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Anisotropic Network Formation by Photopolymerization of Liquid Crystal Monomers in a Low Strength Magnetic Field

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ABSTRACT: Liquid crystalline mixtures of mono- and dimethacrylates were photopolymerized after macroscopic orientation of the monomers under a relatively weak magnetic field or via interaction with a unidirectionally rubbed polyimide substrate. Polymerization kinetics was followed by a thermoanalysis technique, and the transmitted light intensity was measured in real time. The macroscopic order parameter of one of the component comonomers (bearing a cyano group) incorporated into the polymer network prepared under different conditions was evaluated using IR dichroism. The results obtained for the cross-linked polymer network produced under the low strength magnetic field are compared with those for the polymer film produced by surface orientation.

Introduction

Oriented films have many applications resulting from anisotropic physical and optical properties. Consequently, in recent years, there have been a number of papers published dealing with the polymerization of macroscopically oriented liquid crystalline monomers or monomer mixtures.[1-18] In three separate reports,[16-18] it was shown that oriented polymer films could be formed by thermally initiated polymerization of mesogenic monomers in the presence of a low strength magnetic field. In the paper by Perplies et al.,[16] it was clearly demonstrated that rate acceleration of polymerization was only enhanced when higher magnetic field strengths in the range 56–70 kG were employed. Recently, Broer and co-workers,[1-10] Hikmet et al.,[11-14] and Braun et al.[15] in a series of papers demonstrated that highly cross-linked, macroscopically oriented films could be obtained by photoinitiated polymerization of difunctional liquid crystalline (LC) monomers in contact with unidirectionally rubbed thin-film substrates. As a vivid example of these photopolymerization studies, Hikmet and co-workers[13] polymerized a mixture of monofunctional and difunctional liquid crystalline monomers oriented by surface contact with a rubbed polyimide film and demonstrated via infrared dichroism and refractive index measurements that cross-linked, highly oriented films with relatively high degrees of orientation could be achieved. Herein, we compare the photopolymerization process and final optical characteristics of thin polymer films produced by photopolymerization of LC mixtures composed of a difunctional methacrylate and two monofunctional monomers oriented either by contact with unidirectionally rubbed polyimide films or via application of a low power magnetic field.

Experimental Section

All monomers were synthesized by the method of Portugal et al.[19] All products were purified by column chromatography and recrystallized from 2-propanol. 1,1-Dimethoxy-1-phenylacetophenone (Irgacure 651, Ciba Geigy) was recrystallized from ethanol prior to use. Blends of the three monomers and 1 weight % of the photoinitiator were made by dissolving each component in dichloromethane and subsequent evaporation of the solvent. The phase behavior was studied by polarization microscopy and differential scanning calorimetry (DuPont 9900). The LC cell preparation is described in the text.

Polymerization not involving exotherm measurements was carried out on an aluminum block equipped with a heating source and temperature regulation unit. Polymerization exotherms were measured using either a modified Perkin-Elmer DSC-2 or a thin-foil heat flow calorimeter between the aluminum block and the LC cell. A detailed description of the equipment is given elsewhere.[20] Magnetic orientation was induced by placing the LC cell with the heating unit in a low power magnetic field (Alpha Scientific electromagnet with a dc regulated power supply). For each measurement, the LC monomer mixture was first heated to 100 °C for 1 min, ensuring an isotropic state, before quenching to the polymerization temperature under continuous application of the magnetic field. The sample was retained at this temperature for 5 min to allow for stabilization and sample purging by nitrogen prior to UV exposure. A medium pressure mercury lamp with either a 366-nm band-pass filter or a Pyrex filter was used as a light source for photopolymerization. Polarized infrared measurements (16 scans per spectrum) were carried out at room temperature on a Perkin-Elmer Model 1600 FTIR with a wire-grid polarizer at a resolution of 4 cm^{-1}.

In general, transmitted light intensities were determined at 633 nm with a HeNe laser. In each case appropriate references for 100% transmitted light were determined. Percent reflected light intensities in Figures 14 and 15 represent values measured continuously in real time by reflection of a HeNe laser off the bottom of a thin-foil cell with the sample in place. The 100% values were determined for each individual sample prior to polymerization at the given temperature. Samples used for magnetic alignment were 60–70 μm, and samples used for the DSC exotherm measurements were about 160 μm. All other samples used for photopolymerization studies were approximately 10 μm.

Results and Discussion

A. Monomeric Mixture. The primary liquid crystalline monomer mixture investigated was composed of 50 weight % of the difunctional monomer M6P6M, 30% of the monofunctional monomer M66, and 20% of the monofunctional monomer M6CN. A photoinitiator, 1,1-dimethoxy-1-phenylacetophenone (DMPA), at a concentration of 1 weight %, was added to the mixture. The particular mixture of di- and monofunctional monomers was chosen to provide flexible free-standing films after

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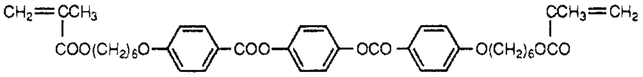
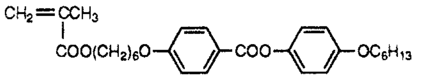
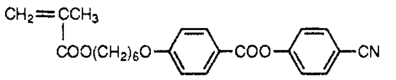
M6P6M



M66



M6CN



the photopolymerization process was complete, thus making it feasible to carry out infrared (IR) dichroism measurements. The M6CN monomer, with the cyano group attached in the para position, served as an orientational probe via infrared dichroism measurements.

The phase transition temperatures and thermodynamic parameters of the three component monomer mixture (with photoinitiator) are given in Table 1, as determined by DSC and polarized optical microscopic analysis. At ~37 °C the mixture melts to a smectic phase (S), followed by conversion to a nematic phase (N) at 66 °C before clearing to an isotropic phase (I) at 89 °C. Both upon cooling to room temperature and on the subsequent second heating, the crystalline state (K) was not observed: The smectic phase is relatively stable at room temperature.

