide. The mixture of mono- and di-substituted products was separated by column chromatography. The pure bisbenzoate intermediate was reacted with

acrylic acid by azeotropic esterification and the reactive monomer purified by column chromatography.

The liquid crystal **2**, 4-*n*-hexyloxyphenyl-4-methoxybenzoate, was prepared by esterification of 4-*n*-hexyloxyphenol with 4-methoxybenzoic acid according to standard methods. The numbers on the structure of molecule **2** in figure 1 serve for the identification of corresponding positions in the NMR spectra. The photoinitiator (Irgacure 651, Ciba-Geigy) was used without further purification.

The mixtures were prepared in standard NMR tubes of 5 mm diameter. The range of concentrations varied from 5 to 20 mol % monomer with 1 wt % photoinitiator dissolved in the liquid crystal **2**; the samples were homogenized in the isotropic phase. For every concentration the solutions were characterized by NMR investigations before polymerization. The polymerization was performed with an external magnetic field directed along the tube axis as shown in figure 2. The samples were exposed to UV-irradiation for about 30 minutes from
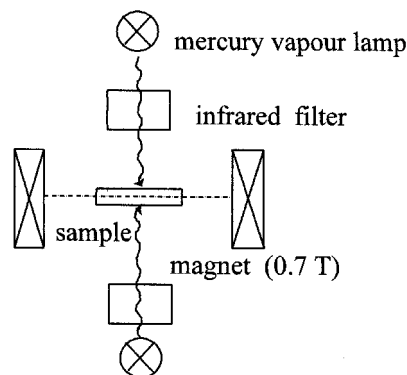

Figure 2. Experimental arrangement for photopolymerisation; the sample is UV-irradiated from both sides for 30 min in a magnetic field of 0·7 T oriented along the tube axis. The infrared filter prevents heating of the sample.
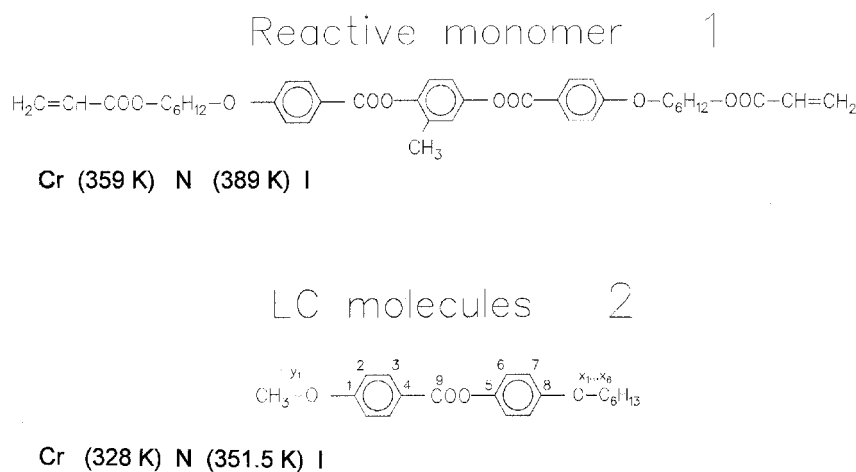

Figure 1. Materials used and their transition temperatures.

both sides at a constant temperature (45°C). In this way well oriented samples were obtained.

2.2. *Experimental technique*

The ^{13}C NMR measurements were performed in a magnetic field of 11·7 T at a frequency of 125 MHz using a Bruker MSL 500 spectrometer. Pulsed proton decoupling was used to remove the interaction with the protons in order to observe the chemical shifts. Accumulations of about 100 were sufficient for most of the spectra.

