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Communications

Third-Order Optical Nonlinearities and Their Wavelength Dispersion in Thin Films of Conjugated Rigid-Rod Polyquinolines and a Random Copolymer

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The focus of current research on polymers and organic materials with large third-order optical nonlinearities[1-6] is directed at (1) a fundamental understanding of the optical properties and their underlying structure-property relationships and (2) optimization of the materials for device applications, including such issues as thin-film processing and ability to fabricate the materials into device structures, the relative figures of merit of the materials compared to device requirements and other classes of materials, robustness of the optical, and other physical properties under laser irradiation, etc. Knowledge of the wavelength dispersion of the third-order nonlinear optical susceptibility $\chi^{(3)}$ is indispensable to a true understanding of the nonlinear optical properties of the materials and a realistic assessment of their potential for technological applications. Therefore, we recently initiated a systematic investigation of $\chi^{(3)}$ and its wavelength dispersion in conjugated polymers and their underlying structure–property relationships. We have previously measured the wavelength dispersion of $\chi^{(3)}$ in thin films of poly(*p*-phenylenebenzobisthiazole) (PBZT) and its molecular composites with polyamides[4b] as well as in thin films of poly(benzimidazobenzophenanthroline) ladder (BBL) and semiladder (BBB) polymers.[5]

Conjugated rigid-rod polyquinolines[7-10] are thermally stable,[7,9] high mechanical strength,[9] film- and fiber-forming materials[7] that can be doped to a high electronic conductivity (10 S/cm)[8]. These polymers are generally stable up to 500–600 °C, show a glass transition temperature (T_g) in the range 275–400 °C, and melt in the range >450 °C. The polyquinolines are soluble to high concentrations in their usual polymerization solvent, di-*m*-cresyl phosphate (DCP)/*m*-cresol,[10,11] or in Lewis acids ($AlCl_3$, $GaCl_3$, etc.)/nitroalkanes[11] to form lyotropic liquid-crystalline solutions and hence are processable to thin films and fibers. One of the most attractive features of this class of conjugated polymers is the flexible synthetic scheme with which the basic polyquinoline molecular structure can be modified.[7] This makes the conjugated polyquinolines an ideal class of polymers, or model systems, for the investigation

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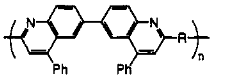
Table I. Intrinsic Viscosity [η], λ_{max}, α, Optical Bandgap, and Resonant and Nonresonant $\chi^{(3)}$ of Rigid-Rod Polyquinolines

polymer	[η], dL/g	λ_{max}, nm	α,[a] 10^4 cm^{-1}	E_g, eV	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, 10^{-12} esu nonresonant (at 2.38 μm)	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, 10^{-12} esu resonant (at 1.2 μm)
PSPQ (E)[b]	31.3	408	11	2.65		
PSPQ (Z)[b]		372	17[c]	2.65	2.2 ± 0.4	8.1 ± 1.6
PBAPQ	8.9	399	24	2.72	2.2 ± 0.4	27 ± 5
PSPQ (E)/PBAPQ	14.3	404		2.72		
PSPQ (Z)/PBAPQ		390	16[d]	2.72	2.2 ± 0.4	18 ± 4

[a] Absorption coefficient at λ_{max}. [b] E (trans) and Z (cis) isomers of PSPQ. [c] Absorption coefficient at 286 nm. [d] Absorption coefficient at 290 nm.

of structure–$\chi^{(3)}$ relationships. The linear and nonlinear optical properties of the polyquinolines have not been reported to date.



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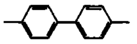
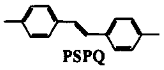
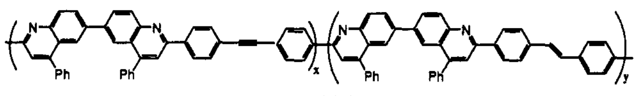


