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Mesomorphic and Orientational Study of Materials Processed by In Situ Photopolymerization of Reactive Liquid Crystals

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The synthesis and in situ photopolymerization of reactive liquid crystals for the preparation of materials with different degrees of cross-linking is described. The molecular orientation of polymeric films can be controlled by orienting the monomeric photopolymerizable materials in the mesomorphic state. The birefringence of photopolymerizable materials and the resulting polymers are described, and its dependence on the temperature has been evaluated. The degree of order of polymeric films has been studied by using a reactive nitrostilbene unit as a probe for performing dichroism measurements. Polymeric films with a low degree of cross-linking showed a memory effect, as observed by optical microscopy, X-ray diffraction, and birefringence measurements.

Introduction

Liquid crystalline (LC) elastomers and networks are produced by the introduction of a low or high cross-linking density, respectively, into liquid crystalline polymeric systems. The anisotropic properties of polymeric films derived from these materials have been extensively investigated because of their applications and interest in them from a fundamental point of view.[1,2] However, the cross-linking strategy plays a very important role in the processing and the final orientation of these films. The photopolymerization of reactive liquid crystals in an oriented mesomorphic state (in situ photopolymerization) has proved to be a versatile and advantageous way of processing anisotropic polymeric films. Inherent advantages are that this method allows the production of any kind of desired pattern in the film and allows the selection of the polymerization temperature and, consequently, the mesophase of the monomer in which the polymer will be produced. This technique has mainly been used in the synthesis of anisotropic densely cross-linked networks,[3] as well as in the preparation of LC gels,[4] side-chain LC polymers,[5] and slightly cross-linked LC polymers (LC elastomers).[6] The processing of LC elastomers into thin films by in situ photopolymerization requires monomeric formulations that usually consist of a monoreactive liquid crystal and a direactive (LC or non-LC) component as a cross-linker, as well as a photoinitiator and a thermal inhibitor that decouples the process of polymerization from the temperature. This is a very important feature of the in situ photopolymerization since it allows the manipulation of monomers in their mesophases before irradiation. As a consequence, macroscopically oriented monomeric samples can be polymerized to give polymeric materials in which the molecular order of the monomers can be frozen-in. Furthermore, cross-linking imposes constraints on the segmental motion, and it might be expected that the molecular order *recorded* (i.e., frozen in) during polymerization should be thermally or mechanically reversible.

In this paper, we report the synthesis and photopolymerization of mixtures of mono- and direactive liquid crystals to yield polymeric materials with different degrees of cross-linking. Some previous works have been published[6,7] in which the order in photopolymerized films has been studied as a function of either the cross-linking density or polymerization temperature. Our main goal has been to combine these two effects to evaluate their relative influence. Thus, the order parameters of several samples with different degrees of cross-linking and photopolymerized at various temperatures (and in different mesophases) have been studied. Figure 1 shows the mono- and the direactive monomers employed in the preparation of photopolymerizable mixtures. The molecular orientation of polymeric films obtained by in situ photopolymerization is a consequence of the orientation of the monomeric mesophase in which polymerization takes place. Birefringence and dichroism measurements of a guest chromophore have been used by several authors to compare the degree of

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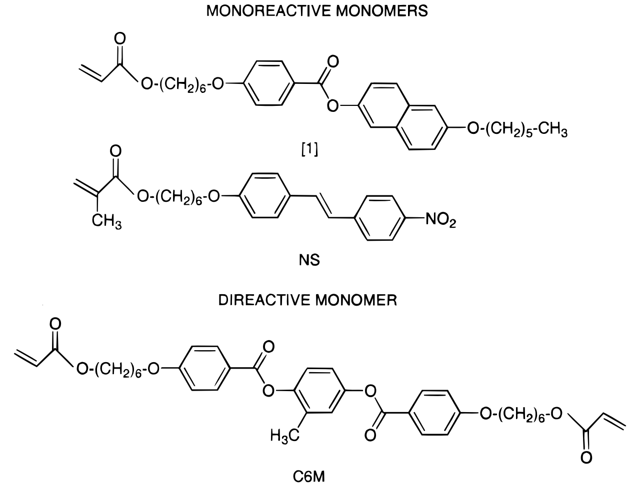

Figure 1. Nomenclature of the mono- and direactive monomers used in the preparation of photopolymerizable samples.

order of monomers and polymers, as well as to monitor the evolution of the order parameter with different thermal treatments.[8-11] We have studied the birefringence of polymeric films formed from monomers, shown in Figure 1, previously oriented in planar LC cells. A reactive nitrostilbene derivative (NS) was added in a low percentage to some of the photopolymerizable samples to act as a probe for dichroism measurements. The evolution of the birefringence of the monomers and polymers as a function of temperature and composition, as well as the changes induced by photopolymerization, are analyzed and discussed. The degree of order of selected polymeric materials has also been studied by measuring the dichroism in the optical absorption spectrum of the nitrostilbene chromophore.

Experimental Section

The synthetic pathway to obtain monomers [1] and NS is depicted in Figure 2. The direactive monomer C6M, which was used as cross-linker, was kindly supplied by Philips.

In Situ Photopolymerization. The photopolymerizable samples were prepared by dissolving the appropriate proportions of the mono- and direactive monomers, 1% (w/w) of the photoinitiator and 200 ppm of 2,6-di-*tert*-butyl-4-methylphenol (thermal inhibitor) in freshly distilled dichloromethane. The solvent was evaporated at room temperature, and the residual solvent was removed by heating the sample at 30 °C under vacuum overnight. The nomenclature and compositions of the photopolymerizable samples are summarized in Table 1.

