



THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF A LADDER POLYMER OBTAINED BY PYROLYSIS OF POLYACRYLONITRILE

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Abstract—We have investigated the nonlinear optical properties of a ladder polymer obtained by pyrolysis of polyacrylonitrile in the presence of oxygen. Undoped and FeCl₃ doped polymer are found to be electrically conducting. Upon doping, the polymer spectra show changes indicative of the presence of polarons. Subpicosecond degenerate four-wave mixing measurements have been performed at 602 nm yielding effective $\chi^{(3)}$ values of the order of 10^{-11} esu for most samples and indicating the presence of longer-lived excitations contributing to the third-order nonlinearity. The characteristic relaxation time constant for these nonlinearity contributions is in the range of 2–7 ps. The influence of doping on the nonlinearity is discussed in terms of contributions from both the undoped chain sections and chemically-induced polarons. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Considerable effort has been directed towards understanding the optical and electrical properties of molecular solids built from molecules with π -electron conjugation [1–3]. In many of these materials the delocalization of π -electrons occurs in a quasi-one-dimensional (1D) strand of bonds. Examples of such structures are molecules with polyenic and/or acetylenic structures, oligomers of benzene and other aromatic molecules and the polymers derived from them such as polyacetylene, polydiacetylene, polythiophene, and poly-*p*-phenylenevinylene. Recently, much interest has also been given to ladder polymers in which the π -electron conjugation is not limited to a single carbon chain but occurs in a ladder-like structure. These systems are also quasi-one-dimensional and therefore expected to support conformational excitations such as solitons in polymers with degenerate ground states, and polarons and bipolarons in structures having nondegenerate ground states [4, 5].

One of the important reasons for investigating the optical properties of π -conjugated polymeric systems including those with single-strand conjugation and those with multiple-strand ladder-like conjugation is the possibility that these systems may yield high optical nonlinearities which can be used in photonic devices. Of special practical interest is the degenerate third-order optical nonlinearity, usually expressed in terms of the third-order nonlinear susceptibility $\chi^{(3)}(\omega; \omega, \omega, \omega)$. High values of $\chi^{(3)}$ have already been reported for several conju-

gated polymers, raising hopes of finding systems suitable for use in e.g. nonlinear optical waveguides, photonic switches, etc. [6–10]. There have already been several studies of the nonlinear optical response of ladder polymers [11–20]. We describe studies performed on a polymer with a pseudo-one-dimensional ladder structure which can be obtained by pyrolysis of polyacrylonitrile (PAN) (see Fig. 1). The pyrolysis leads to ring closure involving the nitrile side groups, and results in a conjugated structure. When the pyrolysis is carried out under anaerobic conditions, the structure obtained consists of a chain of C—C bonds and of a parallel chain of conjugated C=N double bonds. When the reaction takes place under aerobic (oxidative) conditions at a temperature in the range of 200–300°C, the carbon chain becomes partly unsaturated and a fused ring aromatic structure may be formed [21–24]. Examples of structures obtainable by pyrolysis are shown in Fig. 1.

The presence of the conjugated imine system in pyrolyzed PAN leads to the development of semi-conducting properties. As usual for π -conjugated pseudo-one-dimensional polymers, the electric conductivity of these structures can be modified by introduction of suitable dopants. Doping leads to oxidation or reduction of the polymer chain and to the formation of charged polaronic species that may take part in the conduction process and also modify the linear and nonlinear optical properties of the polymer. In this paper we present a study of the dynamics of third-order nonlinear optical effects in pristine and FeCl₃-doped pyrolyzed PAN. One of the problems which is addressed here is the dependence of the third-order nonlinear optical properties of the conjugated polymer on the pre-

