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351 nm, 0·7 ns laser damage thresholds of monomeric liquid-crystalline systems

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The 351 nm laser-damage thresholds (at 0·7 nm pulse length) of monomeric liquid crystals are reported and results from aromatic-core samples are compared with those from fully saturated systems. The role of π-electron conjugation is examined and identified as the key cause for laser damage. For UV laser compatibility of devices, the damage behaviour of an alignment-layer polymer (nylon 6/6) was also investigated.

1. Background

Very high peak-power lasers are currently under development or in use for military applications, for X-ray laser development and for inertial-confinement nuclear fusion research [1, 2]. These lasers show two configurations: they are designed around either ion-doped glass systems, the output frequency of which may be parametrically converted up in an optically non-linear medium, or around high-gain, electrically excited rare-gas halide excimer gas mixtures that lase in the ultraviolet. Maximizing the laser performance for certain applications makes it mandatory that their usually large beams (10 cm $\leqslant$ diameter $<$ 1 m) be modified in terms of polarization, spatial intensity edge profile, etc. For such purposes conventional, crystalline birefringent materials or diffractive elements serve laboratory, table-top lasers very well. At the larger beam diameters, natural size limitations are encountered and scalable, man-made substitutes become essential. That is where a major opportunity for liquid crystal applications has evolved.

We have in earlier accounts [3] reported the scientific and engineering issues related to liquid crystal device applications in the IR (1054 nm) portion of the frequency converted, 351 nm OMEGA laser at the Laboratory for Laser Energetics. Other large scale lasers, operating further in the ultraviolet (248 nm), have also appeared. There is a role for liquid crystal devices at these shorter wavelengths as well.

The devices that currently draw most attention for UV applications are polarization rotators that offer one- [4] or two-dimensional gradients, or binary polarization rotation capabilities in some generalized, checker-board fashion. In addition, soft apertures with higher-order gaussian edge profiles [5] are of interest. In devising a strategy for meeting these application needs, one must resolve one of the thornier issues of any high peak-power laser application: the materials' optical survival strength under repeated irradiation. In this report we summarize recent measurements of 351 nm laser damage thresholds for several monomeric liquid crystal materials intended for UV applications. In addition, similar thresholds are listed for a polymeric thin film (Nylon 6/6) that has proved useful in providing surface alignment and anchoring layers.

2. Experimental

All tests were carried out with pulses of nominally 0·7 ns length. Two different test modes were employed: 1-on-1 measurements and *N*-on-1 measurements. In either case, damage was diagnosed, as in the earlier 1054 nm testing [6], as the appearance within the ~ 3 mm diameter irradiation spot size of a bubble that briefly scatters light. Near the damage threshold, bubbles tend to be small ($\leqslant 100\,\mu$m) and short lived, redissolving into the surrounding matrix within seconds. Only significantly above threshold is photolysis of the material observed with residual carbon formation and shock-wave driven jets disrupting the aligned material far beyond the actual irradiation area. What is listed as a damage threshold in the following must therefore be considered a conservative number. At threshold the monomer invariably recovers. 1-on-1 testing differs from *N*-on-1 testing in two respects. First, in 1-on-1 testing each sample site is irradiated once, and in going from one site to the next, the laser fluence is incremented until bubble formation is encountered. This is repeated over many sites for statistical purposes. Second, *N*-on-1 testing sees the sample sample site irradiated repeatedly at very low repetition rate. From one shot to the next the fluence is ramped up, starting from about the 50 per cent fluence level of the single-shot average damage threshold. In this manner, 1-on-1 and *N*-on-1 thresholds are linked.

Samples were prepared in either one of two configurations: sandwiched between two, laser-quality substrates or in the case of polymers, applied to a single substrate by spin coating. In an improved configuration, one substrate is replaced by a solid glass prism the purpose of which is explained shortly. The thickness for all monomeric samples is uniformly maintained by $100\,\mu$m spacers. Sample fluid is filtered through a $0{\cdot}5\,\mu$m pore membrane filter and filled, in the isotropic phase, into the $100\,\mu$m gap by capillary action. Sample assembly is carried out under cleanroom conditions, as earlier tests identified particulate impurities as a dominant source for lower damage thresholds [6]. It must also be mentioned that great care in substrate cleaning must be exercised, using appropriate particle-free solvents and rinsing fluids.