The tensor character of the chemical shift and the anisotropy of the orientational motion in liquid crystalline phases are responsible for the observed line shifts of the different positions in the ^{13}C NMR spectra [26]. We were mainly interested in the general ordering behaviour of the molecules, but not in details of the orientational order. Therefore, the simplifying assumption of separate averaging of order fluctuations and conformational motions [25] seemed to us appropriate. The observed shift δ_{zz}^{i} for position i is then related to the orientational order parameter S and the biaxiality D by the simple relation

$$\delta_{zz}^{i}(T) = \delta_{\text{isotr}}^{i} + S * \delta *_{\zeta\zeta}^{i}\left(\frac{3}{2}\cos\Phi^{2} - \frac{1}{2}\right) + D/3\ (\delta_{\xi}^{i} - \delta_{\eta\eta}^{i}),$$

$$S = \frac{1}{2}\langle 3\cos^{2}\theta - 1\rangle,$$

$$D = \frac{3}{2}\langle \sin^{2}\theta \cos 2\varphi\rangle. \tag{1}$$

$\delta_{\zeta\zeta}^{i}$ is the tensor component of the chemical shift along the molecular axis and $\delta_{\text{isotr}}^{i}$ the chemical shift in the isotropic phase. Φ is the angle between the director and the direction of the external magnetic field. The order parameters are defined by the angles θ and φ. θ is defined as the angle between the director and the molecular long axis. The azimuth angle φ is defined as the angle between the molecular ξ axis and the projection line of the director onto that plane which is perpendicular to the molecular long axis. We chose the *para*-axis as the reference frame. The experimentally determined ratios of line shifts from aromatic carbon atoms in *ortho*- and *para*-positions are temperature independent for all samples. Therefore, the contribution of the biaxial fluctuations D to the observed shift is neglected.

3.   **Results and discussion**
3.1. *Nematic solutions*

We tested the solubility of the reactive monomer **1** in the liquid crystal **2** for concentrations up to 50 mol %. The nematic–isotropic transition temperature increases almost linearly with concentration. The clearing points are sharp, with biphasic regions smaller than 1 K.

Because of the crystallization temperature decrease, the nematic phases of the mixtures extend over temperature intervals larger than those for the pure system **2**.

In the ^{13}C NMR spectra of the isotropic phase, the lines of the aromatic cores of molecules **1** and **2** are separated. The lines overlap if both cores have identical chemical surroundings (left hand phenyl rings in figure 1). In the nematic phase, however, the lines shift to higher frequencies and the spectral positions are different for equivalent rings. Applying equation (1) and using a tensor component $\delta_{11}^{1} = 84·5$ ppm for position 1 in the *para*-axis system [26], the order parameter for the core can be calculated. The tensor components along the *para*-axis for the other positions follow from the temperature independent ratio of the lines. The order parameters obtained are values averaged over all positions of the core. Figure 3 shows the order parameters of the two liquid crystal components obtained from mixtures of different concentrations. Simple theoretical models based on the Meier–Saupe potential show that the difference in the order parameters of the components in a solution is proportional to the difference in the anisotropic properties of the molecules [27]. This
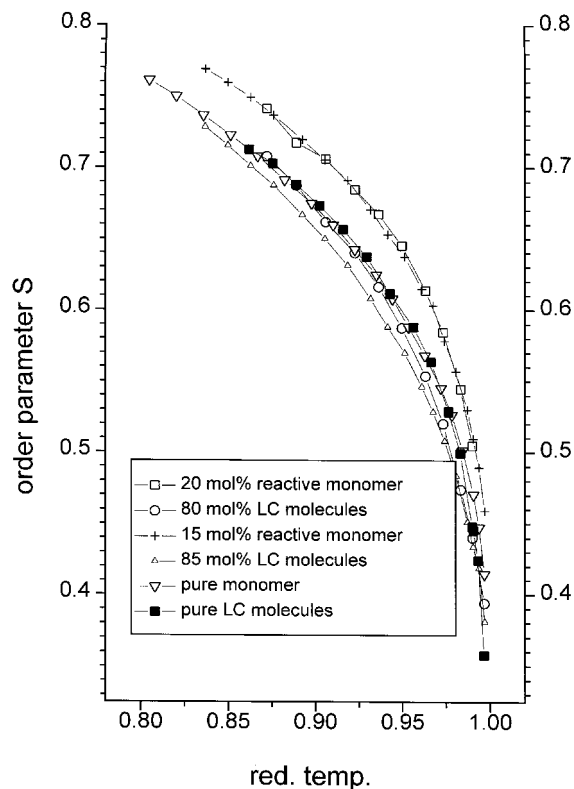