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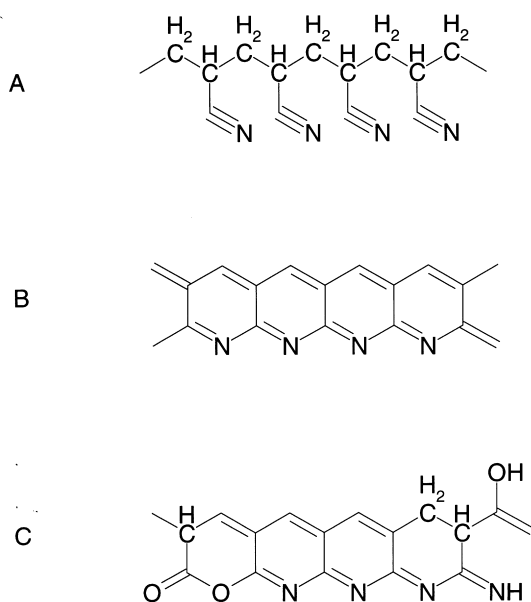


Fig. 1. A scheme of the formation of a ladder polymer from PAN: (a) PAN, (b) ideal structure after pyrolysis in a controlled oxygen atmosphere, (c) structure with various conjugation defects.

sence of a dopant. We discuss the possible involvement of excitons and polarons in doped polymers in the nonlinear optical response as observed by the degenerate four-wave mixing technique using 400 fs, 602 nm light pulses.

EXPERIMENTAL

Sample preparation

Polyacrylonitrile powder of average molecular weight 150,000 (Scientific Polymer Product, Inc.) was dissolved in dimethylformamide (DMF) by heating in a hot water bath (the glass transition temperature of PAN, $T_g = 85^\circ\text{C}$). Thin-film samples of uniform thickness for the degenerate four-wave mixing and electrical conductivity measurements were prepared by spin coating the viscous solutions of PAN or PAN with the dopant (10% PAN by weight dissolved in dimethylformamide) on glass substrates. The films had good optical quality for both doped and undoped PAN and both before and after pyrolysis.

The pyrolysis was carried out at 225°C in air. Its development was monitored by infrared spectroscopy. IR spectra of the samples were obtained using an Alpha Centauri FT-IR spectrophotometer. Figure 2 shows the IR spectra obtained immediately after a sample heated at $5^\circ\text{C}/\text{min}$ reached the temperature of 225°C and those for samples pyrolyzed at 225°C for one and three hours. The peak at 2240 cm^{-1} assigned to the nitrile group decreases, while that of the imine bonds at 1650 cm^{-1} increases as the reaction proceeds. New peaks appearing at 1650 cm^{-1} and 1360 cm^{-1} indicate polymer chain conjugation through the formation of $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds [25,26]. UV-visible spectra also provide evidence of structural changes on pyrolysis. These changes, due to cyclization and formation of charged species by doping, were monitored using a UV-3101PC scanning spectrophotometer. Below 180°C the material remains essentially unchanged. As the temperature is raised, the color changes progressively from yellow to brown. With the onset of coloration the material becomes insoluble in DMF. Typical optical absorption spectra of

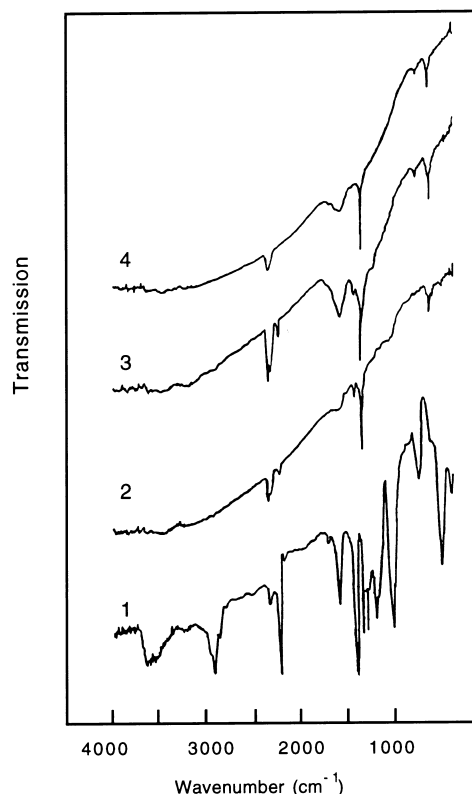


Fig. 2. Infrared absorption spectra: (curve 1) PAN before heating; (curve 2) PAN heated in air, heating rate $5^\circ\text{C}/\text{min}$ immediately after achieving 225°C ; (curve 3) heated at 225°C for 60 min; and (curve 4) 180 min.