To distinguish damage effects driven by alignment layers from those germane to the liquid crystal itself, samples were tested without alignment layers. This was done by heating the substrates with ohmic heating pads to slightly above the isotropic clearing temperature. The temperature was monitored by a thermocouple affixed to the substrate. For the samples discussed in this paper the temperature excursion from room temperature was not significant enough to cause thermal expansion variations in cell thickness that would have to be accounted for in the data analysis. However, the temperature changes were sufficient that sealing the sample cell in final assembly was best done with high-temperature epoxy.

The choice of a backing substrate, either a flat or a prism, is governed by irradiation geometry considerations. The key to the reliability of the measured damage thresholds is the precise knowledge of the local laser fluence (J/cm^2) within the irradiated sample volume. Diagnostic tools for ascertaining this variable can be compromised, however, if the local fluence becomes a superposition of the incident wave that is accurately monitored and a wave back reflected from the sample substrate exit face. One method for suppressing this back reflection is to create a non-reflective interface by matching an absorbing backing plate to the substrate with

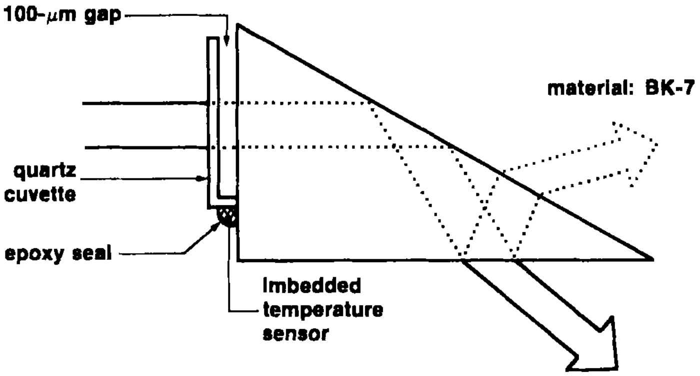

Figure 1. Schematic of sample arrangement for measuring laser damage thresholds of monomeric liquid crystals. For measurements at elevated temperatures, electrical heating pads are attached to the sides of the borosilicate-glass prism. The quartz cuvette gap uniformity is usually better than ± 10 per cent.

the help of an index-matching fluid layer. In most circumstances, this is a satisfactory solution. However, in the investigation of certain liquid crystals it becomes apparent that the sample material's damage threshold exceeds that of the index-matching fluid, especially at UV wavelengths. The apparent damage to the liquid crystal is always accompanied by massive disruption to the index-matching fluid and, although the detailed dynamics of the process remains unresolved, we surmise that a shock-wave originating at the index-fluid interface propagates into the liquid crystal and, by rarefaction and cavitation action, causes bubble formation there.

This challenge is side-stepped by use of a prism as shown in the figure. Multiple bounce reflections at the prism faces take the transmitted beam away from the sample interfaces without back reflection interference. Borosilicate glass is a good choice for prisms for 1054 nm measurements. Experiments in the UV would benefit from quartz prisms. However, BK-7 borosilicate glass prisms do provide a qualitative, independent check on the optical survival strength of the liquid crystals in the UV: the 351 nm fluences employed here solarize the borosilicate glass but leave the liquid crystals (CCH) unaffected. Solarization streaks along the beam paths can be readily observed by the unaided eye. They are irrelevant to the occurrence of damage, since they follow the liquid crystal fluid.

The 351 nm laser pulses are derived from a Nd : glass, mode-locked, feedback-controlled Q-switched oscillator [7] and zig-zag slab amplifier system. This system produces 1053 nm IR pulses of 3 J energy at a repetition rate of 0·3 Hz. The spatially filtered, fundamental-wavelength beam is frequency tripled by a monolithic KD*P frequency conversion cell [8] with efficiencies up to 50 per cent. The unconverted laser light is separated from the UV portion by multiple, dielectric thin-film reflectors. Beam energy in the UV and spatial intensity distribution in a sample-equivalent plane are monitored on each shot by a pyroelectric calorimeter and a UV-sensitive, high-resolution, electronic CID camera, respectively.

3. Materials, results and discussion

The materials investigated in this effort were pure monomers or eutectic mixtures of monomers of commercial origin. They generally are of the phenyl-cyclohexyl core

Table 1. 351 nm, 1 on-1† laser damage thresholds of aromatic and saturated liquid crystal monomers.