Figure 3.   Orientational order parameter S of the central aromatic part; the reduced temperature is normalized to the corresponding clearing temperature. The different symbols denote the values for mixtures of 20 mol % of **1** and 15 mol % of **1** and for pure materials **1** and **2**.

behaviour is well reflected in our results. The order parameter of molecule **1** in the mixtures is larger than that in the pure nematic phase and is larger than that of molecule **2**. The pure materials **1** and **2** have nearly the same order parameters at equivalent reduced temperatures. The good agreement of the experimental results with theoretical predictions for the order parameter and the linear variation of clearing temperature support the assumption of ideal solutions without any micro-phase separation before polymerization. At the polymerization temperature, the order of the monomers is high with values of 0·75.

3.2. *Polymerized mixtures*

We will mainly discuss here the results for samples with 20 and 8 mol % monomer concentration. Although the polymerized samples are now in a gel-like state, the light scattering characteristics are similar to those of the nematic phase. For the ^{13}C NMR measurements, the tube axis, which coincides with the alignment axis of the network, lies perpendicular to the applied magnetic field of 11·7 T. The NMR spectra show only the lines from the LC molecules **2**. The NMR line width increases for the samples containing polymer networks at all temperatures due to the stronger local differences of the diamagnetic susceptibility. However, the magnetic field homogeneity is high enough to resolve all line positions of the molecules **2**, as shown in figure 4. The polymer network itself is not resolved from these experiments. This is because of the broad line width and low intensity of the signals detected.

Above the clearing temperature of the pure substance **2**, low-intensity isotropic lines are detected together with high-intensity lines which are shifted to lower frequencies (figure 4 (*a*), the sample with 20 mol % polymer concentration is shown as an example). This allows a very precise determination of the shift difference. Below the clearing temperature, the lines from the nematic regions shift more to lower frequencies (figure 4 (*b*)). The shift to lower frequencies is a consequence of the orientation of the director perpendicular to the magnetic field ($\phi = 90°$ in equation (1)). The director of the LC phase is influenced by surface coupling and by the magnetic field, but the experimental results reveal that the effect of the field on the orientation of the director is negligible. The magnetic coherence length must therefore be larger than the dimension of the domains. Using typical values for the elastic constant K (10^{-11} N), the diamagnetic anisotropy $\Delta\chi$ ($1·5 \times 10^{-6}$) and $B_0 = 11·7$ T, the magnetic correlation length

$$\xi_{\mathrm{mag}} = \sqrt{\left(\frac{\mu_0 K}{\Delta_\chi B_0^2}\right)^{1/2}}. \qquad (2)$$

is of the order 300 nm. The largest dimensions of the LC regions inside the network in the direction of the external field are therefore smaller than 500 nm. The network itself is not reoriented by the strong perpendicular field.

The position and the width of the lines at a fixed temperature are independent of repeated heating or cooling cycles of the mixture including cooling to the crystalline phase. The preparation technique for the relatively thick NMR tubes used for our experiments generates mainly a homogeneous network. Distortions or defects are responsible for larger LC regions that give the small isotropic lines in the spectra.

Within an accuracy of 1 K, the phase transition temperatures of the gels correspond to those of the pure LC **2**, but with the dissolved photoinitiator. In our mixtures, temperature shifts due to elastic director deformations are absent, although the latter have been observed for liquid crystals which are confined to spheres in mixtures with high polymer concentrations or glasses [28]. With increasing temperature, and above the transition point, the negative shifts of the nematic lines decrease slowly. A few degrees above the transition temperature, the line width begins to increase until the transition point is reached.

Using the same quantities for the tensor components for both mixtures and pure materials, equation (1) allows the calculation of the order parameters of the aromatic core. Figure 5 shows the temperature dependence of the order parameter above and below the phase transition for samples with 20 and 8 mol % of monomer **1** and for the pure liquid crystal. Below the phase transition temperature, the dependence behaves quite normally, but the values lie below the curve of the pure liquid crystal. We explain this by the strong anchoring to the network surface. Above the phase transition, the order remains comparatively high. The transition is still of first order, but an approach to a critical point occurs with increasing concentration. In optical investigations [4, 11, 16, 23] strong pretransitional ordering was also observed. The effect contains contributions from the embedded polymer network and the liquid crystal. A separation of these was only attempted in [23], but our measurements clearly resolve the behaviour of the liquid crystal **2**.

