Section 2
ADVANCED TECHNOLOGY DEVELOPMENTS

2.A Laser Damage in \( \pi \)-Electron Systems

Organic, conjugated \( \pi \)-electron molecular and polymeric materials offer great promise for high-power laser applications. Their advantage over conventional materials lies in the flexibility that organic synthesis offers for their design. By the same approach that leads to the design of other organic compounds, especially pharmaceutical ones, organic materials with specific linear or nonlinear optical properties can now be defined, designed, and calculated in terms of response. The most important properties in this regard are absorption at certain wavelengths, nonlinear susceptibilities, fast response times, and high-power laser-damage thresholds.

The OMEGA laser is among the first to employ organic optical devices in significant numbers. The majority of these devices are liquid-crystal-based circular polarizers developed and manufactured in house. Other devices use the linear birefringence of monomeric liquid-crystal molecules and usually comprise an eutectic mixture of several types of such molecules. In preparing any devices for 5 J cm\(^{-2}\)/1-ns applications, the question arises whether an improved laser-damage threshold can be engineered in an acceptable tradeoff with other parameters by changing the eutectic's composition. After elimination of compounds because of unsuitable linear absorption properties, the choice is between highly conjugated and more saturated compounds.

There are predictions that the nonlinear optical susceptibilities of organic systems are affected by the degree of conjugation. For \( \chi^{(2)} \),
ample experimental evidence\(^2\) supports this contention. For \(\chi^{(3)}\), less data exist. Because \(\chi^{(3)}\) affects self-focusing, and because in the absence of extrinsic impurities self-focusing is a dominant mechanism for laser damage in many transparent materials, we tested the extent to which the damage threshold in some organic materials is affected by the degree of conjugation.

**Experiments**

Three model compounds were chosen for this test: two monomers and one polymer. We report first on the nematic monomers and then on the cholesteric polymer. One monomeric, \(\pi\)-electron-rich compound was 4-octyl-cyanobiphenyl, which is a liquid crystal with a nematic mesophase at room temperature. Its saturated counterpart, 4-octyl-cyanobicyclohexyl, was also tested. As shown in Fig. 35.20, the two compounds differ structurally only in their aromatic and saturated cores. The bicyclohexyl compound is commercially available under the trade name ZLI-S-1185 and has a nematic phase starting at \(62^\circ\text{C}\).\(^3\) Laser interaction tests were conducted at 1053 nm (fundamental of Nd:phosphate glass laser), where neither material exhibits any resonance. This is substantiated by the two absorption scans in Fig. 35.21, obtained from 1-cm-path-length cells at elevated temperatures (Fig. 35.20) keeping the compounds in their respective isotropic phases. The 1053-nm absorption coefficient for the biphenyl compound was \(3.6 \times 10^{-2} \text{ cm}^{-1}\). For the saturated compound, the residual absorption was three times larger. Absorption measurements were done in the isotropic phase to minimize the scattering contribution to the near-IR laser damage threshold.

<table>
<thead>
<tr>
<th>Compound</th>
<th>K-15</th>
<th>ZLI-1185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>(\text{CH}_3\cdot(\text{CH}_2)_4) (\text{O} \rightarrow \text{O} \rightarrow \text{CN})</td>
<td>(\text{CH}_3\cdot(\text{CH}_2)_4) (\text{O} \rightarrow \text{O} \rightarrow \text{CN})</td>
</tr>
<tr>
<td>Mesophase</td>
<td>nematic (22(^\circ)C)</td>
<td>nematic (62(^\circ)C)</td>
</tr>
<tr>
<td>1-on-1 (J/cm(^2))</td>
<td>9.6±2.4</td>
<td>&gt;16.6*</td>
</tr>
<tr>
<td>N-on-1 (J/cm(^2))</td>
<td>5.4±1.3</td>
<td>14.6±0.5</td>
</tr>
</tbody>
</table>

800-ps pulse length, 100-\(\mu\)m path length, 5-mm spot size, linear polarization
*for given spot size, transport optics damage at 20 J/cm\(^2\)

Tests with linearly polarized incident pulses of 800-ps length were conducted identically for both monomeric materials. Unaligned cells of 100-\(\mu\)m path length were prepared from 30-60-90 borosilicate prisms and uncoated, fused-quartz cuvette covers and were sealed by high-temperature epoxy. (A clarification for this choice of sample geometry...
Fig. 35.21
The damage-test experiments were carried out at a wavelength where neither of the liquid-crystal samples exhibit any resonances. The residual linear absorption of 1053 nm of the saturated compound is higher than that of the conjugated, and yet its damage threshold is also higher.

is forthcoming in print. Cells were filled, by capillary action, with materials in their isotropic-fluid phase. Because this involves elevated temperatures, cells were not equipped with the organic alignment layers that are often used in aligning liquid crystals in either homeotropic or homogeneous configurations. It is also important to note that to date we have not found an alignment material that by itself shows a damage threshold in excess of the ones reported here for liquid crystals. What is frequently measured in tests of liquid-crystal/alignment-layer systems is therefore not the damage threshold of the liquid crystal but that of the alignment layer. A project currently under way aims at sorting out the alignment materials with the highest damage threshold.