PBPQ

PBAPQ



PSPQ



PBAPQ/PSPQ

We report here on the cubic optical nonlinearity $\chi^{(3)}$ and its wavelength dispersion in thin films of two polyquinolines, poly[2,2′-(*p,p*′-stilbene)–6,6′-bis(4-phenylquinoline)] (PSPQ) and poly[2,2′-(*p,p*′-biphenylacetylene)–6,6′-bis(4-phenylquinoline)] (PBAPQ), and their random 50/50 copolymer PSPQ/PBAPQ. In the molecular structure of the most commonly studied rigid-rod polyquinoline, poly[2,2′-(*p,p*′-biphenylene)–6,6′-bis(4-phenylquinoline)] (PBPQ), steric hindrance due to the adjacent ortho hydrogens of *p,p*′-biphenylene, among other factors, can be expected to limit coplanarity of polymer repeating units and hence electron delocalization. Introduction of stilbene and biphenylacetylene linkages as in PSPQ and PBAPQ, respectively, is expected to reduce effects of such adverse steric factors on the electronic structure of these polymers. Although it may be argued that the range of the optical and nonlinear optical properties of random or block copolymers would be limited or defined by those of the constituent homopolymers, there are good reasons for investigating random or block copolymers as nonlinear optical materials. The greater tendency of copolymers to form amorphous glassy materials compared to their homopolymers provides one way to achieve smaller optical losses (α) with minimum reduction of Re $\{\chi^{(3)}(-\omega;\omega,\omega,\omega)\}$ and hence an overall improvement of the figure of merit Re $\{\chi^{(3)}\}/\alpha$. However, isotropic materials have reduced optical nonlinearities compared to highly ordered or crystalline forms of the same materials. Random or block copolymer structures as heterogeneous media constitute one possible approach to realize the theoretically predicted[12] and experimentally observed[13] effect of anharmonicity enhancement of $\chi^{(3)}$ in conjugated molecules. Copolymers, as composite materials, also represent excellent model systems for probing the effects of disorder on electronic structure and optical and nonlinear optical properties.

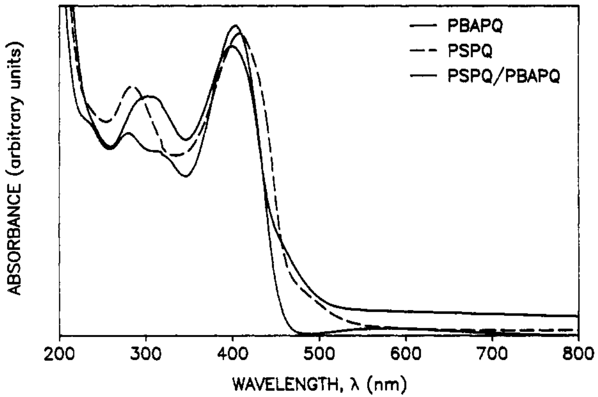


Figure 1. Optical absorption spectra of thin films of rigid-rod polyquinolines.

All monomers, the polymerization solvent di-*m*-cresyl phosphate/*m*-cresol, and polymers were synthesized by using established literature approaches.[10,14] The polymer PSPQ has previously been synthesized and widely studied by Stille et al.[8,14] PBAPQ and the copolymer PSPQ/PBAPQ are new materials synthesized by using techniques similar to those reported for PSPQ and of the other polyquinolines. The polymers were characterized by intrinsic viscosity, spectroscopic techniques, and thermal analysis. The intrinsic viscosity [η] of the polymers in 0.1 mol % DCP/*m*-cresol at 25 °C is shown in Table I. The very high values of the intrinsic viscosity suggests that the molecular weight of the polymers is quite high. Our observed intrinsic viscosity values are generally higher than previously reported for PSPQ and other polyquinolines.[7,8] Typically, the degree of polymerization of the rigid-rod polyquinolines is of the order of 600 for an intrinsic viscosity of ~20 dL/g.[15]

The thin films for third harmonic generation (THG) experiments were prepared from 2–3 wt % polymer solutions in 20 wt % DCP in *m*-cresol.[11] Thin films were obtained by shearing a thin layer of polymer solution between two optically flat silica substrates (5 cm in diameter). The coatings on silica substrates were kept at 95 °C for 4–5 h under vacuum to remove the solvent *m*-cresol. The resulting thin films of polymer/DCP complex were precipitated in 10% triethylamine/ethanol mixture and kept in this solvent mixture overnight. The resulting thin films of pure polyquinolines were dried under vacuum at 95 °C for 4–6 h. Thermogravimetric analysis and optical absorption spectroscopy confirmed the complete removal of *m*-cresol and DCP.[11]

