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Effect of Nematic Order Coupling on the Phase Diagrams of Side-Chain Polymer Gels with Liquid Crystal Solvent

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Abstract: We have explored the influence of nematic order coupling on the swelling and phase diagram of polymer networks in nematogenic low molar weight LC solvent, in view of the increasing importance of such systems in advanced optical devices. Firstly, one isotropic polyacrylate network and one nematic side-chain polyacrylate network is prepared. Immersing these two networks in nematic LC solvent lead to the formation of well-defined polymer gels with LC solvents and allow us to establish the phase diagram of these relatively new materials in the concentration-temperature frame. Results were critically analysed as a function of temperature and network nature (isotropic or nematic). We demonstrate that in the case of gel made from an isotropic polymer network, the LC solvents fails to form a nematic phase inside the gel due to the lack of anisotropic coupling. Moreover, in that case the gel shrinks below $T_{NI}^{Solvent}$ because of a strong "entropic" incompatibility between the isotropic flexible coils and the LC nematogens. However, the situation is drastically different in the case of LC side-chain network due to a strong coupling of the nematic order between the mesogens of the solvents and those of the polymer backbone. In that case, tremendous distortions appear in the phase-diagram, in which we especially emphasize the apparition of a stable nematic gel phase and a miscibility gap between $T_{NI}^{Solvent}$ and T_{NI}^{Gel}. Finally, results are critically examined and compared to the few studies found in the literature.

Introduction

In recent years, materials scientists have devoted enormous effort to the development of new materials for advanced optical device applications. The reasons for continued interests in this area are manifold, encompassing both economic and technological realms. Although conventional liquid crystal systems like twisted nematic currently remain the material of choice for many display application, these materials are still relatively expensive and moderately difficult to fabricate. As a result, new applications requiring alternative materials are presently under development [1].

In this context, mixtures of liquid crystals and polymers have received considerable attention in many laboratories around the world. This interest is motivated by their potential use in many fields of high technology involving electronic equipments, display systems, commutable windows, etc. Today, applications of dispersions containing polymers and liquid crystals are growing in importance [2]. Among the several kinds of polymer / mixtures currently used for display applications, PDLCs (Polymer Dispersed Liquid Crystal) and PSLCs (Polymer Stabilized Liquid Crystals) are among the most popular.

PDLCs consist commonly of micron-sized droplets of low molecular weight LC dispersed in a solid isotropic polymer matrix and can be switched electrically from a light scattering off-state to a transparent on-state [3-5]. On the other end, in PSLCs devices, the concentration of polymer matrix in the material is much lower and its role is to stabilise liquid crystal textures throughout the bulk of the device in order to improve electro-optical performances [6-7]. Moreover, in PSLCs, the polymer network is often made of a LC side-chain backbone.

The concentration as well as the nature (isotropic or LC) of the polymer network in the mixture play a critical role on both PDLCs and PSLCs properties. This parameter will determine the optical performance of the material as well as its mechanical strength and longevity [8-9]. In that framework, it is of great interest to determine the miscibility and the phase diagram of polymer network-LC solvent mixtures. In recent years, the theoretical study of such systems has reached a comprehensive level. But unfortunately, in contrast with the case of linear polymer-LC solvent mixtures [10-11], the experimental study of crosslinked polymer-LC solvent systems has received only little attention until now. The reason is that in technological device, the complex architecture of the polymer matrix (resulting from the in-situ polymerisation of monomers and LC solvent mixtures [12]) prevents us to easily determine the miscibility of the matrix in the LC solvent. A solution is to synthesize homogeneous polymer network for a first time and to study their swelling and phase behavior in LC solvents subsequently. Recently, we have used this concept and reported the influence of crosslinking density on the phase behaviour of isotropic polymer networks in isotropic and nematic liquid crystal solvents [13-15].

In the present article, we aim to investigate the effect of the introduction of LC side-chain on the polymer matrix. In the first step, we have synthesized one isotropic polymer network and one nematic polymer network by a photo-polymerisation technique. Then these networks were swollen in nematic LC solvent in order to create well-defined polymer gels with LC solvent. Using swelling measurements in combination with Polarised Optical Microscopy micrographs, we established the phase diagram of these two systems. We found that in the case of a nematic network swollen in a nematic solvent, the nematic order coupling between these two species induce tremendous distortions in the phase diagram as compared to the case of gels made from isotropic networks.

Results and Discussion

Preparation and Characterisation of the Gel Constituents

The isotropic network was fabricated as follows: an Abu/HDDA/Darocur 1173 mixture (99/0,5/0,5wt%) was prepared and stirred mechanically for several hours in order to ensure a uniform distribution of the monomers and crosslinkers over the sample volume. The initial mixture was transferred into a Teflon holder and placed inside a reaction chamber filled with nitrogen. Subsequently, the sample was exposed to a UV lamp (Philips TL08) with a wavelength of 350nm and an intensity of 1,5mW/cm^2.

The exposure time was fixed to 15 minutes, although 5 minutes was sufficient to achieve a complete conversion of the monomers. After removal from the Teflon mould, the polymer network was obtained as transparent disks, with a diameter of 2,5cm and a thickness of 1,5mm. The network was washed several times in a bath of toluene (good solvent) in order to remove the low molecular species eventually remaining inside the network (monomers and oligomers not attached to the network), dried in air for one day and finally placed under vacuum at room temperature for few hours.

The polydomain nematic network was synthesised as follows: 500 mg (1430 μmol) of 6OCBA, 16,2 mg (72 μmol) of HDDA and 1,31 mg (8 μmol) of Darocur 1173 were dissolved in 2 ml of a mixture of dimethylsulfoxide and toluene (40-60 vol.%) [16]. This isotropic formulation was stirred mechanically, introduced into a Teflon mould and exposed to the UV lamp under nitrogen atmosphere for 20 minutes. It has been checked that the polymerisation was always performed in the fully isotropic phase. The polymerised solution was transferred into a bath of dihloromethane (good solvent of the LC polymer network) and the solvent was exchanged four times in order to eliminate the unattached species. Introducing methanol into the bath gradually decreased the solvent quality.