doped and undoped pyrolyzed PAN are shown in Fig. 3. Doping with FeCl_3 most likely proceeds as [3]: $(\text{PAN})_x + 2\text{FeCl}_3 \rightarrow (\text{PAN})_x^+ \text{FeCl}_4^- + \text{FeCl}_2$. Therefore, the dopant introduces positive charges (polarons) on the polymer backbone. The charges on the polymer chain are compensated with countercharges residing on the FeCl_4^- anions [27].

Measurements

The thicknesses of samples (usually $1\text{--}4\text{ }\mu\text{m}$) were measured with a profilometer (Sheffield Instruments). The refractive index measurements were carried out by Brewster's angle method. The dc conductivity was measured using a four- and a two-probe technique. The third-order nonlinear properties of pyrolyzed pristine and doped PAN films were measured by degenerate four-wave mixing (DFWM) using subpicosecond 602 nm pulses. The experimental setup has been described in Ref. [28]. The laser system consists of a Model 3800 mode-locked Nd:YAG laser with a fiber-optic pulse compressor (Model 3690) and a synchronously pumped Spectra Physics Model 375 B dye laser. The pulses are amplified in a three-stage amplifier (Quanta-Ray PDA 1) pumped by a frequency-doubled 30 Hz Q-switched Nd:YAG laser (Spectra Physics, Model DCR 11A). The resulting pulses are about 400 fs long. The time-resolved degenerate four-wave mixing studies are performed in the forward (BOXCARS) DFWM geometry [29]. The beam from the amplifier is split into three beams that are coincident and synchronized at the sample. The nonlinear interaction of these beams leads to the formation of a fourth beam. This beam intensity is monitored as a function of the delay of one of

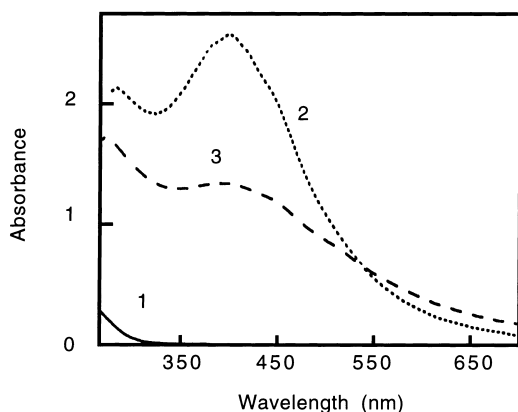


Fig. 3. UV-VISible absorption spectra: PAN before pyrolysis—curve 1, pyrolyzed PAN—curve 2, pyrolyzed, FeCl_3 doped—curve 3.

the input beams (a probe) with respect to the two remaining beams (pump beams). The intensity of the signal is measured by a photodiode (EG&G, Model HAD 1100A) and boxcar (EG&G, Model 4400). All beams have vertical polarization, we therefore measure the $\chi_{1111}^{(3)}$ tensor component of the third-order susceptibility.

RESULTS AND DISCUSSION

Cyclization and doping of polyacrylonitrile introduce characteristic changes in the optical and electrical properties of the polymer. Optical spectra of pyrolyzed and pyrolyzed and doped PAN show significant differences compared to the spectrum of pristine unpyrolyzed PAN (see Fig. 3). The changes induced by pyrolysis are due to the formation of a delocalized π -electron structure along the conjugated C=C and C=N bonds. On doping with FeCl_3 , the absorption peak at 400 nm decreases, as compared to undoped pyrolyzed PAN samples, and there appears a stronger absorption in the range of 570–700 nm which is spectral evidence of the formation of polarons. For our nonlinear optical measurements it is important that the doping itself does not lead to a marked increase of absorption at our measurement wavelength, 602 nm, this wavelength being in the range of the absorption tail (Fig. 3).