In situ photopolymerization was studied by DSC using a Perkin-Elmer DSC-7 suitably modified for studying photopolymerization processes.[12] An aliquot of 2−6 mg of photopolymerizable sample was placed in an open aluminum DSC pan. Experiments were carried out under a nitrogen atmosphere in order to avoid oxygen inhibition. A UV lamp (Philips PL-S 9W/10), at a distance of 13 cm from the sample and reference holders, was used to irradiate the samples. The sample was heated to slightly above the isotropization temperature and then to the selected polymerization temperature at which the sample was maintained for 5 min before irradiation under isothermal conditions. Irradiation was maintained for 15 min and the photopolymerization was detected as an exotherm in the DSC trace. The degree of conversion was calculated from the enthalpy content of this polymerization peak, taking 78 kJ/mol as the polymerization enthalpy of 1 mol of acrylate group.[13]

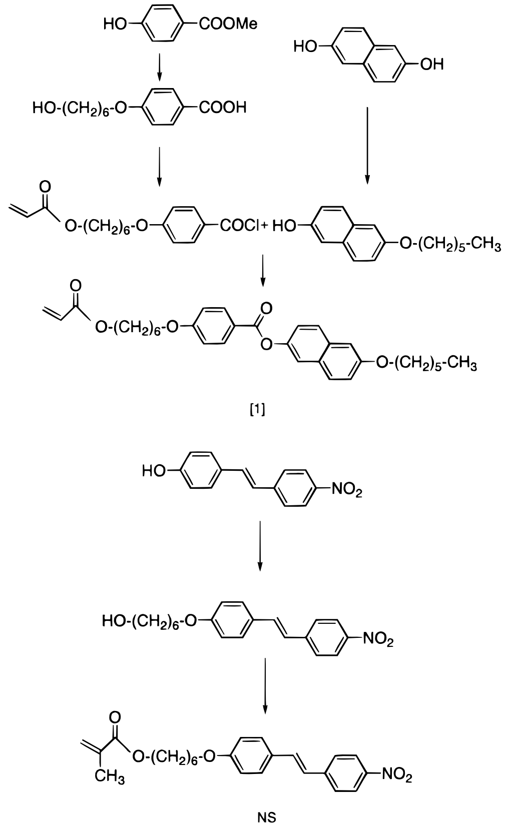

Figure 2. Synthetic pathways for monoreactive monomers.

Table 1. Nomenclature and Composition (in % w/w) of the Photopolymerizable Samples[a]

nomenclature	[1] (%)	C6M (%)	NS (%)
C-0	100		
C-2	98	2	
C-5	95	5	
C-10	90	10	
C-20	80	20	
C-100		100	
C-10-NS	85	10	5
C-95-NS		95	5

[a] (1% in weight of the photoinitiator and 200 ppm of the thermal inhibitor was added to the photopolymerizable samples).

Samples were also photopolymerized in commercial cells for planar alignment (Linkam, 5 μm) in order to produce oriented polymeric films for birefringence and dichroism measurements. The samples were introduced by capillary action at 90 °C in the nematic phase. In all cases, a defect-free planar monodomain was observed by microscopy. Photopolymerization of these samples was performed using an OSRAM Ultravitalux 300 W lamp. A 400 nm long-pass filter was placed between the lamp and the cells in order to prevent irradiation at the absorption bands of [1], C6M, and NS. The lamp was placed at a distance of about 20 cm from the cell, and irradiation was maintained for 10 min.

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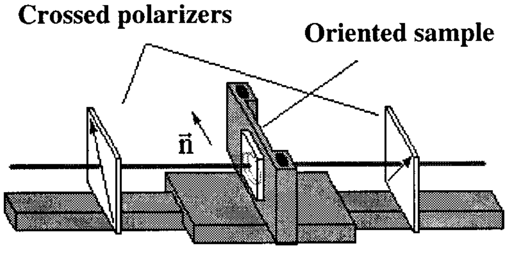

Figure 3. Experimental setup for birefringence measurements.

Table 2. Transition Temperatures and Thermodynamic Parameters (mesophase−mesophase and clearing transitions) of the Reactive Monomers Used in the Preparation of Photopolymerizable Samples (determined by DSC)

monomer	phase transition	T (°C)	ΔH (kJ/mol)	ΔS (J/mol K)
[1]	C−N	69		
	N−I	109	0.77	2.02
	N−S_A	68	0.15	0.43
NS	C−I	98		
C6M	C−N	86		
	N−I	116	1.60	4.11

Techniques. Gel permeation chromatography (GPC) was carried out using a Waters HPLC setup equipped with a 600E multisolvent delivery system and a 996 photodiode array detector. Two Ultrastyragel columns (Waters) of 500 and 10^4 Å pore size were connected in series using THF as the mobile phase (0.8 mL/min) and polystyrene as calibration standards.

Mesomorphic properties were studied by optical microscopy using a Nikon polarizing microscope fitted with a Linkam THMS 600 hot-stage. Transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 at a scanning rate of 10 °C/min. X-ray diffraction patterns were obtained with an evacuated pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. Diffraction patterns were photographically recorded. Free films for X-ray diffraction measurements were obtained by photopolymerization of a molten sample between two glass slides that had been coated with a very fine layer of silicone grease. The silicone grease had been rubbed uniaxially, circularly, or randomly depending on the orientation intended for the mesophase: planar, homeotropic, or random orientation, respectively.

Optical absorption, dichroism, and birefringence measurements were taken using a Hitachi UV−vis−IR spectrophotometer. For dichroism measurements, a linear polarizer was placed in front of the LC cell, which was perpendicular to the light beam. For birefringence measurements, the setup shown in Figure 3 was inserted in the sample beam of the spectrophotometer. The LC cell, with the director ($\vec{n}$) horizontal, was placed between crossed polarizers (polarization directions at 45° from the horizontal). A variable temperature setup was used to measure the birefringence at different temperatures.

