Comment on "Observation of the Photorefractive Effect in a Polymer"

In a recent, very interesting Letter [1] Ducharme *et al.* make what they believe to be the first report of the photorefractive (PR) effect in a polymer. In this Comment we draw attention to electro-optic (EO) conjugated polymers, in which PR effects have also been observed, as reported for *trans*-polyacetylene [t-$(CH)_x$] in 1983 [2], although not described as such at that time.

Above-gap photoexcitation of t-$(CH)_x$ results, at the long times (μs to ms) probed in mechanically chopped cw laser experiments, in a photoinduced absorption (PA) spectrum characteristic of charged solitons [2,3]; peaks appear at "midgap" and in the infrared, together with an associated bleaching of the π-π^* absorption band. In addition, an oscillatory structure (superposed on the bleaching), straddles the absorption edge. The latter reproduces the spectrum obtained in direct electroabsorption (EA) measurements, and is assigned [2] to EO modulation of the absorption due to local fields arising from soliton generation.

Similar photoinduced EA is found in other conjugated polymers, e.g., poly(2,5-thienylene vinylene) [4] (PTV), and is now appropriately recognized [5] as a "photorefractive effect" (N.B. while manifest in PA as a change in the imaginary part, Δk, of the refractive index, there is by necessity an accompanying change, Δn, in the real part of the refractive index). The relative ease with which this PR effect is detected relates to the large third-order EO response. The corresponding complex susceptibility, $\chi^{(3)}(-\omega;0,0,\omega)$, evaluated from the EA data for PTV has a peak $\mathrm{Re}\{\chi^{(3)}\}$ value of 7.5×10^{-9} esu and a peak $\mathrm{Im}\{\chi^{(3)}\}$ value of 6.2×10^{-9} esu. The close correspondence between photoinduced [4] and directly measured [5] EA spectra is demonstrated for PTV in Fig. 1. Comparison of the magnitudes of the two EA signals at their maxima at 1.78 eV [$(-\Delta T/T)_{\max}\approx1\times10^{-4}$ for photoexcitation with 200 mW/cm^2 of 488-nm (2.54-eV) light at 80 K and $(-\Delta T/T)_{\max}\approx5.2\times10^{-4}$ for 100 kV/cm applied electric field at 130 K] allows an estimate of the average space-charge field that results from photoexcitation: We find a value of $\approx$ 50 kV/cm.

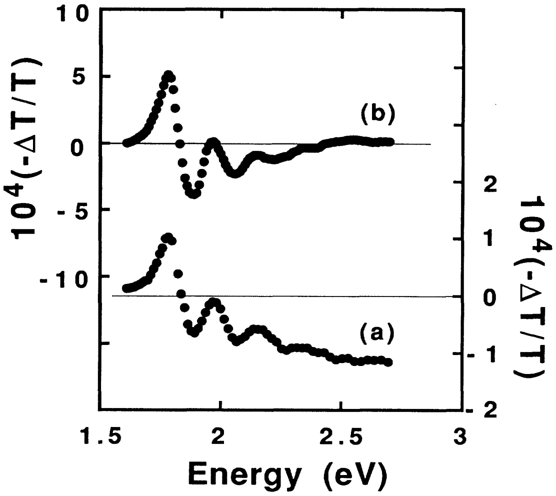

FIG. 1. (a) Photoinduced [4] (right scale, 80 K, 488-nm excitation) and (b) directly measured [5] (left scale, 130 K, 100 kV/cm) EA of PTV. The increasingly negative offset at higher energies for (a) is due to bleaching of the π-π^* absorption by charge-carrier generation [4].

It should be emphasized that the results discussed here differ in two important ways from those reported by Ducharme *et al.* [1].

(i) The PR effect seen in t-$(CH)_x$ and PTV is found in a homopolymer with charge generation and trapping occurring without external bias fields and without the addition of carrier transport agents. Charge generation is assisted by photoexcitation of electron-hole pairs separated between chains, and intrinsic trapping may occur through self-localization arising from electron-phonon coupling [4]. Extrinsic factors including defects and disorder must, however, also play a role.

(ii) The EO effect in conjugated polymers is due to a *third-order* nonlinearity, while that in the materials considered by Ducharme *et al.* [1] has a *second-order* origin. As a consequence, the PR response in conjugated polymers is potentially weaker, but this clearly depends on how large a space-charge field can be achieved. Note also that for second-order materials the polymer must at some stage be poled in order to achieve the EO response, while for conjugated polymers molecular alignment is not required.

Donal D. C. Bradley and Olaf M. Gelsen
Cavendish Laboratory
Madingley Road
Cambridge CB3 0HE, United Kingdom

Received 30 April 1991
PACS numbers: 42.65.Hw, 72.20.Jv, 78.20.Jq, 78.65.Hc

[1] S. Ducharme, J. C. Scott, R. J. Twieg, and W. E. Moerner, Phys. Rev. Lett. **66**, 1846 (1991).
[2] J. Orenstein, G. L. Baker, and Z. Vardeny, J. Phys. (Paris), Colloq. **44**, C3-407 (1983).
[3] N. F. Colaneri, R. H. Friend, H. E. Schaffer, and A. J. Heeger, Phys. Rev. B **38**, 3960 (1988), and references therein.
[4] A. J. Brassett, N. F. Colaneri, D. D. C. Bradley, R. A. Lawrence, R. H. Friend, H. Murata, S. Tokito, T. Tsutsui, and S. Saito, Phys. Rev. B **41**, 10586 (1990), and references therein.
[5] O. M. Gelsen, D. D. C. Bradley, H. Murata, T. Tsutsui, S. Saito, J. Rühe, and G. Wegner, Synth. Met. **41**, 875 (1991).