High-efficiency generation of harmonics in polythiophene

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Abstract. **High-efficiency harmonic generation is observed in a semiconducting polymer RR-P3HT [regioregular poly(3-hexyl-thiophene)], which exhibits a high nonlinear susceptibility [$\chi^{(2)} > 10^{-6}$ m V^{-1}] under pumping by a pulsed fibre laser. The harmonic generation efficiency in RR-P3HT is comparable or higher than that observed for liquid crystals, which are used in reference experiments to estimate the susceptibility [the quadratic susceptibility of a nematic liquid crystal NLC 1289 is $\chi^{(2)} \approx 2 \times 10^{-6}$ m V^{-1}]. No generation is observed in polythiophene with a random structure, RRa-P3HT [regiorandom poly(3-hexylthiophene)], at the same pump power. It is experimentally demonstrated that a necessary condition for generating the second and third harmonics in a polymer, along with a high pump power density, is the presence of a large power density gradient (exceeding 10^{13} W m^{-3}). Based on a preliminary theoretical analysis, we can suggest that the quadrupole mechanism, which is a consequence of the regularity of RR-P3HT structure in the thin near-wall layer, may contribute significantly to the nonlinear radiation conversion in semiconducting polymers.**

Keywords: nonlinear optics, harmonic generation, polythiophene, liquid crystals.

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1. Introduction

Polymer (organic) electronics has become important for many new research and technology fields during the last several decades [1]. This is primarily due to the development of relatively simple techniques for processing and fabricating polymer elements combining the properties of inorganic conductors and semiconductors. The application of these techniques, along with modern nanotechnologies, made it possible to design organic electronic and electro-optic analogues of conventional devices. Despite the evident progress in application of organic semiconductors in electron devices, some of their predicted and expected properties either were not revealed at all or were unsuitable for technological application. An example is nonlinear optical properties of electronic nature (electronic nonlinearity), which provide frequency conversion of radiation. The interest of the experts in the field of nonlinear optics to organic materials has significantly decreased during the last 30 years. The most complete review of achievements in this field by the 1987s–1990s can be found in the two-volume monograph [2], and a unified pattern of optical nonlinearity for media of both classes (organic and inorganic) was presented in [3].

In [3] and other similar works, semiconducting organic media are not considered as an individual subclass, and mathematical models of nonlinearity are built based on expansion of polarisability in powers of only electric field; i.e., the dipole polarisability was taken into account (dipole model). A specific material (polythiophene) was considered later in [4, 5]; however, the results were analysed within the same dipole model. As a result of studying the nonlinear optical properties of different polymer materials, values of nonlinear susceptibility slightly exceeding the corresponding parameters for inorganic media were obtained {for example, $\chi^{(2)} \approx 10^{-11}$ m V^{-1} for NPP (N-(4-nitrophenyl)-L-prolinol) [2]}. A rather pessimistic conclusion (stated most clearly in [3]) about the technological impracticality of polymers in nonlinear optical devices was drawn based on the results of [2–4]. Nevertheless, the research in this field is continued, although not so intensively as before.

High nonresonant nonlinear susceptibilities upon bulk generation of combined frequencies (resonance frequencies are not considered here), exceeding the susceptibilities in solid organic and inorganic semiconductors by several orders of magnitude, were observed in thermotropic nematic liquid crystals (LCs) [6, 7]. Since the optical nonlinearity in LCs is a combined orientational–electronic nonlinearity in its nature, one must perform modelling taking into account the terms of

polarisability expansion in not only electric field powers (dipole component) but also in electric field gradients (quadrupole polarisability) [8–10]. Pure thermotropic LCs (i.e., free of solvents, dyes, nanoadditives, and polymer additives) do not belong to polymer media and have no semiconductor properties of solid crystals. Nevertheless, the orientational structures in LCs (molecules aligned along a selected direction) can be identified to a certain extent with a molecular chain. Based on this, one can suggest the presence of large nonresonant nonlinearities in polymers with semiconducting properties. In particular, some polymers are liquid crystals in the initial state (the so-called polymer LCs); some of them belong to lyotropic LCs [8]; i.e., their orientational properties arise only in a solution with a certain concentration. The object of our study, polythiophene with hexyl substituents (regioregular poly-3-hexylthiophene RR-P3HT), is dissolved well in nonpolar organic solvents [11] (in contrast to the unsubstituted polythiophene, which was used in [12]). In solutions, RR-P3HT may exhibit properties of lyotropic LCs [13]. We used polythiophene in the solid phase, obtained after solvent (chloroform) drying for no less than 24 h.

Thus, polymers can become a 'novel' and technologically more efficient nonlinear optical medium, because many of them, in contrast to LCs, exist in the solid phase, and some are even dissolvable [4]. The solubility of polymers simplifies the preparation technology of polymer samples [1], and their existence in the solid phase, in contrast to the liquid-crystal state (characterised by large orientational, spatial, and temporal fluctuations), reduces significantly the generated radiation scattering and instability.

The third-harmonic generation (THG) in polythiophene RR-P3HT was investigated in [14]. The cubic nonlinear susceptibility $\chi^{(3)}$ was measured to be $\sim 10^{-19}$ m^2 V^{-2}, a value smaller than that for inorganic semiconductors [e.g., $\chi^{(3)} \approx 10^{-18}$ m^2 V^{-2} in GaAs] [15]; this nonlinear susceptibility is obviously insufficient for technological applications. Simultaneous generation of the second and third harmonics was observed in [5]; this effect was used to study the photoelectric properties of mixtures of RR-P3HT with fullerenes; however, no estimates of nonlinear susceptibilities were made.

