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Self-organised poly[(ethynediyl)(arylene)(ethynediyl)silylene]/*N*-ethylcarbazole/polyphenylsilsesquioxane hybrid nanomaterials: photoconductivity and electro-optic response at telecommunication wavelengths*

W. E. Douglas,[a]* *L. G. Klapshina,*[b] *A. S. Kuzhelev,*[c] *W. Peng,*[a] *and V. V. Semenov*[b]

[a]*Laboratoire de Chimie Moléculaire et Organisation du Solide,*
CNRS UMR 5637, Université Montpellier II, 34095 Montpellier cedex 5, France
[b]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603600, Nizhny Novgorod, Russian Federation
[c]*Canadian Space Agency,*
6767 route de l'Aéroport, St-Hubert, Québec, Canada, J3Y 8Y9

The photoconductivity and electro-optic response of a self-organised nanostructured poly[(ethynediyl)(arylene)(ethynediyl)silylene]/*N*-ethylcarbazole/polyphenylsilsesquioxane composite have been investigated with a *cw* diode laser at a wavelength of 1500 nm. For electric field 25 V μm^{-1} and beam intensity 18 W cm^{-2}, the photosensitivity was 0.5 pS cm^{-1} (W $cm^{-2})^{-1}$. The dark conductivity was found to be much less than the photoconductivity and the composite shows photo charge generation at this wavelength. The value of the composite electro-optic coefficient is in agreement with data for polymeric materials active in the visible range. Orientational effects have been observed with modulation frequencies down to several Hz, and quite slow dynamics of the response can be expected.

Keywords: organosilicon polymers, conjugated, self-organization, self-assembly, photoconductivity, electro-optics, charge generation.

Poly[ethynediyl-arylene-ethynediyl-silylene]s (PEAES) exhibit high third order nonlinear optical properties[1] and can be used as optical chromophores for photorefraction (PR) at 633 nm with fullerenes as charge generator.[2] We have also recently described novel organic PR composites, based on PEAES behaving as both optical chromophore and charge generator, active at the very important telecommunication wavelength 1500 nm.[3] The longest wavelengths at which organic PR materials have been previously demonstrated lie in the region 750—830 nm,[4] although inorganic materials[5] and also nanocomposites of inorganic nanocrystals in a polymer matrix[6] active at telecommunication wavelengths have been described. The PR compositions made from PEAES/*N*-ethylcarbazole (EC)/polyphenylsilsesquioxane undergo self-organisation through π—π interactions between the aromatic groups of all three components giving nanostructured hybrid layered materials, thus accounting for the observed PR properties, in particular, the photocharge generation at 1500 nm even though the composition solution has an absorption edge at *ca.* 550 nm.[3] Notably, the self-assembly occurs in the absence of any surfactant. Long-range surfactant-free ordering has been reported recently for bridged silsesquioxanes $X[SiO_{1.5}]_n$ ($n \geq 2$),[7,8] but to our knowledge it has not been observed previously for non-bridged silsesquioxanes ($n = 1$) such as polyphenylsilsesquioxane although surfactant-directed self-assembly is well established,[9] and the use of anthracene-based organogelators has recently been described. Polyphenylsilsesquioxane itself has a random, ladder, or cage structure.[10,11] Here, we report the photoconductivity and electro-optic properties of the nanostructured composite at telecommunication wavelengths.

Results and Discussion

The PEAES polymer was synthesized by Pd-catalysed cross-coupling of diethynyldiphenylsilane with 9,10-dibromoanthracene (Scheme 1), the polymer chains containing *ca.* 50 units.[12] The molecular structure consists of alternating donor anthracene[13—15] and acceptor Ph_2Si [16]