The large paranematic order above the transition point is a consequence of a strong anchoring to the well-aligned network surfaces with a planar axial orientation of the molecules on the surface. Pretransitional nematic ordering due to strong surface coupling in sub-micrometer cavities has been the subject of many publications [29–33]. The calculations of Sheng [34, 35] and Mauger [36] predict an increase of the transition temperature by 0·2 K and a change in character from first to second order connected with an increased
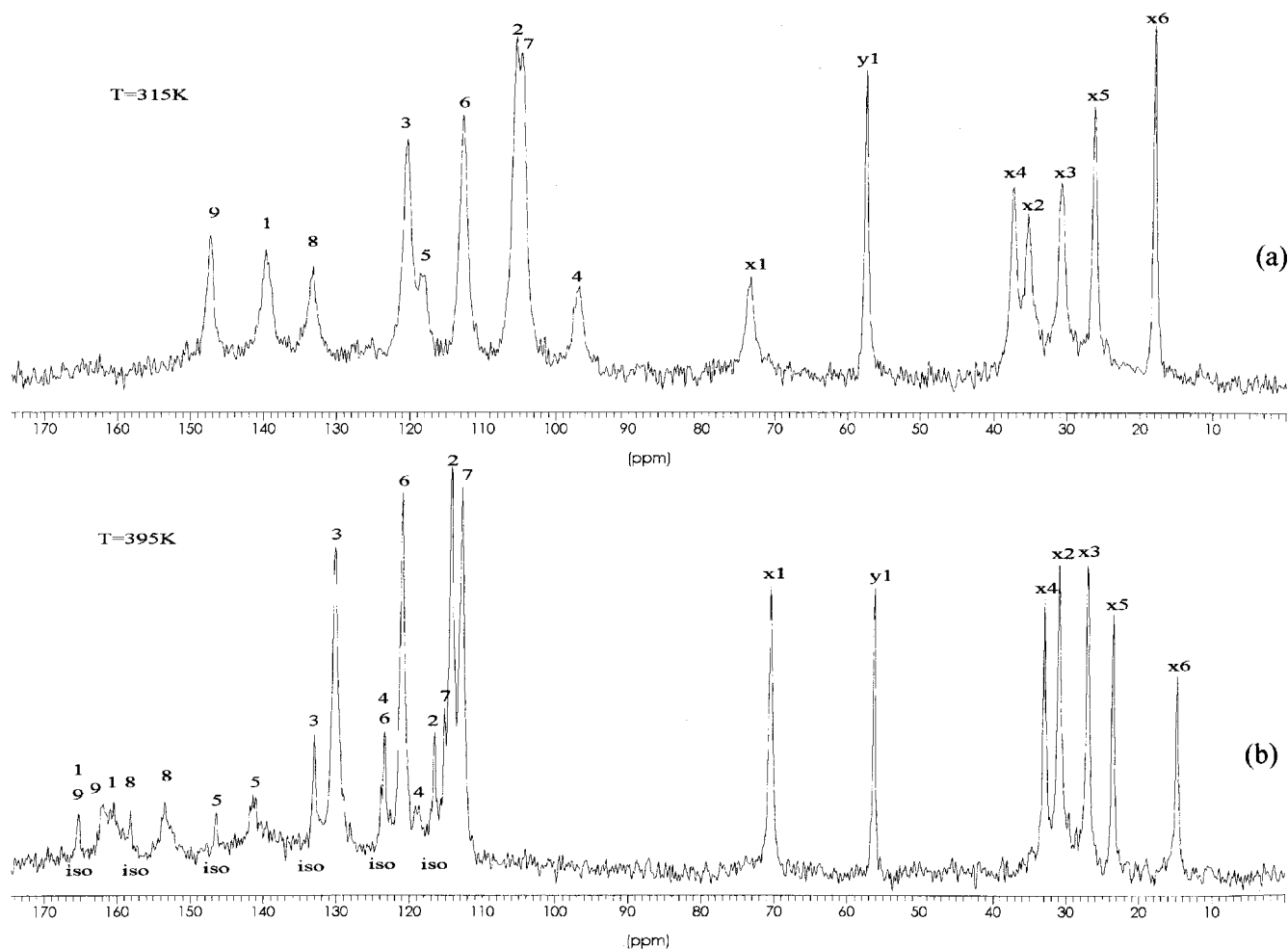
Figure 4. ^{13}C NMR spectra of the polymerized mixture with 20 mol % of monomer **1** below (*a*) and above (*b*) T_{NI}; the spectra are recorded at 125 MHz with 100 accumulations. The numbers refer to figure 1; all carbon positions of molecule **2** are seen. The weak lines in the left hand aromatic part of spectrum (*b*) are from isotropic regions.

