

Optical nonlinearity of fullerene-doped polymer nanocomposites

O.L. Antipov, I.V. Yurasova, G.A. Domrachev

Abstract. The mechanism of optical nonlinearity of new polymer composites based on a conducting polymer [poly(9-vinylcarbazole)] and fullerenes C_{70} and C_{60} is studied both experimentally and theoretically. The nonlinear-optical studies of self-action and coupling of two 633-nm beams from a helium-neon laser are performed, and variations in the absorption spectra of the composites illuminated by a laser beam are investigated. It is shown that a ‘giant’ inertial nonlinearity of organic materials is caused by the difference in polarisabilities of fullerene molecules and their anion radicals, which are formed upon absorption of photons and charge transfer by poly(9-vinylcarbazole) molecules.

Keywords: nonlinear optical susceptibility, organic nanocomposites, photorefraction, polarisability of fullerenes, anion radicals.

1. Introduction

The nonlinear optical properties of organic polymer composites attract recently great interest due to the prospects of their applications in various devices for high-density optical data storage and processing, in broadband switches of optical communication systems, and other fields [1–3]. Organic media possess unique properties such as great nonlinear-optical susceptibilities, structural flexibility, simplicity of their machining, and a comparatively low cost. Organic materials containing fullerene molecules C_{60} , C_{70} , and C_{76-84} feature an increase in absorption with increasing power of the incident light (reverse saturated absorption), which makes them promising for the development of optical power limiters [4, 5].

The photorefractive nonlinearity of organic composites containing a conducting polymer, a sensitiser (generating charges upon exposure to light) and optical chromophores having the electrooptical susceptibility has been studied in recent years in papers [6, 7]. A large photorefractive nonlinearity of such polymer films, which is comparable with

nonlinearity of bulk inorganic materials, is manifested even upon their exposure to a low-power submilliwatt radiation from a helium-neon laser.

Our previous study of organic composites containing a conducting polymer poly(9-vinylcarbazole) (PVC), a sensitiser (fullerenes C_{60} and C_{70}), a plasticiser and a certain amount (no more than 5%) of a nonlinear material, which was used as an optical chromophore, has demonstrated a ‘giant’ optical nonlinearity of these materials [8]. The experiments have demonstrated large nonlinear-optical variations in the refractive index of the composites, which were observed even in the absence of an electrooptical chromophore.

This paper is devoted to the study of the mechanism of optical nonlinearity of composites containing PVC and fullerene C_{70} in the absence of an electrooptical component. Experimental studies of nonlinear-optical self-action and two-beam coupling were supplemented by measurements of the transmission spectra of polymer films before and after laser irradiation, which allowed us to determine the mechanism of optical nonlinearity of the material.

2. Experimental study of self-action of beams in films

We studied composites containing PVC, fullerene C_{70} , and a plasticiser at a percent ratio of 45:0.5:54.5. In some experiments, we used fullerene C_{60} instead of fullerene C_{70} at the same concentration. Thin polymer films of thickness 60–100 μm were prepared from the polymer solution in toluene. The polymer films were placed between two glass plates. In experiments with an electrical field applied to a film, we used glass plates coated with thin conducting layers representing transparent electrodes.

Upon propagation of a 633-nm beam from a cw helium–neon laser of intensity $I_0 \geq 0.2 \text{ W cm}^{-2}$ achieved at weak focusing, the effect of self-defocusing was observed. The characteristic formation time of a nonlinear lens was ~ 10 min, and the relaxation time of a defocusing lens was $\sim 10 - 20$ min. These results show that the observed lens is not thermal because its relaxation time substantially exceeds the thermal diffusivity time τ_t of a polymer film of thickness l . This time is determined from the relation $\tau_t = l^2/4\chi$ (where χ is the thermal diffusivity of the polymer film) and is equal to 25 ms for $l \approx 0.1 \text{ mm}$ and $\chi \approx 10^{-3} \text{ cm}^2 \text{ s}^{-1}$.

When the laser beam was focused in a sample more tightly, an aberration lens was formed. This was manifested in the appearance of a characteristic ring structure of the beam in the far-field zone. Upon focusing the beam by a lens

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with the focal length $F = 7.5$ cm, the structure consisted of three rings. The time of its formation was ~ 10 min and was inversely proportional to the incident beam intensity.

Self-defocusing was observed both in the presence of an external electric field applied to glass electrodes of the cell and without it, the optical strength of the nonlinear lens being independent of the voltage applied, although its formation time somewhat decreased with increasing electric field strength (by 10%–20% with increasing the field strength from zero to $15 \text{ V } \mu\text{m}^{-1}$).