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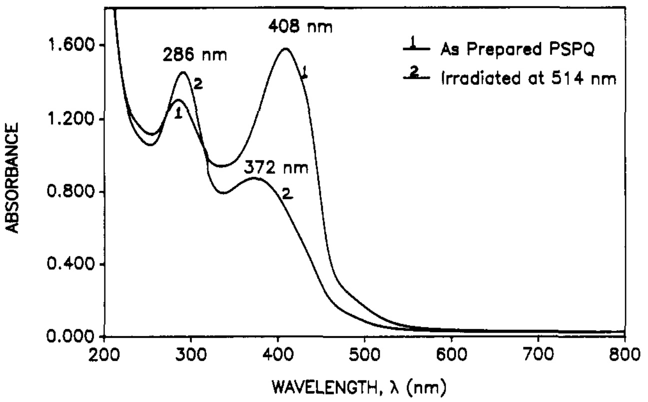

Figure 2. Optical absorption spectra of the same thin film of PSPQ before and after laser illumination, showing photoinduced trans–cis isomerization.

Figure 1 shows the optical absorption spectra of thin films of PSPQ (trans isomer), PBAPQ, and PSPQ/PBAPQ. The yellow polymers absorb near 400 nm and are transparent above 500 nm. The λ_{max} and optical bandgap (E_g) of the polymers are shown in Table I. The absorption maximum of the copolymer is between those of the homopolymers. The naperian extinction coefficients α at λ_{max} for PSPQ, PBAPQ, and PSPQ/PBAPQ are also shown in Table I. The stilbene unit of PSPQ is known to undergo E–Z (trans–cis) isomerization when exposed to UV light.[14] Figure 2 shows the optical absorption spectra of the same thin film of PSPQ before (trans) and after (cis conformation) illumination with an argon-ion laser at 514 nm. It is observed that laser irradiation shifts the absorption peak for the π–π^* transition at 408 nm in PSPQ to 372 nm with a simultaneous decrease of the extinction coefficient (see Table I). This photochromic effect (blue shift of λ_{max}) reduces π-electron delocalization along the polymer backbone. We have observed a similar effect in the random copolymer PSPQ/PBAPQ, where λ_{max} was blue shifted from 404 to 390 nm. In our THG experiments, intense (several GW/cm^2) picosecond near-IR laser pulses could possibly produce the same photochromic effect through a multiphoton process.

THG experiments were performed with a picosecond laser system, continuously tunable in the range 0.6–4 μm. This versatile source, which has been described in detail elsewhere,[16] can be operated at either low (10 Hz) or high (MHz) repetition rate with the possibility of independently selecting the pulse width out of two ranges (typically 3–5 and 30–50 ps), regardless of the choice of wavelength. The average output power is in the milliwatt range for all modes of operation. For this work, the repetition rate was set at 10 Hz and the long pulse width range was selected since THG only probes the electronic contribution to $\chi^{(3)}$. The pulse-to-pulse instability, which is typically 5%, was decreased to 1% by monitoring the pulse energy of a small fraction of the output beam and by rejecting all laser shots that fall outside a predetermined window. The main output beam (attenuated to 100 μJ/pulse) was divided into two optical paths: a reference path and a sample path. In the reference path the THG signal from 0.5-μm film of poly(benzimidazobenzophenanthroline) semiladder polymer (BBB)[5] on a 1-mm fused silica disk was measured with a setup identical with that in the sample path. The BBB film thickness was chosen to be smaller than the coherence length of the THG signal to avoid Maker fringes in the THG signal, yet it is thick enough to give a THG signal that is 2 orders of magnitude larger than that from the substrate (to avoid interference). The use of BBB as opposed to fused silica in the reference arm greatly improves the reproducibility of the measurements. By taking the ratio of the THG signals in the two arms shot after shot, the effect of fluctuations in both power and pulse width of the input beam are effectively eliminated. Finally, by averaging the ratio of the THG signals over some 250 laser shots, the standard deviation of this ratio typically is 0.5%. The sample is located on a computer-controlled rotation stage for obtaining the Maker fringes of the THG signal.