pre-transitional order. Strong surface ordering effects in confined geometries act similarly to an external field, pronounced effects requiring dimensions of the volume elements below a few hundred Å. Experimental tests for planar cells are rare. Strong surface order over a small temperature range has been observed by ellipsometric measurements [33], and well-resolved pretransitional effects have been found for liquid crystals confined to cylindrical pores (Anopore systems) [29–32]. For pore diameters of 200 nm, the pretransitional nematic ordering was one order of magnitude smaller than for our systems.

The recorded NMR spectra reflect the time averaged behaviour of the molecules during the measuring time (20 ms). During this time, the molecules move over distances determined by their translational diffusion constant ($D \approx 10^{-10}$ m^2 s^{-1}) [22, 29, 30] which gives dimensions of 1 μm over which the order parameter is averaged. Because the real dimensions of the pores are smaller than this distance, the observed order parameters are mean values that are averaged over the cross-section of the pores. This explains the sharp lines in the spectra.

We will now use the theoretical predictions to make an estimate of the dimension of the liquid crystalline domains in our network. The theoretical calculations start with a Landau–de Gennes expansion for the free energy density [34, 30]. An analytical solution above T_{NI} can only be obtained if all terms of order higher than second are neglected. In this approximation, the change in the character of the phase transition and the increase in the transition temperature are not taken into account. For simplicity we assume cylindrical volume elements and planar axial orientation. With this simplification, the variation of the order parameter within a cylinder is described by a Bessel function. The cosh-function obtained by Crawford *et al.* [30] or a simple
