Thermal Behavior and Laser Marking of a Novel Nematic Liquid Crystalline Polymer

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SYNOPSIS

The thermal behavior and laser marking of a novel nematic liquid crystalline polymer is explored in this report. The glass transition and mesophase transition temperatures of this material are at 45 and 68°C, respectively, and allow the ready annealing of the nematic phase as well as conversion of the nematic to the isotropic phase by pulsed laser irradiation of metallized or dyed films of the polymer.

INTRODUCTION

The appearance of optical recording as an alternative to magnetic recording has been accompanied by the development of media in which to encode the optical information. While the first media to be developed for this purpose were thin metal films, organic materials have subsequently proven themselves to be useful, particularly for write-once recording.[1] Erasable organic media have seen less development.

Among the classes of candidate erasable media are polymers with mesogenic side chains. In general, films of such materials are prepared for writing by the application of an external electric field to effect molecular alignment. Upon the absorption of laser radiation, this alignment is disrupted and the resultant change in optical properties can be detected as a recorded mark. An early demonstration of this concept was by Shibaev and co-workers,[2] using a polyacrylate having a cyanobiphenyl ether nematic side chain. Laser irradiation of the homeotropically aligned material resulted in the formation of scattering centers that were stable below T_g. Similarly, Coles and Simon were able to do laser writing in dyed films of smectic side chain polysiloxane liquid crystals.[3] Writing was possible in either the homeotropically aligned or scattering textures as a result of material flow along the temperature gradients produced by the laser beam. These marks were stable below T_g but could be erased by either heat or electric field.

A combination of photochemical and thermal effects was used by Eich and co-workers[4] to effect birefringent writing in a polymer having mesogenic cyanoazobenzene ether side chains. Writing was done with linearly polarized green (514 nm) light, and reading of the resultant birefringent pattern was done using 633-nm light whose polarization was 45° to that of the writing beam. Presumably heating of the polymer film above T_g together with *cis–trans* isomerization of the azo linkage resulted in a change of molecular orientation that was frozen in upon cooling. Total erasure with no degradation was achieved by heating to the isotropic phase in an electric field.

The requirement for application of an external electric field is a disadvantage for a practical optical recording medium. A preferable system would be one in which mesophase transitions could be induced by laser irradiation alone. Thus, in a manner analogous to inorganic phase change media, writing might be effected by irradiating the material in its liquid crystalline phase with a short laser pulse so as to convert it to its isotropic phase. Rapid cooling of the thin film would freeze in the isotropic phase. A small temperature interval between T_g and clearing temperature would be expected to aid in quenching the isotropic state. Erasure would be effected by local laser heating to a temperature between T_g and clearing temperature. Reading of the recorded bits would be by the optical changes that accompany the

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phase transitions. It is with this background that our interest in organic optical recording media led us to examine the thermal behavior and laser marking response of a novel nematic liquid crystalline polymer.

EXPERIMENTAL

Synthesis

The synthesis of poly(6-[4-nitrobiphenyloxy]-hexyl)methacrylate (I) has been described elsewhere.[5] For convenience, this material is referred to in this communication as HCC-161. A copolymer designated HCC-166C was made by the same procedure.

Samples were prepared for testing by coating onto glass from solutions containing 12.5 and 25 wt % HCC-161 in trichloropropane. A Headway spin coater was used to coat samples, the spin rate controlling the final sample thickness. After coating, the samples were dried under partial vacuum at 90°C for 4 h, then annealed at atmospheric pressure at 60°C for 48 h. Thicknesses of the coated films were measured using a Dektak surface profilometer and were in the range of 0.43–4.8 μm. A plot of film thickness versus spin rate is shown in Figure 1. The relation of thickness t to spin rate ω is given by the equation

$$t = k\omega^{-b}$$

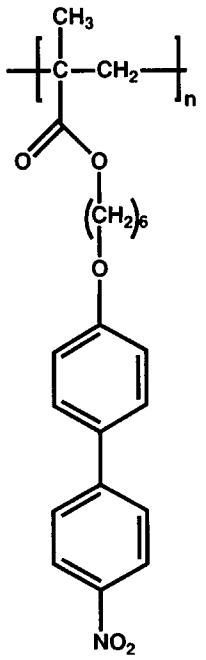
where the value of the exponent was found to be 0.58, in reasonable agreement with the theoretical value[6] of 0.5.