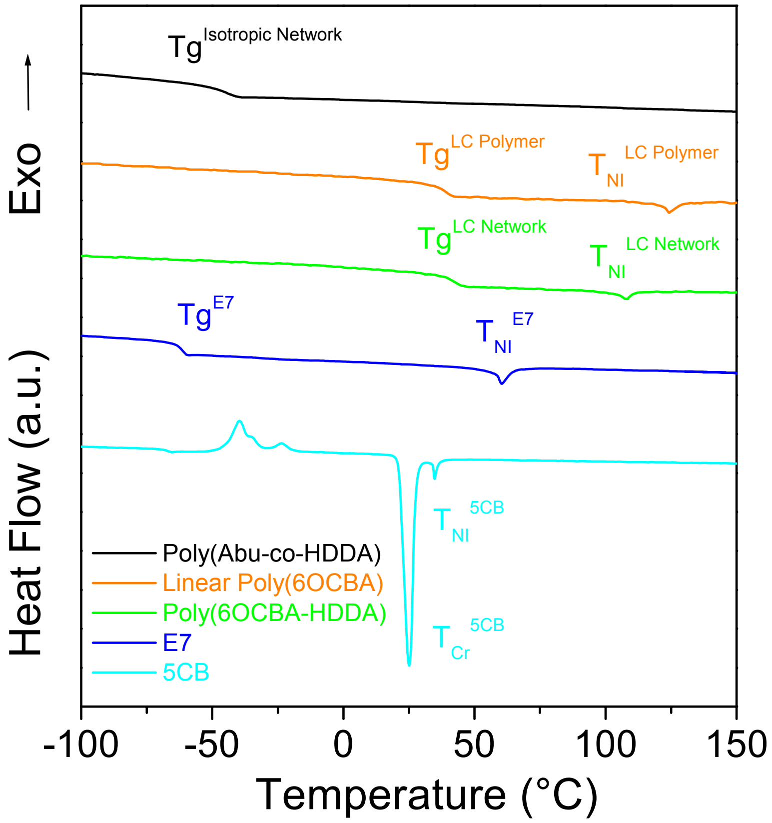

Fig.1. DSC thermograms of the gels constituents prior to swelling.

At the end of the process (5 days), the LC network is obtained as a white disc in a pure methanol bath. Subsequently, the network was dried at 40°C for 2 days and then at room temperature under vacuum for one day. The conversion of the acrylate double bonds was estimated to be 92% by weighting the final network and compared this value to the mass of the precursors previously introduced in the initial reactive solution. A linear nematic polymer poly(6OCBA) was also synthesised by the same technique but without adding HDDA in the initial reactive formulation.

DSC thermogramms of the different constituents of the gel (networks and solvents) are presented on Figure 1. The isotropic poly(Abu-co-HDDA) network presents a unique transition at -45,9°C corresponding to the glass transition temperature. The liner LC polymer poly(6OCBA) displays a glass transition temperature at 38,4°C and a nematic to isotropic transition $T_{NI}^{LC\ Polymer}$ at 124,5°C. Between Tg and $T_{NI}^{LC\ olymer}$, the Schlieren texture characteristic of nematic phases was observed using a polarised optical microscope by sandwiching a small quantity of poly(6OCBA) between two clean glass slides. Below Tg, the LC texture did not disappear and is frozen. The LC network poly(6OCBA-co-HDDA) presents a glass transition slightly higher than the non crosslinked polymer (42,4°C) and a T_{NI} significantly lower (108,2°C). It is suspected that the introduction of crosslinking points in the materials tend to decrease the molecular mobility of the network (augmentation of the Tg) and also diminish the size and perfection of the nematic domains formed by the LC side-chains (reduction of $T_{NI}^{LC\ Network}$) [17]. The nematic schlieren texture was not observed for the crosslinked LC polymer, which only showed birefringence. As the LC polymer, the eutectic mixture E7 displays both a Tg (-62,1°C) and a nematic to isotropic temperature transition T_{NI} (60°C). On the other end, 5CB possesses a crystallisation temperature ($T_{Cr\text{-}N}$=23,7°C) in addition to its nematic to isotropic temperature (T_{NI}=35,4°C).

Swelling and Phase Behaviour of an Isotropic Polymer Network in a Nematic Solvent

Although it is a question of primary importance in a wide range of current high-tech applications like PDLCs nowadays, it is still not clear in the literature whether a LC can form an organised phase inside an isotropic polymer network. Ballauf studied the swelling behaviour of poly(butadiene) (PB) networks in the nematic liquid crystals p-azoxyanisole (PAA) and N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) [18-19]. They emphasized on the swelling behaviour of the gels but did not discuss the phase of the solvent inside the gel.

Later, Urayama et al. investigated the swelling properties of cylindrical shaped PB [20-21] and poly(styrene) [4] (PS) networks in few nematic liquid crystals including EBBA and discussed the phase behaviour of a the solvent inside the gel. For the case of PB networks [20-21], they concluded that the phase behaviour of EBBA inside the gel strongly depends on whether there is surrounding EBBA or not. Without the surrounding solvent, EBBA in PB networks fails to form the nematic phase but in the presence of the surrounding EBBA, the nematic phase is formed inside the gels at a temperature T_{NI}^{Gel} slightly lower than the T_{NI} of the pure solvent (approximately one degree). For a PS network surrounded by a nematic solvent [22], they observed a nematic phase in the gel, which they attributed to the faculty of the nematic molecules to localise in the network mesh so that they can form nearly pure nematic domains. This result contradicts the prediction of mean field theories of polymer and LC mixtures [23-25]]. But the greater stiffness of the PS chains compared to PB chains and the glass transition of PS significantly higher than the T_{NI} of the solvent used in this study may interfere in the phase diagram of the gels.