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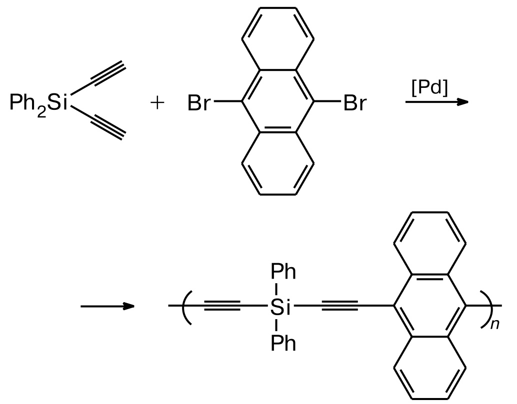
groups linked by acetylene bridges giving a conjugated electron system. Indeed, acetylene itself is a strong acceptor,[17] thus reinforcing the acceptor effect of the silicon-containing units. Hence, in our design of a low-bandgap conjugated polymer we followed the approach previously used of alternating donor and acceptor groups in the polymer chain.[18] This alternation together with the long conjugated chain gives rise to a red-shifted absorption spectrum in solution, which in the solid-state extends into the IR region up to 1600 nm (Fig. 1).

Scheme 1



PEAES

Reagents and conditions: $(PPh_3)_2PdCl_2$, CuI, PPh_3, Et_3N, PhMe, 16 h, 89 °C.

Such differences between the solution and solid-state spectra can arise from formation of aggregates and intermolecular charge transfer complexes as has been observed in different conjugated polymer systems.[18–20] In particular, the large increase in the value of the electronic $\chi^{(3)}$ (*ca.* two orders of magnitude) for a similar PEAES derivative observed on going from solution to the solid-state film[21] should be noted. The same mechanisms responsible for IR-tailing obviously may provide the traps in the composite necessary for the observed PR.[3]

In addition, the long conjugated polymer backbone giving rise to a high hyperpolarizability makes PEAES useful as an optical chromophore.[1,21] Indeed, the PEAES molecule being centrosymmetric, the microscopic second-order susceptibility (β_{ijk}) must be zero. At first sight, this might appear to preclude PR effects. However, it has been shown in a number of works that in practice the dominating role in the creation of refractive index gratings by PR processes in low glass-transition temperature composites can be attributed to the orientational nonlinearity, *i.e.* a third-order response.[22–24] Another mechanism of the third-order response that can result in field-induced birefringence (and thus contribute to the PR process) is the fast electronic $\chi^{(3)}$. Typically, the value of the electronic $\chi^{(3)}$ is much less than the orientational $\chi^{(3)}$ for most components of PR composites, and thus its contribution can be neglected.[25] However, in the case of conjugated polymers with large numbers of units, the orientational and electronic $\chi^{(3)}$ can be of the same order of magnitude. This effect becomes crucially important for molecules with zero second-order susceptibility, where the electronic $\chi^{(3)}$ provides the sole mechanism affording fast field-induced birefringence. In other words, the second-order electro-optic (EO) response provided by electronic $\chi^{(3)}$ can be used for PR.

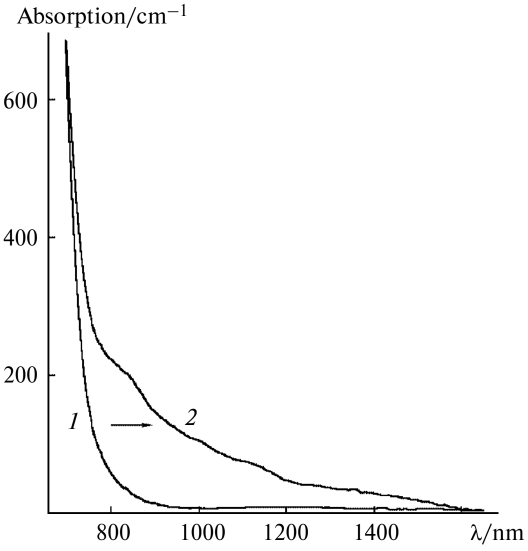


Fig. 1. The absorption spectra of the composite made from PEAES(36%), EC(28%), and phenyltrimethoxysilane (PTMS, 36%) (*1*) in toluene solution with solvent spectrum subtracted (measured in cell of 1 cm thickness with concentration such that the number of absorbing PEAES molecules is identical to that in the 20 μm composite film) and (*2*) the amorphous solid-state (film of thickness 20 μm). The arrow indicates the spectrum transformation from solution to solid-state.

