Adjusting the Third-Order Nonlinear Optical Properties of a Conjugated Polymer Film

S. A. Hambir,[†] **D. Wolfe,**[‡] **G. J. Blanchard,* and G. L. Baker***

Contribution from the Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

Received February 18, 1997[⊗]

Abstract: We demonstrate the ability to adjust and control the magnitude of the third-order nonlinear response of a conjugated polymer, the processable polydiacetylene poly(4BCMU), through macroscopic polymer processing techniques. The demonstration of control over $\chi^{(3)}$ in a conjugated polymer is accomplished by using stimulated inverse Raman scattering. The control is achieved through the balance of two opposing effects introduced by processing: the enhancement in nonlinear response per chromophore unit and the misalignment of the chromophores relative to the incident linearly polarized electric field. We observe a significant enhancement of the nonlinear response in the stretch-aligned material compared to the non-aligned material, with the enhancement limited in our measurements by the extent to which the optically active polymer and supporting substrate can be elongated.

Introduction

Over the past decade, the field of nonlinear optics has attracted substantial research interest, with most of the attention being focused on establishing the fundamental relationship between nonlinear optical response and chemical structure, and more applied efforts aimed at photonic and photoelectric device applications. Conjugated organic materials have been the target of much of this work because of the range of structural and mechanical properties they exhibit. π-Conjugated systems possess characteristically large electronic polarizabilities and, because the nonlinear response of a material is a manifestation of higher orders of the molecular polarizability, it is reasonable to expect conjugated molecules to possess substantial hyperpolarizabilities. Conjugated molecules have been used extensively in work on the optimization of the first hyperpolarizability, β, in organic materials. Early treatments of β related the difference in permanent dipole moment between the ground and excited electronic states of the molecule to the magnitude of the second-order nonlinear response.[1] Following this model, significant research effort has been expended in creating the largest possible charge separation in the excited electronic state by using "push−pull" compounds, but the results do not always yield a β response as large as expected. Marder and co-workers have developed an elegant model for understanding the relationship between chemical structure and second-order nonlinear optical response based on the extent of bond alternation that exists in polyene chains connecting donor and acceptor terminal functionalities.[2−7] Their work demonstrates clearly that it is

not only a charge separation in the excited state that influences the second-order nonlinear response, but also the extent to which the donor and acceptor functionalities communicate through their connecting polyene chain. Their work serves as a useful guide in the design of materials with tailored β properties.

Despite the substantial advances that have been made in understanding the chemical basis for second-order nonlinear optical effects, the same level of success remains to be achieved for higher order processes. We are interested in understanding the chemical basis for third-order nonlinear optical properties, which depend on the second hyperpolarizability, γ. Our interest stems from the many nonlinear optical processes (*e.g.* third harmonic generation, stimulated Raman scattering, degenerate four-wave mixing) that are described in terms of γ, and the fact that all molecules possess a third-order nonlinear optical susceptibility. This latter property stands in contrast to second-order processes, which operate only in molecules or materials that do not possess a center of inversion. Achieving a predictive understanding of the relationship between chemical structure and γ has proven to be challenging, at least in part because of the derivative nature of the relationship between the orders of the polarizability.[8] A further complication is that there are many different experimental means to access γ. Because each optical method interrogates some subset of the γ tensor elements, the relationship between the results of different measurements is often unclear. There have been several attempts at understanding the relationship between γ and chemical structure and, from this work, two approaches appear to show promise. Both rely on the adjustment of the electron density distribution within the nonlinear chromophore. In the case of polar molecules, Marder demonstrated the utility of the bond alternation approach, which is related to his treatment of the β ($\chi^{(2)}$) response, and relies on the electronic properties of the nonlinear chromophore. While this approach is useful and versatile for individual molecules, its application to polymer systems is not necessarily straightforward. Our approach to the optimization of γ ($\chi^{(3)}$), especially in polymer systems, is based on using both the electronic and the vibrational structure of the polymer, where the characteristically strong coupling between electronic and