Irradiation by high-peak-power laser pulses occurred at normal incidence. The beam was weakly focused to a spot size of about 3 mm. Laser-induced sample changes that in liquid crystals usually appear as small bubbles can be observed with a long-working-distance microscope. The detectability of bubbles was limited by the lifetime of bubbles that redissolve into the liquid matrix. One-on-1 and N-on-1 irradiation modes were chosen. In N-on-1 testing, each separate sample site was irradiated by series of ten pulses each (8% pulse-to-pulse energy stability) of slowly increasing fluence levels. In that mode, occurrence of damage was checked after each shot. After the appearance of a bubble, irradiation was terminated even if that bubble happened to redissolve. In N-on-1 testing, the interval between pulses was 5 s. A record of peak fluence and its location within the beam was obtained for each shot.

Results
Results for the monomeric materials are listed in Fig. 35.20. For both the aromatic and saturated compounds, the N-on-1 threshold is lower than the 1-on-1 threshold. This is in general agreement with many other monomeric liquid-crystal compounds tested earlier. However, in both 1-on-1 and N-on-1 results, a significant difference is
apparent between the \( p \)-electron-rich and the fully saturated nematic. In fact, the beam transport optics for this experiment suffered damage of its own before any site of the saturated compound showed single-shot bubble formation. The corresponding fluence level is twice that of the single-shot threshold average for the aromatic compound. The \( N \)-on-1 threshold comparison shows an improvement over the aromatic compound by nearly a factor of 3.

To eliminate from consideration that impurities may cause these threshold differences, we analyzed sample stock by gas chromatography. At the one-part-in-\( 10^5 \) sensitivity level, no extraneous signals were observed from either compound. The only unusual feature was an isomer signature from the bicyclohexyl material. Within the stated sensitivity limit, impurities must be ruled out as a damage-dominating mechanism. Similarly, the opposing trends of damage thresholds and linear-absorption coefficients between the two nematics make linear absorption an unlikely damage mechanism.

The polymeric material was tested in a different approach. Here, the \( \pi \)-electron-rich phenyl functional group, one of several of the polymer's functional groups, was simply removed in the preparation of the control-sample polymer. The liquid-crystal polymer comprised a polysiloxane backbone with lateral, mesogenic side groups. The structure of the repeat unit is shown below:

\[
\begin{align*}
\text{Chol} \quad &\text{stands here for cholesterol; } m \text{ is usually 4 or 5. The cholesterol} \\
&\text{functional group with its alkyl tail introduces chirality into the} \\
&\text{polymer, offering interesting optical properties. Among them is} \\
&\text{the coupling between the molecular helix and the proper-handed,} \\
&\text{circularly polarized light of a wavelength } \lambda \text{ that matches the pitch of} \\
&\text{the helix. By varying the pitch of the chiral structure, tuned optical} \\
&\text{devices can be prepared.}^5 \text{ One method for varying the pitch of a chiral nematic} \\
&\text{polymer is to prepare a variable-weight copolymer of the design}
\end{align*}
\]

\[
\begin{align*}
H_3C - Si - (CH_2)_n - O - &\bigcirc - COO - Chol_m \\
O \quad &\bigcirc \quad &\bigcirc \\
\end{align*}
\]

Chol stands here for cholesterol; \( m \) is usually 4 or 5. The cholesterol functional group with its alkyl tail introduces chirality into the polymer, offering interesting optical properties. Among them is the coupling between the molecular helix and the proper-handed, circularly polarized light of a wavelength \( \lambda \) that matches the pitch of the helix. By varying the pitch of the chiral structure, tuned optical devices can be prepared.\(^5\) One method for varying the pitch of a chiral nematic polymer is to prepare a variable-weight copolymer of the design:

\[
\begin{align*}
H_3C - Si - (CH_2)_n - O - &\bigcirc - COO - Chol \\
O \quad &\bigcirc \quad &\bigcirc \\
\end{align*}
\]

\[
\begin{align*}
H_3C - Si - (CH_2)_n - O - &\bigcirc - COO - Chol \\
O \quad &\bigcirc \quad &\bigcirc \\
\end{align*}
\]

\[
\begin{align*}
H_3C - Si - (CH_2)_n - O - &\bigcirc - COO - Chol \\
O \quad &\bigcirc \quad &\bigcirc \\
\end{align*}
\]
in which the density $x$ of interleaved copolymer pendants determines the degree of pitch dilation along the backbone direction. By virtue of the $\pi$-electron distribution in the copolymer, changing this density means increasing or decreasing the nonlinear optical susceptibility of the total system in accordance with copolymer content. Testing the damage threshold of chiral copolymer samples tuned to different (nonresonant with regard to the 1053-nm incident wavelength) wavelengths provides further corroboration for the postulated link between $\chi^{(3)}$ and the degree of conjugation.