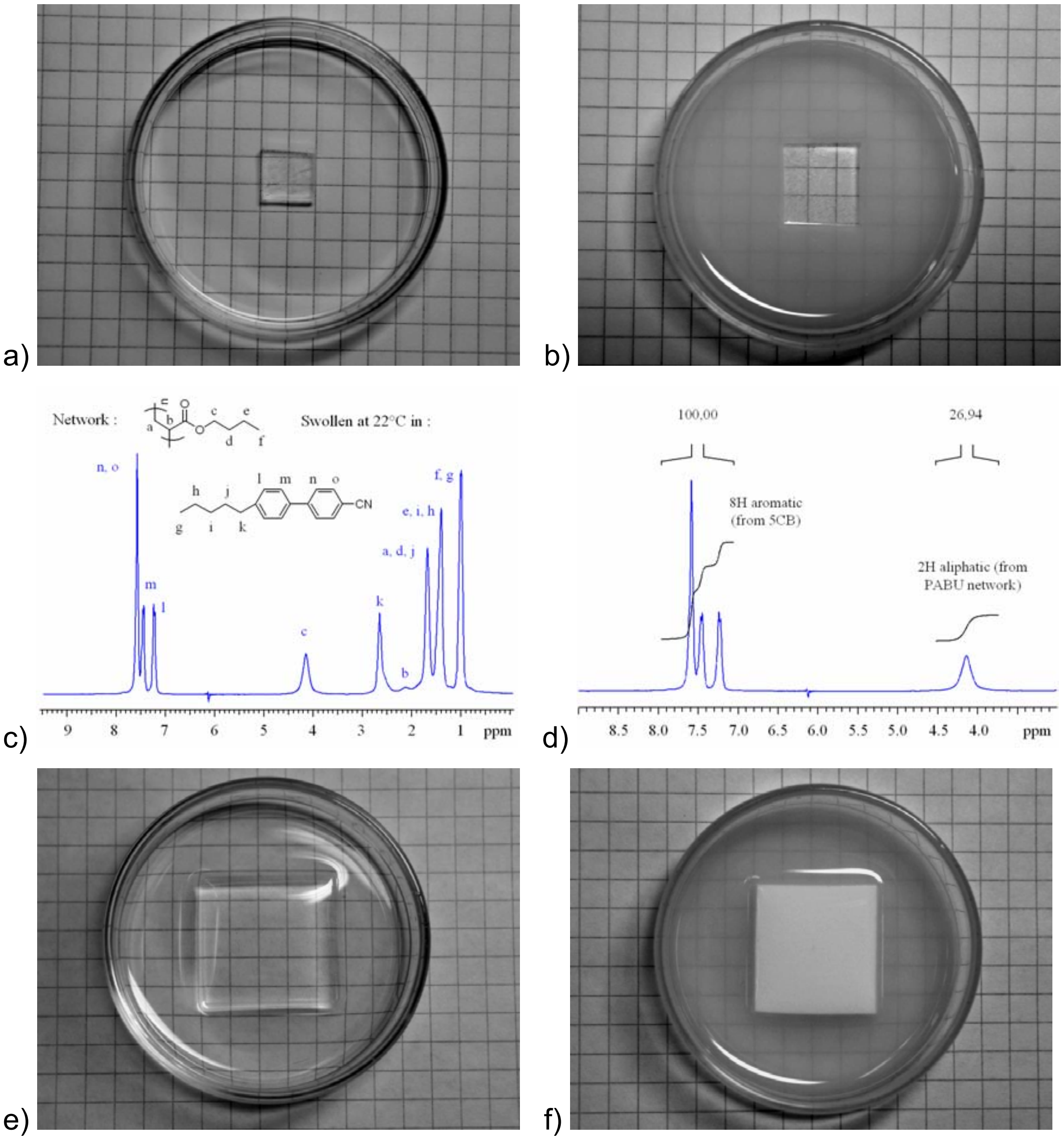

Fig. 2. Swelling of an isotropic rubber in 5CB. a) Dry piece of a poly(Abu-co-HDDA) network; b,c) Micrograph of the network swollen at room temperature in 5CB and corresponding solid state ^{1}H NMR spectra of the gel phase; d) enlarged view of the solid state ^{1}H NMR spectra of the gel phase at room temperature with the corresponding integrations; e) Micrograph of the system at 90°C in the isotropic phase of 5CB; f) Gel quenched from the isotropic phase (90°C) to room temperature.

Recently, we undertook a new study by Optical Microscopy on the influence of crosslinking degree on the swelling and phase behaviour of poly(Abu-co-HDDA) elastomers in the nematic solvents 5CB and E7 [15]. We observed that the LC that penetrates the isotropic network looses its nematic properties and discussed our result in terms of concentration-temperature phase diagrams. Here we would like to show new macroscopic optical micrographs supporting the hypothesis of an isotropic gel phase. Immersing a macroscopic piece of dry poly(Abu-co-HDDA) network (Figure 2a) in 5CB at 22°C lead to a substantial swelling of the gel (Figure 2b), which is confirmed by the increase of the gel size and the solid state NMR spectra (Figure 2c) of the gel phase. The transparency of the gel on Figure 2b) indicates the optically isotropic nature of the gel phase, which is drastically different from the excess of nematic 5CB inside the petri dish.

Besides direct measurement of the gel dimensions by optical microscopy, the swelling degree of the gel phase can be also evaluated from the NMR spectra, as we show on Figures 2c and 2d. The height aromatic protons of 5CB “l, m, n and o” appear clearly between 7 ppm and 8 ppm whether the two protons “c” of the network appear around 4,1 ppm, without overlapping with any other peaks. The relative intensity for one aromatic proton of 5CB is given by 100 / 8 = 12,5 and the relative intensity for one proton “c” of the network is 26,94 / 2 = 13,47. Assuming that the relative intensity of a peak is proportional to the volume fraction of the component into the gel, we can roughly evaluate the swelling degree of the network as Q = 1 + [13,47 / (12,5 + 13,47)] = 1,52. This value is coherent with the optical microscopy result within a margin of 15%. After heating the system from room temperature to 90°C, in the isotropic phase of 5CB, we observe macroscopically that the swelling degree of the gel significantly increases, as shown on Figure 2e). As a result, Figures 2b) and 2e) indicate that under thermodynamic equilibrium conditions, an isotropic network swollen in a nematogenic solvent remains always isotropic, even below the transition temperature of the solvent.

However, an interesting question is what happens to the gel phase if we bring the system out of the equilibrium conditions? As suggested long ago by Brochard in her pioneering theoretical work on polymer gel with LC solvents [26], one may eventually obtain a nematic gel by “supercooling” the gel from the isotropic state into the nematic phase of the solvent. Following this idea, we undertook quenching experiments of the gel from its isotropic state into the nematic phase of the solvent. A representative result of such a quenching experiment is presented on Figure 2f) which brings several conclusions.

In contrast with the surrounding solvent, which becomes turbid and translucid like conventional nematic fluids upon cooling, we observe that the gel adopts a white and opaque appearance. This observation suggests that instead of obtaining a homogeneous nematic gel, the fast cooling of the gel leads to a syneresys (phase separation) inside the gel. The LC phase tend to phase separate from the gel but, due to the macroscopic size of the sample and the long diffusion time of solvent molecules, the segregated LC phase is entrapped in the matrix. In that state, the gel is not monophasic anymore but contains two distinct phases: a polymer rich phase, made of the isotropic polymer chains swollen by 5CB in the isotropic phase, and a pure nematic phase, made of the LC which has phase separated and migrate into pure nematic domains. The white and opaque appearance of the gel after quenching indicates that the size of the segregated LC domains inside the gel phase is large enough to diffract the light. Finally, after a certain period of time necessary for the equilibration of the system (two weeks in the present conditions), the gel shrinks and recovers its isotropic character (as shown on Figure 2b).

A representative swelling curve and a phase diagram of a poly(Abu-co-HDDA) network swollen in the nematic solvent 7CB is presented on Figure 3). This diagram, obtained from monitoring the swelling of small piece of gel under a polarized optical microscope [15], can be divided into three zones. On the left part of the coexistence curve, we found a large monophasic domain characteristic of the isotropic network phase. On the right part of the coexistence curve, we observe two biphasic regions. If we add some solvent to the system in these zones, solvent molecules will directly go in the excess of pure solvent because the network has already reached its saturation limit [27].