Results and Discussion

Monomers and Photopolymerizable Samples. The monoreactive monomers [1] and NS were synthesized according to the synthetic route shown in Figure 2 and were purified in the appropriate manner. The mesomorphic properties and transition temperatures of these monomers were studied by polarizing optical microscopy and DSC, and the results are collected in Table 2. This table also includes the properties of the diacrylate, C6M, used as a cross-linker.[14] Monomer [1] exhibits both an enantiotropic nematic mesophase at temperatures similar to those of C6M and a monotropic smectic A phase. The monomer NS does not exhibit mesomorphism, as has been previously reported.[15] The methacryloyl group was selected as the photoreactive unit of this monomer since lower yields and cross-linking through the stilbene group has been described for the polymerization of the acrylate derivative.[16]

Table 3. Transition Temperatures of the Photopolymerizable Samples of Monomer [1] and C6M Determined by DSC[a]

sample	phase transition	T (°C)
C-2	C−N	66
	N−I	104
	N−S_A	65
C-5	C−N	67
	N−I	105
	N−S_A	61
C-10	C−N	66
	N−I	106
	N−S_A	53
C-20	C−N	65
	N−I	109
	N−S_A	40

[a] (C-0 and C-100 exhibit the same transition temperatures as the corresponding monomers, see Table 2).

A study of the photopolymerization of the monomer [1] and its mixtures with C6M was carried out by DSC. The mesomorphism of the resulting polymeric materials was characterized by optical microscopy and DSC. The nomenclature used for photopolymerizable mixtures is summarized in Table 1, along with that for samples with a low percentage of NS used for performing dichroism measurements. The monomers [1] and C6M do not absorb above 350 nm and, consequently, the polymerization can be induced by a photoinitiator absorbing at 365 nm, the wavelength of emission of the lamp adapted to our photo-DSC experimental setup. For this reason, the DSC study of photopolymerization of mixtures of these monomers was carried out using samples containing 1% (w/w) of Irgacure 651, which absorbs at this wavelength (λ). In addition, 200 ppm of the thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol was added to avoid thermal polymerization. The samples were completely miscible in the range of concentrations investigated. In addition, low percentages of C6M do not considerably modify the phase transitions and the mesophase range of [1] except for the monotropic N−S_A transition, which shifts to a lower temperature (see Table 3).

Monomer NS shows an absorption band at about 380 nm. For this reason, samples used in the birefringence and dichroism study were photopolymerized using the photoinitiator Irgacure 784 DC, which shows some absorption bands in the 400−500 nm region.[17] Visible light was used to initiate the photopolymerization process.

In Situ Photopolymerization Study of Photopolymerizable Samples of [1] and C6M. Before inves-

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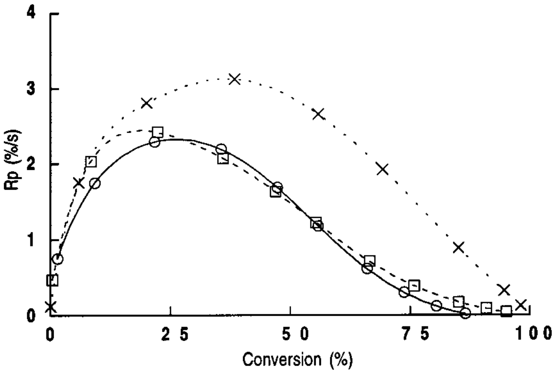

Figure 4. Polymerization rate vs conversion for the photopolymerizable sample C-5 at different temperatures: ○ 45 °C (S_A), × 90 °C (N), □ 120 °C (I).

tigating the photopolymerization of mixtures of the mono- and direactive monomers, the photopolymerization of [1] (see entry C-0 in Table 1) and the mesomorphic properties of the resulting polymer were studied. The DSC study reveals a polymerization exotherm that provides evidence of a high rate of polymerization. The conversion calculated from this exotherm is 99%, and no traces of residual monomer were detected by GPC. Photopolymerization of C-0 at different temperatures in the N, S_A, or I phase gives rise to a side-chain liquid crystalline polymer (coded as P-C-0), which exhibits a smectic C phase with a blurred *schlieren* texture over a wide temperature range, as characterized by optical microscopy and DSC. The phase transitions detected by DSC for polymer P-C-0 obtained by photopolymerization at 90 °C were g 27 °C S_C 183 °C I, and the thermodynamic data of the isotropization transition were $\Delta H_i = 4.56$ kJ/mru and $\Delta S_i = 10.0$ J/mru (mru = moles of repeating units) according to a smectic−isotropic phase transition. The molecular weight detected by GPC for this polymer, M_n, was 2.6×10^5 (polydispersity $M_w/M_n = 3.5$). On the other hand, the transition temperatures of P-C-0 hardly change on performing the polymerization in other phases. The mesophase of P-C-0 was also characterized by X-ray diffraction. Thus, the X-ray diffraction pattern of a polymeric film obtained by photopolymerization of C-0 is consistent with a lamellar structure having an interlayer spacing that increases from 48 to 52 Å over the mesophase temperature range. Taking into account that the repeating unit length is estimated to be approximately 36 Å by Dreiding stereomodels, it can be concluded that the polymer exhibits a bilayer tilted smectic structure. The different mesophases exhibited by the monomer and resulting polymer imply that a phase transition occurs during polymerization.

The photopolymerization of mixtures of [1] with different percentages of C6M was also studied by DSC and optical microscopy. The conversion versus irradiation time and polymerization rate versus conversion relationships were evaluated from the photopolymerization exotherms of the DSC curves. As an example, Figure 4 displays the dependence of the polymerization rate (R_p) on the conversion for sample C-5, which was photopolymerized in the isotropic (120 °C), nematic (90 °C) and smectic A (45 °C) phases. The final conversion determined by DSC is ca. 100% at 90 and 120, but is slightly lower (90%) at 45 °C. A higher polymerization rate is observed at 90 °C, and similar curves are observed for photopolymerization at 45 and 120 °C despite the different initial molecular ordering at these temperatures. These results indicate a higher influence of the polymerization temperature in comparison to phase ordering.[18] Figure 5 shows the influence of the percentage of C6M in the polymerization of samples of monomer [1] at 90 °C in the nematic state. The polymerization rate increases as the percentage of cross-linker increases because a higher degree of cross-linking hinders the mobility of macroradicals and, consequently, makes the termination step more difficult.