The magnitude of nonlinearity and its sign were determined by the z -scan method. This method involves the measurement of the optical nonlinearity constant from the dependence of the intensity of a beam propagated through a thin nonlinear layer on its position with respect to the lens focus [9, 10].

In experiments, a polymer film was placed along a focal waist (Fig. 1). We measured the beam intensity in the far-field zone on the axis (the power of the beam of diameter ~ 20 mm propagated through an aperture of diameter ~ 1.2 mm) as a function of the film position. The results of two series of measurements presented in Fig. 2 demon-

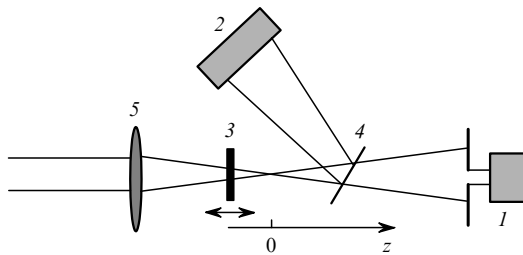


Figure 1. Experimental z -scan scheme: (1, 2) photodetectors; (3) sample; (4) beamsplitter; (5) lens with the focal length $F = 15$ cm.

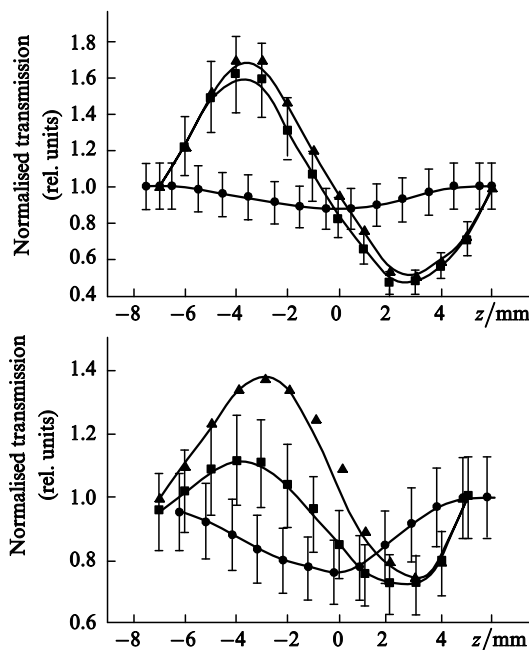


Figure 2. Results of two series of z -scan experiments at partially closed (■) and completely open (●) apertures, and the results of z -scan normalised to an actual transmitted power (▲). Position $z = 0$ corresponds to the geometrical focal point.

strate a great scatter, which can be explained by the inhomogeneity of the distribution of fullerene molecules in the sample. The total power of the beam propagated through the film was also measured at different positions of the film with respect to the focus. This power proved to be minimal near the geometrical focal point, which is explained by an increase of absorption in the sample with increasing light intensity caused by reverse saturated absorption. For the same reason, the z -scan curves detected within a small aperture differ from each other upon normalisation to the power of the incident beam or the beam transmitted by the cell. Scattering from film inhomogeneities also distorted the z -scan curves.

We assumed in our estimates that optical nonlinearity of the films is locally related to the light field, so that the relation $\Delta n = n_2 I$ is valid for the film (this assumption was confirmed later). We also neglected small variations in the absorption coefficient $\Delta\alpha$ of the medium resulting in the additional modulation of the amplitude in the cross section of the light beam (one can easily estimate that the contribution of this effect to nonlinear refraction of the beam is insignificant compared to the contribution of a nonlinear change in the refractive index of the medium under the condition $\Delta\alpha \ll \Delta n k$, where k is the wave number.) For such a local nonlinearity, caused by variations in the refractive index Δn , the z -scan is described by the self-focusing theory, which gives the expression

$$\Delta n = \frac{\Delta T}{0.4(1-S)^{0.27} k L_{\text{eff}}}, \quad (1)$$

for determining small values of Δn , where S is the transmission coefficient of a detector unit, i.e., the ratio of the radius of a limiting aperture on the axis to the beam radius; $L_{\text{eff}} = [1 - \exp(-\alpha l)]/\alpha$ is the effective length of nonlinear interaction; α is the absorption coefficient of the medium; $\Delta T = T_{\text{max}} - T_{\text{min}}$ is a change in the lens transmission defined as the difference of transmission coefficients (the ratio of the power of the beam propagated through a small aperture on the axis to the total power of the beam propagated through a nonlinear layer) at the maximum and minimum of the experimental z -scan curve. Knowing the beam intensity on the axis and measuring the value ΔT , we can determine the nonlinear coefficient n_2 .