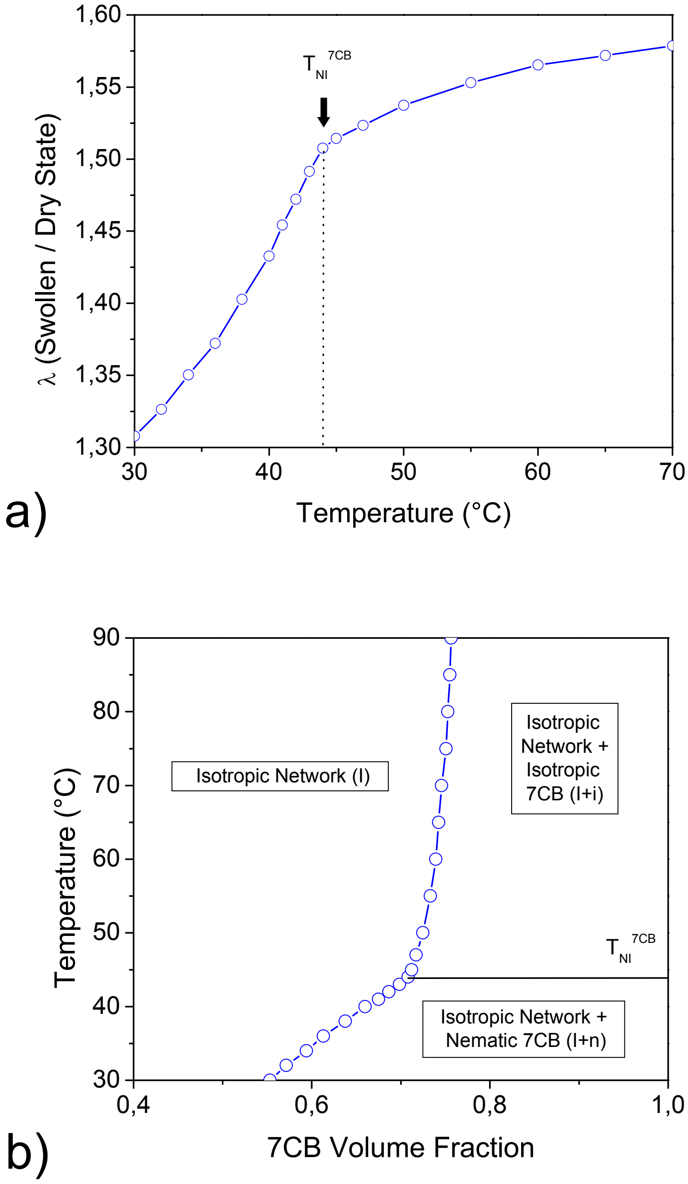

Fig. 3. a) Swelling curve and b) phase diagram of a poly(Abu-co-HDDA) network in the nematic solvent 7CB.

On the upper right zone of the diagram, the isotropic network phase is in equilibrium with an isotropic phase of pure 5CB. Finally, below T_{NI}^{5CB}, we observe in the right bottom corner another biphasic domain where an isotropic network phase coexists with a nematic phase made of pure 5CB. The miscibility of 5CB in the matrix is strongly depressed under T_{NI}^{5CB}. This effect can be understood by using simple entropic argument. In fact, below T_{NI}^{5CB}, the coexistence of an isotropic phase (the gel) and a nematic phase (the excess of solvent) creates a phenomenon of “entropic” incompatibility and the nematic species tends to phase separate from the isotropic flexible coils. As a result, 5CB molecules are expellled outside of the gel phase into the surrounding solvent and the gel shrinks [12-15].

We conclude from these observations that it is not possible to fabricate a nematic gel from an isotropic polymer network and a LC solvent because the lack of anisotropic coupling between the mesogens of the solvent and the isotropic polymer backbone prevent the formation of a homogeneous nematic phase. Even the quenching technique did not work and led to a phase separated gel rather than a homogeneous nematic media.

Swelling of a Nematic Polymer Network in a Nematogenic Solvent

Following again the suggestions of Brochard [26], another possibility to obtain a nematic gel is to swell a side-chain nematic network in a nematic solvent. The swelling behaviour of LC network in LC solvents has been the subject of several theoretical studies since decades but surprisingly attracted experimental investigations only very recently. Urayama et al. first reported the equilibrium swelling behaviour of LC networks in nematic [28-29] and isotropic [30] solvents and show that the principal features of the swelling can be qualitatively reported by a mean field theory. Unfortunately, their study concentrate only on the swelling behaviour of the nematic gel in a narrow temperature window centred on the transition temperatures and no concentration-temperature phase diagrams were plotted. Yusuf et al. studied the dynamic swelling behaviour of dry poly-domain or mono-domain LC elastomer in nematic solvent [31]. In the present paper, we aim to investigate the swelling of a nematic network in a nematic solvent in a wide range of temperature, in order to enlarge the amount of information accessible from swelling measurements. A representative series of optical micrographs under parallel and crossed polarizers showing the equilibrium phase behaviour of a nematic network swollen by the nematic solvent 5CB is presented on Figure 4).

Immersing a small piece of dry nematic network (Figures 4a and 4b) into an excess of nematic solvent lead to the formation of a nematic gel surrounded by a pure phase of nematic solvent (Figures 4c and 4d). Visually, we note that the swelling degree of the gel is important which denotes a good miscibility between the nematic network and the nematic solvent. After increasing the temperature slightly above the transition temperature of the solvent T_{NI}^{5CB}, the surrounding solvent becomes isotropic but the gel phase remains nematic (Figures 4e and 4f). It seems that in this region the network tend to shrink (the size of the gel square visually decreases). Finally, at 49°C, the gel phase undertake a transition from the nematic to the isotropic state (T_{NI}^{Gel}), and the resulting isotropic network is swollen in an excess of isotropic solvent (Figures 4e and 4f). In this last domain, the swelling degree of the gel is important which denotes a good miscibility between the isotropic network and the isotropic solvent. As we can comment from Figure 4, the swelling process of a nematic network in a nematic solvent can be divided into three characteristic regions, which are separated by two different transition temperatures, denoted as $T_{NI}^{Solvent}$ and T_{NI}^{Gel}. Optical micrographs of the gel during these two transitions are displayed on Figure 5. We emphasize on Figure 5c) that the network during its transition from the nematic state to the isotropic state is not homogeneous but is composed of both nematic and isotropic domains.