The electrical conductivity in pyrolyzed PAN was found to be an increasing function of the dopant concentration and the room temperature specific conductivity rises from approximately 10^{-4} Sm^{-1} to 10^{-3} Sm^{-1} at the concentration of 3.0 wt.%, thereafter the conductivity is approximately independent of the dopant content. This behavior is to be expected. Doping introduces positively charged species on the polymer chains, while the countercharges remain on FeCl_4^- ions. The conductivity should depend on the concentration of positive charges on the polymer chains. However, the electrical conductivity is also found to increase with the degree of cyclization, even in the absence of dopant. This increase of the conductivity in undoped PAN on pyrolysis is probably due to a change in conjugation of the polymer chain which leads to increased charge carrier mobility and also to the

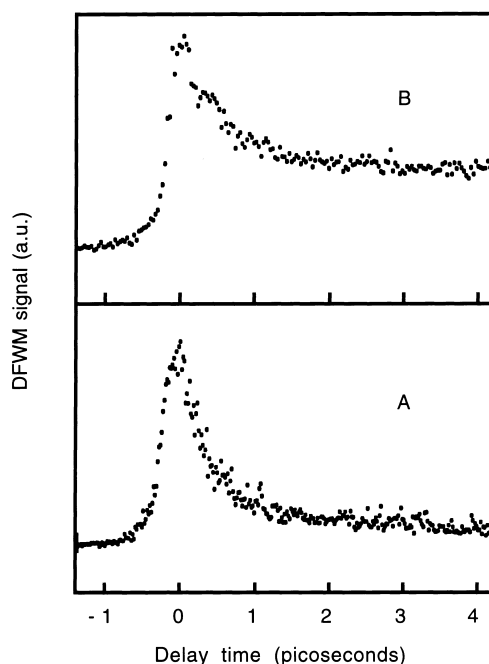


Fig. 4. Degenerate four-wave mixing signals for undoped pyrolyzed PAN (a) and FeCl_3 doped pyrolyzed PAN (b) plotted as a function of the probe beam delay.

formation of charges on the polymer chain by spurious dopants, for example, by oxygen.

The nonlinear optical properties of thin films of doped and undoped pyrolyzed PAN were investigated by time-resolved degenerate four-wave mixing. Examples of the DFWM signals recorded as functions of the delay of one of the beams are given in Fig. 4. Since our working wavelength (602 nm) lies in the region of moderately strong absorption (for undoped pyrolyzed PAN, the linear absorption coefficient α is in the range 3×10^2 – $2 \times 10^3 \text{ cm}^{-1}$; for doped pyrolyzed PAN with different %wt. ratio of dopants in the range 8×10^2 – $4 \times 10^3 \text{ cm}^{-1}$), the observed effects obviously involve one-photon resonant processes. The DFWM signals may be considered to arise from changes induced by pump beams in both the real and the imaginary parts of the complex susceptibility ($\chi^{(1)}$) of the films, i.e. in both the refractive index and the absorption coefficient. These changes, in turn, may be due either to the instantaneous interaction of optical fields through the third-order susceptibility $\chi^{(3)}$ or to the formation of excited species whose presence modifies the complex susceptibility. The latter contribution is noninstantaneous, since the excited species can persist for a certain period of time, limited, for example by their radiative or nonradiative lifetimes or recombination speed. The intensities of the DFWM signals depend therefore on at least two contributions and involve real and imaginary parts of both of them. In the zeroth approximation, however, just for the sake of comparison between PAN films processed in different manner, it is convenient to disregard these complications and to compare the peak intensities of DFWM signals ascribing to them "effective $\chi^{(3)}$ " values. These effective $\chi^{(3)}$