In general, for magnetic field strengths above a threshold level, orientation of domains is possible if the anisotropic diamagnetic susceptibility of the molecular structure comprising the domain is positive. Since anisotropies of the mesogenic group of compounds like M6P6M, M66, and M6CN are mainly determined by the anisotropy of their aromatic rings, their long axes are expected to translate into domain orientation in the direction of the applied magnetic field. In order to assess the effect of the magnetic field on achieving alignment of the mixture in a configuration convenient for the light induced polymerization to be discussed later in this paper, samples (thicknesses of 60–70 μm) were placed on microscope cover slips and the temperature was maintained constant by means of a thermostated aluminum block. The light transmitted through the samples was measured as a function of magnetic field strength. The light source was a polarized HeNe laser, and the transmitted light was analyzed before reaching the detector with a Nicol prism having a polarization axis perpendicular to that of the laser polarization. In the isotropic phase, the system is not birefrigent and thus the polarization direction of the transmitted light is perpendicular to the polarization axis of the Nicol prism. In this case, the transmitted intensity is attenuated before reaching the detector. In the nematic phase the birefringence is nonzero and the polarization direction of the transmitted intensity is rotated relative to that of the incident beam. Hence, polarization components of the transmitted intensity exist parallel to that of the Nicol prism and the light reaches the detector. Figure 1 shows the transmitted polarized light intensity (in terms of relative units) for the three component mixture in the nematic phase under the influence of a magnetic field. The transmitted polarized light intensity started to increase at ~0.1 T and reached a maximum around 0.3 T in the nematic phase. Essentially no transmitted light was observed in the isotropic phase upon application of the magnetic field. The response time of the orientation process was estimated to be less than 10 s for the nematic phase. Such a rapid orientation is much faster than for polymer main chain or side chain liquid crystalline materials, thus making it possible to create rapidly an oriented monomeric medium with a relatively low strength magnetic field (generated by an electromagnet) prior to photopolymerization. This paper deals only with results for magnetic field application to the mixture in the nematic and isotropic phases.

Table 1. Transition Temperatures and Thermodynamic Parameters for the M66/M66M/M6CN Monomer Mixture with a Photoinitiator[a]

1st heating	K	37 °C	S	66 °C	N	89 °C	I
ΔH (J/g)		30.2		0.67		0.93	
ΔS (mJ/(g·K))		97		2.0			
1st cooling			S	62 °C	N	85 °C	I
ΔH (J/g)				0.70		1.08	
ΔS (mJ/(g·K))				1.9		3.0	

[a] Heating/cooling rate of 10 °C/min.

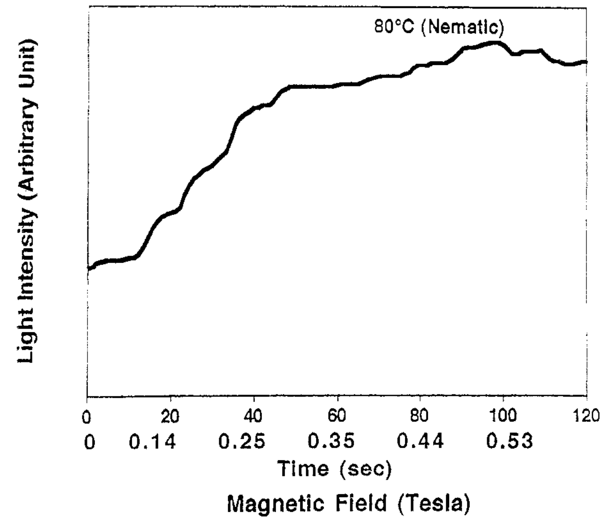


Figure 1. Transmitted HeNe polarized light through a M66/M6P6M/M6CN mixture as a function of magnetic field strength at, 85 °C.

B. Photopolymerization Rates. Before proceeding to the process of an orientational analysis of substituent groups in the polymerized films, the kinetics of the mixture, as well as the individual components, was investigated using a photo-DSC system described previously.[21] In each case, about 2 mg of material was placed in the sample compartment, which was flushed with nitrogen for 5 min. In order to maintain a uniform sample thickness (~160 μm), modified aluminum pans[21] were used. The polymerization was initiated using a medium pressure mercury lamp with a 366-nm band-pass filter (0.024 mW/cm^2).

Time–conversion curves calculated from the heat of polymerization for M6P6M (K61S76N132I) and M66 (K48S51N57I) containing 1 weight % DMPA (1,1-dimethoxy-1-phenylacetophenone), as well as the three component mixture, at 80 °C are shown in Figure 2: Characteristic polymerization kinetics are demonstrated by each of the three samples. A rapid initial instantaneous increase of conversion was observed for M6P6M, a difunctional monomer, due most likely to early gel formation followed by cessation of the reaction at 50–60% conversion. This Trommsdorff-like phenomenon is typical for conventional difunctional methacrylate or acrylate monomers and has been observed for polymerization of difunctional LC monomers by Broer et al.[5] In the case of M66, which is isotropic at 80 °C, a rapid increase in conversion and a corresponding sudden acceleration of the reaction at a conversion of about 30–40% were observed. This can be explained by a phase transition induced acceleration upon conversion to a medium with

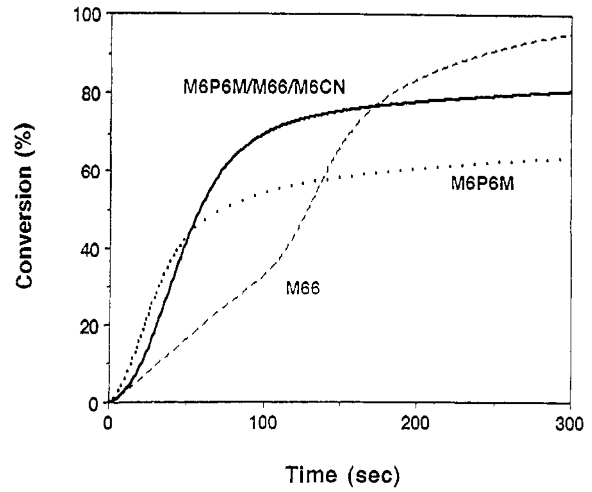


Figure 2. Percent conversion versus time plots for photopolymerization of the M66/M6P6M/M6CN mixture, M66, and M6P6M at 80 °C using a medium pressure mercury lamp (λ_{ex} = 366 nm; I = 0.024 mW cm^{-2}).