Thermal-optical analyses were carried out using a Mettler FP80 with the photometer placed in one ocular tube of a Leitz polarizing microscope. For pulsed laser irradiation experiments, a simple test rig, schematically shown in Figure 2, was used. By means of this device it was possible to vary both pulsewidth and power (up to 10 mW) delivered to the sample from the 830-nm diode laser. A low-power read beam was used to interrogate the sample before and after exposure of the sample. The difference in light intensity reflected from the surface of the sample before and after irradiation reveals marking of the sample.

RESULTS AND DISCUSSION

Examination of HCC-161 by differential scanning calorimetry (DSC) revealed its glass transition temperature at 45°C and the nematic to isotropic transition at 68°C. The mesophase transition temperature of 68°C was confirmed by hot stage microscopy. At this temperature the material went from a cloudy, scattering texture to a clear texture. If the sample was removed from the hot stage at a temperature above 68°C and cooled quickly by placing it on a cool surface, the isotropic phase was quenched, and the nematic phase did not reform on extended standing but could be recovered upon annealing overnight at 60°C. The optical density change that occurred at the clearing temperature was quantified by thermal-optical analysis (TOA). With a sample of HCC-161 having a thickness of 4.8 μm and using bright-field optics, the increase in transmitted light intensity at the clearing temperature was 43%. The phase transition was even more easily seen using crossed polarizers, in which case an annealed (nematic) sample was bright with fine texture and became dark at the clearing temperature. The transmitted light intensity above 68°C was only 5% of that for the sample in the nematic phase. Thinner samples showed less pronounced changes in transmitted light intensity.

The isotropic to nematic transition was also examined by TOA using samples coated on glass slides at a thickness of 3.3 μm and annealed for 68 h at 60°C. These samples were placed on the microscope hot stage between crossed polarizers and the transmitted light intensity monitored photometrically. In