† Present Address: Department of Chemistry, University of Illinois at Urbana−Champaign, Urbana, IL 61801.
‡ Present Address: Department of Chemistry, Rice University, Houston, TX 77251.
* Authors to whom correspondence should be addressed.
⊗ [Abstract published in *Advance ACS Abstracts*]

(1) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Academic: New York, 1986.
(2) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103.
(3) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 3006.
(4) Risser, S. M.; Beratan, D. N.; Marder, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 7719.
(5) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186.
(6) Meyers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

(7) Meyers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. L. *Chem. Phys. Lett.* **1994**, *228*, 171.
(8) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.
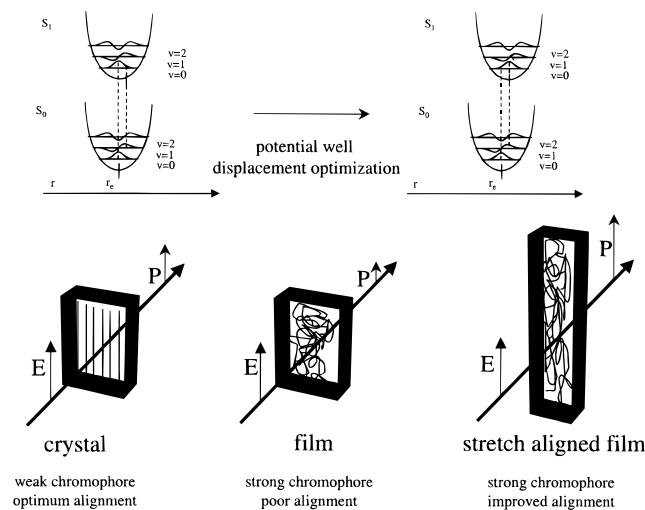
Figure 1. Schematic representation of adjustment of the $\chi^{(3)}$ response in a processable polymer. Top: Change in potential well displacement to optimize Franck−Condon factors due to short-range disorder in the polymer chromophore. Bottom: Schematic of variation in the nonlinear response as a function of processing. E = incident polarized electric field, P = induced third-order polarization.

vibrational structure in conjugated polymers can be used to advantage. This approach is comprised of two parts. The first is the optimization of γ for individual chromophore subunits by adjustment of the polymer effective conjugation length.[9] The conjugation length of the nonlinear chromophore is determined by the distance between defects (bends, breaks, twists, etc.) in the polymer backbone, and the density of defects can be controlled by macroscopic processing techniques, such as spin casting, for certain conjugated polymers. The disorder-induced optimization of the optical nonlinearity per chromophore unit competes with misalignment between the chromophore and a polarized incident electric field. For the polydiacetylene poly(4BCMU), the enhancement in γ per chromophore achieved through disorder is overcome by the misalignment introduced to the polymer film, yielding a third-order nonlinear response that is less than that of the crystalline material.[9] To change the balance between these competing effects, we report here that the magnitude of the nonlinear response for the film can be increased to equal that of the crystal through stretch alignment, where the orientational distribution of nonlinear chromophores is partially re-aligned with the incident electric field. A schematic of this concept is shown in Figure 1.

While there is a great deal of interest in the chemistry and materials communities in achieving process-level control over the fundamental optical properties of materials, this connection, for the most part, remains to be made. The work we present here marks a step toward realizing this goal. The significance of this work is that it demonstrates our ability to *adjust* the nonlinear response of a conjugated polymer using macroscopic processing techniques. This is not simply a controlled means of diminishing the $\chi^{(3)}$ response of this material, but rather it is the first demonstration of processing a disordered film to recover the nonlinearity characteristic of the crystalline polymer. Gaining control over the third-order nonlinear optical response in a conjugated polymer is the direct result of understanding the fundamental chemical and structural basis for the optical nonlinearity.