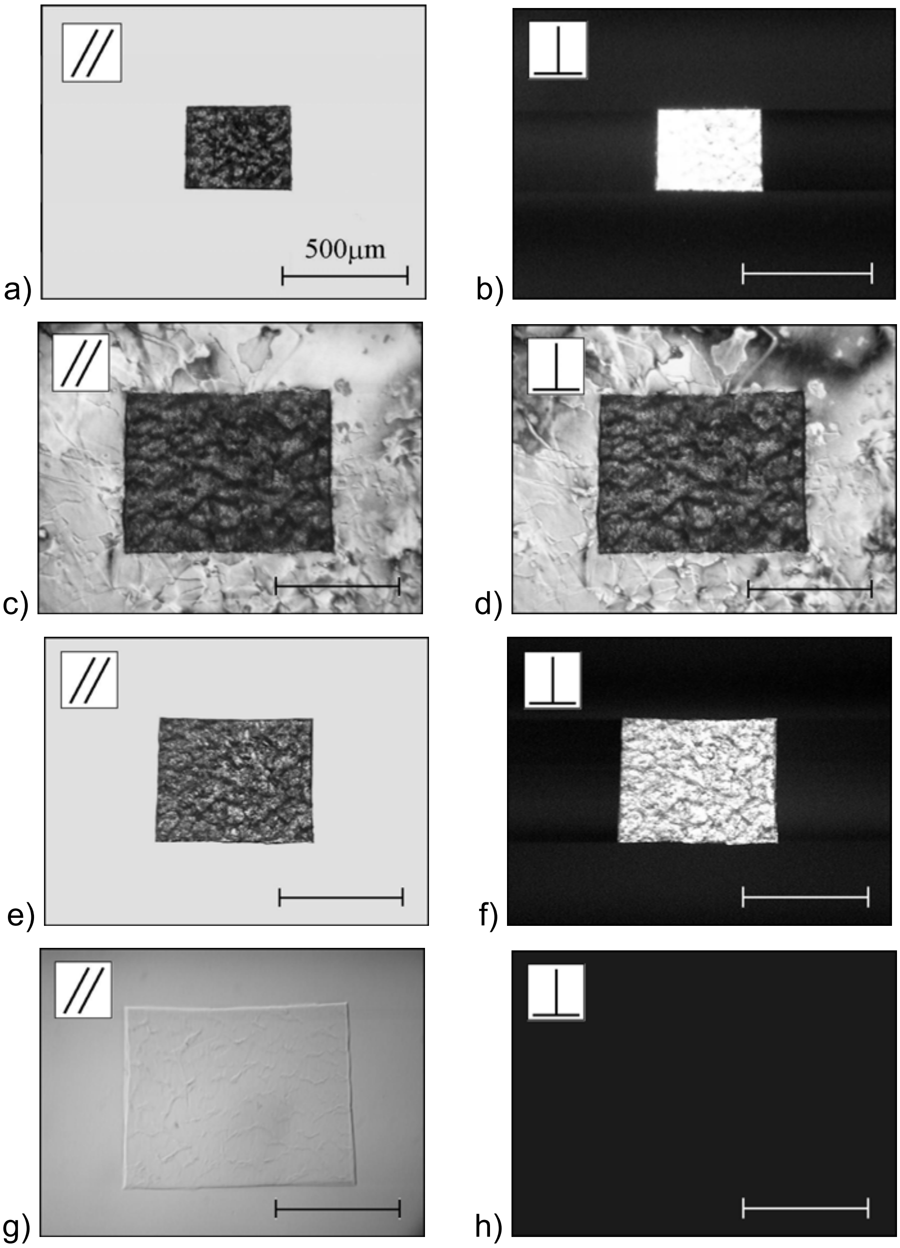

Fig. 4. Representative optical micrographs showing the phase behaviour of a nematic network poly(6OCBA-co-HDDA) swollen in 5CB under parallel polarizers (symbols //) and crossed polarizers (symbols ⊥) as a function of temperature. a,b) Dry nematic network at room temperature; c,d) Nematic network swollen in nematic 5CB at 25°C; e,f) Nematic gel surrounded by isotropic 5CB at 47°C; g,h) System at 70°C in the fully isotropic phase.

From the optical micrographs presented on Figure 4, we have determined the unidirectional swelling degree λ, calculated from averaged length/width/diagonals in the dry and the swollen state. Network shape appears distinctly in every domain, even in the fully isotropic region, and allowed the precise monitoring of λ in the complete temperature range. Unless no significant gel deformation is observed during the swelling process, measurement of the gel dimension in six different directions will average and annihilate the eventual phenomenon of non homogeneous swelling. It is important to note that even the gel in the nematic phase swells isotropically because of the polydomain structure of the gel, which annihilates the local nematic orders on a macroscopic scale.

