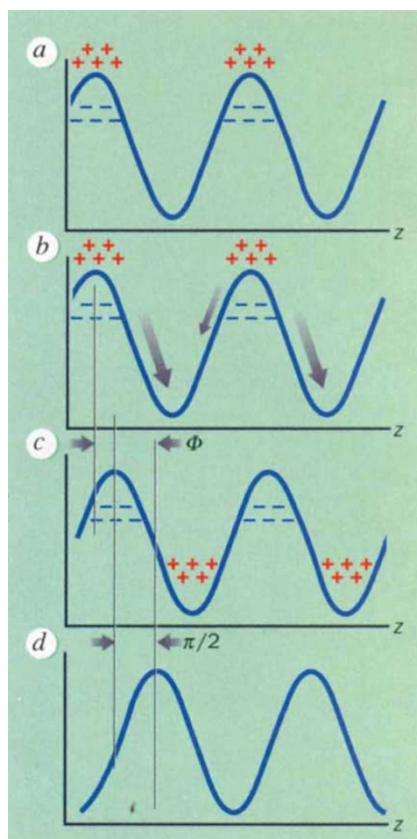


The photorefractive effect

WHEN two light beams intersect to create an interference pattern in a photorefractive material, mobile charges are produced at the intensity peaks by optical absorption in charge-generating sites (a). If a uniform external field is applied, or if diffusion can occur, the positive and negative charges separate and drift apart to produce a 'grating' of electric charge throughout the volume of material (b, c). This produces an internal electric field that is also modulated at the periodicity of the original light intensity pattern, but is not in phase with it (d). If the material's optical index of refraction depends on the local electric field, as in the polymer developed by Meerholz *et al.* (page 497 of this issue), then a refractive index grating is set up. This refractive index grating is a hologram which can diffract light. Its diffraction efficiency, defined as the ratio of intensity of the diffracted beam to that of a probing beam, depends on both the amplitude of modulation of the refractive index (Δn) and the thickness (L) of material, because the overall phase shift introduced into the beam is proportional to ΔnL .

In summary, if a material is to show the photorefractive effect it must contain a photoionizable charge generator and a charge-transporting medium, and its refractive index must depend on the local space-charge field. Deep charge-trapping sites, although not strictly necessary, are also desirable for long-



term storage of the space-charge field. These may be defect sites produced by the imperfect structure of the polymer, or the result of deliberate doping.

A key point is the phase difference ϕ between the pattern of light intensity and the refractive index grating, which arises from the physical motion of charges in the material (they can move by as much as a few micrometres). This spatial non-locality allows for the asymmetric exchange of energy between two light beams in the material to yield optical gain. To see how it works, consider the two 'writing' beams that are interfering in the material to produce the index modulation. Each transmitted writing beam is accompanied by a diffracted beam in the same direction, produced by the other writing beam diffracting off the grating. As a result of the spatial phase shift, the transmitted and diffracted beams in one direction add constructively, yielding gain; the beams in the other direction add destructively, producing loss.

Beam coupling is at the root of many fascinating optical properties such as optical limiting, optical image amplification, or 'novelty filtering', in which a photorefractive material and simple optics are used to display only the features of an image that are changing with time. There are many other ways in which the refractive index of a material can be modified by an incident light beam — photochromism, thermorefraction and optical generation of electronic excited states, to name a few — but none produces the essential nonlocal effect and consequent phase shift. W. E. M.

are conjugated organic molecules with an asymmetric charge distribution produced, for example, by a donor substituent on one end of the molecule and an acceptor substituent on the other. To make the entire sample optically nonlinear, the nonlinear chromophores must be partially aligned (or poled) by an applied electric field in order to make the sample noncentrosymmetric⁴.

Charge-transporting polymers are already familiar as the organic photoconductors used in xerographic copying machines⁵. Generally, these contain a high concentration of 'transport agents', molecules which provide a network for charge to hop through the polymer. The sensitization of photoconductivity at a particular wavelength can be provided by a suitably chosen dye molecule in low concentration.

The first confirmed photorefractive polymer, developed in 1991 (ref. 6), was an optically nonlinear host polymer doped with a high concentration (30 weight per cent) of a charge-transporting hydrazone molecule. This material provided an important proof-of-principle that photorefractive polymers could be fabricated, but the maximum diffraction efficiency was

small (10^{-2} per cent in 350 μm thickness) and the grating growth times were large (minutes at 1 W cm^{-2} writing intensity). Additional polymeric photorefractives were quickly found, with substantial improvements in both diffraction efficiency and speed⁷. Recently we⁸ and independently workers at SUNY Buffalo⁹ took a different tack: start with the well-known photoconductive host polymer poly(*N*-vinyl carbazole), and dope it with a nonlinear optical chromophore in high concentration and a dash of sensitizer. Our approach proved fruitful, producing diffraction efficiencies greater than 1 per cent for the first time (in 125- μm -thick samples). More importantly, net gain was achieved in this polymer: the two-beam coupling gain coefficient was measured to be larger than the optical absorption coefficient (see box for explanation of the two-beam coupling process).

To understand the significance of the new result by Meerholz *et al.*, some simple facts about volume gratings are required. The diffraction efficiency of a volume hologram is proportional to the amplitude of the index of refraction modulation Δn as $[\sin(\pi\Delta nL/\lambda)]^2$, where L is the thickness of the sample and λ is the optical

wavelength. Thus, when (ΔnL) is small compared to λ , the diffraction efficiency grows proportional to $(\Delta nL)^2$. One might think that diffraction efficiencies could be made larger and larger by increasing the sample thickness, and (ignoring absorption) this is true up to a point for most inorganic materials where millimetre- or centimetre-thick samples can be fabricated (albeit with some difficulty). With the new photorefractive polymers, however, millimetre-thick samples are difficult to make at present, mostly because high electric fields are needed to align the nonlinear chromophores and to assist in charge motion.

When (ΔnL) becomes large enough, the sinusoidal function reaches unity (100 per cent diffraction efficiency) and then oscillates. Thus the actual diffraction efficiency never actually exceeds 100 per cent, but the index modulation (Δn) is large enough for 100 per cent efficiency to be attained with an even thinner sample. The new material¹ enters this regime and beyond, producing several oscillations in diffraction efficiency even with 105- μm -thick samples. (The maximum diffraction efficiency measured was only 86 per cent because of optical absorption and reflec-