Experimental Section

Nonlinear Laser Spectroscopy. We use a pump-probe laser spectrometer[10] for our stimulated inverse Raman scattering[11] measurements. An intense, linearly polarized "pump" laser pulse provides subresonant excitation, and a weak, linearly polarized "probe" laser pulse, approximately one vibrational resonance higher in energy than the pump pulse and of parallel polarization, interrogates the result of the excitation. The spectrometer used for these measurements produces two trains of picosecond pulses that are independently frequency-tunable while maintaining a well-defined temporal relationship. The source laser is a mode-locked CW Nd:YAG laser that produces 3 W average power at 532 nm and ∼1.2 W average power at 355 nm. The repetition rate of this laser is ∼76 MHz and the pulse width is ∼100 ps fwhm. The second and third harmonic outputs of this laser are used to excite two cavity-dumped dye lasers synchronously. The dye laser pulse widths are typically 5 ps fwhm and the cross correlation between the two dye lasers is ∼10 ps fwhm. For these experiments the pump laser wavelength was varied between 579 and 627 nm (Rhodamine 590 and Rhodamine 610, Exciton) and the probe laser was varied over the range 512 to 575 nm (Coumarin 500 and Pyromethene 567, Exciton). The pump-probe signals are detected by using radio- and audio-frequency triple modulation signal encoding with synchronous demodulation detection, allowing shot noise limited sensitivity and at least 4 orders of magnitude of dynamic range.[12] This wide dynamic range is necessary for the quantitative measurement of the subtle features present in inverse Raman data.[13,14]

Linear Spectroscopy. The absorption data for spin-coated and stretch-aligned films of poly(4BCMU) were recorded with ∼1 nm resolution with a Hitachi U4001 absorption spectrophotometer. Polarized FTIR measurements were made on a Nicolet Magna 550 system with 8-cm^{-1} resolution and a Cambridge IR polarizer.

Materials and Processing. Poly(4BCMU) was synthesized in our laboratories as described previously.[19] Films used in optical experiments were spin cast (1000 rpm, 60 s) from 5 wt % solutions of poly-(4BCMU) in cyclopentanone onto an optically transparent polymer substrate attached to a glass microscope slide. After drying *in vacuo*, the poly(4BCMU)/substrate composite was annealed at 100 °C for 2 h and stretched to the desired elongation ratio (l/l_0) with an in-house apparatus. Samples were examined by using a polarizing optical microscope to detect flaws and crystallinity.

Substrate. The substrate support material used in this work is a copolymer poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP). This polymer was chosen as the substrate material because it is amorphous, is insoluble in the cyclopentanone spinning solvent, and does not undergo stress-induced crystallization. Other substrates, such as polyethylene, could be stretch aligned to a higher elongation ratio than FEP, but elongation causes these substrates to form stress-induced microcrystalline domains. Optical scattering from these domains precluded their use for inverse Raman scattering measurements.

Because of the nearly complete fluorination of this polymer, it possesses a low surface tension and thus does not adhere well to poly-(4BCMU). We modified the surface of the FEP copolymer using a method similar to that used by Bening and McCarthy[15] and Dwight and Riggs.[16] The copolymer substrate was treated with benzophenone and metallic sodium in tetrahydrofuran at 60 °C for 24 h under a N$_2$ atmosphere and was subsequently rinsed with water, acetone, and *n*-hexane, in that order. The purpose of this treatment is to abstract fluorine from the FEP copolymer surface and create carbon−carbon double bonds so that poly(4BCMU) can adhere to the polymer substrate. Spontaneous resonance Raman spectra of the modified substrate

(9) Hambir, S. A.; Blanchard, G. J.; Baker, G. L. *J. Chem. Phys.* **1995**, *102*, 2295.

(10) Jiang, Y.; Hambir, S. A.; Blanchard, G. J. *Opt. Commun.* **1993**, *99*, 216.

(11) Jones, W. J.; Stoicheff, B. P. *Phys. Rev. Lett.* **1964**, *13*, 657.