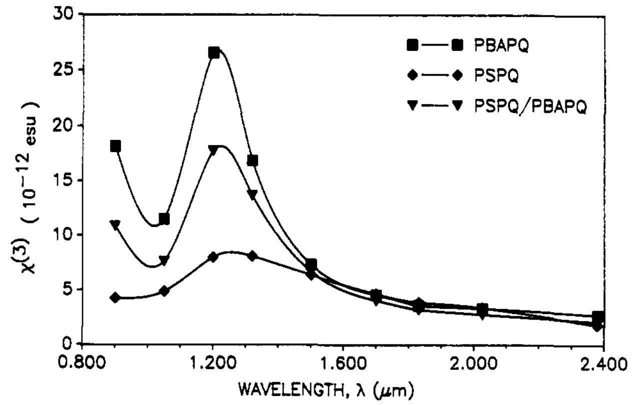

Figure 3. Wavelength dispersion of the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of polyquinolines (PSPQ and PBAPQ) and their random 50/50 copolymer (PBAPQ/PSPQ). The solid lines are a guide for the eye only.

The magnitude of the third-order susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the sample is obtained relative to fused silica in the following way. First, the Maker fringe pattern of the sample (thin film on a fused silica substrate) is compared to the Maker fringe pattern of a blank substrate also placed in the sample path. Following the procedure outlined in ref 17, a value of $\chi^{(3)}$ of the thin film is inferred. This $\chi^{(3)}$ value is then used as a starting value for an exact determination of $\chi^{(3)}$ by a theoretical fit of the Maker fringe pattern of the sample,[18] using an optical transfer matrix technique.[19] In addition to being exact, our method has the advantage of requiring a minimal set of fitting parameters ($\chi^{(3)}$ for fused silica, the film and substrate thicknesses, and indexes of refraction), thereby eliminating all other experimental calibration factors such as transmission of filters, beam splitter ratios, and analog/digital gain factors in the computerized data acquisition system.

THG measurements were performed at a fundamental wavelength of 0.9–2.4 μm. The reported $\chi^{(3)}$ values are average values, corrected for absorption at the third harmonic wavelength, and are obtained relative to $\chi^{(3)}$ for fused silica. For the latter we used $\chi^{(3)} = 2.8 \times 10^{-14}$ esu at 1.9 μm.[20] The error for $\chi^{(3)}$ of the films, typically ±20%, reflect mostly the error in film thickness measurements since the repeatability of individual results for each material is ±5%.

Figure 3 shows the wavelength dispersion of the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of PSPQ, PBAPQ, and their random copolymer PSPQ/PBAPQ in the wavelength range 0.9–2.4 μm. The $\chi^{(3)}$ spectra of the three materials exhibit a resonance peak at about 1.2 μm and off-resonance values for wavelengths longer than 1.8 μm. The nonresonant $\chi^{(3)}$

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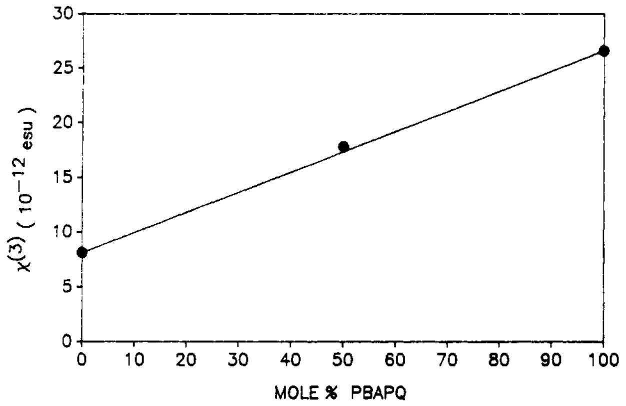

Figure 4. Resonant $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ versus the mole percent of PBAPQ in random copolymer PSPQ/PBAPQ.

values for the three materials at 2.38 μm, as shown in Table I, are all the same (2.2 × 10^{-12} esu) within experimental errors. Thus, the structural differences between PSPQ, PBAPQ, and the random copolymer have no effect on the off-resonance $\chi^{(3)}$ of these polyquinolines.