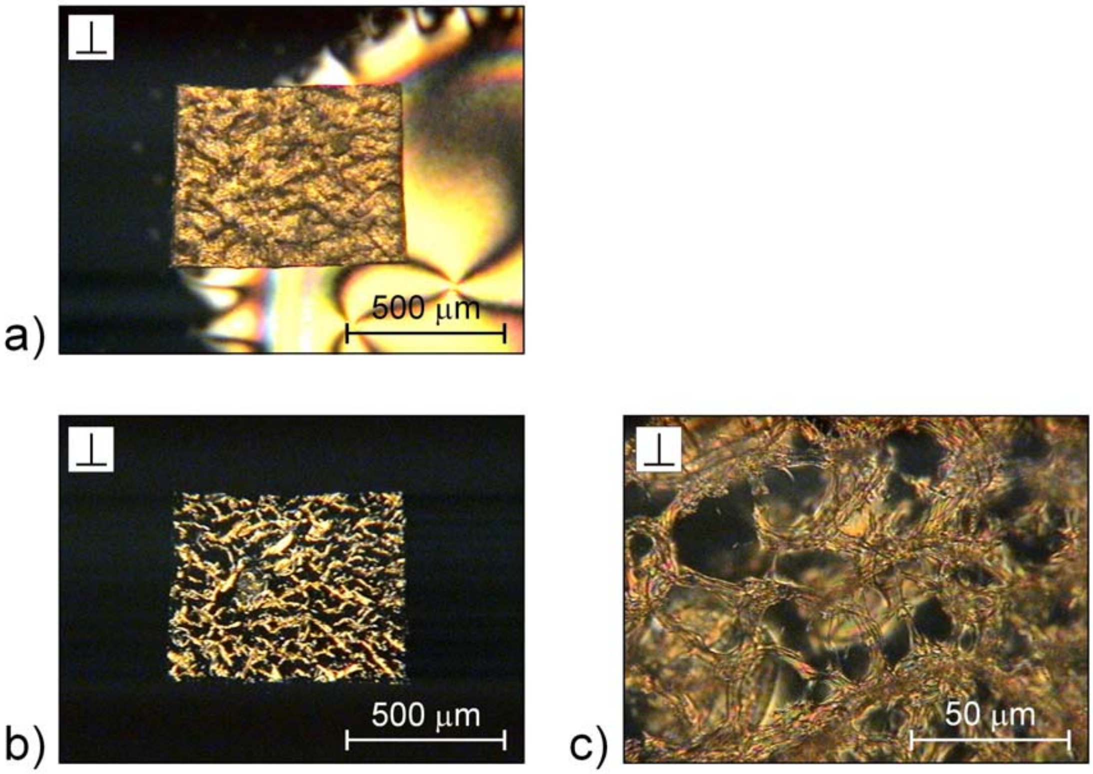

Fig. 5. Optical micrographs showing the phase transitions of the nematic network poly(6OCBA-co-HDDA) swollen in 5CB. a) System at T_{NI}^{5CB} = 35,4°C; b) System at T_{NI}^{Gel} = 61°C during the phase transition of the gel; c) enlarge view of the gel at T_{NI}^{Gel} showing its biphasic nature (isotropic network + nematic network).

The swelling data presented in Figure 6 are an average of several data measured from at least three distinct samples, prepared and analysed separately but in the same conditions. These curves were measured during a heating process, in which we increased stepwise the temperature from one to five degrees and subsequently waited at this “plateau” temperature so that the gel reaches his swelling equilibrium. In order to check the relevance of this technique, we also measured the gel size on a cooling process (deswelling of the gel). The curves measured by the two methods (heating / cooling) did not show significant difference and fits together within a margin of 0,5°C, indicating that the swelling curve corresponds to a true thermodynamic equilibrium. Swelling curves of the poly(6OCBA-co-HDDA) network in the nematic solvents 5CB and E7 displayed on Figure 6 presented the same general features. Below $T_{NI}^{Solvent}$, the swelling degree is a constant for the gel made of 5CB and slightly increases for the gel made of E7. Just above $T_{NI}^{Solvent}$, the solvent becomes isotropic whether the gel remains nematic and the swelling degree start to decrease. Further increase in the temperature tends to depress the strength of anisotropic interactions inside the gel phase and results in the shrinking of the gel. As noted by Urayama [32], the transition of the gel from the nematic to isotropic state induces a large discontinuous volume phase transition. Finally, above T_{NI}^{Gel}, the isotropic network is not saturated and continues to absorb some nematic solvent (5CB or E7) even at elevated temperature (160°C). As a result, the swelling of a nematic network in nematic solvent is strongly correlated to the phase of the LC molecules inside or outside the gel.

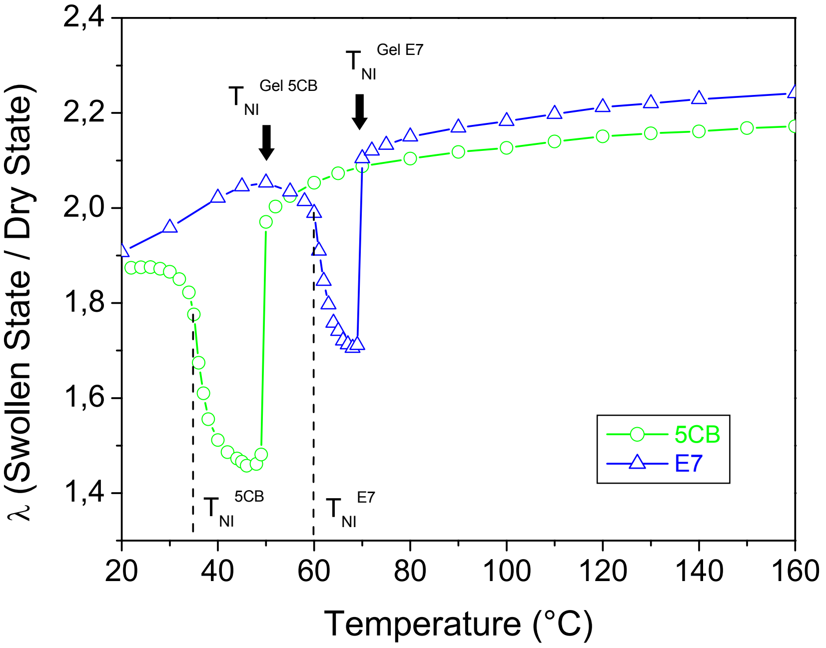

Fig. 6. Swelling curves of the LC network poly(6OCBA-co-HDDA) in 5CB and E7.

Influence of Nematic Order Coupling on the Phase Diagram of Nematic Gels

Considering the swelling degree in volume of the gel $Q = \lambda^3$ and assuming the incompressibility of the system, we can write $Q = 1/\Phi_{\text{Network}}$, where Φ_{Network} is the volume fraction of polymer in the gel phase. Following this idea, the volume fraction of LC in the gel is defined as $\Phi_{\text{LC}} = 1- \Phi_{\text{Network}} = 1- (1/\lambda^3)$. The coexistence curves (binodals) of the phase diagrams can be constructed by plotting $\Phi_{\text{LC}} = f(T)$. As shown on Figure 7a), a typical phase diagram for a nematic network swollen with a nematic solvent is divided into six domains.

Two monophasic and one biphasic domains can be distinguished on the left part of the coexistence curve while three biphasic zones appear on the right part of the diagram. As for the case of a gel made of an isotropic network, the upper left and upper right regions of the diagrams are respectively composed by a monophasic isotropic network phase and a biphasic isotropic-isotropic phase where the isotropic network is in equilibrium with an excess of isotropic 5CB. Below $T_{\text{NI}}^{\text{5CB}}$, we found a biphasic nematic-nematic zone on the right of the coexistence curve. Interestingly, the volume fraction of 5CB in the gel in this nematic-nematic region (0, 83) is comparable to the volume fraction of 5CB in the isotropic-isotropic zone. Between, $T_{\text{NI}}^{\text{Gel}}$ and $T_{\text{NI}}^{\text{5CB}}$, another biphasic region, composed of a nematic network surrounded by an excess of isotropic 5CB is found on the right of the binodal. As we already observe from the swelling curves, the miscibility between the solvent and the network in this zone is greatly depressed and reaches the value of 0,6 at 48°C. Again here, the concept of entropic incompatibility is helpful and can give, in a first approximation, a simple explanation of the phenomena. In contrast with the bi-isotropic (above T_{NI}^{Gel}) and bi-nematic (below T_{NI}^{5CB}) biphasic domains, this biphasic region is characterised by an organised phase (the gel) in equilibrium with an isotropic phase (the surrounding solvent). Therefore, the nematic chains tend to phase separate from the isotropic solvent molecules.