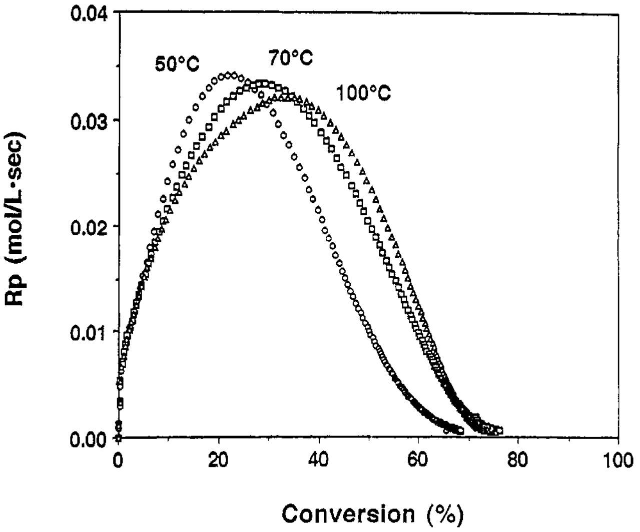


Figure 3. Polymerization rate (R_p) versus percent conversion for photopolymerization of the M66/M6P6M/M6CN mixture at 50, 70, and 100 °C using a medium pressure mercury lamp (λ_{ex} = 366 nm; I = 0.024 mW cm^{-2}).

a polymer-rich smectic phase during the course of polymerization. A detailed study of this monomer, which is characterized by phase separation between the monomer and polymer during polymerization, is described elsewhere.[22] The three component mixture shows an intermediate rate behavior between the monofunctional and difunctional monomers. An autoacceleration, which begins in the early stages of the polymerization process of the mixture, leads to a reaction with ultimate conversion of about 80%.

The temperature dependence of the kinetics of polymerization of the three component mixture has been investigated, and the calculated polymerization rates at different temperatures as a function of conversion are shown in Figure 3. The polymerization initiated from three different phases [smectic at 50 °C, nematic at 70 °C, and isotropic at 100 °C] showed no large (at least under the dictates of the experimental conditions) differences in the initial rate for the three temperatures at less than 10% conversion. Figure 4 shows a plot of k_t/k_p versus percent conversion at 50 °C as determined by an exotherm decay method:[14] The k_t/k_p ratio decreases significantly with conversion. A preliminary kinetic analysis at higher temperatures also indicates that a decrease in the k_t/k_p ratio with conversion occurs. Finally, returning to Figure 3, we note that an ultimate conversion of about 65–70% was attained for the polymerization at 50 °C compared to ~75% conversion at 70 and 100 °C. The lower ultimate conversion at 50 °C could well be due to the T_g of the polymer surpassing the polymerization temperature at 50 °C. This supposition is supported by DMA measurements of polymerized films (high conversions) of the mixture which show glass transitions around 70 °C.

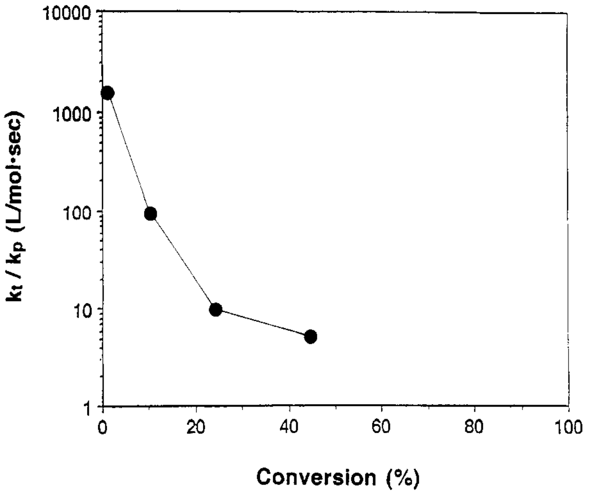


Figure 4. k_t/k_p ratio versus percent conversion for photopolymerization of the M66/M6P6M/M6CN mixture at 50 °C (no orientational field applied).

C. Surface Orientation Effect. For comparison with the results for magnetic alignment to be discussed in the next section, orientation of the three component mixture was induced by a surface effect, followed by photopolymerization. We know from the detailed work of Broer et al.[5] that relatively highly oriented cross-linked networks can be produced by photopolymerization of LC monomers between unidirectionally rubbed polyimide coated glass surfaces. In the present case, we polymerized our macroscopically oriented LC mixture (surface contact with a rubbed polyimide film) for comparison with the results from the magnetic field induced orientation. The LC mixture was sandwiched between two polyimide coated microscopic cover glasses which were repeatedly rubbed in one direction. To maintain a constant cell gap, a small amount of glass beads, which had 10-μm diameters, was added to the sample. The sample cell was heated to above the clearing temperature, then placed on a thermostated aluminum block, and cooled at a constant rate to the polymerization temperature. A high degree of orientation with respect to the rubbing direction of the monomer mixture was observed in both the nematic and smectic phases via polarized optical microscopy. Polymerization was initiated by irradiation with a medium pressure mercury lamp through a Pyrex glass filter. Figures 5 and 6 show the polarized FT-IR spectra of polymerized samples at 75 °C. At least some nematic-type order, as identified by optical microscopy, was maintained in both cases in the cross-linked films. The film in Figure 5 was not oriented (the polyimide base coating was not rubbed): Accordingly, the polarized infrared absorption spectra are independent of the angle of the polarized infrared light source (see Figure 5a,b). When the base coat polyimide was unidirectionally rubbed, there was a marked difference between the polarized infrared spectrum in the direction of the film orienation and the spectrum recorded with the infrared light source polarized 90° to the orientation direction (see Figure 6a,b). This is especially prominent for the cyano stretching band at 2227 cm^{-1} (due exclusively to M6CN monomer incorporated into the polymer network during polymerization) expanded in the insets in Figure 6. Figure 7 shows plots of the band absorbance ratio versus