Structure I

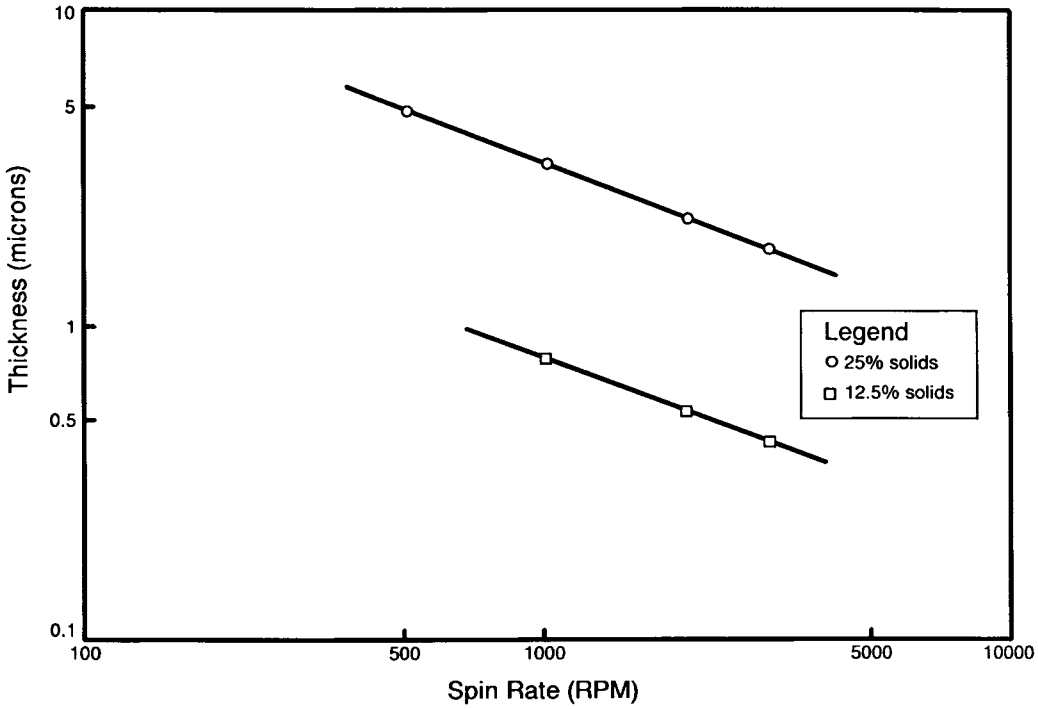


Figure 1 Film thickness as a function of spin coating speed for HCC-161 solutions.

two separate runs the samples were heated at 1°C/min from 40 to 70°C in order to convert them to the isotropic state and then let cool to a temperature between the clearing and glass transition temperatures. In one case the sample was held at 60°C, in the other at 65°C. The results of this experiment are summarized in Figure 3 where the temperature ramp–cool–hold sequence is shown. In both cases the nematic to isotropic transition occurred rapidly, while the reverse occurred much more slowly, and the initial degree of ordering was not achieved after one hour of annealing. The initial rate of recovery was faster for the sample held at 65°C, but leveled off sooner and at a lower level than the sample held at 60°C. The TOA data may be used in a first-order kinetic treatment to estimate the rates of annealing at the two temperatures. When this is done, a half-life for the recovery of the nematic phase is obtained: 546 s for annealing at 60°C and 311 s at 65°C.

TOA experiments on the material revealed some effects of thermal history on its ability to be cycled. Replicate samples were coated on glass slides and observed by hot stage microscopy with crossed polarizers, using transmitted light intensity as a mea-

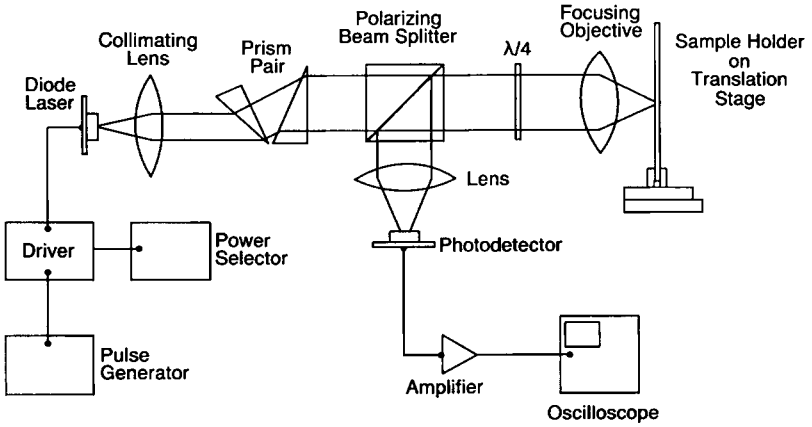


Figure 2 Schematic of static media tester.