The estimate of the maximum change in the refractive index of the sample from (1) using our experimental parameters gave the value $\Delta n = -3 \times 10^{-3}$ (the negative sign corresponds to the defocusing nonlinearity).

Therefore, self-defocusing of a laser beam observed in a polymer layer revealed strong optical nonlinearity of the composite under study. This effect can be explained neither by photorefractive nonlinearity (because an electric field does not affect the value of a nonlinear lens) nor by thermal nonlinearity, because the relaxation time of the lens greatly exceeded the thermal diffusion time over the polymer film thickness. We also did not observe any nonlinear variations in the refractive index of the sample caused by photochemical processes during our experiments (no new stable chemical compounds were formed during our experiments). Some photochemical transformation were observed only after very prolonged exposures (when films were illuminated by a focused beam from a helium–neon laser for several hours).

3. Experimental study of two-beam coupling in polymer films

We studied nonlinear interaction of two collimated beams from a cw helium–neon laser, which were intersected in a $\sim 100\text{-}\mu\text{m}$ thick polymer PVC:C₇₀:plasticiser film (Fig. 3). The pump beam intensity was $\sim 100\text{ mW cm}^{-2}$, and that of the probe beam was 0.16 mW cm^{-2} . The interference field of the intersecting laser beams modulated the refractive index of the medium. Self-diffraction of the incident waves from a refractive-index grating being formed resulted in asymmetric energy transfer between the interacting beams. The energy of an intense pump wave transferred at the output from the layer to a weak probe beam.

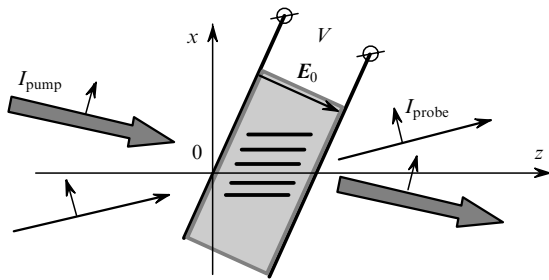


Figure 3. Scheme of two-beam coupling ($l = 60\ \mu\text{m}$, $I_{\text{pump}}/I_{\text{probe}} = 625$).

Unlike the photorefractive effect, two-beam coupling was observed both in the presence and absence of an electric field. The field strength was varied from 1 to $10\text{ V }\mu\text{m}^{-1}$. However, an increase in the electric field strength did not enhance energy transfer but only reduced the characteristic time of formation of the refractive index grating.

The intersection angle θ of two interacting waves also was varied in experiments from 0.01 to 0.45 rad, energy transfer being observed for different angles. An example of the dynamics of this process for $\theta = 0.03$ rad is shown in Fig. 4. For small angles between the beams ($\theta \sim 0.01$ rad), energy transfer was accompanied by the formation of higher diffraction orders, which can be observed visually. Such energy transfer between the waves, which are intersected at a small angle and excite a dynamic grating, involving higher diffraction orders is well known for nonlinearities of different types [11]. Energy transfer from an intense wave to a weaker wave intersecting at a large angle (~ 0.45 rad) also

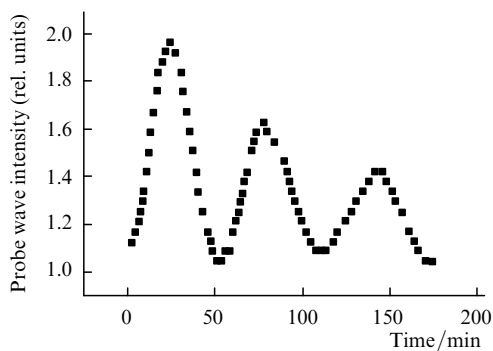


Figure 4. Oscillogram of a signal beam upon two-beam coupling for the intersection angle $\theta = 0.03$ rad.

cannot be an indicator of classical photorefraction in a spatially-displaced grating because such energy transfer can occur in a nonstationary regime even in the case of a purely local nonlinearity.

Thus, our experiments demonstrate energy transfer from an intense to a weak wave in a polymer film; however, they do not allow us to make a definite conclusion about the nature of nonlinearity of the polymer composite.

4. Spectral measurements

A nonlinear change in the refraction index of the composites under study can be explained by the dynamic (reversible) modification of fullerene C₇₀ (or C₆₀) caused by laser irradiation. This effect should be accompanied by a change in the transmission spectrum of the polymer composite after exposure to laser radiation. To elucidate the mechanism of nonlinearity, we measured the transmission spectra of samples before and after their irradiation by a helium–neon laser.