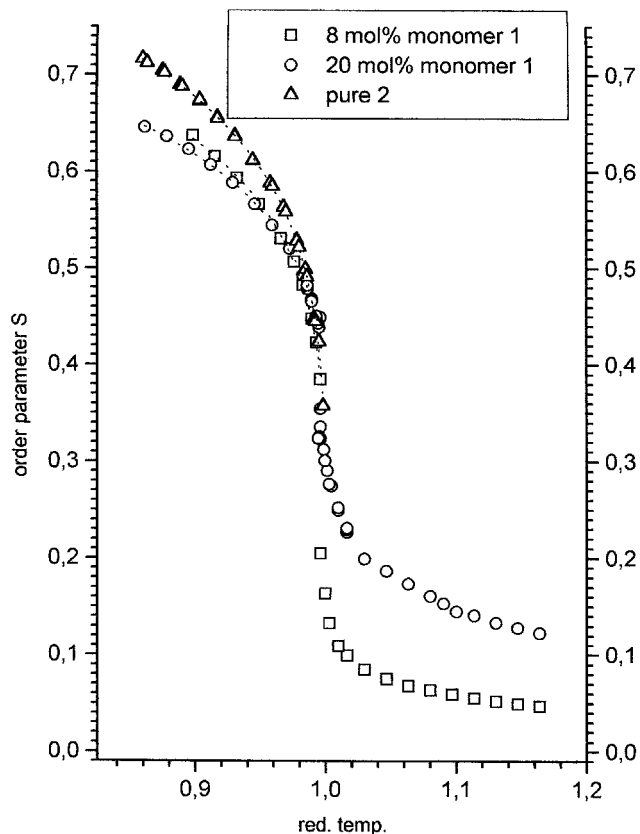
Figure 5.   Order parameter S of the central part of the LC molecules **2** in polymerized systems with 8 and 20 mol % of monomer **1** and for the pure system. The reduced temperature is normalized to the clearing temperature (~ 345 K).
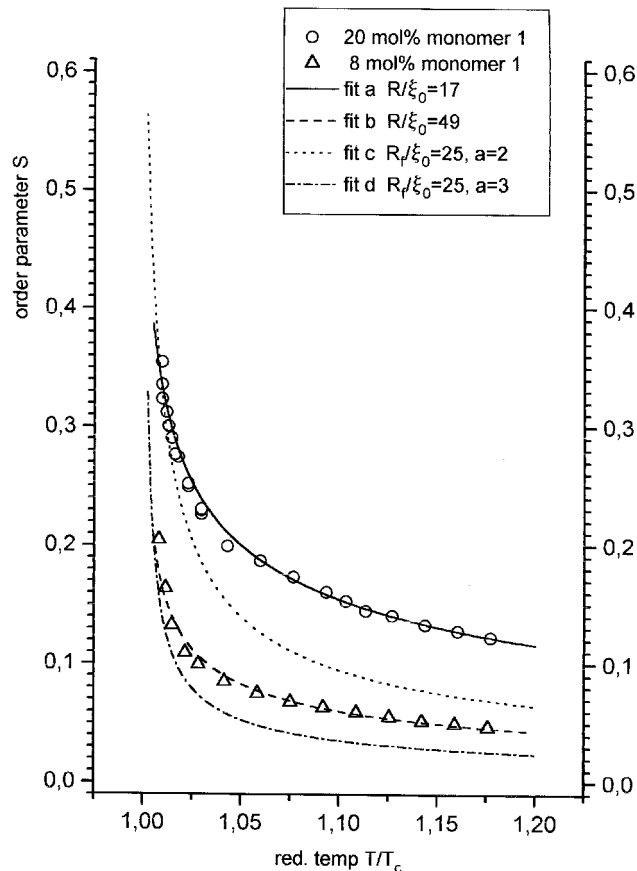

Figure 6.   Pretransitional order parameter S of the molecules **2** over a range of 55 K above T_{NI}. The experimental points are fitted for a cylinder model according to equation (4) with (*a*) $R/\xi_0=17$ (20 mol %), (*b*) $R/\xi_0=49$ (15 mol %) and $S_0=0.5$; and for fibres with (*c*) $R_f/\xi_0=25$, $R_a/\xi_0=50$, (*d*) $R_f/\xi_0=25$, $R_a/\xi_0=75$ and $S_0=1$.

exponential decay gives nearly the same dependence on the distance r from centre to wall of the cylinder of radius R

$$S = S_0 \cosh (r/\xi)/\cosh (R/\xi). \qquad (3)$$

Here S_0 is the order parameter at the wall and $\xi = \xi_0[(T - T^*)/T^*]^{-1/2}$; T^* is the supercooling limit temperature in the Landau expansion and ξ_0 is the zero temperature correlation length [34]. The observed first order transition temperature T_{NI} for bulk samples lies about 1 K above T^*. Using this function, the averaged order inside the cylinder can be analytically calculated.

$$\langle S \rangle = 2S_0\xi_0^2/(R^2t)(-1 + 1/\cosh (Rt^{1/2}/\xi_0)$$
$$+ Rt^{1/2}/\xi_0 \tanh (Rt^{1/2}/\xi_0) \qquad (4)$$

where $t = (T - T^*)/T^*$ is the reduced temperature difference. As already mentioned, this expression is valid if S is not too large. Nevertheless, we apply equation (4) to fit our experimental results above T_{NI}. The T^* used for the fits are 2–3 K below the observed transition temperatures T_{NI} that can be accepted, because T_{NI}