Another peculiarity of the phase diagram presented on Figure 7a) is the apparition of a large and stable monophasic nematic network domain on the left bottom corner. Moreover, a new biphasic region named “nematic network + isotropic network” appears between this monophasic nematic network phase and the monophasic isotropic network phase. However, this new zone, which appears as an elongated triangle on the phase diagram, is different from the other biphasic regions observed on the right part of the coexistence curve. In fact, this biphasic region is not characterised by a monophasic and homogeneous gel phase in equilibrium with excess of solvent, but by a biphasic gel without any surrounding solvent. A representative micrograph of this new phase was previously shown on Figure 5c). It is interesting to note that the experimental phase diagrams presented on Figure 7a) qualitatively agreed with those previously reported in the literature [33-36].

Comparison of Figures 3 and 7a clearly reveals the tremendous distortions induced by the mesogenic coupling on the phase diagram of crosslinked polymers swollen in nematic solvents. The nematic network + nematic solvent systems present a great richness and variety of phases, in which we especially note the formation of a stable nematic gel (due to the strong anisotropic coupling between the LC side-chain of the network and the LC solvent) and also a wide miscibility gap between $T_{NI}^{Solvent}$ and T_{NI}^{Gel} (which we attributed to an entropic phase separation process). The situation is drastically different for systems containing an isotropic network because in that case the lack of anisotropic coupling between the LC molecules and the polymer backbone always prevent the formation of a LC phase inside the gel.

In order to check the universality of the phase diagram presented on Figure 7a), we extended the study on the phase diagram of the nematic network swollen in E7, as presented on Figure 7b). This phase diagram possesses the same general features than the phase diagram in 5CB, and the six characteristic regions can be observed. However, as E7 is a mixture of four molecules, it is eventually possible for this system that the concentration of E7 inside the gel is slightly different from the pure eutectic mixture because of the preferential miscibility of some E7 components into the matrix [37]. Moreover, we note that the shape of the coexistence curve, notably around the miscibility gap between T_{NI}^{Gel} and T_{NI}^{E7}, is slightly different than the system made of 5CB. In the case of bi-nematic mixtures with crosslinked architecture, theoretical studies have shown that several parameters can influence the phase diagrams of nematic network in nematic solvent. Among these factors, the difference between $T_{NI}^{Network}$ and $T_{NI}^{Solvent}$ or the strength of the nematic coupling, which is notably determined by the chemical structure of the mesogens, have a preponderant role. In that framework, the presence of 8OCB in the E7 mixture may reinforce the coupling with the 6OCB side-chains of the network (because both contain the same oxycyano biphenyl mesogens). In addition, the transition temperature of E7 is significantly higher than 5CB, which is a favourable factor towards the reduction of the temperature window of the miscibility gap.

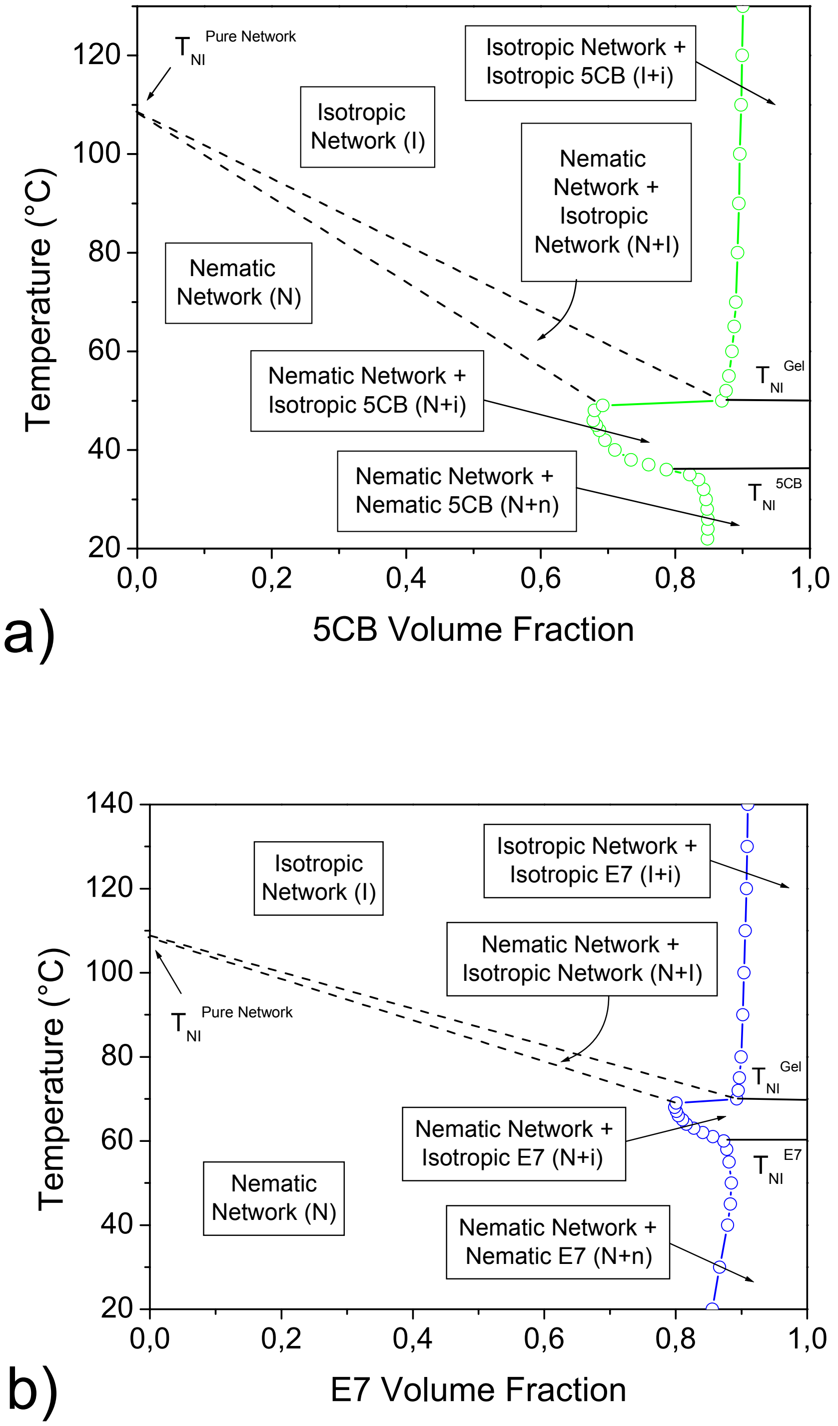

Fig. 7. a) Phase diagram of the system poly(6OCBA-co-HDDA) / 5CB in the composition-temperature frame; b) Phase diagram of the system poly(6OCBA-co-HDDA) / E7.