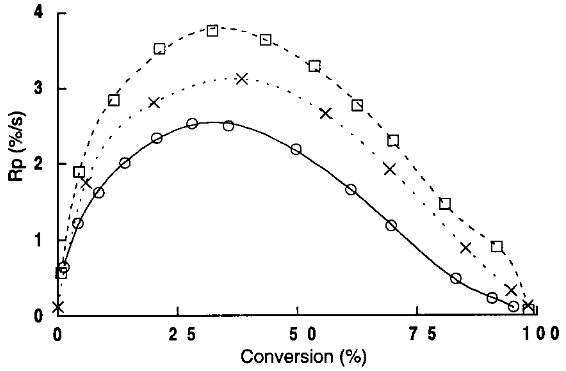

Figure 5. Polymerization rate vs conversion for the samples with a different percentage of C6M at 90 °C in the nematic state: ○ C-2, × C-5, □ C-10.

Table 4. Transition Temperatures and Thermodynamic Parameters Determined by DSC of the Polymers Obtained by in Situ Photopolymerization at 90 °C in the N Phase

polymer	phase transitions (°C)	ΔH_{M-I} (kJ/mru)[a]	ΔS_{M-I} (J/mru K)[a]
P-C-0	g 27 S_C 183 I	4.56	10.00
P-C-2	g 27 S_C 181 I	4.42	9.74
P-C-5	g 28 S_C 180 I	2.19	4.83
P-C-10	g 28 N 191 I	0.56	0.96
P-C-20	g 28 N[b]		

[a] mru: mol of repeating unit. [b] Isotropization transition is not observed.

The mesomorphic properties of the cross-linked materials obtained by in situ photopolymerization at 90 °C in the DSC study are gathered in Table 4. The DSC curves of these photopolymerized materials exhibit a glass transition (T_g) and a broad endothermic peak at high temperatures. The glass transition appears in a similar range of temperatures for all the materials, and there is not a clear tendency toward increased T_g with increasing cross-linking density. This effect has been previously observed, especially if the cross-linkers have flexible chains.[19] The endothermic broad peak can be assigned to isotropization by taking into account the optical microscopy observations. The transition temperatures are similar to those detected for the side-chain polymer P-C-0. However, when the percentage of C6M is ≥10%, isotropization is barely detectable by DSC. The study of these polymers by optical microscopy reveals that materials with low percentages of C6M (P-C-2 and P-C-5 resulting from C-2 and C-5, respectively) exhibit textures similar to those of the side-chain polymer P-C-0, which were assigned to an S_C mesophase. Fur-

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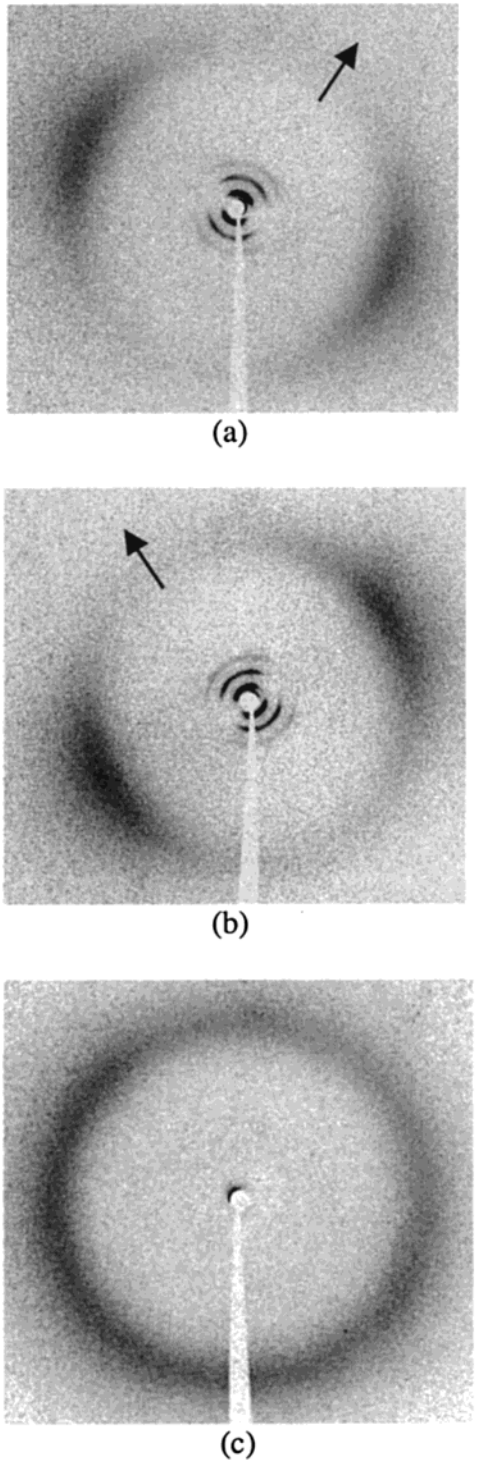
(a)

(b)

(c)

Figure 6. Room temperature X-ray diffraction patterns of free-standing films derived from C-2 (P-C-2): (a) photopolymerized at 90 °C in the N phase between glass plates uniaxially rubbed and (b) after heating the films above the isotropization temperature and cooling to room temperature (the arrows show the rubbing direction). (c) Pseudohomeotropic S_C film of a sample photopolymerized at 60 °C (S_A monomeric phase) between glass plates rubbed in a circular manner.