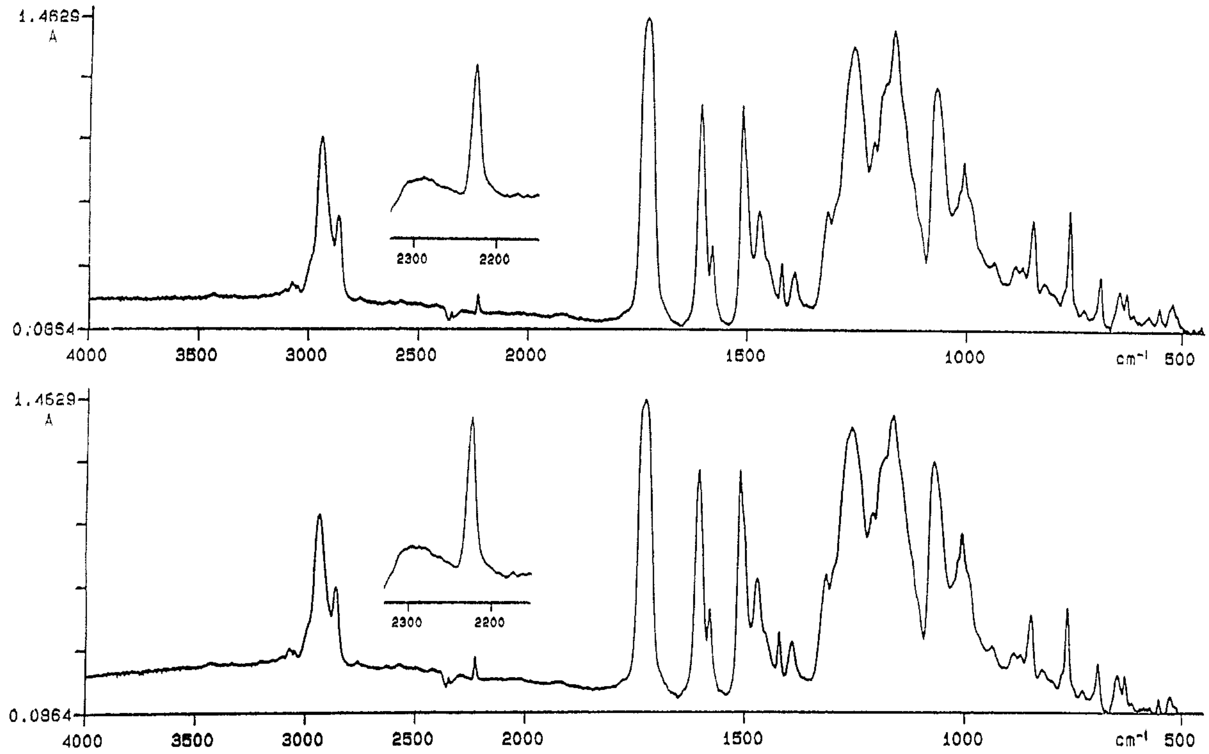


Figure 5. IR dichroism for the network generated by photopolymerization of M66/M6P6M/M6CN at 75 °C in contact with polyimide films (not unidirectionally rubbed).

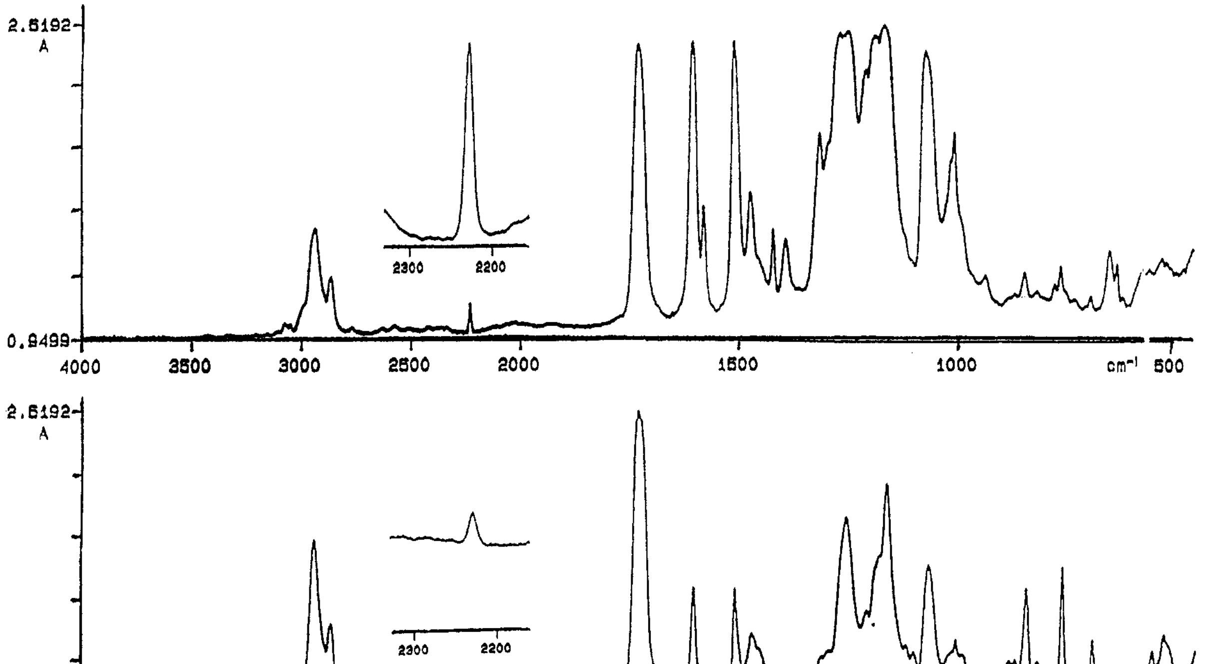


Figure 6. IR dichroism for the network generated by photopolymerization of M66/M6P6M/M6CN at 75 °C in contact with unidirectionally rubbed polyimide film.

the infrared polarization angle from 0 to 90° for several characteristic bands. The absorbances at 1606 cm^{-1} (assigned to a stretching band of the phenyl ring), 1256 cm^{-1} (assigned to a C–O–C ester stretching bond), and 2227 cm^{-1} (cyano stretching) decreased continuously as the polarization angle increased from 0 to 90°. On the other hand, the absorbances at 847 cm^{-1} (assigned to an out of plane vibration of phenyl hydrogen atoms) and at 2937 cm^{-1} (assigned to a C–H stretching frequency of the hydrocarbon chains) increased to varying extents as a function of the polarizer angle. The absorption intensity of the bond at 1731 cm^{-1}, assigned to carbonyl stretching, was independent of the polarizer rotation angle. The results in Figure 7 clearly indicate a marked degree of alignment of mesogenic groups in the direction of rubbing in the photo-cross-linked networks. Interestingly, not only the orientation of the mesogenic groups but also some minor, but observable, orientation of the hydrocarbon groups in the direction of rubbing are suggested by the results for the absorption at 2937 cm^{-1}.