(12) (a) Bado, P.; Wilson, S. B.; Wilson, K. R. *Rev. Sci. Instrum.* **1982**, *53*, 706. (b) Andor, L.; Lorincz, A.; Siemion, J.; Smith, D. D.; Rice, S. A. *Rev. Sci. Instrum.* **1984**, *55*, 64. (c) Blanchard, G. J.; Wirth, M. J. *Anal. Chem.* **1986**, *58*, 532.

(13) Blanchard, G. J.; Heritage, J. P.; von Lehmen, A. C.; Kelley, M. K.; Baker, G. L.; Etemad, S. *Phys. Rev. Lett.* **1989**, *63*, 887.

(14) Blanchard, G. J.; Heritage, J. P. *J. Chem. Phys.* **1990**, *93*, 4377.

(15) Bening, R. C.; McCarthy, T. J. *Polym. Prepr.* **1988**, *29*, 336.

(16) Dwight, D. W.; Riggs, W. J. *J. Colloid Interface Sci.* **1974**, *47*, 650.

exhibited a resonance at $\sim$1560 cm^{-1}, which we assign to a C≡C stretching mode. The untreated substrate did not exhibit this resonance.

Results and Discussion

To gain control over the nonlinear optical properties of a material, the essential physics of the optical response must be understood and related to macroscopic materials properties. In our investigations, we have focused on polydiacetylenes as the materials of choice because of the wide range of accessible morphologies and their favorable linear and nonlinear optical properties. We access a $\chi^{(3)}$ optical response in polydiacetylenes that depends on the coupling between the electronic and vibrational coordinates of the polymer backbone. The use of stimulated inverse Raman scattering allows us to exploit the structural richness of these materials and not simply use them as a support structure for an extended π-system. In our initial investigations,[13,14] we focused on the inverse Raman scattering spectroscopy of the polydiacetylene PTS because of its high degree of crystallinity and well-understood optical properties. While investigations of PTS have revealed a great deal about the optical properties of conjugated polymers, this material does not possess the morphological versatility that allows the relationship between $\chi^{(3)}$ optical response and polymer morphology to be explored fully. For this reason we have studied the inverse Raman scattering behavior of the polydiacetylene poly-(4BCMU). This conjugated polymer possesses the same nonlinear chromophore polymer backbone as PTS, but poly-(4BCMU) is a processable material, owing to the labile nature of side groups. With this material, it is possible to explore the relationship between polymer morphology and nonlinear optical response.

The inverse Raman $\chi^{(3)}$ response of poly(4BCMU) *increases* per nonlinear chromophore unit when the material is transformed from crystalline to amorphous form. This behavior is non-intuitive and we understand it quantitatively.[9] Briefly, the introduction of disorder in the polymer backbone shortens the conjugation length of the system compared to that of the crystalline polymer, giving rise to a blue shift of the $\pi \rightarrow \pi^*$ absorption band (*vide infra*). The disorder-induced change in conjugation length increases the change in bond order associated with electronic excitation. The polymer backbone experiences a greater geometric change (elongation) on excitation for the disordered material than for the crystal. The greater modulation of bond length in the disordered material gives rise to an enhancement in the Franck−Condon factors associated with the inverse Raman signal. This behavior is one of the factors that allows us to control the optical response of polydiacetylenes macroscopically.