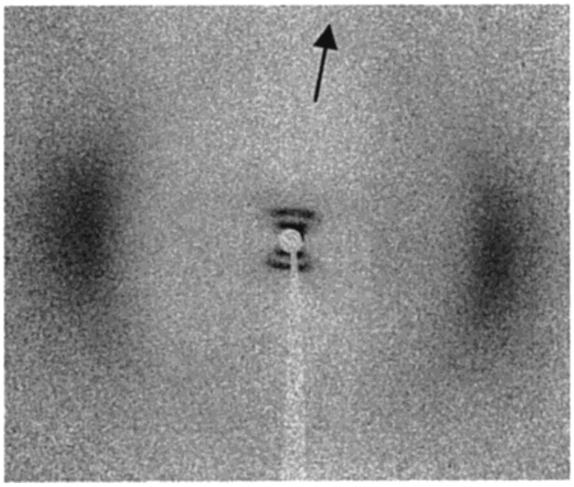

Figure 7. Room temperature X-ray diffraction pattern of a free-standing film derived from C-10 (P-C-10) photopolymerized at 90 °C (N phase) between glass plates uniaxially rubbed at room temperature (the arrow shows the rubbing direction).

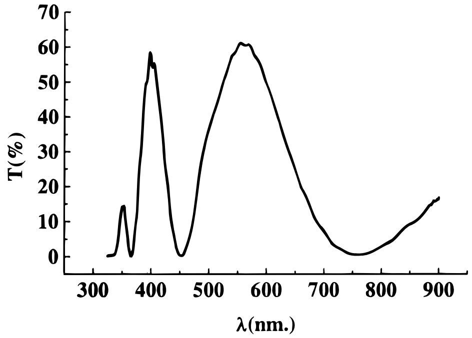

Figure 8. Typical measurement of the transmitted intensity vs wavelength in a birefringence experiment (see eq 1).

thermore, the as-polymerized S_C textures exhibited by these slightly cross-linked materials are re-formed when the samples are heated above their isotropization temperatures and then recooled to the polymerization temperature, indicating that this material exhibits a memory effect typical of LC elastomers. Both facts were also corroborated by the study of the X-ray diffraction patterns of free-standing films obtained by photopolymerization of C-2 at different temperatures. Photopolymerization was performed at 90 °C in the N phase, between two glass plates coated with a very thin layer of uniaxially rubbed silicone grease. Unfortunately, by using this technique, a monodomain with a planar orientation could not be obtained. However, a certain orientation of the molecular axes is induced in the plane of the glass plate, as can be seen in Figure 6a for P-C-2. The peaks observed at low angles are reinforced as a diagram of four points and correspond to diffraction of the smectic C layers having a layer spacing about 49 Å (bilayer structure) and a tilt of about 35°. When the free-standing film was heated above the isotropization temperature and then recooled to room temperature, the same pattern was obtained, as can be seen in Figure 6b. Films obtained by photopolymerization at 60 °C in the homeotropically aligned S_A phase give rise to patterns such as that shown in Figure 6c. This diagram corresponds to a sample having a homeotropic or pseudohomeotropic orientation, which is also recovered after heating the sample above isotropization and recooling to room temperature.

In the cases of materials having a higher percentage of cross-linker, especially in P-C-20 but also in P-C-10, the texture of the monomeric samples is frozen by photopolymerization, and consequently, a nematic mesophase is obtained. Birefringence is also observed to a

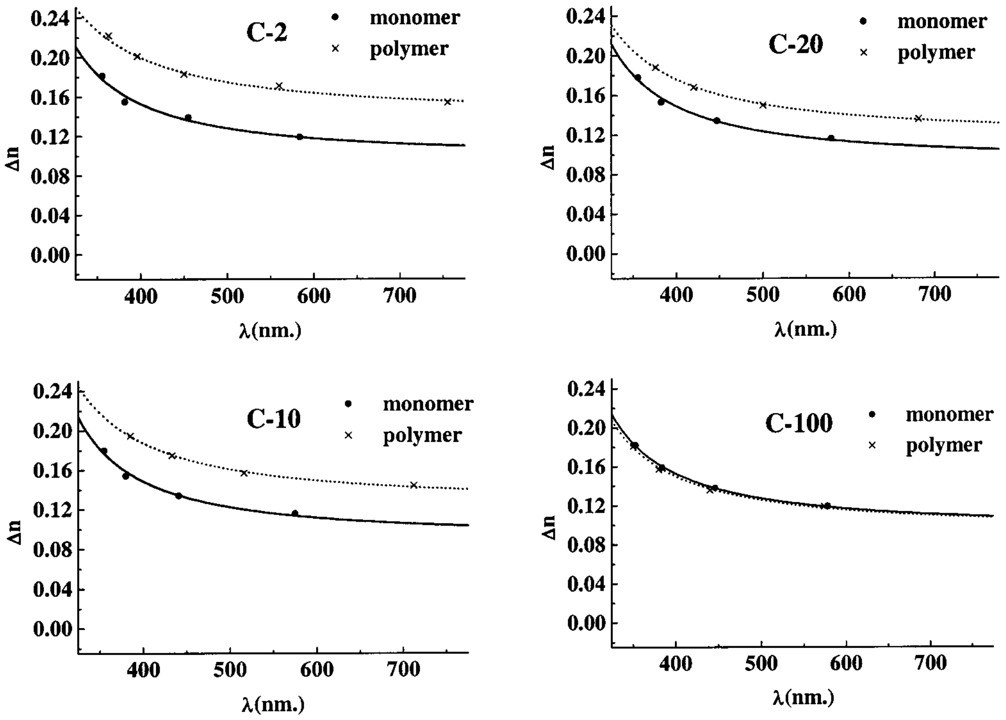

Figure 9. Birefringence of the different mixtures as a function of wavelength. The circles and crosses give the values corresponding to maxima and minima of the I vs λ curves (see Figure 8) for monomers and polymers, respectively. Solid lines and dotted lines give the fittings using eq 4. The samples were measured and photopolymerized at 100 °C.

small extent at temperatures higher than the isotropization temperature of P-C-0 taken as reference. From these optical observations, it can be deduced that samples with a percentage of cross-linker ≥10% behave as polymeric networks. Figure 7 shows the X-ray pattern of a film obtained by photopolymerization of sample C-10 (P-C-10) at 90 °C in the nematic state. It can be seen that the diagram is similar to Figure 6a but the peaks at low angle are more diffuse and the diagram is consistent with a nematic phase with smectic C fluctuations.