In this paper, we analyze oriented films that are produced by both surface contact and magnetic field application (to be discussed) methods using IR dichroism to measure the ordering of the M6CN groups which are

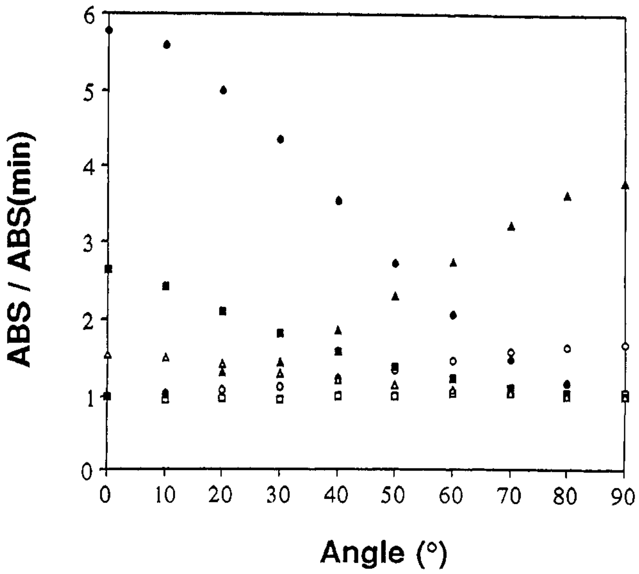


Figure 7. Plot of the ratio of IR absorbance/minimum IR absorbance versus IR beam angle for several characteristic IR bands of groups in the network generated by photopolymerization of M66/M6P6M/M6CN at 75 °C in contact with unidirectionally rubbed polyimide film. Key: (○) 2937 cm^{-1}; (●) 2227 cm^{-1}; (□) 1731 cm^{-1}; (■) 1606 cm^{-1}; (△) 1256 cm^{-1}; (▲) 847 cm^{-1}.

incorporated into the polymer network. The order parameter, P_2, as defined by eq 1, is related to the infrared

$$P_2 = 3(\langle \cos^2 \theta - 1 \rangle)/2 \qquad (1)$$

$$P_2 = \frac{(R_o + 2)(R - 1)}{(R_o - 1)(R + 2)} \qquad (2)$$

absorbances parallel and perpendicular to the direction defined by the magnetic field or rubbed direction of the polyimide film using eq 2, where θ is the angle between the long axis of the M6CN moiety in the network and the field direction[23] and

$$R = \frac{A_0}{A_{90}}$$

$$R_o = 2 \cot^2 \alpha$$

A_0 = absorbance at an angle of 0°

A_{90} = absorbance at an angle of 90°

α = angle between the axis of the mesogen and the transition moment of the cyano IR absorption band (11° according to ref 23)

We chose to utilize the cyano transition of the M6CN group at 2227 cm^{-1} in the IR to illustrate, by example, the relative extent of macroscopic orientation achieved by the network in contact with the unidirectionally rubbed polyimide film. As specified herein by eq 2, the order parameter, P_2, is an average macroscopic property (see ref 23) exhibited by the M6CN groups and, in our case, is controlled by the alignment of nematic-type domains composed of three components: M66 moieties, M6P6M groups, and the M6CN chromophores themselves.

Table 2. Order Parameter and Transparency of Anisotropic Networks Obtained by Surface Treatment

polymerization temp (°C)	P_2[c]	transmitted light intensity[d] before	after
50 (smectic)[a]	0.48	~100	89
75 (nematic)[a]	0.65	~100	98
75 (nematic)[b]	0.06	~90	83
120 (isotropic)[a]	0.02	100	100

[a] Placed between uniaxially rubbed polyimide films spin coated onto Pyrex cover glasses. [b] Placed between polyimides films (not uniaxially rubbed) spin coated onto Pyrex cover glasses. [c] Values for the M6CN moiety in an oriented network. [d] Intensity for the isotropic taken as 100% value for reference.

Table 2 shows the P_2 values for the network M6CN groups obtained by use of eq 2 and the intensity of light transmitted through the cross-linked films obtained by polymerization of the three component mixture in contact with rubbed polyimide surfaces at several temperatures. The transmitted light intensity of a HeNe laser beam (λ = 633 nm) was measured for 10-μm thickness films before and after polymerization. Analysis of the polymer produced from the nematic phase gives a P_2 value of 0.65, while that generated from the smectic phase gives a lower value (P_2 = 0.48). [The film produced by polymerization from the isotropic phase exhibited essentially no order for the M6CN groups (P_2 = 0.02).] The percent light intensity of the 633-nm laser beam transmitted also decreased after polymerization from the monomeric smectic phase at 50 °C. The lower value of P_2 obtained from the film produced from the smectic phase of the monomer mixture and the decreased transparency suggests that a general disordering may take place during the polymerization process. It is possible that shrinkage during the polymerization destroys the layer structure originally in the monomeric smectic phase to some extent. Finally, we found that polymerization exotherms (not shown) monitored by a thin-foil heat flow sensor attached between the sample and a heated aluminum block showed no significant difference between the sample in contact with the rubbed and nonrubbed polyimide substrate, indicating that macroscopic alignment via surface interaction does not significantly alter, within our ability to measure, the polymerization kinetics.

D. Magnetic Field Effect. Anisotropic networks can also be prepared by photopolymerization of the liquid crystalline monomer mixture under the influence of a low strength magnetic field. About 3 mg of the monomer mixture was spread to give a uniform 60–70-μm film on a glass cover slip previously coated with an unrubbed thin polyimide film. The sample was then placed in a low strength magnetic field, 0–0.6 T, throughout the polymerization process. The temperature of the sample was held constant by a thermostated aluminum block. The sample was purged in nitrogen for 5 min prior to polymerization and then exposed to the Pyrex-filtered output of a medium pressure mercury lamp. The polymerization was monitored via exotherm measurement to ensure that a high degree of polymerization was achieved in each case.