The charge transporting properties were provided by both PEAES and EC.[26] Good optical quality films with a glass transition temperature around room temperature were obtained for the composition PEAES(36%) : EC(28%) : PTMS(36%). The large concentration of PEAES served to increase the EO coefficient and charge generation efficiency.

Photoconductivity measurements

The spectral range of operation of organic PR materials is limited by the sensitivity of the sensitizer. Thus, the most important step in realizing PR in the near-IR region is the attainment of efficient charge generation. We examined our samples for charge generation and electroconductivity by the simple dc technique (by measuring the photocurrent through the film) successfully used in a large number of studies. A voltage up to 500 V was applied through a resistor between the indium tin oxide (ITO) electrodes. The current was measured by monitoring the voltage across the resistor when a *cw* laser beam was directed into the sample, as well as under dark conditions. The photoconductivity σ_{ph} was determined as the difference between the conductivity measured under illuminated conditions and the dark conductivity $\sigma_{d.}$. It depended on both the dc electric field value E and the laser beam intensity I (Fig. 2). Both dependences can be well approximated by the power laws $\sigma_{ph} \propto E^q$, and $\sigma_{ph} \propto I^p$. The photoconductivity was best fitted for $q = 0.8 \pm 0.1$ and $p = 1.2 \pm 0.1$. Such dependences are typical of PR organic materials and reflect the increase in charge generation efficiency and reduction in recombination probability at increasing field and intensity.[27] Using the magnitude of the measured photoconductivity 2—9 pS cm^{-1}, we calculated the sample photosensitivity σ_{ph}/I commonly used as a figure-of-merit for charge generation efficiency and carrier transporting properties. For electric field 25 V μm^{-1} and beam intensity W cm^{-2}, we obtained photosensitivity 0.5 pS cm^{-1} (W cm^{-2})$^{-1}$. Note that this value is in agreement with those for a number of PR polymeric materials, for example, the well-studied NPDA:DEN-based composites in the visible range.[28—30] The dark conductivity was found to be much less than the photoconductivity. Thus, our polymer composite shows photo charge generation at 1.5 μm and sufficient conductivity for a PR response to be expected at this wavelength.

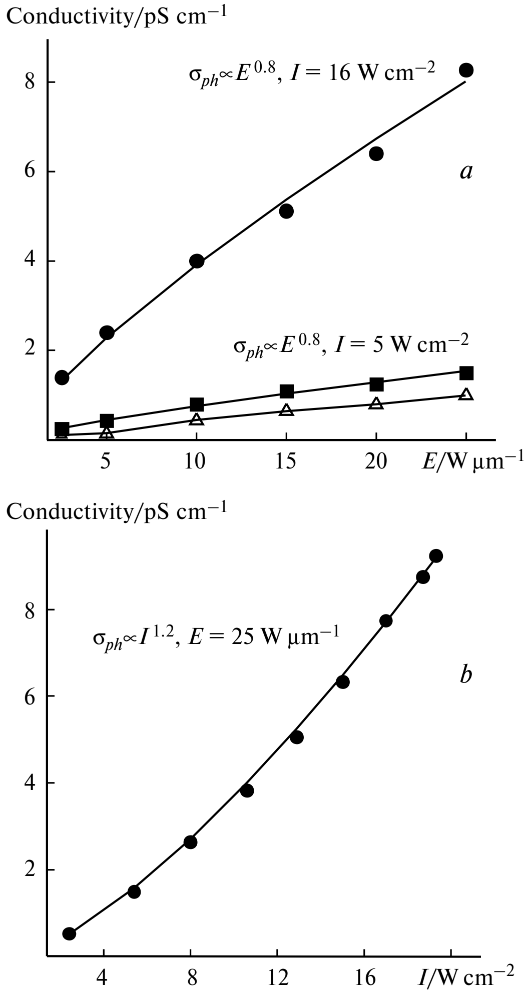


Fig. 2. The dependences of photoconductivity σ_{ph} and dark conductivity σ_d on the dc field value E (*a*) and laser beam intensity I (*b*). The curves are power law approximations.