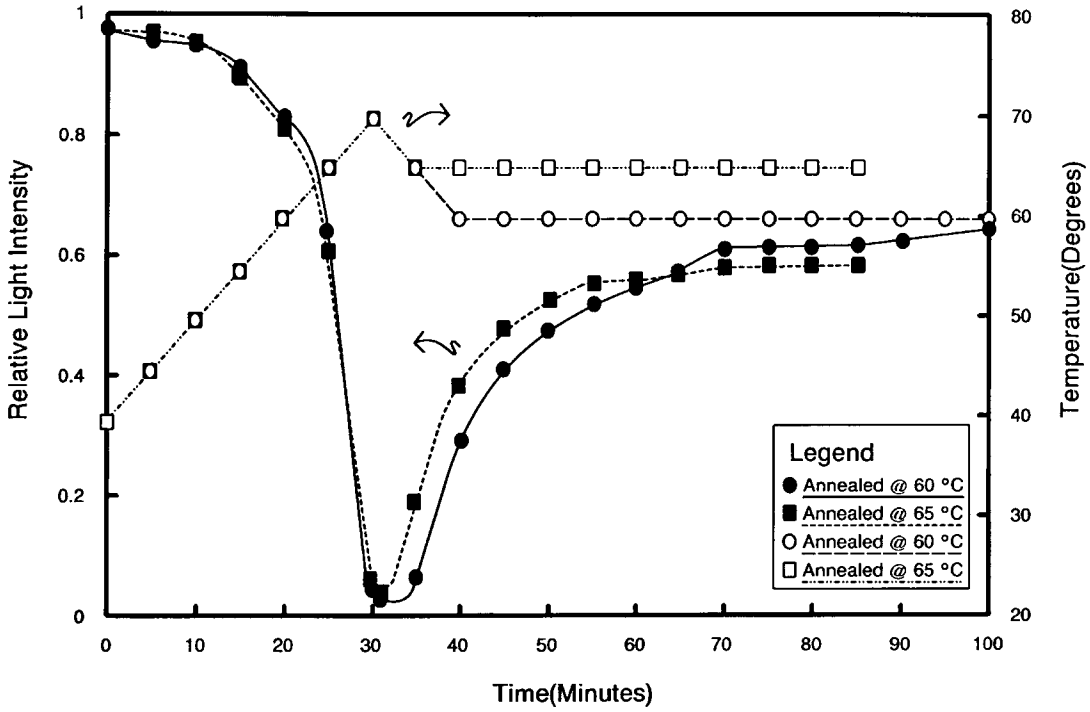


Figure 3 TOA curves for HCC-161 films. The temperature is ramped, then held while the sample is placed between crossed polars.

sure of degree of ordering in the sample. The light intensity initially measured after annealing 72 h at 60°C was taken to be indicative of material completely in the nematic phase. Duplicate samples were then heated to 70 and to 80°C, converting them to the isotropic state. The sample that had been heated