In an initial experiment, a sample was polymerized at 79 °C from the nematic phase of the mixture to generate a cross-linked, oriented film while a magnetic field of 0.53 T was applied. A control film was also produced in the absence of any applied magnetic field. The angle between the orientation direction and the analyzing infrared source was varied between 0 and 90° in order to assess the magnitude of the orientation of the M6CN groups with respect to the direction of the applied magnitude field used in production of the polymerized films. Figure 8 shows a plot of the absorbance of the cyano group at 2227 cm^{-1} versus the infrared polarization angle. Results for the film produced with the magnetic field showed a greater angle dependence of cyano band absorbance than those for network films generated without the magnetic field applied. Since the orientation of liquid crystalline materials varies with temperature and applied magnetic field

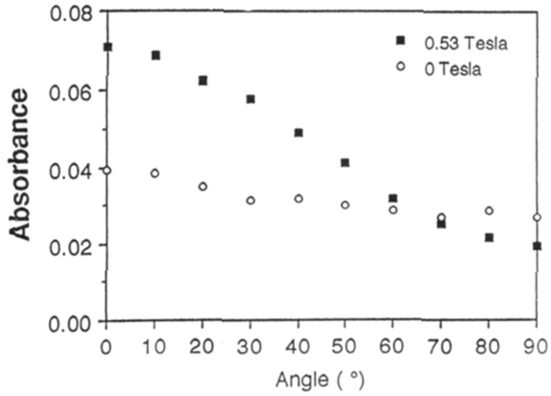


Figure 8. Absorbance of the IR band at 2227 cm^{-1} (C≡N stretching of M6CN group) for the network obtained by photopolymerization of the M66/M6P6M/M6CN mixture at 75 °C with a medium pressure mercury lamp (I = 1.3 mW cm^{-2}) in the absence and presence of a 0.53-T magnetic field.

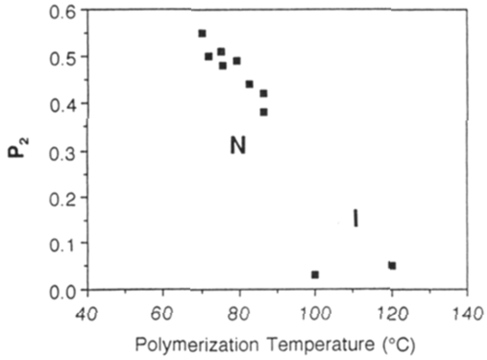


Figure 9. P_2 value obtained for photopolymerization in the presence of a 0.53-T magnetic field, as described in Figure 8, as a function of polymerization temperature.

strength, the values of P_2 obtained from the resultant polymer networks formed by photopolymerization of monomer mixtures subjected to a magnetic field are expected to depend on such factors. The effect of the polymerization temperature on the samples produced while a 0.53-T magnetic field is being applied is shown in Figure 9, where the P_2 order parameter determined by IR dichroism of the M6CN groups and equation 2 is plotted as a function of polymerization temperature in the nematic and isotropic phases. It can be seen that the alignment originally induced by the magnetic field in the monomeric mixture in the nematic phase is frozen into the polymer network, as exhibited by the P_2 order parameter of the M6CN groups. The orientation level is markedly affected by the polymerization temperature. Maximum ordering of the M6CN moieties (P_2 = 0.55) is observed at 65 °C, just above the smectic–nematic transition temperature of the original monomeric mixture. This probably reflects the large carryover of the alignment induced in the nematic phase of the monomeric mixture prior to polymerization. In summary, we project, on the basis of the results obtained for the M6CN groups polymerized into the network from the magnetically aligned nematic monomer mixture, that photopolymerization is capable of locking in relatively high orientation in the cross-linked polymer film with low strength magnetic fields. A similar result was obtained by Clough et al.[18] for thermal polymerization of a different liquid crystalline mixture at high temperatures to give cross-linked, oriented films.

Before continuing with additional IR dichroism analysis, we should note that the small angle X-ray analysis of the cross-linked film polymerized at 75 °C with the magnetic field applied showed both sharp meridional peaks as well as diffuse equatorial arcs, thus confirming significant orientation in the direction of the applied magnetic field. A layer spacing of approximately 40.0 Å is calculated from the integration of the meridional peaks of the X-ray diffraction pattern. This value is consistent with a layer structure characterized by a density fluctuation in the film. The equatorial arcs indicate an intermolecular spacing of about 4.3 Å. Similar X-ray diffraction patterns exhibiting a layer structure for cross-linked oriented networks generated from polymerization of aligned mixtures achieved via surface induced orientation have been described in the literature.[13,18]

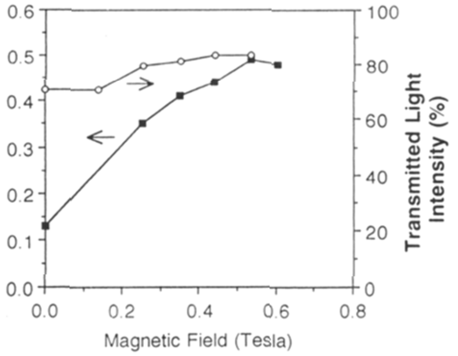


Figure 10. Plots of P_2 and network transmitted light intensity (%) obtained by photopolymerization of the M66/M6P6M/M6CN mixture at 75 °C while applying a magnetic field with the strength as indicated on the x-axis.

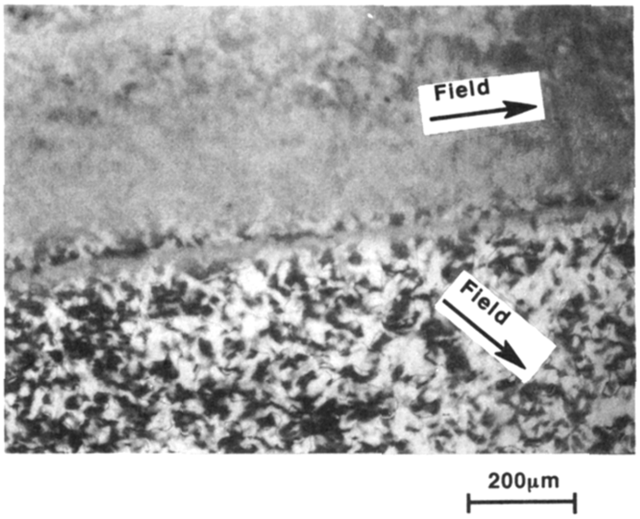


Figure 11. Polarized optical micrograph of an anisotropic cross-linked network obtained by photopolymerization of the M66/M6P6M/M6CN mixture at 75 °C through a cutoff mask while applying 0.53-T magnetic field (two directions consecutively).