Birefringence and Dichroism Measurements. Birefringence measurements have been performed on photopolymerizable samples derived from mixtures of [1] and C6M before and after polymerization. The light intensity (I) transmitted through the crossed polarizers in the experimental setup represented in Figure 3 was measured at fixed temperatures as a function of wavelength (λ) for the pure monomers [1] (C-0) and C6M (C-100), as well as for different photopolymerizable mixtures (C-2, C-10, and C-20). A typical result is shown in Figure 8. The transmitted intensity I is given by the equation:

$$I = I_0 \sin^2(\pi d|\Delta n|/\lambda) \qquad (1)$$

where I_0 is the intensity transmitted under parallel polarizers, d is the film thickness, and Δn is the birefringence. The thickness (d) of the sample region in each cell was determined by interferometry before filling the cell with the photopolymerizable sample. We assume that this thickness does not change during polymerization and subsequent thermal treatments. The positions of the minima and maxima of eq 1 are given by the following equations:

$$d|\Delta n|/\lambda = m \text{ (minima)} \qquad (2)$$

$$d|\Delta n|/\lambda = (m + {}^1/_2)\text{(maxima)} \qquad (3)$$

where m is a natural number that indicates the order of the corresponding maximum or minimum. To obtain the value of m we followed the procedure described by Broer et al.[8] The sample was placed under crossed polarizers in the polarizing microscope with the director at 45° with respect to the transmission direction of the polarizers. A red filter was placed in front of the light source such that only red light passed through the sample. The sample was then slowly cooled from the isotropic phase to the nematic phase. Because of the orientational surface effect, the LC domains become oriented in the nematic phase and the birefringence increases in a continuous way. This increase is accompanied by oscillations in the transmitted light, and the number of observed minima gives the birefringence order corresponding to the first minimum in the low-energy side of Figure 8. In the case described here, the m value corresponding to this minimum was $m = 1$.

By fitting eqs 2 and 3 to our experimental results, the values of Δn were obtained at 100 °C in each of the samples for a number of wavelengths corresponding to the maxima and minima of the I versus λ curves. In a single-band model,[20] the birefringence (Δn) as a function of wavelength and temperature is given by the following expression:

$$\Delta n(\lambda,T) = G(T)(\lambda^2\lambda_m{}^2)/(\lambda^2 - \lambda_m{}^2) \qquad (4)$$

where λ_m is an effective wavelength associated with the absorption bands of the compound.

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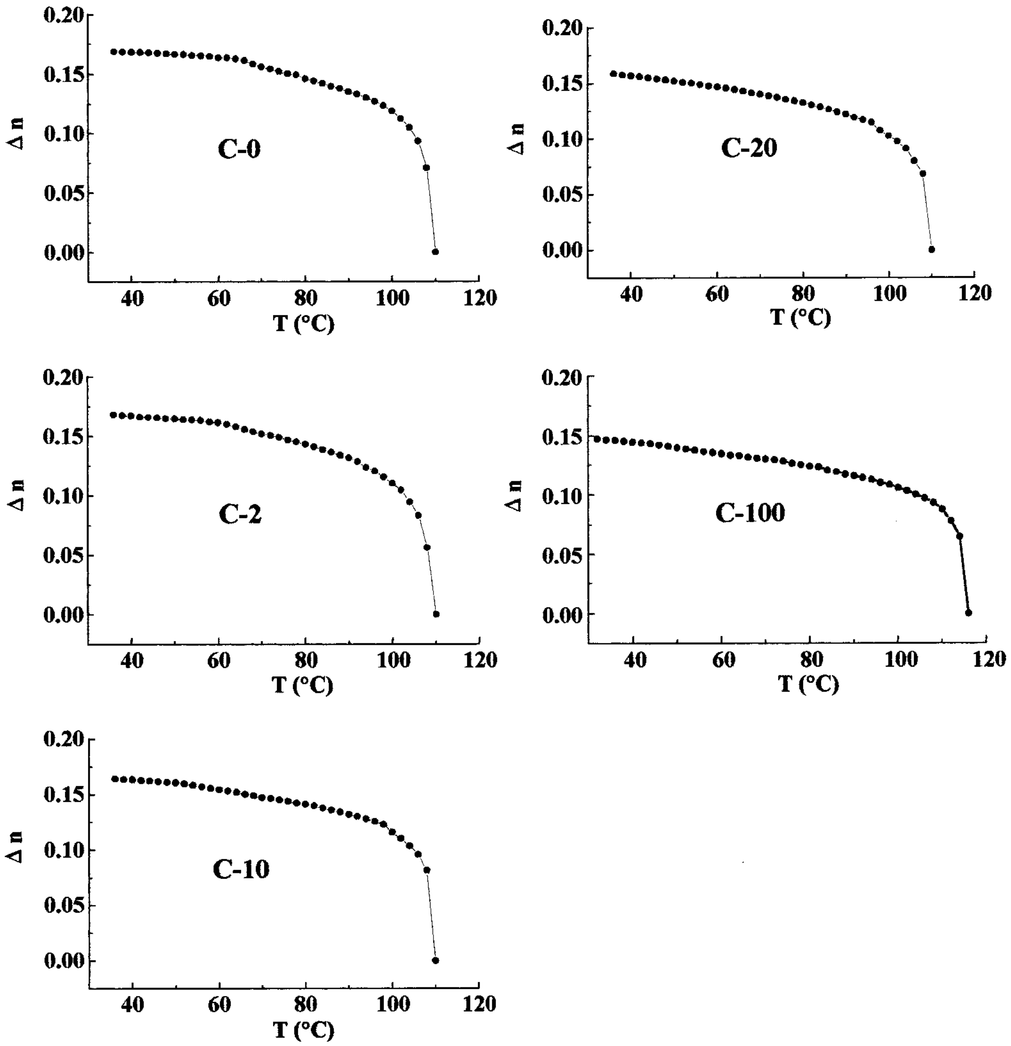