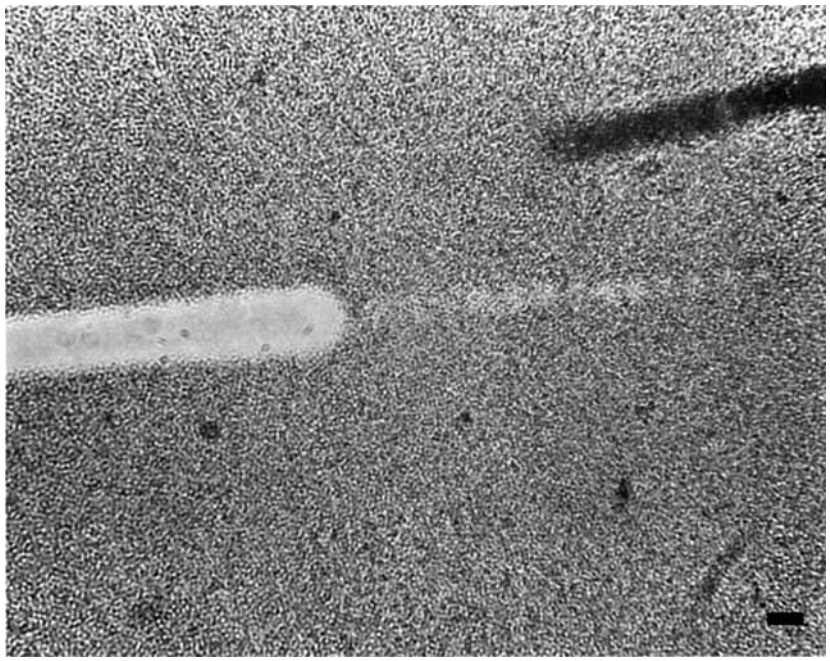
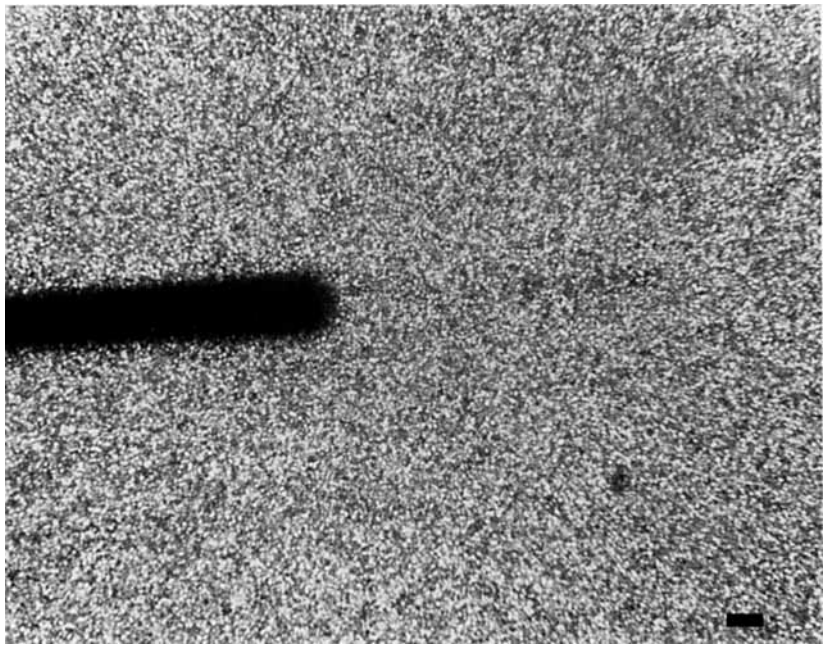
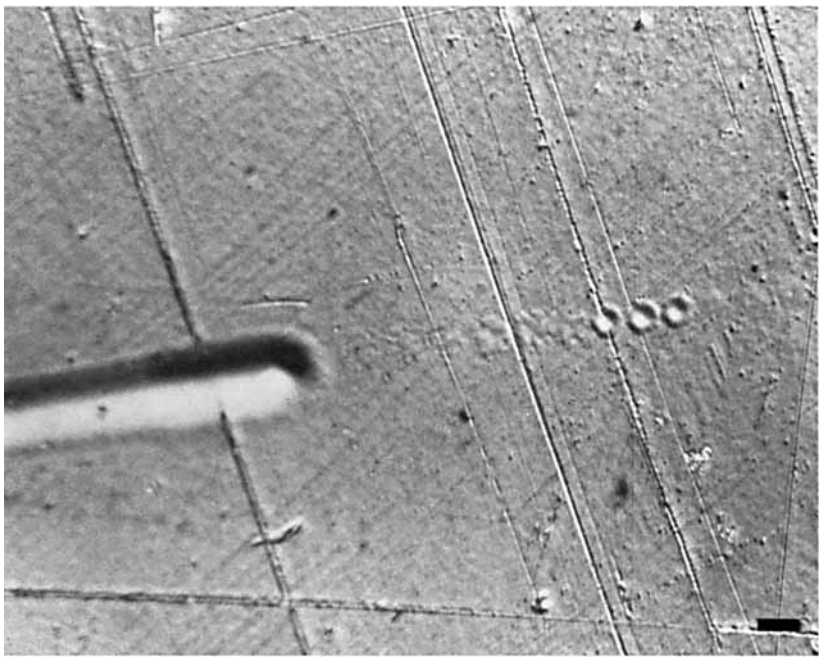


Figure 4 Optical micrographs of HCC-161 films, annealed, metallized, and irradiated. Bars indicate 10 μm. (a) Transmission bright field. (b) Transmission crossed polars. (c) Reflection DIC.



(b)



(c)

Figure 4 *(continued from the previous page)*

to 70°C recovered 39% of its nematic character after 16 h annealing at 60°C, while the sample heated to 80°C showed only 29% recovery after an identical annealing treatment.