In this work we showed for the first time that a necessary condition for implementing more efficient (as compared with previous studies) harmonic generation in polymers, along with the high pump power density, is the presence of a high pump power density gradient (above 10^{13} W m^{-3}). Conditions for harmonic generation, implementing susceptibilities $\chi^{(2)} > 10^{-6}$ m V^{-1} under pumping by a pulsed fibre laser were found for the polymer RR-P3HT. The harmonic generation efficiency in RR-P3HT is close to that of the liquid crystals used in comparative experiments aimed at estimating susceptibilities (or even higher) [6, 7]. It follows from a preliminary theoretical analysis of the obtained results that the quadrupole mechanism, which is due to the regularity of RR-P3HT structure in a thin layer adjacent to the substrate, makes a significant contribution to the nonlinear radiation conversion in polymers.

Structurally, RR-P3HT is 'semicrystalline', in contrast to its regiorandom, completely amorphous analogue (RRa-P3HT) [1]. Crystalline regions with sizes from several hundred nanometres to a micrometre alternate (are randomly mixed) with amorphous regions in RR-P3HT films. The volume ratio of the amorphous and crystalline regions depends on the way of preparation of RR-P3HT film and its thermal history. The RR-P3HT and RRa-P3HT chemi-
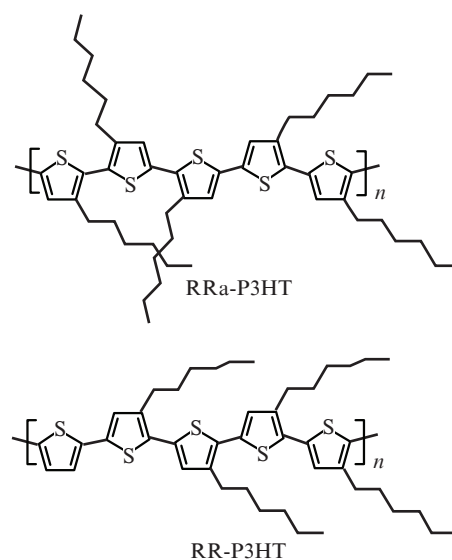

Figure 1. Arrangement of hexyl substituents in RRa-P3HT and RR-P3HT.

cal structures differ by the arrangement of hexyl substituents (Fig. 1). Note that, in correspondence with the EU Regulation No. 1272/2008, RR-P3HT and RRa-P3HT are nontoxic and ecologically safe materials.

2. Specific features of harmonic generation in organic polymers and liquid crystals

The interest in the problems of nonlinear optics of organic media [1–4, 16, 17] is primarily due to the possibility of revealing large (in comparison with inorganic materials) nonlinear susceptibility coefficients for them. However, an organic material satisfying all necessary requirements for applied nonlinear optics has not been obtained until now. Wang et al. [4], who studied the THG in the most promising semiconducting polymer, i.e. regioregular poly-3-hexylthiophene (RR-P3HT), showed (based on comparative experiments) the susceptibility coefficient for the third harmonic (TH) to be lower than for GaAs. Nevertheless, the theoretical prerequisites reported for semiconducting polymers [2, 16, 17] are quite justified, and the absence of experimental data confirming high nonlinearity may be caused by the neglect of peculiar properties of polymers, differing them from solid inorganic crystals. In our opinion, to take into account these properties, one would to proceed from an analogy with high-efficiency frequency conversion of radiation in LCs [9, 18], despite the difference in the aggregate states of LCs and solid polymers [19].

The bulk harmonic generation in LCs is characterised by a number of features that are absent in inorganic materials [20]. In particular, an unstrained (homogeneous) NLC has no inversion centres in the bulk. However, in contrast to solid crystals, LCs belong to the so-called soft media, and their structure, along with the bulk symmetry, can easily be changed under external factors. The latter include impacts that can be classified by one term: nonlinear self-action of radiation [21]. As a result, the generation of even harmonics is arbitrarily divided into two successive stages. First, bulk deformation occurs under the action of a wave electric field, which generally changes the uniform direction of the NLC

optical axis (director) in space and removes the central symmetry. Second, nonlinear generation of even harmonics occurs, as in solid crystals due to electrons. In particular, the generation thresholds are generally determined by the onset thresholds of LC structure deformation. Here, an important factor is that there must be a corresponding change in the LC structure for efficient SHG (as well as for THG, but without any requirements on symmetry). The issues of harmonic generation in LCs were considered in [22], where an analogy with inorganic crystals was laid in the basis and the orientational processes of nonlinear wave self-action were not discussed.

The specific features of nonlinear optical properties of LCs, including their high (several orders of magnitude higher than that for inorganic crystals) nonlinear susceptibility, are due to the orientational structure of nematic and smectic states of LCs [6, 7, 18, 20, 23], which is similar to some extent to the planar structure of RR-P3HT molecules in the region contacting the substrate [1]. In accordance with these considerations, as well as for LCs in [20], we suggested that the generation mechanism is quadrupole and, as a consequence, that the frequency conversion of radiation in polythiophene is affected by an additional factor: pump intensity (or electric-field) gradient. As was expected, the efficiency of radiation conversion into harmonics depends fairly strongly on this factor.