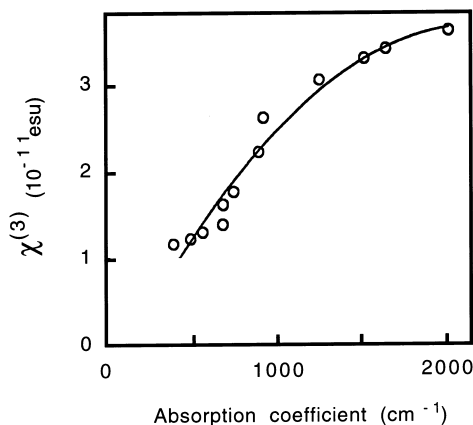


Fig. 5. The dependence of $\chi^{(3)}$ on the linear absorption coefficient α in pyrolyzed PAN. Saturation behavior is observed.

values were determined by comparing the strength of the DFWM signals from the polymer films with that from a reference which in our measurements was a 1 mm cell of liquid CS_2 . The calculation was performed according to the formula [29]:

$$\frac{\chi_s^{(3)}}{\chi_c^{(3)}} = \frac{n_c^2 l_c l_s^{1/2}}{n_c^2 l_c l_s^{1/2}} \times \frac{\alpha l_s}{\exp(-\alpha l_s/2)[1 - \exp(-\alpha l_s)]} \quad (1)$$

In the above equation n is the refractive index, l is the interaction length, and α is the linear absorption coefficient. The subscripts c and s refer to CS_2 and the sample, respectively. CS_2 is transparent at the wavelength used in our experiments, but the losses due to absorption of the polymer samples are taken into account. The nonlinear susceptibility for CS_2 was taken as $\chi^{(3)} = 6.8 \times 10^{-13}$ esu.

We have studied the dependence of the DFWM signal magnitude (at a fixed input power) on the degree of cyclization in undoped pyrolyzed PAN. The dependence of $\chi^{(3)}$ on α (linear absorption coefficient), which is a measure of the cyclization, shows a saturation of $\chi^{(3)}$ (Fig. 5). This behavior may be reminiscent of that described previously for the third-order hyperpolarizability γ , the microscopic analogue of $\chi^{(3)}$, which shows a saturation at some effective conjugation length [28, 30]. However, the present results concern a third-order nonlinear optical phenomenon containing a resonant contribution. Therefore, the analogy with the behavior of nonresonant third-order nonlinearity may be superficial. On the other hand, $\chi^{(3)}$ also depends on the concentration of the dopant. The values of $\chi^{(3)}$ attained for lightly doped pyrolyzed PAN samples (Table 1) are higher than those for pure PAN. However, at higher doping levels there appears to be a decrease in the value of the effective $\chi^{(3)}$.

Our intention was also to investigate changes in the dynamics of the third-order nonlinearity as a function of both the cyclization degree and the dopant content. Examples of DFWM temporal profiles are shown in Fig. 6. The presence of a delayed part of the signal (the "tail" of the signal) indicates that the nonlinear process involves creation of excited species of relatively long lifetime. We there-

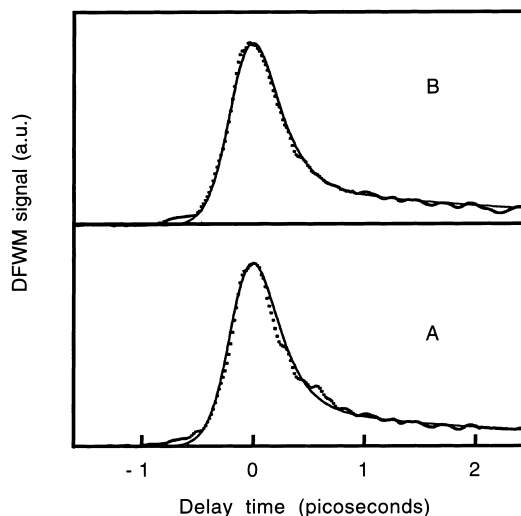


Fig. 6. Typical temporal profiles of a DFWM signal for lightly doped pyrolyzed PAN (5 %wt. of FeCl_3 , $\alpha = 2.5 \times 10^3 \text{ cm}^{-1}$) (a) and pyrolyzed undoped PAN ($\alpha = 1.5 \times 10^3 \text{ cm}^{-1}$) (b) plotted together with numerical fitting results (full lines).