It was of particular interest to examine the optical response of HCC-161 when the source of thermal energy was pulsed laser radiation. Two approaches are possible for capturing the laser light and effecting thermal marking of the medium. The polymer film may itself absorb light either because it is inherently absorptive or because an absorbing dye is intimately admixed with the sample. Alternatively, the functions of light absorption and thermal marking may reside in two physically distinct layers, the first of which captures the light and converts it to thermal energy and that then transfers this thermal energy to an adjacent layer capable of undergoing some physico-chemical change. This latter approach was

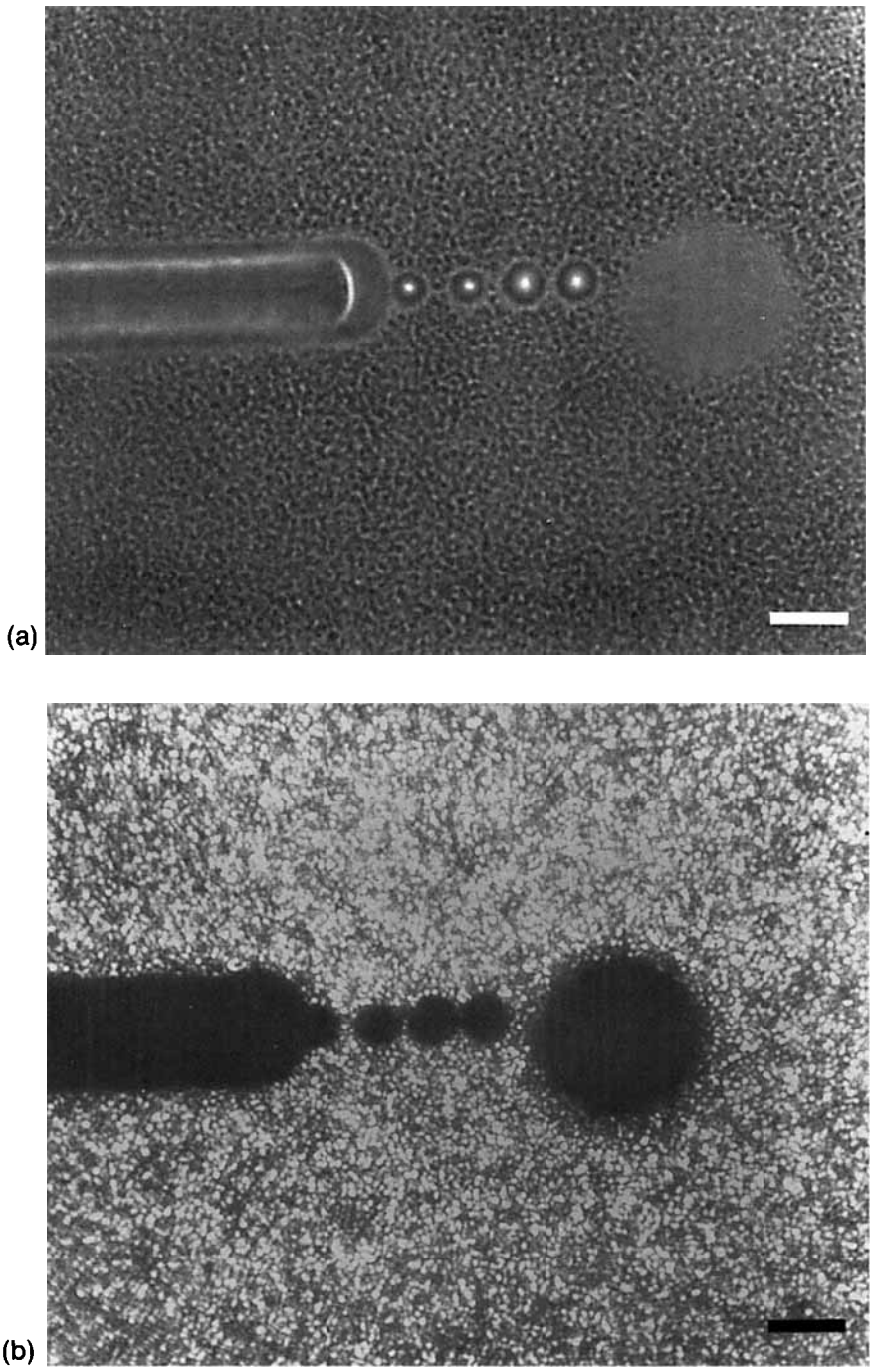
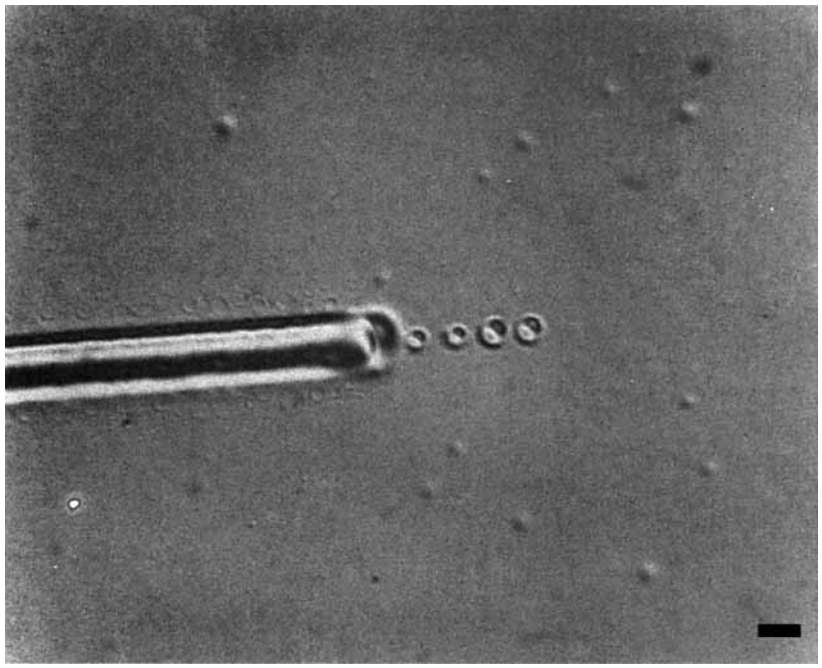