Figure 10. Birefringence of the different monomer mixtures as a function of temperature. Measured at $\lambda = 589$ nm.

The birefringence results corresponding to the different monomeric photopolymerizable samples are given in Figure 9. Δn values (represented by black circles) correspond to maxima and minima of the I versus λ curves (see Figure 8), and solid lines give the fitting using eq 4. The λ_m values are in the 220−250 nm range in all of the samples.

Birefringence measurements were also performed after photopolymerization at 100 °C. The photopolymerization of samples C-10, C-20, and C-100 gave rise to films having a defect-free monodomain structure, as observed by optical microscopy. However, polymeric films derived from samples C-0 and C-2 showed some scattered light associated with a distribution of domains with the director close to the alignment direction of the cells. In the polymeric films derived from C-0, the scattering was too strong to obtain meaningful values for the birefringence and, consequently, was not measured. The Δn values, obtained in a similar way to those of the monomers, are represented as crosses in Figure 9. The dotted line corresponds to the fitting using eq 4, with λ_m values in the same range as those in the monomers. Results of the photopolymerization of C-2 were obtained using a diaphragm to select a single LC domain with planar orientation (a few square millimeters in area).

The results in Figure 9 show that the birefringence of the monomer mixtures measured at 100 °C is the same for all samples, within experimental error. On the other hand, Δn increases in all the samples after the photopolymerization process except for C-100. Similar behavior has been reported[21] for samples photopolymerized at temperatures close to the clearing point. This increase has been tentatively associated with an increase of the order during the polymerization process.

On the other hand, the birefringence of the films increases as the content of [1] increases. This could also be due to a higher degree of order in the films. Dichroism measurements (see below) also show a higher order in samples with a higher content of [1].

The birefringence of the different films was also determined at a fixed wavelength (589 nm) as a function of temperature. The results are shown in Figures 10 and 11 for the photopolymerizable samples and polymers, respectively. In the monomers, a step increase in Δn was observed at temperatures below the clearing point, followed by a slow increase when the temperature was decreased. A small jump was also observed at the transition from the nematic to the smectic A phase in the case of samples C-0 and C-2, with a larger value of

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[21] Kelly, S. M. *Liq. Cryst.* **1998**, *24*, 71.

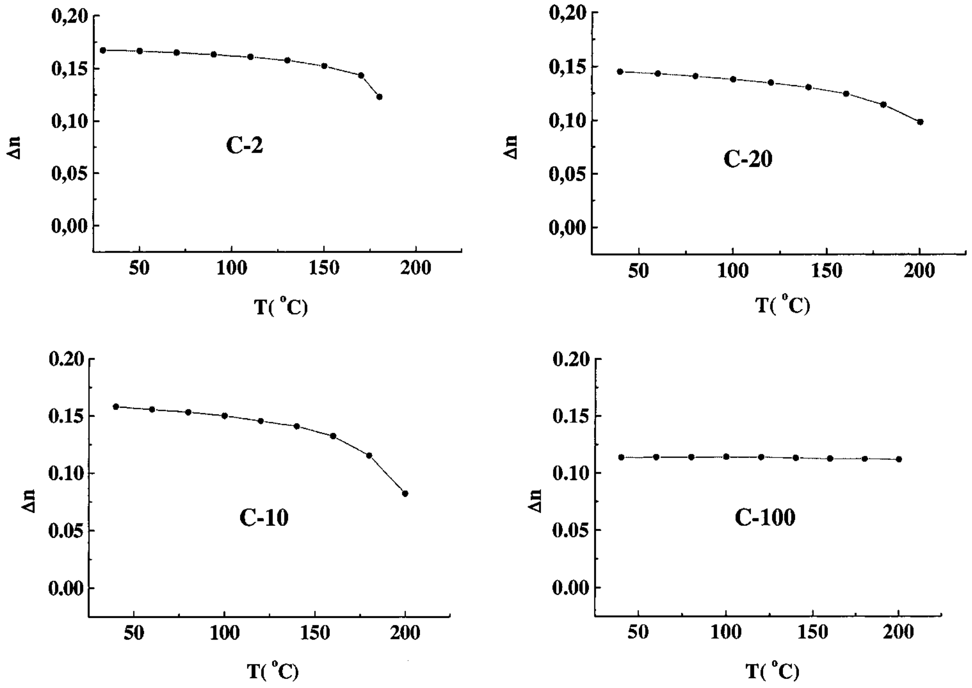

Figure 11. Birefringence of the different polymers as a function of temperature. Measured at $\lambda = 589$ nm. The photopolymerization temperature was 100 °C.

Δn in the smectic A phase. This increase in the birefringence can also be associated with an increase of the molecular order.