3. Experimental

A pulsed fibre laser system (laser + amplifier) with a radiation wavelength $\lambda \approx 1560$ nm was used for pumping in our experiments. A schematic of the experimental setup is shown in Fig. 2. The pulse repetition rate is 15.6 MHz, the pulse duration is 50 ps, the average radiation power is 400 mW, the peak power is $\sim$480 W, and the pulse energy is $\sim$25 nJ. A fibre controller is installed at the laser system output to drive the radiation polarisation state. A standard SMF-28e fibre with a core diameter $w_0 = 8.2$ μm was used. The output end face of the polarisation controller fibre formed a divergent conical beam with a profile close to Gaussian and a width at the end face equal to w_0. The second-harmonic ($\lambda/2 = 780$ nm) generation power did not exceed 20–30 pW on average due to the pump-laser intrinsic nonlinearity; no THG was observed. The spectrum of transmitted radiation in the visible and near-IR ranges was recorded using a QEPro spectrometer (Ocean Optics). When measuring intensity, the spectrometer was replaced by a power meter with filters for selecting harmonics.
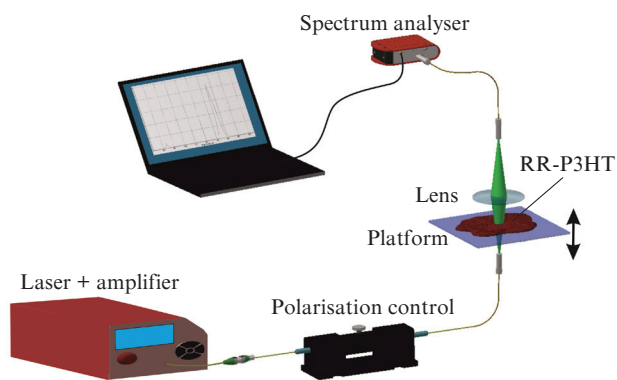
Regioregular P3HT with a regularity higher than 98.5 % (Ossila Ltd) was used without any additional purification; the other necessary agents – acetone, ethanol, and chloroform (Sigma Aldrich) – were not additionally purified as well. Glass and quartz substrates were purified mechanically in a detergent solution and then processed with ultrasound in distilled water, acetone, and ethanol, for 10 min in each stage. In the end of purification, substrates were dried in a pure air flow and exposed to an UV lamp in air for 30 min, which led to ozone generation. The residues of organic materials on a substrate were oxidised as a result of interaction with ozone. RR-P3HT solutions were prepared by dissolving 1.7 mg RR-P3HT in 1 mL chloroform by 2-min heating at 60 °C. To prepare a RR-P3HT layer, 300 mL solution were deposited on a substrate with sizes of 23×23 mm. The layer obtained after evaporating chloroform had a uniform brownish-goldish colour. To prepare thicker RR-P3HT films, the polymer concentration in the solution was proportionally increased.

Comparative experiments were performed with an NLC that was not subjected to any purification; it was a commercial mixture of NLC 1289 biphenyls (NIOPIK, Russia).

To study the dependences of harmonic generation on the pump parameters, the substrate with a RR-P3HT layer could be displaced (using a micrometer table) to change its position (distance h) relative to the immobile fibre end face. This displacement made it possible to change gradually the diameter w of the Gaussian pump beam incident on the sample. The laser and diagnostic equipment used in the experiments did not reveal any generation of harmonics from pure substrates and other elements of the system.

A characteristic transmission spectrum of polythiophene samples is shown in Fig. 3. It can be seen that, with allowance for the scattering and Fresnel reflection from boundaries in the vicinity of pump ($\lambda = 1560$ nm) and second harmonic ($\lambda/2 = 780$ nm) wavelengths, the samples are fairly transparent. There is significant absorption at the TH wavelength ($\lambda/3 = 520$ nm), whose influence on THG will be discussed below.
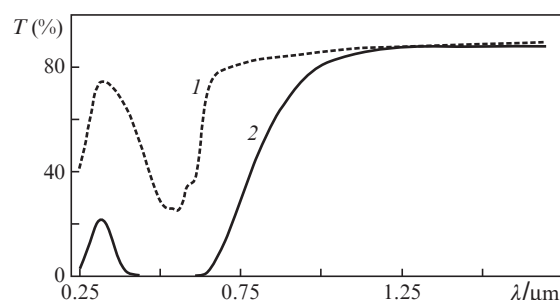

Figure 3. Transmission spectra of RR-P3HT films with thicknesses of (*1*) 0.12 and (*2*) 0.7 μm on a glass substrate.

Figure 2. Schematic of experimental setup.

The thickness of RR-P3HT films was measured using a scanning nano-hardness tester Nanoskan-3D (http://nanoscan.info/eng/). To this end, a scratch was made by a diamond tip on the sample surface, so as to make the polymer film peel off from the solid substrate. To visualise the residual trace of scratches and determine the film thickness, we applied the same instrument in the regime of atomic-force microscope
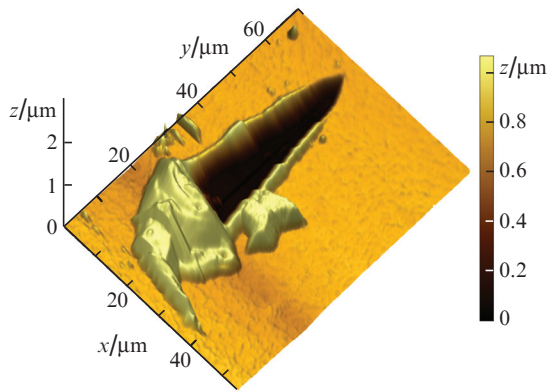
Figure 4. (Colour online) AFM image of a residual trace of a scratch in an RR-P3HT film on a quartz substrate. The uniform-layer thickness is ~0.7 μm.

(AFM) (Fig. 4). The visible inhomogeneity is the consequence of polymer extrusion when making a scratch. The equipment in use made it possible to determine locally the coating thickness with an error no larger than 5%. The film thickness was taken to be the result of averaging several measurements.

Comparative experiments were performed according to the scheme similar to that reported in [18]. A drop of polythiophene solution or LC was deposited on a polished end face of a telecommunication fibre connector (ceramic ferule 2.4 mm in diameter) of the FC/PC type (flat end face without a bevel) with a single-mode fibre (Fig. 5). The fibre with an external diameter of ~100 μm was located at the centre (within the ferule). First, we performed experiments with the polythiophene obtained by drying the solution. Then the coating thickness was measured (see above). After this procedure, the ferule end face was carefully purified, NLC 1289 was deposited on it by dropping, and necessary optical measurements were performed. Finally, the LC thickness was measured using a horizontal microscope equipped with a CCD camera. An additional advantage of this measuring technique is that the direct contact of the media studied with the ceramic ferule provides an efficient heat sink, which excludes sample overheating.