One important means of processing poly(4BCMU) is annealing. Differential scanning calorimetry (DSC) traces of spin-cast poly(4BCMU) films show two broad transitions: one beginning just above room temperature and extending to 110 °C, and a second endothermic transition at 165 °C.[17] The first transition is associated with melting of the hydrogen-bonded lattice formed within the side chains of poly(4BCMU), while the second transition reflects gross disordering of the polymer backbone. Annealing poly(4BCMU) films at $\sim$100 °C sharpens the first DSC transition and causes a corresponding increase in the intensity of the excitonic transition. Annealing allows the chains to relax locally and enables re-formation of the hydrogen-bonded lattice. For annealing at $T > 110$ °C, the hydrogen-bonded lattice "melts" and the chains rearrange to form ordered domains that scatter light.
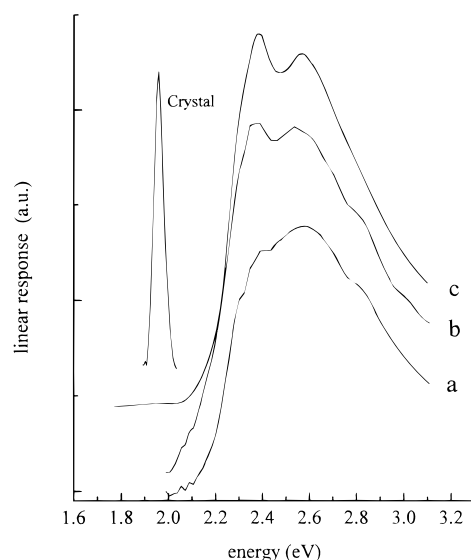

Figure 2. Linear absorption of a poly(4BCMU) film cast on FEP for elongation ratios of (a) $l/l_0 = 1$, (b) $l/l_0 = 5$ and (c) linear absorption of a four year old spin-cast poly(4BCMU) on a quartz substrate ($l/l_0 = 1$). Also shown is the exciton resonance for crystalline poly-(4BCMU).

Heat, solvent, and pressure cause backbone conformational changes in poly(4BCMU), and these changes are manifested as thermo-, solvato-,[18] and piezochromism.[19] Particularly striking are chromic effects that reflect conformational disorder on length scales shorter than the size of a relaxed exciton on a crystalline polydiacetylene chain. For example, blue single crystals of poly(4BCMU) turn red on exposure to solvent vapors,[20] and form yellow solutions in good solvents.[18] Similarly, heating poly(4BCMU) crystals yields first a red phase and then a tacky orange-yellow solid at higher temperatures. In both cases, the red phase materials are less ordered than the single crystals, and the yellow phase materials correspond to the most extensively disordered polydiacetylene chains.

The linear vibrational and electronic responses of polydiacetylenes provide important information on the conformation and orientation of the polymer backbone (Figure 2) and side groups (Figure 3). Both the center frequency and the bandwidth of the $\pi \rightarrow \pi^*$ electronic transition, localized on the polymer backbone, depend on the processing history of the material, and we can exploit this relationship to characterize and quantitate the extent of backbone disorder in the polymer.[20] We use anisotropy in the electronic response to infer the extent of backbone ordering in stretch aligned poly(4BCMU). While stretching clearly improves the overall alignment of the chains, the local environment on the length scale of the chromophore can remain disordered because of twists in the polymer backbone and side chain disorder. Spectra of stretch-aligned poly-(4BCMU) show a higher optical dichroism than unstretched spin cast films (*vide infra*), but the shape of the absorption band for light polarized along the polymer backbone is largely unchanged from that of unstretched film cast onto the same substrate (Figure 2).

(17) Baker, G. L.; Shelburne, J. A., III; Townsend, P. D. *Inst. Phys. Conf. Ser.* **1989**, *103*, 227.

(18) Chance, R. R.; Washbaugh, M. W.; Hupe, D. J. NATO Advanced Research Workshop; Polydiacetylenes, Synthesis, Structure and Electronic Properties, 1985, No. E102, p 39.

(19) Variano, M. J.; Sandroff, C. J.; Baker, G. L. *Macromolecules* **1991**, *24*, 4376.