Electro-optic measurements

In addition to light induced charge generation and transporting, another necessary property for the composite to be PR is EO response. Note that in the case of the centrosymmetric PEAES molecule, only the presence of second order EO responses can be expected (the linear EO coefficient should be zero, or negligible). However, the macroscopic manifestation of second order EO in polymer composites of low glass transition temperature should be the same as that for linear EO owing to the linear dependence of the linear EO coefficient on the strength of the poling field.

In our measurements the poling dc electric field E_{dc} up to 9 V μm^{-1} and a modulating electric field with amplitude E_m = 1 V μm^{-1} were applied to the ITO electrodes of the sample. An ellipsometry setup (similar to the simple reflection technique) was used for measurements of the electro-optic response (Fig. 3).[24,31] The laser beam with polarization 45° to the plane of incidence was directed on the sample at an angle θ = 60°. After the first passage through the sample the beam was reflected at 0.5° to the backward direction by a mirror. After the second passage, the beam passed through the compensator and polarization analyzer, and was directed to the detector. The compensator was adjusted as described[31] to maximize the measured signal. A lock-in amplifier measured the modulated part of the beam. The modulation was a manifestation of

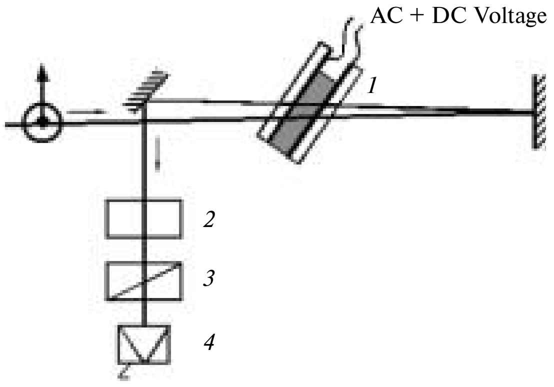


Fig. 3. The setup for measurements of field-induced anisotropy and electro-optic response of the composite film: sample (*1*), compensator (*2*), analyzer (*3*), detector (*4*).

the field-induced anisotropy of the sample caused by the phase shift difference of the *p*- and *s*-polarized components of the beam induced by the modulating voltage in the sample. The electric field induced phase shifts for these components of ac-modulation frequency can be derived by the procedure developed previously[31] from symmetry relationships for electronic $\chi^{(3)}$ tensor components or second order EO s_{ijkl} tensor components ($s_{3333} = 3s_{3311}$, where 1 and 3 are the directions perpendicular and parallel to the film normal). Thus, the following expression for the magnitude of the second order EO tensor component s_{3333} can be obtained:

$$s_{3333} = \frac{3\lambda I_m}{4\pi E_{dc} V_m n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{\sin^2\theta (n^2 - 2\sin^2\theta)}, \qquad (1)$$

where I_m is the measured amplitude of the intensity modulation normalized to the time-averaged intensity at the detector, V_m is the amplitude of the modulating voltage, and n is the refractive index. To distinguish the field induced anisotropy associated with the electro-optic response from that caused by molecular reorientation, a modulation frequency greater than 1 kHz should be used.[23,24] In our experiments, the value of the electro-optic tensor component s_{3333} was found to be $4.7 \cdot 10^{-19}$ m^2 V^{-2} (for $n = 1.6$) at a modulation frequency of 10 kHz.