4. Results

The characteristic spectra beyond the wavelength range of the pump radiation ($\lambda = 1560$ nm), incident on sample from the side of polythiophene layer, for a RR-P3HT film with a thickness $d \approx 1$ μm are shown in Fig. 6. The spectra with elliptical polarisations, implementing maximum and minimum harmonic intensity, are presented. TH is more sensitive to polarisation than SH. A similar influence of polarisation at small thicknesses (beyond the phase-matching conditions) is also observed in NLCs [20]. The harmonic peak amplitudes and their ratio depended on not only the polarisation state but also on the location on the substrate surface. Choosing an appropriate irradiation point, one could obtain a larger second-harmonic amplitude in comparison with the TH. This dependence, provided that the polymer thickness is sufficiently homogeneous (Fig. 4, uniform brown surface), is primarily explained by the orientational inhomogeneity of polymer molecules in the film.

At film thickness $d > 1-2$ μm, the harmonic generation power decreases and begins to depend strongly on the side
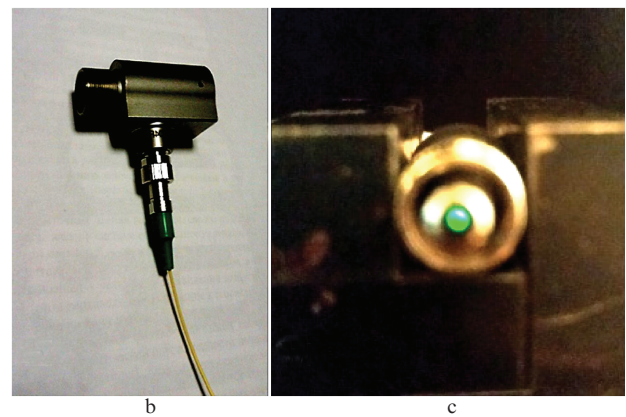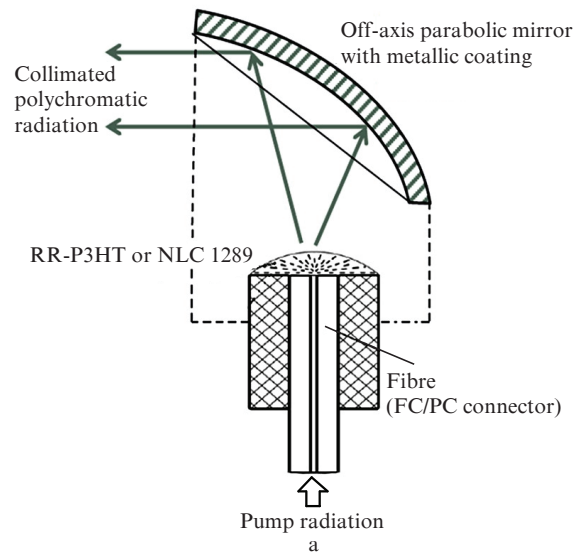

a

b   c

Figure 5. (Colour online) (a) Schematic of a sample of a studied medium (polythiophene or LC), deposited on a fibre connector end face by dropping. (b) Appearance of a collected sample with feeding fibre and collimator. (c) Connector without a collimator, emitting TH from RR-P3HT.
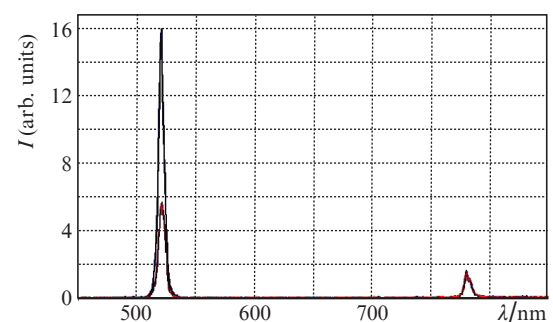

Figure 6. (Colour online) SH and TH emission spectra of an RR-P3HT layer with a thickness $d \approx 1$ μm. Pumping is performed from the polythiophene side. The red and blue lines correspond to minimum and maximum THG, depending on the pump polarisation ellipticity.

from which the pump beam arrives. With a decrease in the initial radiation power from the substrate side the intensity of harmonics decreases with an increase in thickness, up to their disappearance (at $d \approx 6-7$ μm); however, this does not occur when radiation is incident from the side of the RR-P3HT film. Note that the TH power decreases more rapidly and dis-

appears much earlier than the SH power. The THG asymmetry is most pronounced in thick samples: the THG is observed only when the pump beam arrives from the polymer side. Based on the analysis performed, it was concluded that harmonic generation involves a thin (no more than several hundred nanometres) RR-P3HT layer adjacent to the substrate, in which anisotropy occurs due to the dominance of planar (along the glass surface) orientation of polymer chains. This is also evidenced by the presence of SH, which cannot be generated in an isotropic medium with central symmetry. If we take into account the high absorption at the TH wavelength (see Fig. 3) and film transparency for pump radiation, the suggestion about the necessity of orientational order and small thickness of generating layer becomes quite justified. A decrease in radiation conversion efficiency into TH with an increase in the film thickness was also indicated in [4].

The use of modified (regiorandom) polythiophene RRa-P3HT did not give any significant result. With the pump powers in use, even when harmonic generation was observed, its power was several orders of magnitude lower than that for RR-P3HT.