Material/trade Name	Pure/mixture	Core	Temperature/°C	Damage threshold/J/cm^2	Comments
ZLI-1185	Pure	CCH	RT	8·9 ± 0·9	
ZLI-1167	Mixture	all CCH	55°	7·3 ± 0·5	
ZLI-3125	Mixture	all CCH	65°	9·1 ± 1·3	
BDH 14616/14627	Mixture	fluorinated CCH	RT	10·5 ± 2·5	
ZLI-1114	Pure	PCH	RT	< 0·9	Not outgassed
ZLI-1114	Pure	PCH	RT	< 0·5	Outgassed

† *N*-on-1 thresholds fall within the error bars of listed 1-on-1 thresholds.

type or of the all-saturated kind. Except for filtration and outgassing at elevated temperatures, the materials were used as received.

Our earlier measurements [6] established the importance of π-electron delocalization in the liquid crystal core for laser damage at 1054 nm. A comparison between phenyl-cyclohexyl (PCH) compounds and fully saturated compounds (CCH) yields particularly striking differences in the UV. In table 1 we list the 1-on-1 thresholds for the monomeric mixtures and pure compounds, all obtained from 0·7 ns pulses.

From table 1 the order-of-magnitude disparity between fully saturated and partly conjugated compounds is evident. It is also clear that, at the UV wavelengths, damage in conjugated systems is virtually independent from preparation parameters such as outgassing, i.e. the dominant factor in short-wavelength damage is π-electron delocalization. This finding agrees with 500 μs, flash lamp-pumped, broadband UV (> 356 nm) photostability results for commercial bicyclohexyl- and biphenyl-core liquid crystals, undertaken by Lackner, Margerum, and Van Ast [9]. Their result: the less electron delocalization, the more UV stable the compound. Since flash lamp-triggered effects are inherently absorptive or thermal in nature while laser-driven effects may be absorptive, thermal or refractive (i.e. non-absorptive, acting via self-focusing) or may be a combination of relative contributions from all three mechanisms, the close agreement between laser-driven and flash lamp-driven results suggests that absorption effects also dominate in the laser-driven case. To what extent this absorptive energy transfer results from non-linear absorption cannot be resolved with our fixed-wavelength source and from damage observations alone. Certainly in the case of phenyl compounds, $\pi \rightarrow \pi^*$ electronic transitions ($^1A_{1g} \rightarrow {}^1E_{1u}$) of benzene that occur near 180 nm are accessible via 2-photon processes from the 351 nm source used here. Given the relaxation of selection rules in the condensed phase, this 2-photon absorption mechanism must be considered the key limiting process for damage resistance in the PCH compounds. The *N*-on-1 threshold for several of the fully saturated compounds of table 1 was measured as well. The thresholds fell within the error margin of the respective 1-on-1 results, indicating an absence of either multiple-irradiation hardening or degradation effects in these compounds.

For device operation at 351 nm, the role of surface alignment layers in optical damage must be studied separately. To this end, nylon 6/6 films were spin cast on fused-silica substrates from 0·2 wt % formic acid solutions. Samples were prepared both in mechanically buffed and in unbuffed form—buffing being the process of

Table 2. 351 nm damage thresholds of nylon 6/6 films.

	1-on-1/J/cm^2	*N*-on-1/J/cm^2
Unbuffed	5·1 ± 0·6	6·8 ± 0·1
Buffed	3·0 ± 0·4	5·0 ± 0·1

modifying the film surface to optmize the liquid crystal orientational anchoring [10]. As the buffing process is technically essential yet chemically least understood or controlled, impurities are believed to be introduced into the film by the process, rendering the film locally absorptive and susceptible to damage. Comparing measurements from the untreated film with those from an equivalent, buffed sample helps in identifying the effect of buffing on damage.

This comparison is shown in table 2. Clearly, the buffing process degrades the material's optical survival strength. The high thresholds of the untreated material are consistent with the high degree of saturation in this compound, i.e. the repeat unit carries only one π-conjugated carbonyl group. Cleanliness improvements during alignment-layer preparation should permit liquid crystal device development and use at UV fluences in excess of 5 J/cm^2. This work suggests that, especially for pulsed UV applications, the liquid crystal anchoring layer composition should not contain any aromatic moieties. There are many known compounds [11] that fit this requirement. The improvement in optical survival strength of the polymer during multiple irradiation is not yet understood. It contrasts with findings from polymethacrylate [12] obtained in the near IR where multiple irradiation by laser pulses of 20 ns pulse length weakens the material.

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