Conclusions

In summary, we have explored the phase behaviour of side-chain polyacrylate networks swollen in low molar weight nematogenic solvents in order to elucidate the role of the nematic order coupling on the phase diagram of polymer network/solvent mixtures. To achieve this purpose, we prepared isotropic and nematic networks by a photo-polymerisation technique and swelled them in well-characterised nematic low molar solvents 5CB and E7. In the case of small isotropic side-chains like poly(n-butyl acrylate) network, 5CB fails to form a LC phase into the network and the gel tends to collapse below T_{NI}. Fast cooling of the isotropic gel into the nematic phase of the solvent did not result in the formation of a nematic gel but instead led to a syneresys inside the gel.

However, the situation is drastically different if the polymer network possesses side-chain LC moieties. In that case, anisotropic coupling between LC solvent molecules and LC side-chains of the network promotes the appearance of a large and stable nematic phase in the phase diagram, both for 5CB and E7. In the bi-nematic systems, we interestingly observe the appearance of a wide miscibility gap between T_{NI}^{5CB} and T_{NI}^{Gel}, which was attributed to an entropic demixing process. Until now, we mainly explained the phase diagrams of crosslinked polymer gels with nematic solvents in terms of simple entropic arguments, arguing that two LC components tend to mix but a LC phase tend to phase separate from an isotropic phase. But enthalpic reasons should not be under estimated for such systems. For example the polymer/solvent interaction parameter may be significantly different depending on the respective phases (isotropic or nematic) of the gel constituents (polymer network or solvent). Further analysis including theoretical simulations of the phase diagrams are currently under progress and will surely help to refine our understanding of this phenomenon. Finally, we hope that this study will help to give a clear picture of the influence of nematic coupling on the phase diagrams of nematic gels and will motivate further investigations related to these fascinating materials, which hold great promise for the next generation of functional polymer gels in advanced optical and telecommunications technologies or as artificial muscles.

Experimental Section

Materials

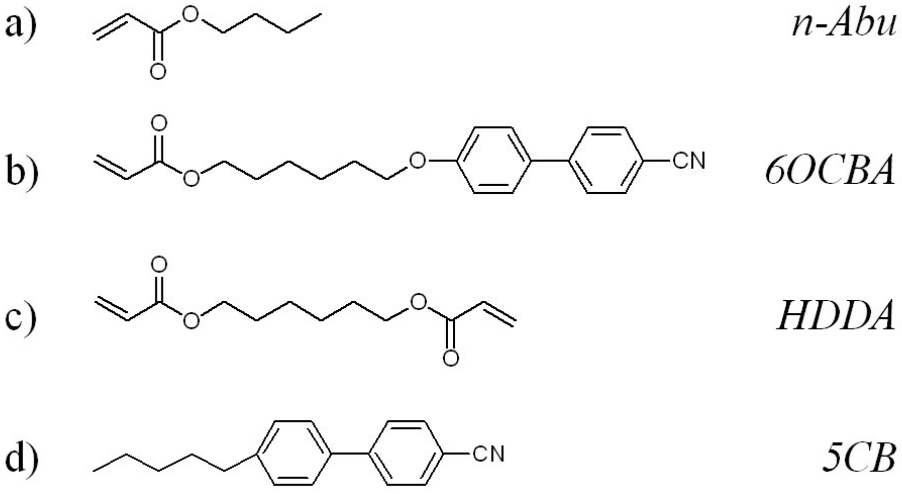

Fig. 8. Molecular structures of a) isotropic monomer n-Abu; b) mesogenic monomer 6OCBA; c) crosslinker HDDA and d) nematic solvent 5CB.

The monomer n-butyl acrylate (Abu) and the photoinitiator 2-hydroxy-2-methyl-1-phenylpropane-1 (Darocur 1173) were respectively obtained from Aldrich and Ciba whereas the crosslinking agent hexanediol diacrylate (HDDA) was donated from Cray Valley. The mesogenic monomer 6-(4’-cyanophenyl-4’’-phenoxy)hexyl acrylate (6OCBA) was synthesised by the conventional procedures found in the literature [38-39]. The LCs, 4-cyano-4’-pentylbiphenyl (5CB), 4-cyano-4’-heptylbiphenyl (7CB) and E7 were purchased from Merck Eurolab GmbH (Darmstadt, Germany). The eutectic LC mixture E7 exhibits a single nematic-isotropic transition temperature and contains 51 wt.% of 5CB, 25 wt.% of 4-cyano-4’-heptylbiphenyl (7CB), 16 wt.% of 4-cyano-4’-oxyoctylbiphenyl (8OCB) and 8 wt.% of 4-cyano-4’’-pentyl-p-terphenyl (5CT). Chemicals structures of Abu, HDDA, 6OCBA and 5CB are presented in Figure 8.

Microscopy

The thermo-microscopy studies were performed on a Leitz polarized optical microscope (POM), equipped with a Linkam heating/cooling stage THMS 600 together with a temperature-controlling unit TMS 92. For the swelling measurements, thin sheets of dry polymer networks (thickness of approximately 50μm) were sliced with a scalpel, cut into approximately 500*500μm squares and placed in a THMS-Q quartz cell (Linkam Instruments), which allows the thermo-microscopic observation of liquid samples without being sandwiched between two glass plates. The THMS-Q cell was filled with low molecular weight liquid crystal (LMWLC) and placed in the heating stage under a nitrogen atmosphere. Ratios of the gel dimensions in the swollen to dry states allow the precise determination of the swelling degree of the gel in a wide range of temperature. The temperature was increased in a stepwise manner, the typical size of one step being generally 5°C and has been reduced to 1°C around the transition temperatures.

Thermal analysis

DSC measurements were carried out on a Mettler DSC 30 equipped with a liquid nitrogen system allowing cooling experiments. The DSC cell was purged with 50 ml/min of nitrogen. Data analysis has been carried out on the second heating ramp at a speed of 5°C/min for both polymer networks and the solvents. Glass transition temperatures were determined from the midpoint of the transition range.

Solid State Nuclear Magnetic Resonance (NMR)

Solid State NMR spectra were measured at room temperature using Brucker DSX console together with a 2,5mm MAS (Magic Angle Spinning) double resonance probe (Rotating conditions: 25 kHz MAS, 300 Mhz 1H Larmor frequency; Pulse technique: 1H single pulse excitation; Frequency of magnet: 100 kHz B1 filed strength).

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