OPTICAL MATERIALS

High Gains for Polymer Dynamic Holography

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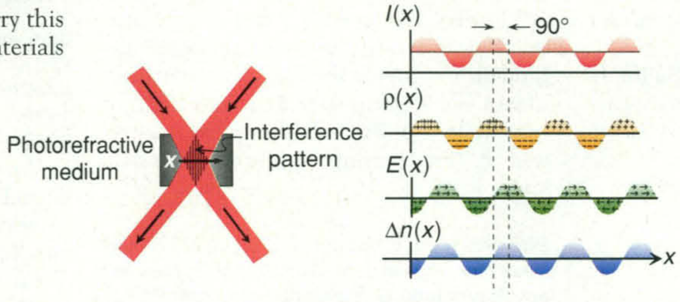
Photorefractive materials are dynamic holographic media that respond to the interference pattern between two or more laser beams. Certain photorefractive materials also exhibit two-beam coupling gain, in which energy from one beam is diffracted into another beam, a phenomenon useful in image amplification (or attenuation) and a host of dynamic optical devices. Within the optics literature, one finds uses of photorefractive materials that range from optical storage to wave front correction and from spatial solitons to optical machines that learn by themselves. A few years ago, polymers began to show promise as a less expensive, more manufacturable, and more flexible alternative to the exotic inorganic crystals that presently dominate photorefractive applications. With the demonstration of large net two-beam coupling gain in a photorefractive polymer, Grunnet-Jepsen *et al.* (*1*) report results on page 549 of this issue that carry this young class of nonlinear optical materials across a threshold.

The photorefractive effect in inorganic crystals takes place as a sequence of three steps. When two or more light beams illuminate a crystal, they give rise to an interference pattern (see figure). The first step is the excitation of charges, which sit in defects sites within the crystal, to the conduction band. In the second step, conduction band charges move around for a short time and are transported to other locations. As the charges become trapped again, they tend to pile up in regions of relatively lower intensity, because here they are less likely to be excited into the conduction band again. The redistribution of charge carriers into lower intensity regions leads to an electric field. Finally, through the electro-optic effect, the electric field induces a variation in the index of refraction that essentially mimics the original interference pattern. The index variation is called the "index grating," and it is the hologram. With no light on the medium, no charge transport takes place, and the hologram stays put. Such is the basis of optical storage in photorefractive media: Only a small dark conductivity (the background value in the absence of light) leads to loss of the stored hologram over time.

Energy transfer between two beams may or may not take place as the beams that form the interference subsequently diffract into each other off of the index grating, depending on the charge transport mechanism. For transport by diffusion, it turns out as one beam diffracts off of the grating, it travels in the direction of the other beam and adds constructively to the intensity in that direction, while the second beam diffracts destructively and leads to a decrease in the first beam's intensity.

To mimic their inorganic counterpart, a polymer must provide the three crucial components to the photorefractive effect suggested above: charge generation, charge transport, and the electro-optic effect. Organic synthesis assembles the requisite components by taking advantage of the properties of distinct chemical species. Grunnet-Jepsen *et al.* (*1*) used C_{60} to provide charge generation, poly(*n*-vinyl carbazole) (PVK) to provide charge transport, and 4-piperidinobenzylidene-malononitrile (PDCST), a nonlinear optical chromophore, to provide an electro-optical response. The latter was established by applying a dc electric field across the medium.



Hologram formation. (**Left**) Two beams interfere in a photorefractive medium, producing an index grating across a spatial dimension *x*. (**Right**) Relations between spatial light intensity $I(x)$, charge density $\rho(x)$, electric field $E(x)$, and change in index of refraction $\Delta n(x)$. The 90° phase shift between the interference pattern and the index change is indicative of gain, that is, energy transfer from one beam to the other.

Polymer photorefractive materials began to make their appearance in the literature about 6 years ago (*2*). The first materials showed promise but were plagued by a number of problems. From the user's perspective, two of these problems were particularly severe. First, the materials absorbed too much light, so that even when they displayed two-beam coupling gain, absorption loss caused no net amplification of the signal. Second, these materials were unstable and decomposed after an unacceptably short time. The instability arises partly from the large permanent electric field that must be applied to the material to provide it with an electro-optic response. (Inorganic photorefractive crystals are ferroelectric and are made to have a permanent electro-optic response if a large electric field is temporarily applied at high temperature.)

Investigators have made substantial progress in improving the stability and gain in a short time (*3*). Inorganic crystals, however, have a leg up in the high-gain arena because thick crystals are easily had, whereas polymer media are made in thin layers for both practical and technical reasons. Large gain is essential for many uses; inorganic crystals have exponential gains of tens per centimeter. A barium titanate crystal a few millimeters thick, for example, can show huge net gains, on the order of 10^4 to 10^5. This value means that a 1-μW signal can be amplified to 10 to 100 mW (provided that the other supplied beam has more than that same 10 to 100 mW).

Grunnet-Jepsen *et al.* achieved a net gain of 5 by stacking several layers of their material optically in series while the orientation of the electro-optic PDCST was done electrically in parallel. The gain of 5, although not huge, is sufficient to demonstrate self-pumped phase-conjugation, a particular optical oscillator configuration used to correct or undo wavefront and image distortions.