increases for small dimensions. As figure 6 shows, the theoretical values are in good agreement with the experimental data. Values of $R/\xi_0=17$ and $R/\xi_0=49$ for 20 and 8 mol %, respectively, were used for the calculations. To obtain the diameters of the cylinders we need to know correlation length ξ_0. For 5CB and MBBA, ξ_0 is smaller than 1 nm [30, 34]. Assuming $\xi_0=1$ nm for our system, we obtain radii of 17 and 49 nm for the pores in the mixtures of 20 and 8 mol %, respectively. Note, that these results are strongly coupled to the initial assumptions on ξ_0. The optimized temperature-independent surface-order parameter $S_0=0.5$ for both probes seems an acceptable value for strong anchoring. The factor S_0 only extends the theoretical curves along the ordinate and its influence on the optimized R/ξ_0 is very small.

From the results of best fits using experimental data for LC molecules in Anopores, a temperature dependence of S_0 with $(T - T^*)^{1/2}$ was derived [29–32]. With such an assumption the calculated order for our probes

decreases too rapidly with increasing temperature and no reasonable fits could be obtained. The application of more complicated models with a finite thickness of surface layer does not seem appropriate. Here we use the simple theoretical approach to estimate the structure of polymer network.

The model of parallel polymer fibres formed by the network and passing through the liquid crystal contradicts our experimental results. In this model the liquid crystal is a more open system, because the molecules at the cylindrical surface of the fibre induce order in the radial surroundings. We assume a nearly cylindrical shaped volume of the liquid crystal with an outer radius $R_a = aR_f$ influenced by one fibre of diameter R_f and an exponential decay of order with r. The averaged order parameter for a fibre system with $R_f/\xi_0 = 25$ is calculated and shown in figure 6. The outer radii $50\xi_0$ and $75\xi_0$ are used for the calculations. Such values or still larger dimensions are derived from structural investigations [17, 19, 20, 23]. To approximate the observed values, $S_0 = 1$ is chosen for the fit. The results obtained deviate significantly from the experimental data, as does their temperature dependence. Our results in fact confirm the model of Hikmet [9, 21] and Braun *et al.* [16] of liquid crystal domains surrounded by nearly closed walls of polymer network. The rough surface of the network causes the strong anchoring of the liquid crystal molecules and may be responsible for the temperature independence. Calculations with $R/\xi_0 = 16$ and $R/\xi_0 = 18$ for the 20 mol % sample in figure 6 give results that are outside the experimental errors, which means our experiments are very sensitive to the dimension of the structure formed by the network. The radius for the lower polymer concentration is remarkably larger. Concentration obviously determines the radius of the pores and not only the thickness of the walls. The absolute values of the diameters obtained depend somewhat on the applied model. The phase transition is still of first order; the 20 mol % sample, however, is near to the critical first to second order phase transition point. The first order character for the 8 mol % mixture is clearly pronounced. The exact concentration dependence is to be the object of further studies, and diffusion measurements are being made to study the diffusion length of the liquid crystalline molecules; this should allow a direct decision between open and closed domains.

4. Conclusions

The studies described here are used to obtain information about the structure of polymer networks included in samples of large dimensions. The ^{13}C NMR technique is a well suited method for the investigation of order parameters.

The starting conditions before polymerization by UV-irradiation are homogeneous mixtures with order parameters of 0·75 and 0·7 for the reactive monomer **1** and the liquid crystal molecules **2**, respectively. The process of cross-linking and micro-phase separation within the 5 mm tube is not expected to occur simultaneously. In spite of this complication, the samples appear uniform and the NMR spectra result from a homogeneous system of domains. At the time of polymerization, the network is perfectly aligned in the direction of the external field.

The polymerized mixtures are models well suited to investigations of the influence of confined geometries on the properties of liquid crystalline phases. The surface interaction is strong and generates an axial planar, homogeneous director field of the liquid crystal domains. We observed a very strong orientational order above the isotropic–nematic transition temperature never seen before in other types of confined systems. The phase transition is still of first order. However, the jump in S is reduced to 0·05 for 20 mol % of monomer. The explanation is a polymeric network with pores of an averaged diameter of the order 35 and 98 nm for the 20 and 8 mol % samples, respectively.

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