Damage-test samples of the copolymer were prepared by dissolving the material in toluene and spraying about 100-\(\mu\)m-thick films onto carefully cleaned, 30-60-90 borosilicate glass prism surfaces. Film thicknesses were uniform to better than 10% across individual samples but varied by up to 20% from sample to sample. The three copolymers reported here had cholesteric weight percents of 14%, 21%, and 35%, corresponding to tuned-response peak wavelengths of 1170 nm, 760 nm, and 450 nm, respectively. In 1-on-1 tests conducted in the same way as for monomeric materials, an important trend emerged: the copolymer with the highest cholesterol content—i.e., that with the lowest volume density of conjugation—showed the highest damage threshold; the one with the lowest cholesterol content and therefore the highest volume density of conjugation showed the lowest threshold. This trend is evident in Table 35.III.

<table>
<thead>
<tr>
<th>Weight % Cholesteric</th>
<th>Peak Wavelength (nm)</th>
<th>Film Thickness ((\mu)m)</th>
<th>1-on-1 Threshold (J/cm²)</th>
<th>N-on-1 Threshold (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1170</td>
<td>108</td>
<td>0.8±0.1</td>
<td>&lt;0.8</td>
</tr>
<tr>
<td>21</td>
<td>760</td>
<td>104</td>
<td>2.4±0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>35</td>
<td>450</td>
<td>83</td>
<td>5.1±1.2</td>
<td>&lt;0.8</td>
</tr>
<tr>
<td>smectic-C</td>
<td>not applicable</td>
<td>105</td>
<td>5.8±0.3</td>
<td>13.8±3.0</td>
</tr>
</tbody>
</table>

Catalysts used in the synthesis of these polymers were thought to affect these thresholds through platinum trace residues. Platinum inclusions in laser glass have been widely acknowledged as prime damage-inducing impurities. However, tests with especially purified copolymer samples yielded only marginally higher damage thresholds than those listed in Table 35.III. We surmise that the role of impurities in the IR laser damage of these materials is as insignificant as in the monomeric compounds. The damage morphology in polymers differed from monomers in that no bubbles were observed. Damage was monitored at the same spatial resolution as in the case of bubbles, except that here permanent structural modifications in the form of microscopic pits were recorded.
Finally, a cholesteric polymer was prepared that totally lacked the copolymer pendants used in the previous examples for wavelength tuning. It also lacked the phenol group in the cholesteric pendant. Except for one conjugated bond on the cholesterol itself, this system was entirely $\pi$-electron free. These reductions affected not only the laser damage threshold but other physical properties as well. The polymer glass transition temperature, affecting the material's processability, was raised and its mesogenic phase behavior changed. The chiral nematic room-temperature phase changed to smectic-C. Again, special efforts were made to keep this compound platinum-free. The platinum content was verified to be $<1$ ppm. When films of this material were prepared from a toluene solution in the same manner as for previous polymer samples, laser-damage thresholds could be measured. The 1054-nm, 1-on-1 threshold was $5.8 \pm 0.3$ J/cm$^2$, a 10% improvement over the best copolymer mentioned earlier. A more dramatic improvement was observed for the $N$-on-1 threshold. Whereas the $\pi$-electron-rich copolymers exhibited a common, precipitous threshold drop with large scatter in data to about 0.8 J/cm$^2$ when tested in the $N$-on-1 mode, the smectic-C sample showed a significant rise in threshold to $13.8 \pm 3.0$ J/cm$^2$. To date, we have no compelling explanation for these diverging trends. These measured thresholds compare well with the ones obtained for traditional, dielectric thin films.7

Summary
To summarize, we conclude that, once impurities have been removed as a major cause of damage in organic optical materials, the volume density of conjugation in a compound becomes the dominant laser-damage factor. Because of this link, a reformulation of liquid-crystal polarizer compositions is under way that will enhance the damage resistance of liquid-crystal optical elements used in the OMEGA laser. The guiding principle here is to substitute, wherever possible, highly saturated compounds for conjugated ones. One trade-off in this case is a drop in birefringence associated with the loss in conjugation, a trade-off easy to accommodate. The same principle will also help make other liquid-crystal devices high-power compatible, such as soft apertures,8 cholesteric laser end mirrors,9 or active devices, such as shutters and modulators.10

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Dr. F. Kreuzer of Consortium fur Elektrochemische Industrie, Munich, West Germany, kindly provided the polymeric sample materials and their analytical characterization. He also offered valuable advice.

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REFERENCES