(20) Nowak, M. J.; Blanchard, G. J.; Baker, G. L.; Etemad, S.; Soos, Z. G. *Conjugated Polymeric Materials: Opportunities in Electronics, Opto-Electronics and Molecular Electronics;* Bredas, J. L., Chance, R. R., Eds.; Kluner Academic Publishing: Dordrecht, 1990; Vol. 182, pp 421−4 27.
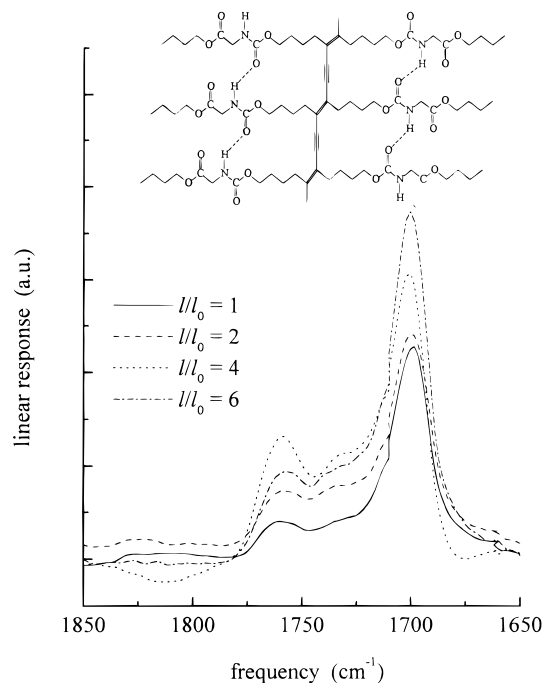
Figure 3. Polarized infrared spectra of stretch aligned poly(4BCMU) in the C=O stretch region for film elongation ratios of $l/l_0 = 6, 4, 2,$ and 1 from top to bottom. The structure of poly(4BCMU) is shown at the top of the figure. These data sense side group orientation in this material.

A particularly sensitive marker for local disorder in poly-(4BCMU) is the relative intensity of the exciton in polydiacetylenes. In addition, the energy of the excitonic transition depends sensitively on polymer morphology. For single crystals, the excitonic resonance appears at ~1.96 eV and dominates the optical properties of polydiacetylenes. For spin cast poly-(4BCMU) films, the exciton appears at ~2.29 eV in accord with the increased disorder seen for films (Figure 2). In crystalline materials the exciton is one dimensional to within the width of the backbone π system, with a characteristic length of ~38 Å.[21] The observed exciton binding energy of 400 meV and very large transition cross-section are direct results of its one-dimensional character and make this resonance useful for room temperature nonlinear optical signal processing applications. Both the shift and the transition line width can be used to characterize disorder in these materials.

As discussed above, the linear response of polydiacetylenes is known to depend on disorder in the polymer backbone. Our recent inverse Raman scattering measurements on poly-(4BCMU) films[9] spin cast on a quartz substrate demonstrate that the nonlinear response of this material is also quite sensitive to polymer morphology, and in a manner that is advantageous for photonic signal processing applications (Figure 4). While aging of the spin-cast films changes the linear response of this material measurably (Figure 2), its nonlinear inverse Raman response is largely unaffected, implying long-term stability of this material for photonic signal processing applications. Previous inverse Raman measurements on the crystalline polydiacetylene PTS show that the nonlinear optical response of polydiacetylenes can be modeled effectively in the context of a strongly coupled three-level system.[13,14] For crystalline poly-(4BCMU), the inverse Raman scattering response is virtually identical with that for PTS, while for spin-cast films of poly-(4BCMU), the vibronic transition cross sections, resonance
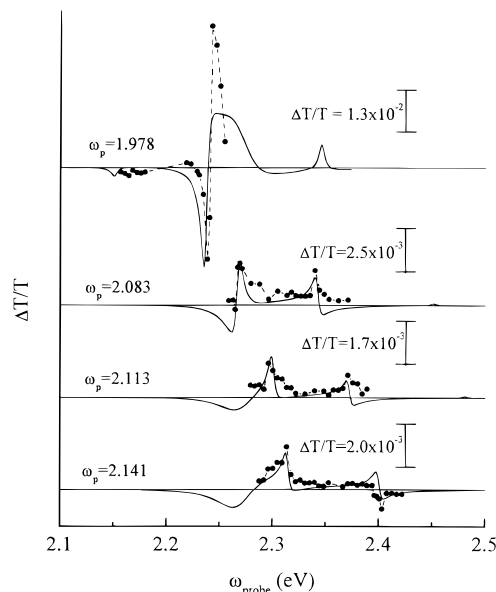
(21) Greene, B. I.; Orenstein, J.; Millard, R. R.; Williams, L. R. *Phys. Rev. Lett.* **1987**, *58*, 2750.