From a functional view, a single photorefractive medium might be likened to an operational amplifier in electronics: Its optical properties make it applicable to a wide range of tasks, and its specific behavior depends on how one uses it in detail, for example, whether one employs feedback in such a way as to produce an optical oscillator or an optical amplifier. The variety and breadth of photorefractive systems that have been demonstrated is remarkable (*4*). In addition to storage and wave-front correction, photorefractive materials have been used in adaptive interferometry for precision measurements without the need for high-quality optical wave fronts. In the past few years, the

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photorefractive effect has been used extensively as a medium for studying nonlinear dynamical phenomena such as the breakup of solitary waves and pattern formation. Photorefractives are popular for image processing devices, such as the novelty filter, which is an optical system that displays changes in a visual scene arising from motion or some other dynamical cause. Other photorefractive-based image processing systems have been used to find edges or to otherwise spatially filter an image. Photorefractive-based systems have furthermore been used to optically implement neural network models for pattern classification and recognition of both spatial and temporal information.

Like their complex electronic circuit counterparts, complex photorefractive optical circuits often require several crystals, yet a single cube of photorefractive crystal measuring 5 mm on a side typically costs a few thousand dollars. Needless to say, a low-cost alternative can make a substantial impact on both applications and research in the field. Those of us who work with inorganic crystals appreciate the flexibility that organic synthesis provides as well: Crystal properties are mostly fixed by nature and modified only in a coarse way by the addition of dopants. Furthermore, the crystal growth process is long and tedious compared with the combine-and-stir approach of polymer chemistry. With their high-gain medium, Grunnet-Jepsen *et al.* demonstrated some of the core building blocks of photorefractive systems. Their research, along with the work of others on photorefractive polymers, suggests that organic synthesis may be a viable approach to manufacturing general purpose photorefractive materials.

References

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BIOMEDICINE

Proinsulin C-Peptide–Biological Activity?

Donald F. Steiner and Arthur H. Rubenstein

Insulin—a hormone critical for the control of blood glucose—is first synthesized as a longer prohormone. During its maturation, a peptide, C-peptide, is cleaved from the protein, but has been thought to be biologically inert. Defying the rule that peptide hormones act only by binding to stereospecific receptors, Ido *et al.* (*1*) report on page 563 of this issue that C-peptide not only produces biological effects, but does so by an unusual mechanism that depends on structural features of the C-peptide related to its sequence but independent of its direction or chirality. These effects include a restoration toward normal of the diabetes-induced decrease in cellular sodium-potassium adenosine triphosphatase (ATPase) activity and impaired nerve conduction, and reductions in the diabetes-induced increase in vascular permeability and blood flow, changes that are concomitants of the hyperglycemia associated with diabetes. These beneficial effects are seen after prolonged treatment of diabetic rats with pharmacological doses of C-peptide, as well as in specially designed skin chambers in which granulation tissue can be exposed to various agents while blood flow is maintained to supply nutrients and endogenous hormones. Normalization of these parameters, argue the authors, could prevent or slow the progression of some of the complications of this chronic and often debilitating disorder.

Human proinsulin with its C-peptide. Insulin A chain (purple), B chain (yellow), and C-peptide (blue). The CA and BC junctions, the dibasic processing sites (R31-R32 and K64-R65), are shown suitably poised for interaction with the prohormone convertases (*3*). Pro^{48} (P48) corresponds to Pro^{16} [in figure 6 of (*1*)]. [Model by G. Lipkind, with Biosyn Technologies Software]

The C-peptide seems to accomplish these effects without reducing hyperglycemia. It has no insulin-like action and so acts without changing any of the usual metabolic parameters that are deranged in diabetes. In addition to hyperglycemia and hyperlipidemia, these include elevation of sorbitol in tissues, a consequence of hyperglycemia that can lead to cataracts and degenerative changes. C-peptide administration also does not prevent the increased nonenzymatic glycation of proteins, which has also been implicated in retinal, nerve, kidney, and general vascular degenerative processes in diabetes. [In support of these results, in diabetic humans (*2*) C-peptide shows beneficial effects on microcirculation, vascular permeability, and sodium-potassium ATPase, but in contrast it also improves glucose utilization and glycemia.]

What is even more remarkable about this action of C-peptide is that it seems not to follow the usual rules of ligand and receptor chemistry. Its action does not require the normal chirality of the peptide, a property that may be attributable to the glycine-rich central portion. A C-peptide made up of D-amino acids is equally active, as is a peptide synthesized with amino acids in the reversed order, carboxyl terminal to amino terminal. The central glycine-rich region is largely achiral, is extremely flexible, and is well conserved in most, but not all, of the mammalian C-peptides. Both the rat and the human peptides are active in their systems, whereas the porcine (and possibly also bovine) peptides, which have deletions in the central region, appear to be inactive or less active. It should be noted that complications in type II diabetes, in which insulin and C-peptide secretion are significantly retained, do not differ from those of insulin-dependent diabetes, characterized by absent C-peptide (endogenous and exogenous).

How can these new observations be explained? The authors suggest that C-peptides may function like some antibiotic peptides, which assemble into bacterial membranes to form pores or channels that disrupt normal ion flow and membrane integrity and thereby inhibit cellular function. The C-peptides, however, differ significantly in their structure from these antibiotic peptides. It seems unlikely that they could form membrane channels, especially since the C-peptides show no tendency to self-associate and are rather polar (negatively charged).

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