fore numerically fitted some DFWM profiles assuming that the signal can be described by a superposition of an instantaneous interaction of the input beams with a delayed part which is due to a transient grating formed by excited states. In the calculation we assumed for simplicity that the laser pulse temporal profile can be described by a *sech*² function and used the following equation for fitting:

$$I_{\text{DFWM}}(t_D) = \text{const} \times \left[\int_{-\infty}^{\infty} \left[A E(t)^2 + B \int_{-\infty}^t E(t_1)^2 \exp\left(-\frac{t-t_1}{\tau}\right) dt_1 \right] E(t-t_D) dt \right]^2 \quad (2)$$

In this equation, τ is the lifetime of the excited species, t_D is the probe beam delay, and A and B are constants. From fitting studies, lifetimes τ in the range 3–9 ps were obtained for doped and undoped samples. The ratio between the instantaneous and the delayed part of the response (A/B) obtained by fitting DFWM profiles lies in the range 0.5–1.0. These values exhibit some variations for different samples (see Table 1), but based on the present studies, no interpretation of the observed trends can be provided. To summarize, we observe the following trends in the nonlinear optical behaviour of pyrolyzed PAN:

- (i) The effective $\chi^{(3)}$ increases with the degree of cyclization (or linear absorption coefficient α) for undoped pyrolyzed PAN,
- (ii) the dependence of the effective nonlinearity on the dopant concentration is not simple: depending on the degree of cyclization of PAN (which depends on the time of pyrolysis) we observe either an increase of $\chi^{(3)}$ with the dopant con-

Table 1. Nonlinear optical parameters of PAN samples

Sample	α (cm ⁻¹)	$\chi^{(3)}$ (esu)	%wt. of dopant	A/B ratio	Lifetime τ (ps)
Undoped	7.5×10^1		0	1.12	1.92
	4.8×10^2	2.6×10^{-11}	0	0.91	3.2
	5.5×10^2	1.3×10^{-11}	0	0.71	7.4
	8.8×10^2	2.8×10^{-11}	0	0.59	5.8
	1.5×10^3	3.1×10^{-11}	0	0.32	5.2
	2.0×10^3	3.3×10^{-11}	0	0.51	6.2
FeCl ₃ doped	8.7×10^2	2.1×10^{-11}	5	0.91	2.9
	2.4×10^3	4.1×10^{-11}	5	0.92	5.8
	2.8×10^3	5.3×10^{-11}	5	0.67	3.0
	4.0×10^3	4.5×10^{-11}	5		7.4

tent or a decrease or even nonmonotonic behavior.

The experimentally observed behavior is rather complex which is not unexpected since we are dealing with a complicated system under resonant conditions. One can try, nevertheless, to rationalize the data. It can be expected that the nonresonant contribution to the effective $\chi^{(3)}$ will be mostly due to the delocalized π -electrons and therefore will increase with the degree of π -conjugation of the polymer. Thus, this part of the nonlinearity should increase with cyclization but may decrease with doping. This decrease can be expected if one considers that the presence of chemically induced polarons breaks the translational symmetry of the polymer backbone leading therefore to a decrease of the effective π -conjugation. From a spectroscopic point of view, this means that, on doping, the band-to-band transition in the polymer is bleached and/or blue shifted while at the same time a polaronic band is formed in the longer wavelength part of the spectrum. Whether the nonresonant nonlinearity will actually increase or decrease upon doping will depend on the relative contributions to $\chi^{(3)}$ from the π -electron band transitions and polaron absorption. While the polaron absorption occurs at a lower energy, it is more localized in character, therefore it is not straightforward to predict whether the net effect of bleaching the band-to-band transition and introducing the polaronic bands will be a higher or a lower nonlinearity.