The generated harmonic intensity may depend on time at elevated (above 150 mW) average pump powers. The power level at which time dependence occurred, as well as some other parameters, depended on the chosen area on the substrate. Figure 7 shows the time dependences of SH and TH intensities after switching on a pump beam with an average power of 250 mW at $h = 0$.
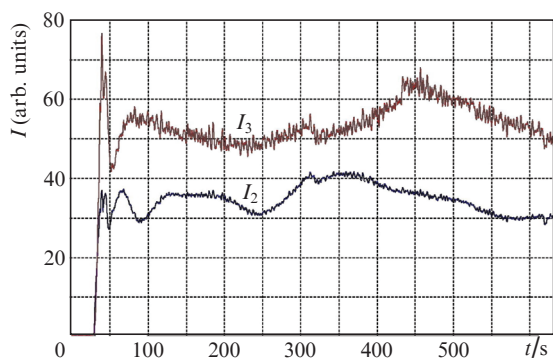

Figure 7. Time dependences of the SH (I_2) and TH (I_3) intensity after switching on a pump beam with an average power of 250 mW.

The time-dependent regime includes arbitrarily a settling period and subsequent fast (less than ~1 s) and slow (from ~10 s to ~3 min) changes in intensity. The nature of fast oscillations and jumps is yet unclear. Slow changes are apparently due to the thermal processes (initiated by radiation absorption), which may lead, in particular, to structural changes in the polymer. Long-term (more than 5 min) measurements were performed with allowance for possible instability of the pump laser system, which did not exceed 3 % per hour.

Figure 8 shows the dependences of the SH (I_2) and TH (I_3) intensities on the pump power prior to the time-dependent regime onset. The data were obtained on a 0.7-μm-thick RR-P3HT film at $h = 0$ (the contact between the film and fibre end face provided a heat sink and excluded overheating in short-term measurements), with the pump polarisation tuned to a maximum THG. Note that similar tunings are
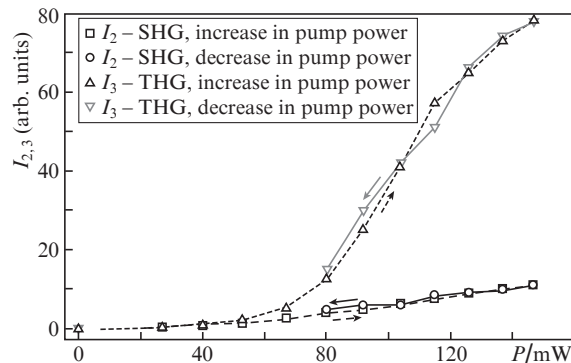

Figure 8. Dependences of the maximum SH and TH intensities on the pump power. Arrows indicate an increase or decrease in pump power.

characteristic of polarisation dependences of harmonic generation in NLC [20]. The shape of curves in Fig. 8 suggests the absence of a threshold and hysteresis in the dependences of harmonic generation on the pump power.

A decrease in the gap width h led to a significant increase in the intensity of harmonics and their generation efficiency. This dependence was fairly sharp, which suggested the influence of the pump power density (intensity) gradient on the harmonic generation. An experiment was performed, in which the influence of the gradient of intensity I could be separated from the influence of the average pump power density P/w^2 (P is the total power and w is the waist width). In our case, the pump power density is proportional to I, $|\nabla I| \sim I_0/w$, where the intensity is described by a Gaussian: $I = I_0 \times \exp[-\rho^2/w^2(h)]$. For small divergence angles, the conical Gaussian shape of the radiation emerging from the fibre end face forms a beam waist w that approximately linearly depends on the distance h (according to the relation $w = w_0 + 2h\sin\alpha \approx w_0 + 2h\alpha$)) for small angles α. Correspondingly, one must measure the dependence of harmonic intensity on h, while keeping $P/w^2 \approx P/(w_0 + 2h\alpha)^2 = $ const.

Figure 9 shows a dependence of the TH intensity I_3 on the waist width w at a constant average pump power ($P/w^2 = $ const) in a 0.7-μm-thick RR-P3HT film. To plot this dependence from the condition of Gaussian beam divergence, the necessary total pump power was calculated so as to retain the average power density. During the measurements, it was necessary to displace the sample, increasing or decreasing the distance h between it and the connector end face and thus increasing or decreasing the pump power according to its precalculated quadratic dependence on h. As can be seen in Fig. 9, the harmonic intensity rises by an order of magnitude when decreasing w by a factor of about 1.5–2 (the value $|\nabla I| \sim I_0/w$ increases correspondingly, which is not characteristic of inorganic nonlinear crystals [15]. Under the same experimental conditions we could not plot the dependence for narrower waists ($w < 22$ μm) because of the polymer film overheating by the pump beam, whose influence becomes pronounced even at $w \approx 25$ μm. The laser source parameters provide the following characteristics on the fibre end face ($w = 8.2$ μm, $P = 0.4$ W): maximum average power density $P/w^2 = 5 \times 10^9$ W m^{-2}, average power gradient $P/w = 4.5 \times 10^4$ W m^{-1}, and average power density gradient $P/w^3 = 5.6 \times 10^{14}$ W m^{-3}. In the experiment with $22 < w < 37$ μm (Fig. 9) we maintained the value $P/w^2(h) \approx 3.5 \times 10^8$ W m^{-2}; under these conditions, the gradients varied in the following ranges: $5 \times 10^3 < P/w < 1.3 \times 10^4$ W m^{-1} and $0.9 \times 10^{13} <$