Spectral measurements were performed in two stages. First, we measured the transmission spectrum of a freshly prepared film. Then, the film was irradiated by a laser beam for some time (the exposure was chosen in accordance with the characteristic time of the two-beam coupling). Five minutes later after irradiation, the transmission spectrum of the film was measured again. The aim of this experiment was to detect the appearance of the absorption lines of anion radical of fullerene lying in the near-IR region.

Comparison of the spectra recorded before and after irradiation showed stable changes in the absorption spectrum of the film, which exceeded the experimental error (Fig. 5). The absorption of the composite after irradiation increased by 10%–20% in the wavelength range between 500 and 1500 nm.

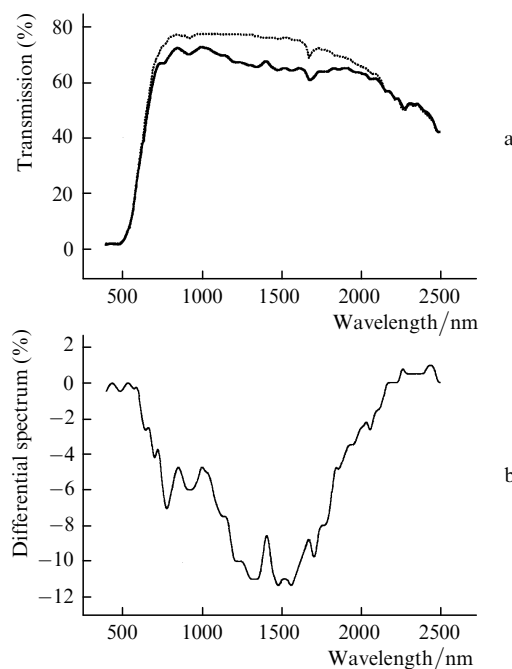


Figure 5. Transmission spectrum of the composite before (dotted curve) and after (solid curve) irradiation (a) and the difference spectrum of the composite (b).

Our spectral measurements confirmed the assumption that the contribution of the change in the absorption coefficient at the operating wavelength to nonlinear refraction is negligible. Indeed, a change in the absorption coefficient measured at the laser frequency was $\sim 10^{-4} \mu\text{m}^{-1}$, which is substantially lower than $\Delta nk \sim 3.2 \times 10^{-2} \mu\text{m}^{-1}$.

The changes in the spectrum relaxed during ~ 10 min after laser irradiation. Note that this relaxation time corresponds to the dynamics of two-beam coupling and self-action.

The results of the spectral studies can be explained by the appearance of anion radicals of fullerene (C_{70}^- , C_{70}^{2-} , etc.) induced by irradiation. It is well known that the absorption spectrum of anion radicals of fullerene differs from that of a fullerene molecule [12]. A similar transformations of absorption spectra was earlier observed for organic photo-refractive composites doped with C_{60} [13].

5. Discussion

Our experiments showed that variations in the refractive indices of polymer films are most likely caused by changes in their transmission spectra due to transformation of fullerene C_{70} (or C_{60}) to anion radicals C_{70}^- , C_{70}^{2-} , etc. induced by laser irradiation.

The mechanism of nonlinearity can be described as follows (Fig. 6). After absorption of a photon by a fullerene molecule, its electron undergoes a transition from the ground state to higher singlet states and then experiences nonradiative relaxation over excited singlet levels $S_1 - S_2$ to the excited triplet level T_1 . An electron from a nearest energy level of a PVC molecule occupies the electron vacancy that appeared at the ground level. This process results in the formation of a stable structure – an anion radical of fullerene. A hole formed after transition of the electron to the anion radical migrates over the electron system of PVC until it is captured by a trap. The concentration of anion radicals decreases after irradiation due to recombination.

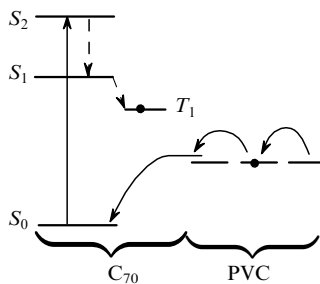


Figure 6. Scheme of formation of a fullerene anion radical.

Such a scenario also takes place in the case of classical photorefractive nonlinearity; however, only in the presence of an additional electrooptical component in a polymer composite, which provides a change in the refractive index induced by the field of a spatial charge of anion radicals and electrons captured by traps.

A peculiarity of our case is that the refractive index of the composite containing anion radicals changes even in the absence of the electrooptical component due to the difference between polarisabilities of anion radicals and fullerene

molecules. The matter is that the excited triplet level T_1 has a rather long lifetime (up to a few tens of milliseconds), which strongly depends on the fullerene surrounding, and its polarisability substantially differs from polarisability in the ground S_0 state.