It should be noted that no substantial electro-absorption was observed that could contribute to the EO measurements. For comparison with other PR materials we calculated the "effective" EO coefficient $s_{3333}E_{dc}$ analogous to the linear EO coefficient (Fig. 4, *a*). The value of the "effective" electro-optic coefficient is in agreement with data for polymer PR materials active in the visible range.[32]

Orientational effects have been observed with modulation frequencies down to several Hz (Fig. 4, *b*). A substantial increase in the signal for the field-induced anisotropy was noted. This is in good agreement with the orientational enhancement effect.[23,24] Since our polymer has no side-chain chromophores, this contribution may result from reorientation of the PEAES main chain. It should be emphasized that the growth of the signal is sharply increased at the lowest rate (5 Hz). Thus, one may expect an interruption in the growth at frequencies much less than several Hz, and, as a consequence, characteristic reorientation times (comparable with the period of modulation at which the birefringence reaches a maximum) in the range of seconds or even more. Therefore, quite slow dynamics of the PR response can be expected.

Experimental

The PEAES was prepared as previously described.[12] The samples for the optical studies were prepared by placing a sufficient amount of the composite [PEAES(36%) : EC(28%) : PTMS(36%)] dissolved in toluene on a glass slide coated with a transparent ITO electrode, followed by drying at room temperature until the solvent was removed, and then covering with a second ITO coated glass slide. The sandwich contained a layer of composite material of thickness $L = 20$ μm determined by the Teflon® spacer. It should be noted that due to the very low transparency of the samples in the visible range at this thickness, the control of film quality in thicker samples was hampered. Hence, samples of thickness in excess of 40 μm exhibited low breakdown voltages. Thus, films of thickness 20 μm were found to be optimal for the optical studies.

The testing of the material for the presence of all the necessary features for PR activity, namely, light-induced charge generation, electro-conductivity, and electro-optic responses was performed with a *cw* diode laser at a wavelength of 1500 nm with fibre Bragg grating stabilization of the wavelength. The total power of the optical beams was up to 200 mW.

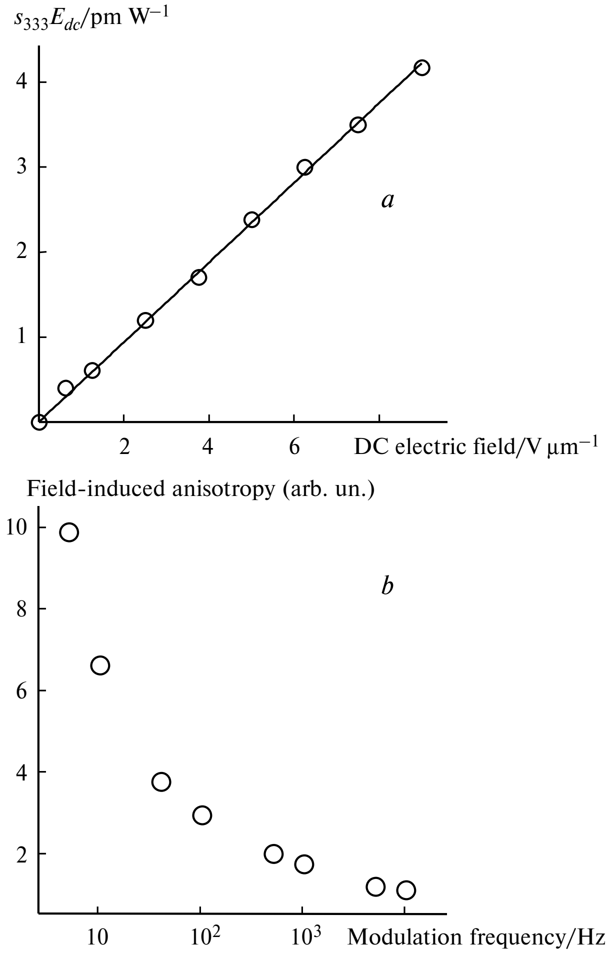


Fig. 4. The dependence of the "effective" electro-optic coefficient $s_{333}E_{dc}$ on the applied poling field at 10 kHz modulating field (circles denote experimental data; the curve is a linear fit) (*a*), and of the field-induced anisotropy on the frequency of the modulating field at a dc electric field of 9 V μm^{-1} (*b*). A tenfold increase in the signal was observed.

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