The effect of the magnetic field strength on the orientation of the polymer network was investigated using IR dichroism of the cyano band to calculate P_2 for the M6CN groups in the network. P_2 values for the polymer network formed at 79 °C via photopolymerization of the three component mixture plotted as a function of the applied magnetic field in Figure 10 reached a plateau of 0.49 at around 0.5 T. Interestingly, the percent transmitted light intensity (Figure 10) of the polymerized film, determined with a HeNe laser, shows that the relative amount of light transmitted through the film increases dramatically as the applied magnetic field strength increases, suggesting that indeed nematic domains appear to align as the field strength increases.

Figure 11 shows the polarized optical micrograph of an anisotropoic network produced while applying a low strength magnetic field of 0.53 T. Two different regions, one brighter than the other, are observed corresponding

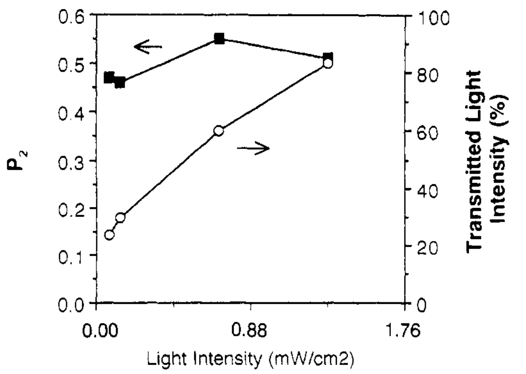


Figure 12. Plots of the order parameter and transmitted light intensity of network obtained by photopolymerization of the M66/M6P6M/M6CN mixture at 75 °C as a function of mercury light intensity (through Pyrex).

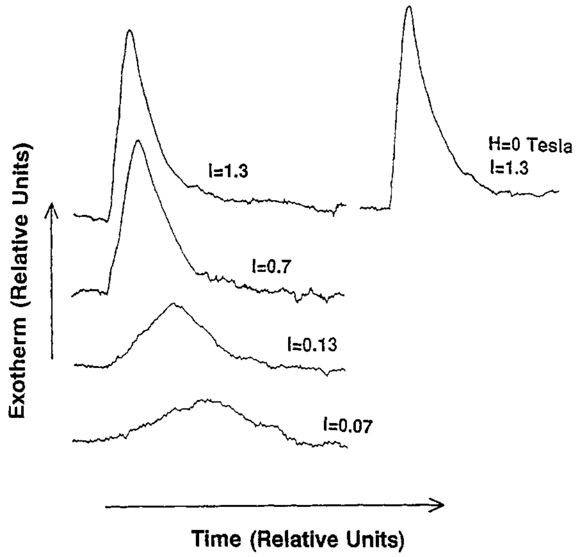


Figure 13. Exotherm curves for photopolymerization in a thin-foil exotherm unit of the mixture of M66/M6P6M/M6CN at 75 °C as a function of filtered (Pyrex) mercury light and applied magnetic field (in the case of highest light intensity).

to switching of the direction of the applied magnetic field during UV exposure (mercury lamp, 10.5 mW cm^{-2}) through a photomask. The direction of the applied magnetic field is noted in the figure caption. Examination of the micrograph in Figure 11 reveals that orientation is frozen into the cross-linked network in the direction of the applied magnetic field to generate a pattern reflective of the orientation at the instant of polymerization.

Figure 12 shows quantitative results of the effect that the polymerization light intensity has on both the P_2 values and the percent light transmitted through the films as a function of temperature (observed upon cooling the polymerized films to room temperature). In spite of a reduction in the transmitted light intensity of the film produced with low light intensity, the value for P_2 did not change. The low amount of light transmitted results from crystallization of residual monomer which did not react under low light intensity irradiation; i.e., a lower degree of conversion is obtained when the polymerization is induced with low light intensity. This is confirmed by the results in Figure 13, which show exotherm curves measured by a thin-foil exotherm unit during the polymerization using various light intensities to initiate the process. We also show exotherm results in Figure 13, for comparison, for polymerization of the mixture at the same temperature in the absence of the applied field: As in the case of the surface oriented samples, we see no appreciable effect on the rate when the sample is oriented by the low field strength magnetic field applied during polymerization.

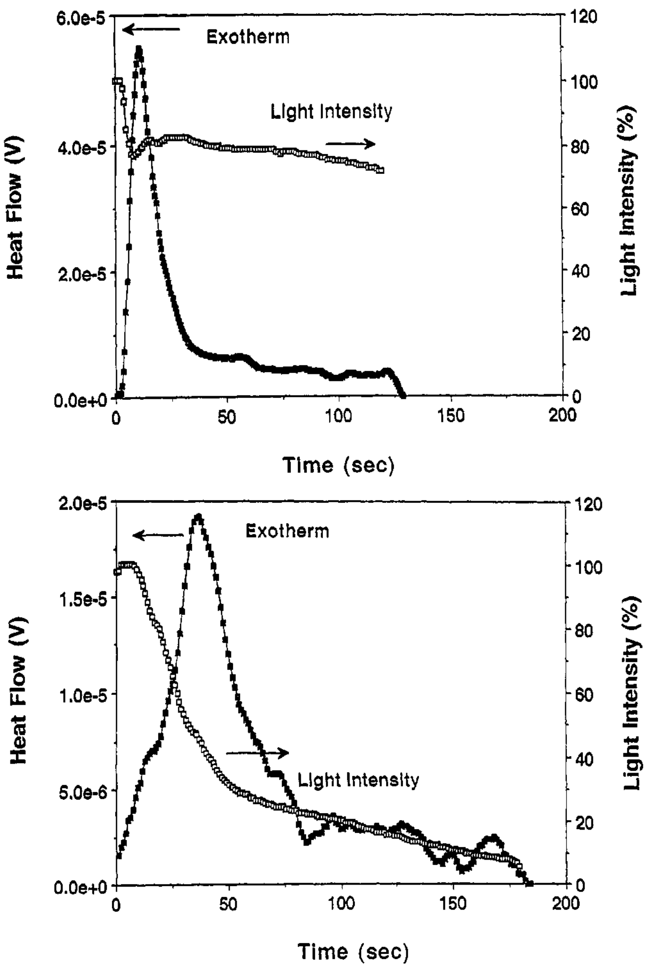


Figure 14. Exotherms (thin-foil unit) and reflected light intensity versus photolysis time for photopolymerization mixtures using a Pyrex filtered medium pressure mercury lamp (I = 1.3 mW cm^{-2}) at (a) 75 °C, M66/M6P6M/M6CN mixture, and at (b) 51 °C, M66/M6CN mixture, while applying a 0.53-T magnetic field.