The observed resonance peaks at about 1.2 μm in the $\chi^{(3)}$ spectra of the three materials and the lack of any absorption features in the 0.5-2.4-μm region in their optical absorption spectra (Figure 1) show that the peaks are due to a three-photon resonance. The magnitude of the three-photon resonance-enhanced $\chi^{(3)}$ of PSPQ, PBAPQ, and PSPQ/PBAPQ was 8.1 × 10^{-12}, 2.7 × 10^{-11}, and 1.8 × 10^{-11} esu, respectively (Table I). Thus, the off-resonance optical nonlinearities of PSPQ, PBAPQ, and PSPQ/PBAPQ are enhanced at resonance by a factor of 4, 12, and 8, respectively. The systematic decrease in resonant $\chi^{(3)}$ value (PBAPQ > PSPQ(Z)/PBAPQ > PSPQ(Z)) correlates with the decrease in the degree of π-electron delocalization expected from the absorption spectra: PBAPQ (λ_{max} = 399 nm) > PSPQ(Z)/PBAPQ (λ_{max} = 390 nm) > PSPQ(Z) (λ_{max} = 372 nm). Since the E or trans isomer of PSPQ has a higher π-electron delocalization (λ_{max} = 408 nm) than PBAPQ, it is clear that the observed smaller resonant $\chi^{(3)}$ of vinylene-linked polyquinoline (PSPQ) compared to the acetylene-linked polyquinoline (PBAPQ) is due to photoinduced E–Z (trans–cis) isomerization of PSPQ and the associated decrease in π-electron delocalization.

In Figure 4, the resonant $\chi^{(3)}$ is represented as a function of copolymer composition. The $\chi^{(3)}$ of copolymer PSPQ/PBAPQ (50:50) lies on a straight line joining the $\chi^{(3)}$ values of the two constituent homopolymers, suggesting the absence of enhancement in the third-order nonlinearities with the introduction of disorder in the copolymer backbone. In fact, the $\chi^{(3)}$ value of the copolymer is, within experimental errors, equal to the molar average of the $\chi^{(3)}$ values of the homopolymers over the entire spectrum.

In preliminary measurements of the optical loss (α) of thin films of the conjugated rigid-rod polyquinolines, defined as the absorbance per unit thickness, we have found α values of the order 1–10 cm^{-1} in the wavelength range 0.80–2.0 μm.[11] This suggests that low optical loss thin films can be fabricated from the polyquinolines. Also, this gives a figure of merit $|\chi^{(3)}|/\alpha$ estimate for the current thin films to be about 10^{-11}–10^{-13} esu cm.

In summary, we have prepared optical-quality thin films of conjugated rigid-rod polyquinolines, PSPQ and PBAPQ, and their random 50/50 copolymer PSPQ/PBAPQ and investigated their wavelength dependent third-order optical nonlinearities by third harmonic generation. The $\chi^{(3)}$ spectra of the three materials in the 0.9–2.4-μm wavelength range showed a peak near 1.2 μm that was identified as a three-photon resonance. The magnitude of the three-photon enhanced $\chi^{(3)}$ was respectively 8.1 × 10^{-12}, 2.7 × 10^{-11}, and 1.8 × 10^{-11} esu for thin films of PSPQ, PBAPQ, and PSPQ/PBAPQ. Off-resonance at 2.38 μm, it was found that the $\chi^{(3)}$ of the three materials was the same, 2.2 × 10^{-12} esu. Over the entire spectrum, the $\chi^{(3)}$ value of the copolymer is, within experimental errors, equal to the molar average of the $\chi^{(3)}$ values of the homopolymers, suggesting the absence of enhancement or reduction in the third-order optical nonlinearities with the introduction of disorder in the copolymer backbone. The relative resonant $\chi^{(3)}$ values of the three materials correlate well with their degree of π-electron delocalization. The smaller resonant $\chi^{(3)}$ of vinylene-linked polyquinoline (PSPQ) relative to the acetylene-linked polymer (PBAPQ) appears to be due to photoinduced E–Z isomerization and the associated decrease in π-electron delocalization. The measured magnitude of the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the polyquinolines over a wide wavelength range, using THG, makes possible the theoretical modeling of the optical nonlinearity of the materials based on the essential states mechanism.[4b] From such a modeling, we can then predict the real and imaginary parts of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$. Such modeling studies on the polyquinolines are currently in progress and will be reported in the future.

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Registry No. PBAPQ (SRU), 135614-64-1; PSPQ (SRU), 94751-99-2; PSPQ (copolymer), 106500-72-5; PBAPQ (copolymer), 135663-13-7; PSPQ/PBAPQ (copolymer), 135695-37-3.

Electrochemical Synthesis of Metal Nitride Ceramic Precursors in Liquid Ammonia Electrolyte Solutions

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We report a new electrochemical method for synthesizing a range of metal nitride, M_xN_y, ceramic precursors. The experimental conditions (NH_4Br/liquid NH_3 electrolyte solutions and inert atmosphere manipulation of reactants and products) lead to a significant reduction in the levels of C and O contamination compared to previously reported electrosynthetic schemes.[1] Moreover, the

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