In the case of the polymeric films derived from C-2, C-10, and C-20, Δn slowly decreases with increasing temperature and disappears at about 180 °C for the films derived from C-2, whereas in films derived from C-10 and C-20, a decrease in Δn was observed at about 200 °C. This can be related to an increase in the disorder in the system, which is mainly associated with the monofunctionalized [1] molecules. However, light transmission with the samples under crossed polarizers was observed up to temperatures as high as 250 °C. This indicates that some anisotropy remains in the film even at high temperatures. On the other hand, the change in Δn with T is very small in the case of the polymer obtained from C-100, and in this case, the birefringence does not disappear up to 250 °C. This can be understood because the order parameter in the network is only slightly temperature dependent due to the high density of cross-linking of the molecules, which precludes their reorientation. Besides, in the case of the polymers derived from C-2, C-10, and C-20, the birefringence is recovered after annealing at 250 °C, a phenomenon that is associated with the elastomeric properties of these polymers.

Photopolymerization was also performed at 80 and 60 °C, and the birefringence of the monomers and polymers was measured at these temperatures. In the polymeric samples derived from C-2, the scattering was too strong to obtain reliable results. The Δn values corresponding to the other samples at $\lambda = 589$ nm are given in Table 5. It can be seen that on going from the monomer to the polymer the birefringence of the C-10 and C-20 samples shows an increase when the polymerization temperature is 80 or 100 °C. This increase is smaller when the polymerization temperature is 80 °C. Furthermore, the birefringence actually decreases in the polymerization process when it is performed at 60 °C. In polymers derived from C-100, there is a decrease in the birefringence at all the polymerization temperatures, with the decrease being especially marked at low temperatures.

Table 5. Birefringence of the Mixtures of [1] and C6M Measured at the Photopolymerization Temperature for the Monomeric Sample (m) and the Polymer (p)

sample	Δn (100 °C) m→p	Δn (80 °C) m→p	Δn (60 °C) m→p
C-2	0.115 → 0.165		
C-10	0.113 → 0.150	0.143 → 0.155	0.158 → 0.155
C-20	0.114 → 0.141	0.137 → 0.145	0.151 → 0.145
C-100	0.118 → 0.116	0.135 → 0.124	0.144 → 0.130

To check the order parameter of some of the mixtures after the photopolymerization process, the dichroism in the optical absorption spectrum of the NS chromophore incorporated to the C-10-NS and C-95-NS samples photopolymerized at 100 °C was measured. The optical absorption spectra of the two polymers, measured with light polarized parallel and perpendicular to the director, are shown in Figure 12. The dichroic ratio R is related to the order parameter S_2 by the following expression:

$$R = D_{\mathrm{par}}/D_{\mathrm{perp}} = (1 + 2S_2)/(1 - S_2) \qquad (5)$$

where D_{par} and D_{perp} are the optical densities measured with light polarized parallel and perpendicular, respectively, to the orientation direction of the cell. In eq 5, the corrections associated with the local field anisotropy have been neglected. These D-values were corrected from the background absorption, which was measured in films without the chromophore. The dichroic ratio and the order parameter for the C-10-NS and C-95-NS samples are given in Table 6. Under the commonly employed assumption that the order parameter derived from the dichroism of the chromophore is the same as that of the matrix, it can be concluded that the degree

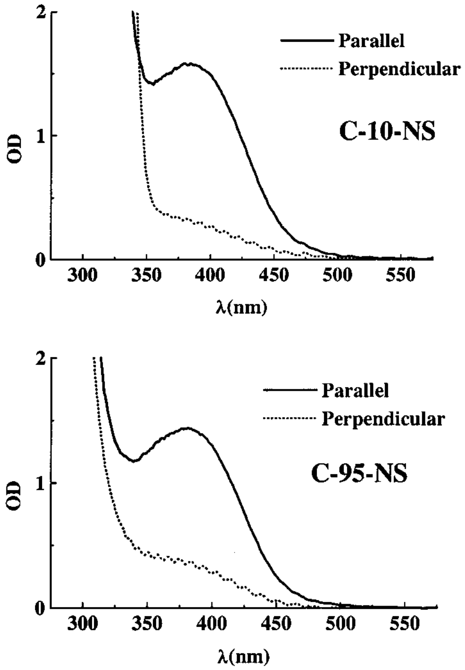

Figure 12. Optical absorption spectra of the C-10-NS and the C-95-NS polymers measured with light polarized parallel (—) and perpendicular (...) to the director.

Table 6. Dichroic Ratio and Order Parameter of Samples C-10-NS and C-95-NS Photopolymerized at 100 °C and Measured at Room Temperature

sample	R	S_2
C-10-NS	8.3	0.71
C-95-NS	5.9	0.62

of order in the C-10 sample is higher than that in the C-100 sample. As stated above, this result is in agreement with those obtained from birefringence measurements.

Summary

Polymeric films with different degrees of cross-linking can be obtained by in situ photopolymerization of samples consisting of mono- and direactive liquid crystals. DSC studies of the in situ photopolymerization provide evidence of a high conversion rate and a high rate of polymerization, which seems to depend on the polymerization temperature and the proportion of cross-linker (C6M). In photopolymerizable samples based on C-0 and those with a low content of C6M (C-2 and C-5), a phase transition occurs during photopolymerization and a S_C mesophase is detected by optical microscopy and X-ray diffraction. Photopolymerized materials with a C6M content higher than 10% seem to behave as polymeric networks.

Oriented films can be processed by controlling the orientation of the monomeric mesophase in which photopolymerization takes place. The birefringence of both photopolymerizable samples and polymeric films has been evaluated, as well as its dependence on temperature. The birefringence of the films increases as the content of the monoreactive naphthalene derivative [1] increases. Dichroism measurements, using a reactive nitrostilbene derivative (NS) as a probe, indicate a higher degree of order in polymeric films having a higher content of [1].

Finally, the dependence of the orientation of the polymers on the temperature was evaluated by X-ray diffraction and birefringence measurements. The results indicate that polymeric films having a low degree of cross-linking have a temperature-reversible orientation.

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Supporting Information Available: Synthesis and characterization of the monoreactive monomers and their optical absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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