Another contribution which appears in our experiment is that of the resonant nonlinear response. Our experimental DFWM curves contain pronounced tails characterized by lifetimes of the order of a few picoseconds. Absorption of light in a ladder polymer should lead to the formation of excitons – excitations across the band gap. In a similar way like for well-known one-dimensional π -conjugated polymers, the lattice then will deform and single and double bond lengths will change to adapt to the new charge distribution. The excitation formed in such a way is a relaxed (self-trapped and thermalized) exciton. Another type of excitation is a P^\pm bipolaron, i.e. a charge carrier geminate pair. The results of femtosecond transient absorption studies performed on another ladder-type polymer [31] indicate that the thermalization of P^\pm can be as fast as 2 picoseconds and longer lifetimes (8 picoseconds) may be involved in the case of decay of the exciton population. Longer decay and nonexponential decay behavior have been observed for polaro-

nic species in other studies. Therefore, the decay time of about 6–9 ps observed by us cannot be the indication of the character of states contributing to the nonlinearity.

The doping effect is an additional complication. The doping introduces chemically induced polarons (bipolarons). Light absorption by polaronic states also leads to a contribution to the nonlinear optical response. Therefore, on doping, one can expect a decrease of the excitonic and geminate pair contribution to the nonlinear optical response because of the bleaching of the band absorption as well as modification of geminate pair properties, e.g. by facilitating their recombination. On the other hand, chemically introduced polarons will bring a contribution of their own which may in part or totally compensate for loss of the other contributions. To illustrate the point we simulated the doping effect using a simple model. The nonlinearity of the polymer chain can be considered to be a combination of two contributions: that of the unmodified sections of the polymer chain and that of polarons. Therefore, one can present the $\chi^{(3)}$ as a function of the concentration of the dopant N_d in the following form:

$$\chi^{(3)} = \sum_i \gamma_i(l_i) + N_d \gamma_d \quad (3)$$

where the first term is the sum of contributions brought about by the sections of the polymer chain having different lengths l_i and the second term is the contribution of polarons. In a nonresonant case one should expect that $\gamma_i(l_i)$ should be a function of the length of the chain section which is similar to those observed for oligomers of π -electron molecules (e.g. [28, 30]), that is, it should increase with some power of the chain length and the hyperpolarizability per unit saturating at some length. The doping will increase N_d , while reducing l_i . Depending on the details of the two counterbalancing contributions to the nonlinearity, this may lead to an increase of $\chi^{(3)}$ on doping or to a decrease.

In a resonant case one can predict a similar behavior. According to the phase space-filling model of Greene *et al.* [32], the third-order nonlinear susceptibility is proportional to the product of the effective exciton length x_0 and the absorption coefficient α . For the polymer consisting of short chain segments, the exciton will be confined to the unmodified chains, i.e. x_0 will be equal to the average length of a conjugated segment $\langle l_i \rangle$, while for longer chains x_0 should reach a saturation value. The absorption coefficient will behave in a similar

way, i.e. it will be constant for longer chains and reduced (due to blue shift of absorption) for chains shorter than x_0 . In effect, under resonant conditions the contribution of the undoped sections of the polymer chain should depend on doping in a way similar to that of the nonresonant nonlinearity. Thus, we reiterate that depending on the relative contributions of the two terms in Equation (3), the doping can either enhance or reduce the effective $\chi^{(3)}$ and even a nonmonotonic behavior can be rationalized. It should be mentioned that the problem of the influence of doping on $\chi^{(3)}$ of poly(bithiophene) is discussed in [33].

In conclusion, we observe a picosecond phase conjugate response from a conjugated ladder polymer. The value of the effective $\chi^{(3)}$ is relatively high, due to a superposition of various resonant processes. It should be mentioned that the merit factor $\chi^{(3)}/\alpha$ at 602 nm is of the order of 10^{-14} esu cm, which is quite unsatisfactory. The major part of the nonlinear response derives from relatively long-lived (5–9 ps) species. Doping leads to a modification of the third-order nonlinear optical behavior, however, depending on the dopant and other parameters, it may lead to either enhancement or a decrease of the effective nonlinearity.

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