$P/w^3 < 1.6 \times 10^{13}$ W m^{-3}. The neglect of such a sharp dependence on the intensity gradient can explain the small susceptibility values obtained in [4] and other similar studies devoted to optical nonlinearities in semiconductor polymers, where the main efficiency factor was considered to be only the pump power density. The revealed influence of pump intensity gradient suggests a quadrupole mechanism of susceptibility formation in RR-P3HT; this mechanism is discussed below.
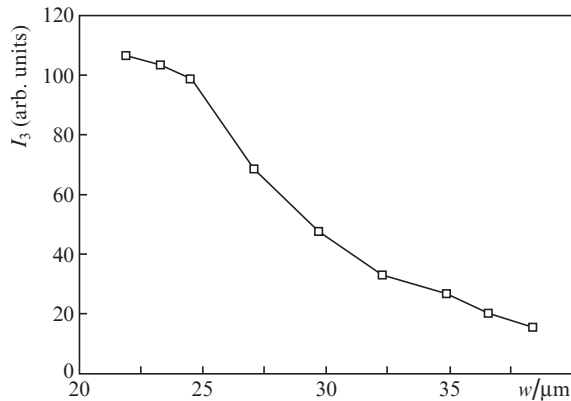

Figure 9. Dependence of the THG intensity on the waist width $w = w_0 + 2\alpha h$ at a constant average pump power density: $P/w^2(h) \approx 3.5 \times 10^8$ W m^{-2}.

The harmonic generation intensity depended on the choice of the irradiation point in the RR-P3HT film, despite the fact that the film thickness is fairly constant. In our opinion, this spatial ambiguity is explained by the inhomogeneity of the orientational structure (alternation of crystalline and amorphous domains) of RR-P3HT polymer chains in the near-wall layer, which is similar in some respect to instabilities during bulk harmonic generation in LCs due to the thermal (temporal and spatial) fluctuations of molecular orientation. In contrast to LCs, molecules of a solid polymer change much weaker their configuration as a result of variation in temperature, but may have significantly different orientational structures in space on plane, especially in the case of sufficiently high localisation of the region of interaction with radiation. Therefore, we report some 'record' (maximum among all measurements) value of harmonic generation efficiency, obtained in our experiments for a 0.55-μm thick RR-P3HT layer deposited on the connector end face ($h = 0$), which turned out to be $\sim5 \times 10^{-4}$ for THG (and, correspondingly, an order of magnitude lower for SHG). This result, even with the absorption in RR-P3HT disregarded, exceeds by a factor of more than 10 the corresponding values for NLC layers with thicknesses of ~100 μm [6, 7]. Figure 10 shows a photograph of TH emission from a sample on a substrate at the point of maximum conversion efficiency.

To reduce the influence of film structural inhomogeneity, some preliminary studies had been performed before the experiments. It was noted that the technology used to form films on a substrate leads to harmonic generation inhomogeneities with characteristic sizes of 0.5–1 mm. Visible defects were excluded from consideration. The pump beam width w varied from 8 to 33 μm in all cases. First, a sample was scanned in its plane relative to the chosen point on the substrate within 50–100 μm, and the harmonic amplitudes were measured on a spectrometer. If the variations in the harmonic

Figure 10. Photograph of the TH beam ($\lambda/3 = 520$ nm) for generation in a 550-nm-thick RR-P3HT film on a substrate and pumping from the polymer side by near-IR radiation ($\lambda = 1560$ nm), fed to the sample through a fibre.

amplitude peaks did not exceed 5%–10%, the chosen position was accepted for main measurements. This preliminary procedure excluded the possibility of changes in harmonic generation because of the RR-P3HT inhomogeneity in further experiments with variable $w = w(h)$.

High-power nonlinear generation of harmonics was observed during a month in an RR-P3HT sample specially selected for long-term measurements; then the sample was destructed to perform further analysis. The polymer film was not damaged under long-term irradiation, and its colour did not change.

To estimate the absolute nonlinear susceptibility, we performed comparative (relative) experiments with a medium most similar from the point of view of harmonic generation: NLC. The generation processes in NLC were studied by us previously [6, 7, 18, 20]. In particular, the quadratic susceptibility $\chi^{(2)}$ under conditions of difference-frequency generation was measured for NLC 1289 at room temperature in [6]; it was found to be $\sim2 \times 10^{-6}$ m V^{-1}. Note that the comparison method yields a rather approximate value; more specifically, the order of magnitude of effective susceptibility is estimated. It is assumed that the media under comparison have the same mechanism of harmonic generation, and that the error introduced by the dispersion of the properties of media is small. In our case, a factor contributing to the measurement error is the impossibility of determining the thickness of the RR-P3HT layer adjacent to the substrate, in which harmonics are generated. Taking all this into account, the measurement result should be considered as only an estimate from below in the form of an inequality, which was calculated proceeding from the entire thickness of the RR-P3HT film. In comparative experiments an RR-P3HT layer was first deposited on the fibre connector end face, and the SHG power was measured. Then an NLC layer was deposited after purification, and the SHG power was measured again. The comparison formula, with the absorption disregarded (at the SH wavelength of 780 nm the absorption in NLC and RR-P3HT is low, see Fig. 3), has the form [24]

$$\frac{\chi_{RR}^{(d)}}{\chi_{NLC}^{(d)}} \approx \sqrt{\frac{P_{RR}}{P_{NLC}} \frac{l_{NLC}}{l_{RR}}}.$$

The technique used for comparative measurements is fairly simple and does not involve any additional elements in the form of a substrate or limiting glasses for NLC. Since the

thickness of measured media is smaller than the coherence length, the problems with self-matching are excluded. A drawback is the impossibility of changing the generation region: the medium is fixed relative to the fibre centre. However, since the experiment is fairly simple, it can be repeated several times with new coatings. In our case, the comparison formula contains an uncertain factor: the length l_{RR} of the RR-P3HT generation region. To eliminate this factor, six independent measurements were performed, and the measured thickness of the entire RR-P3HT layer was used in the calculation. The least value was chosen from the obtained results: $\chi^{(2)} > 10^{-6}$ m V^{-1}. Taking into account the approximate character of the comparison formula, which was derived for plane waves and identical conditions of their propagation in both media, one can accept the obtained estimate in the form of a inequality accurate to an order of magnitude. In relative experiments, when a contact with the connector end face was provided, the pump beam width was determined by the diameter of the inner part (the core, in which up to 80%–90% power was concentrated): $w_0 = 8.2$ µm. In contrast to the schemes with a remote substrate, which did not make it possible to perform measurements at $w < 22$ µm, RR-P3HT or NLC films were not overheated in comparative experiments because of the good heat sink provided by the ceramic ferule.