E. Role of Difunctional Monomer in Film Properties. In this section we focus on the significance of the role of the difunctional monomer in the properties of films produced under the magnetic field. We have recently found that phase separation of M66 readily occurs during the course of polymerization of M66.[22] Such a phenomenon causes structural disorder that can affect the final optical property of the resultant films (scattering of light occurs). The question arises as to the effect of the difunctional monomer on the phase separation normally seen for M66 at all temperatures regardless of the initial phase of the monomer. Figure 14 shows simultaneously the polymerization exotherm and the transmitted light intensity of a HeNe laser during the polymerization of the M6P6M/M66/M6CN mixture (Figure 14a) as well as a 80:20 mixture of M66 and M6CN while a 0.53-T magnetic field is applied at 75 and 51 °C, respectively (both mixtures are in their respective nematic phases). In the case of the monofunctional monomer mixture (M66/M6CN), the reflected light intensity decreased continuously during the polymerization process (Figure 14b). For the trimolecular mixture (M66/M6CN/M6P6M) (Figure 14a) containing the difunctional monomer, however, the amount of reflected light intensity decreases only modestly. The limited decrease in reflected light intensity which does occur happens at the initial stage of the polymerization of the M66/M6CN/M6P6M mixture. Apparently, extensive phase separation does not take place when M6P6M is present and a cross-linked network is formed.

To illustrate the response of the phase separation in the

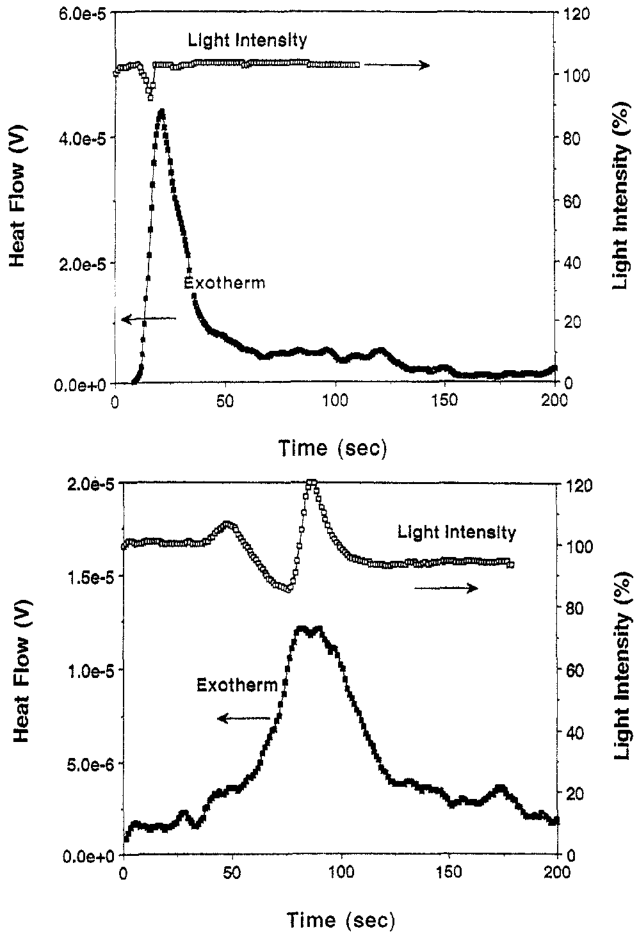


Figure 15. Exotherms (thin-foil) and reflected light intensity versus photolysis time for photopolymerization of the M66/M6P6M/M6CN mixture using a Pyrex filtered mercury lamp (I = 1.3 mW cm^{-2}) at (a) 75 °C, M66/M6P6M/M6CN mixture, and at (b) 51 °C, M66/M6CN mixture, for a system between unidirectionally rubbed polyimide films.

M66/M6CN system when in contact with a unidirectionally rubbed polyimide surface, the same experiment was conducted on the monomer mixtures aligned by contact with a rubbed polyimide film: Figure 15 shows the results for the M66/M6CN and M66/M6CN/M6P6M systems. In both cases, the reflected light intensity remains at almost the initial level, despite some fluctuations for the M66/M6CN mixture at intermediate conversions. [Interestingly, the appearance of the final film prepared from the M66 and M6CN monofunctional monomers was transparent and the P_2 values for the M6CN groups in the film generated were estimated as 0.58 by IR dichroism using eq 1.] The results in Figure 15 indicate the role of the surface in maintaining the uniform orientation of the monomer mixture which was induced prior to polymerization. Apparently, the structural disordering produced by phase separation during the polymerization of M66 and M6CN can be rapidly overcome by the influence of the surface orientation effect. Of course, as exhibited in Figure 15a, when M6P6M is present, there is almost no fluctuation in the reflected light intensity during polymerization since, as already discussed for the results in Figure 14, phase separation is limited during the course of formation of the cross-linked network.

Conclusion

Monofunctional and difunctional liquid crystalline monomers were synthesized and a three component mixture was photopolymerized under the influence of either a low strength magnetic field or surface orientation. The cross-linked networks formed exhibit optical anisotropy if the polymerization is initiated from the monomeric nematic phase with the magnetic field in the range from 0.3 to 0.6 T. The maximum orientation of nematic type ordering with respect to the field direction obtained for a cyano bearing IR probe group (M6CN) incorporated into the network was obtained when the polymerization was conducted at 65 °C, just above the transition temperature from the smectic to the nematic phase of the monomer mixture. This indicates that initial monomer orientation under the weak magnetic field (0.53 T) can be fixed by photopolymerization in the liquid crystalline temperature range. We have also demonstrated the formation of oriented patterns in a polymer film, a phenomenon potentially useful for optical imaging, recording, or other applications. The rapid cross-linking inherent to the difunctional monomer plays an important role in preventing phase separation during the course of polymerization. There is little question that the difunctional monomer is indispensable in maintaining the orientation of the final films produced, particularly in the case of low strength magnetic field application.

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