Figure 5 Optical micrographs of dyed HCC-161 films, annealed and irradiated. Bars indicate 10 μm. (a) Transmission bright field. (b) Transmission crossed polars. (c) Reflection DIC.

tried first. To this end the laser marking response of polymer films sputter coated with 400 Å of PdAu was examined.

A number of runs were made with the apparatus described above, the results of which are best illustrated by examination of Figure 4. This shows optical micrographs of an annealed HCC-161 sample, 3.3 μm thick on glass, metallized with 400 Å of PdAu and irradiated through the substrate. The micrographs were taken with transmission optics (bright



(c)

Figure 5 *(continued from the previous page)*

field and crossed polarizers) and in reflection by differential interference contrast (DIC). Extending from the left-hand side of each micrograph is seen a line that resulted when the sample was moved while the laser was on continuously at 10 mW power. The result is the conversion of the nematic phase (recognized by its fine grainy texture) to the isotropic phase. The isotropic phase appears light with bright-field optics and dark with crossed polarizers. The corresponding micrograph taken with DIC reflection optics shows that this phase change was accompanied by deformation of the surface and the formation of a trough. (The trough made by moving the sample while the laser was on served as a convenient marker for locating marks made subsequently by pulsed irradiation.) Extending in a line to the right of the trough may be seen the marks made at 10-μm intervals by pulsed irradiation at 10 mW power. Contained in the line are two groups of three marks made with 2-μs pulsewidth and two groups of three made with 20-μs pulsewidth. Additional traces resulting from 90-μs pulsewidths are outside the field of the micrograph. The beam was refocused between each group of three pulses.

Although the marks produced by pulsed irradiation are not as clearly distinguished from the background as that produced by the continuous scan, they were clearly detected by the change in the read detector voltage. For the three different pulsewidths the average signals (mV) are summarized as follows:

	Before	After	Change
2 μs	136	144	8
20 μs	144	177	33
90 μs	144	267	123

Note that the contrast is positive, in keeping with the decrease in scattering that accompanies the partial transformation from nematic to isotropic. One of the groups of three pulses resulted in pits with rims, the others resulted in minimal surface deformation.