5. Discussion

The results obtained and some of their specific features in comparison with the previous studies on harmonic generation in polythiophene, performed by other researchers, put a question about the dependence of generation processes on the internal structure of RR-P3HT. However, we cannot unambiguously answer this question yet. Qualitative considerations can be reduced to the following. Primarily, the observed nonlinearity should be related to polymer electrons. The outer orbital electrons, forming a conjugate π system in the polymer, make the main contribution to this process. The electrons in these bonds are least rigidly bound with atoms and are most subjected to the influence of the electrons of neighbouring chain regions and the electrons of neighbouring molecules. However, the same electrons are responsible to a greater extent for the structural state of the polymer and its semiconductor properties and can be most susceptible to external effects. Hence, one can draw the following qualitative conclusion: specifically a regular RR-P3HT, which is characterised by a higher crystallinity near the ordering substrate surface, implements appropriate conditions for binding electrons with neighbours (both within one chain and in the chain of nearest molecules), which allow them to deviate nonlinearly with the largest amplitude from equilibrium under an external impact of electromagnetic field.

Currently, it is generally accepted to describe nonlinear optical phenomena in terms of expansion of polarisability of a medium in a Taylor series in powers of the wave electric field E_j [15]. To describe most of solid inorganic media, it is sufficient to take into account the quadratic and cubic terms in the form of the relation for the nonlinear part of polarisability P^{nl}:

$$P_i^{nl} = P_i^{nl(2)} + P_i^{nl(3)} + \ldots = \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots,$$

$$i, j, k, l = 1, 2, 3 = x, y, z, \tag{1}$$

where $\hat{\chi}^{(2)}$ and $\hat{\chi}^{(3)}$ are, respectively, the quadratic and cubic susceptibility tensors; the repeating indices imply summation. The nonlinear additives in (1) have a relatively simple form. However, the expression becomes much more complicated for more complex media, e.g., LCs, where two terms with electric fields are insufficient to describe the optical nonlinearity. In particular, to describe the quadratic nonlinearity of NLC, it was proposed [9] to consider a more complex [as compared with (1)] relation taking into account the quadrupole expansion terms, for which the dependence of polarisability on field gradients must be introduced:

$$P_i^{nl(2)} \Rightarrow \chi_{1,ijl}^{(2)} E_j E_i + \chi_{2,ijlk}^{(2)} E_j \frac{\partial E_l}{\partial x_k}. \tag{2}$$

In the last term one can select an isotropic additive with radiation intensity $I \sim E_l E_l / 8\pi$, whose contribution to harmonic generation is determined experimentally (see Fig. 9). The isotropic part of nonlinear polarisability can be written in the form

$$P_i^{nl(2)isotrop} = \chi_{2,ijlk}^{(2)isotrop} E_j \frac{E_l}{x_k} = (a\delta_{ij}\delta_{kl} + b\delta_{ik}\delta_{jl} + c\delta_{il}\delta_{jk})$$

$$\times E_j \frac{\partial E_l}{\partial x_k} = aE_i \frac{\partial E_l}{\partial x_l} + bE_l \frac{\partial E_l}{\partial x_i} + cE_j \frac{\partial E_i}{\partial x_j}$$

$$= aE_i \operatorname{div}\boldsymbol{E} + 4\pi b\nabla_i I + c(\boldsymbol{E}\nabla)E_i \sim \nabla_i I,$$

where a, b, and c are combinations of components $\chi_{2,ijlk}^{(2)isotrop}$ with allowance for the convolution over repeating indices and δ_{ij} is the Kronecker delta. In particular, the consideration of quadrupole polarisability terms made it possible to explain the SHG in the isotropic LC phase [7]. The susceptibility tensors depend on the structural LC parameters, which include the scalar order parameter Q and the orientational components of the long axes of NLC molecules: director $\boldsymbol{n} = \boldsymbol{n}(t, \boldsymbol{r})$, which coincides with the optical axis direction changing under the action of field wave [9, 21]. To describe the cubic nonlinearity and quadrupole mechanism of generation, dependence (1) for structured media of the LC type should contain a larger number of Taylor expansion terms (up to the cubic power when taking into account the THG), with allowance for the field gradients, considering the fields and their gradients as independent variables [7, 10]:

$$\boldsymbol{P}^{nl} = \hat{\chi}_1^{(2)} : \boldsymbol{E} : \boldsymbol{E} + \hat{\chi}_2^{(2)} : \boldsymbol{E} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} + \hat{\chi}_3^{(2)} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} + \hat{\chi}_1^{(3)} : \boldsymbol{E} : \boldsymbol{E} : \boldsymbol{E}$$

$$+ \hat{\chi}_2^{(3)} : \boldsymbol{E} : \boldsymbol{E} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} + \hat{\chi}_3^{(3)} : \boldsymbol{E} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} + \hat{\chi}_4^{(3)} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}} + \ldots. \tag{3}$$

Here, a formal recording of gradients via $\partial/\partial \boldsymbol{r}$ and operator (vector–tensor) multiplication in the form of a colon is used for brevity. In the generalised form of (3) for NLC, one must take into account the dependence of susceptibilities on not only the structural parameters but also on their gradients:

$$\hat{\chi}_{1,2,3}^{(2),(3)} = \hat{\chi}_{1,2,3}^{(2),(3)}\left(Q, \boldsymbol{n}; \frac{\partial Q}{\partial \boldsymbol{r}}, \frac{\partial \boldsymbol{n}}{\partial \boldsymbol{r}}\right). \tag{4}$$