The effect of a change in the refractive index of various substances upon excitation of molecules having different polarisabilities in the ground and excited states is well known and is described by the expression [14]

$$\Delta n = 2\pi \frac{F_L^2}{n_0} \sum_q \Delta N_q \Delta p_q, \quad (2)$$

where $F_L = (n_0^2 + 2)/3$ is the local field factor (Lorentz factor); n_0 is the unperturbed refractive index; Δp_q is the difference between polarisabilities of ions in the ground state and in the excited q th level, whose population changes by ΔN_q upon excitation.

It is known that the polarisability of a level is determined by the probabilities of all transitions from this level induced by radiation at the frequency ν of measurements:

$$p_q^0(\nu) = \frac{e^2}{4\pi^2 m} \sum_l \frac{f_{ql}(\nu_{ql}^2 - \nu^2)}{(\nu_{ql}^2 - \nu^2)^2 + (\gamma_{ql}\nu)^2}, \quad (3)$$

where e and m are the electron charge and mass, respectively; f_{ql} is the oscillator strength of the transition between energy levels with subscripts q and l ; ν_{ql} and γ_{ql} are the resonance frequency and linewidth of this transition, respectively.

The difference between polarisabilities of fullerene molecules in the ground state and in the excited triplet state appears because the oscillator strengths for transitions from the excited T_1 state are substantially greater than those for transitions from the ground state. Indeed, it is this property that determines the effect of reverse saturated absorption (or ‘darkening’) of fullerene-doped compounds.

An additional factor, which enhances nonlinearity of polymer composites, is diffusion (or drift) of free charge (hole) carriers, which facilitates the population of an excited level during formation of anion radicals with populated S_0 singlet and T_1 triplet levels. Relaxation of an anion radical can occur due to its recombination with a hole, which is substantially hindered when holes leave the irradiated region and recombine with traps in a dark region. For this reason, the relaxation time of nonlinear perturbations, which we have measured after laser excitation, proved to be equal to the relaxation time of captured holes and noticeably decreased in the presence of an external electric field facilitating a fast drift of free charge carriers.

A large optical nonlinearity of fullerene-doped composites was confirmed by two-beam coupling and laser-beam self-action experiments. The fact that the energy transfer rate does not increase with increasing voltage proves the ‘non-electrooptical’ nature of nonlinearity. The increase in the rate of energy transfer from an intense wave to a weak wave can be reasonably explained by an increase in the rate of formation of anion radicals due to a faster separation of charges and their drift in the electric field.

Energy transfer upon two-beam coupling can be also explained by the formation of a concentration grating of fullerene anion radicals in the sample, whose polarisability differs from that of fullerene molecules. The refractive index grating caused by such nonlinearity is locally related to the

interference pattern, which excludes, as is known, stationary energy transfer upon Bragg diffraction. At the same time, it is known that stationary energy transfer can occur upon two-beam coupling in samples with local nonlinearity under conditions of Raman–Nath diffraction taking place at small angles of intersection of the interacting waves. Indeed, according to our estimates, the phase mismatch Δkl of the wave vectors of the nearest diffraction order in a film of thickness $l = 100$ nm was ~ 0.3 .

Energy transfer upon wave-mixing in the case of large intersection angles of the waves ($\theta > 0.1$ rad) can be explained by a nonstationary energy transfer due to the motion of the refractive index grating with respect to the interference pattern inducing the grating [11]. This is proved by oscillations of a probe wave observed in experiments.

6. Conclusions

We have shown that organic films containing a conducting polymer poly(9-vinylcarbazole), fullerenes C_{70} (or C_{60}), and plasticisers possess a strong photochromic optical nonlinearity, which is explained by the difference of polarisabilities of fullerene C_{70} and its anion radicals produced upon laser irradiation. Variations in the refractive index and related changes in the absorption spectrum of the polymer composite are reversible (they relax with the relaxation time ~ 10 min).

The results of nonlinear-optical experiments on two-beam coupling and self-action confirm the giant nonlinearity of the composites. Energy transfer from a strong wave to a weak wave upon two-beam coupling was observed both in an external electric field and without it. The two-beam coupling coefficient does not depend on the electric field strength, which affects only the characteristic time of the grating formation.

Note that such nonlinearity can be obtained not only in polymer composites but also in other fullerene-doped media such as, for example, fullerene-doped glasses.

A disadvantage of polymer composites is the film degradation after prolonged exposure to laser light. At the same time, the giant nonlinear-optical susceptibility of fullerene-doped polymer composites make them promising for using in devices for optical data processing (for example, in devices for separating signals against a random noise background, etc.).

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