Laser marking of HCC-161 was also attempted using dyed films rather than metallized films. The dye used for this purpose was a 2 : 1 mixture of HDITC (**II**) and PA-1006 (**III**), both of these being commercially available materials. It was felt that these flat molecules could readily be added to the liquid crystalline polymer without disrupting the nematic structure. In fact, it was not possible to anneal in the nematic phase with a 10% dye loading although this could be done at a 5% loading. It was possible to produce laser-induced marking of an annealed sample containing 5% dye, although at somewhat longer pulsewidths than was the case with metallized films. Optical micrographs of this laser marked sample are shown in Figure 5. It is noteworthy that the large mark that appears in the right-

hand side of the transmission micrographs is absent in the micrograph obtained with the DIC reflection technique, i.e., there is no surface deformation accompanying the phase change. It is likely that the relatively long laser pulse (> 1 ms) used to produce this feature resulted in lower temperature gradients than is the case when pit formation occurs.

It was of interest to observe the effect of higher transition temperature on marking behavior in the same type of polymeric media. Such a material, designated HCC-161C, was obtained and consisted of a 65 : 35 copolymer of HCC-161 with methyl methacrylate. As for HCC-161, samples of this material were prepared for thermo-optical and laser marking experiments by dissolution in trichloropropane and spin coating onto glass substrates, followed by drying and annealing. Hot stage microscopy of an annealed sample of this material revealed a clearing temperature of 100°C, with no evidence for the reverse transition (isotropic to nematic) upon annealing 16 h at 90°C. Examination of this compound by DSC showed a T_g of 75°C and T_m of 98°C, the latter being in good agreement with the observed clearing temperature of 100°C.

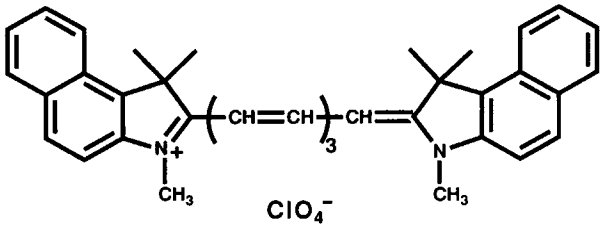
Samples of the copolymer, annealed to the nematic state, were metallized and subjected to pulsed laser irradiation. It was possible to mark these samples with 2-μs pulses at 10 mW power producing a decrease in read signal. Subsequent microscopic examination showed that these marks were due to pit formation, which was not accompanied by a phase change. Evidently, the lower degree of order in the copolymer did not favor the same behavior as seen in the related homopolymer.

SUMMARY

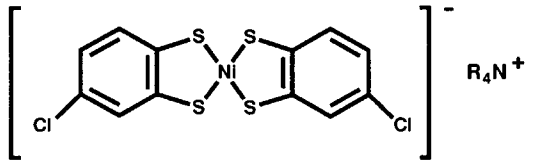
The thermal and laser marking behavior of a novel nematic liquid crystalline polymer, designated HCC-161, was examined. The temperature for the nematic to isotropic transition was determined to be 68°C by DSC and by thermal-optical analysis of thin samples spin coated onto glass slides. The isotropic phase is readily frozen in when a sample initially in the nematic phase is heated above 68°C and allowed to cool rapidly. Reconversion to the nematic state occurs only with prolonged annealing.

The nematic to isotropic conversion of HCC-161 can also be effected by addressing metallized films of the polymer with focused diode laser irradiation. In this case the transition is generally accompanied by deformation of the film surface, indicative of surface tension gradients in the sample that follow the Gaussian intensity profile of the impinging laser beam. The marks produced in this manner are clearly readable from the change in reflected light intensity when interrogated by a continuous low-power laser beam. Similar results were obtained with annealed films of the polymer containing 5% by weight of a compatible dye.

The pit formation observed upon pulsed laser irradiation of HCC-161 is similar to the response of other dye/polymer recording media reported in the literature. Pit formation together with a mesotropic phase transition upon pulsed laser irradiation appears to be novel and could provide an attractive approach to sensitive laser recording media.



Structure II



Structure III

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