The set of dependences (3) and (4) determines the complex electronic–orientational mechanism of optical nonlinearity in NLCs with the simplest structure. In particular, the term with $\hat{\chi}_3^{(3)}$ was responsible for the sharp temperature dependence of THG in NLC, $\hat{\chi}_3^{(3)} > (T^* - T)^{-1}$, near the point of phase transition to an isotropic liquid [10]. These sharp dependences in the quadrupole types of LC interaction with fields, determined by the order parameter and its dependence on T, were noted previously in theoretical studies on flexoelectricity in an inhomogeneous electric field (see, e.g., [8] and references therein).

To date, the theory of LC orientational nonlinearity has been developed well [21]. However, this theory does not consider the processes of spectral changes in the emission caused by electronic nonlinearity or the relationship between the structural and electronic forms of LC interaction with radiation. A model providing a complete description of nonlinear bulk generation of radiation in LCs with a change in radiation frequency, which is a fairly complex combination of nonlinear 3D Maxwell equations and LC material equations, has not been developed yet. Studies [21, 22] do not give a complete pattern of orientational–electronic nonlinearity processes. Nevertheless, based on the form of (3) and dependence (4), one can draw some justified conclusions acceptable for not only NLCs but also, in our opinion, for polymers.

The consideration of electric field derivatives in (3) was confirmed in an experiment, which showed that, with a change in the field (power density) gradient by less than half, the harmonic intensity increases by an order of magnitude (see Fig. 9). Expression (3) has a fairly general form; the a medium (not necessarily LC) is specified by the dependence of type (4) on the parameters characterising the medium. Apparently, one scalar order parameter and its gradient, $n =$ const, $\partial n/\partial r =$ const, will be sufficient to set anisotropy for some polymers. This is quite justified if we assume that a physically small volume does not contain (after averaging over it) a macroscopic dipole moment. Here, we will not give a definition for the polymer order parameter and specify the dependence of susceptibility coefficients (4) on it, because a detailed theoretical analysis is beyond the scope of this study. We should only note that the existence of polymers in the solid phase simplifies the model of optical nonlinearity in comparison with LCs, because in this case it is not necessary to take into account the influence of radiation on the orientation n of the molecules of the medium because of their immobility.

The question about the quadrupole mechanism of optical nonlinearity formation, implemented by the gradient of femtosecond-pulse electric field, was considered in [25]. Simultaneous generation of the second and third harmonics was observed and used when studying the photoelectric properties of RR-P3HT mixtures with fullerenes in [5]. The SHG, a necessary condition for which is central symmetry breaking, was explained by the presence of local structural defects in the mixture deposited by centrifugation on a substrate. When using low-boiling solvents (for example, chloroform) for pure RR-P3HT [4], this technique provides (10–200)-nm-thick amorphous films. Harmonic generation was used in [5] as a tool of nonlinear spectroscopy, and the corresponding absolute susceptibilities were not reported.

As follows from (3), the radiation frequency conversion is determined at least by seven coefficients. In this stage, it does not appear possible to determine which of them (or they all)

makes a dominant contribution to the SHG and THG. In addition, the comparison method in use yields a fairly approximate result [15, 24], because it is based on many assumptions. Correspondingly, we do not report separately susceptibilities, as this was done in [4], and limit ourselves to the value of measured ('total') efficiency and report some estimate (on the order of magnitude), obtained from a comparative experiment with NLC, in the form of a inequality of 'averaged susceptibility' for only a simpler second-order process. The conclusion about the influence of intensity gradients on the harmonic generation (see Fig. 9), which is determined by the terms with spatial derivatives of electric fields, is in agreement with relation (3).

6. Conclusions

The obtained values of harmonic generation efficiency in RR-P3HT exceed the corresponding parameters for semiconductors and are comparable with orientational–electronic bulk nonlinearities in LCs. Good prospects of semiconducting polymers as nonlinear optical media were experimentally confirmed in this study.

The conversion efficiency of pulsed fibre laser radiation into TH in RR-P3HT polymer layers with thicknesses of 0.5–5 μm turned out to be $\sim 5 \times 10^{-4}$, which exceeds the harmonic generation efficiency in NLC layers 100 μm thick or thicker. In contrast to NLC, one does not need to spend part of wave energy on the deformation of the orientational structure in a polymer. To increase the THG efficiency, it is necessary to increase the polythiophene film thickness; however, this cannot be done for this polymer because of the high absorption at a wavelength of 520 nm. Nevertheless, the possibility of existence of ultrahigh nonlinear susceptibility coefficients in semiconducting polymers ($\chi^{(2)} \sim 10^{-6}$ m V^{-1}), which was demonstrated in experiments, indicates the necessity of searching for and studying other semiconducting polymers with more appropriate absorption parameters.

It was experimentally shown that a necessary condition for harmonic generation in polymers, along with a high pump power density, is the existence of high power density gradient (more than 10^{13} W m^{-3}). A qualitative theoretical analysis of the data obtained showed that the nonlinear radiation conversion in polymers may be determined by the quadrupole mechanism of generation, implemented by the regular RR-P3HT structure in the thin near-wall layer.

Despite the approximate character of the reported susceptibility estimates, the results obtained can be used as a base for designing high-efficiency portable (including all-fibre) converters or parametric oscillators to expand the frequency range of laser systems of relatively low average power. To make progress in this field, it is necessary to continue studies aimed at revealing all specific features of harmonic generation in semiconducting polymers and searching for other similar but more appropriate materials.

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