Figure 4. Experimental data (points) and calculated fit (solid line) of the stimulated inverse Raman spectra of the C=C and C≡C stretching resonances for spin-cast poly(4BCMU) on a quartz substrate for ω_p energies from 1.978 to 2.141 eV, as indicated. The magnitudes of the signals are as indicated for each spectrum.

energies, and line widths all differ from those for the crystalline material and depend sensitively on the morphology of the polymer.[9]

We show in Figure 5 the stimulated inverse Raman responses of stretch-aligned poly(4BCMU) films supported on FEP copolymer substrates. These responses, as for the inverse Raman spectra we have reported previously, are characteristic of a system with strong electronic-vibrational coupling. In the small signal limit, the nonlinear response induced in the material at a (probe) frequency ω_t by the action of an intense (pump) electric field at ω_p, the inverse Raman response, can be modeled qualitatively with eq 1[22]

$$\chi^{(3)}(\omega_t) = \frac{|\mu_{0x}|^2|\mu_{vx}|^2}{\hbar^3} \frac{1}{(\omega_{0x} - \omega_t - i\gamma_{0x})^2(\omega_{0v} - \omega_t + \omega_p - i\gamma_{0v})} \quad (1)$$

where the terms μ are transition dipole moments and ω_{0v}, ω_{0x}, ω_p, and ω_t are vibrational, excitonic, pump (p), and probe (t) laser frequencies, and the terms γ are the line widths for the indicated transitions, where 0, x, and v are ground, excitonic, and vibrational energy levels, respectively.[13,14] The transition dipole moments and the line widths both depend on the morphology of the material. The signal we detect experimentally is related to the change in linear absorption through eq 2.

$$\Delta T/T \cong \Delta\alpha l \quad (2)$$

$\Delta\alpha l$ is related to $\text{Im}\{\chi^{(3)}\}$ through the complex dielectric response of the material.[13] By taking the dielectric response of the polydiacetylenes into account in our calculation of the signal, we achieve virtually quantitative agreement between theory and experiment for spin-cast and stretch-aligned poly-(4BCMU) films. In all of our inverse Raman measurements on the poly(4BCMU)/modified FEP system, we observe a positive ($\Delta T/T > 0$) displacement of the experimental data from the calculated responses. This slight difference between the

(22) Saikan, S.; Hashimoto, N.; Kushida, T.; Namba, K. *J. Chem. Phys.* **1985**, *82*, 5409.
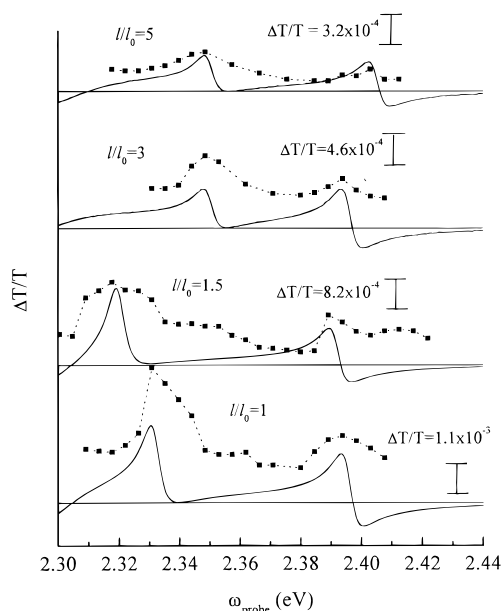
Figure 5. Experimental data (points) and calculated fit (solid line) of the stimulated inverse Raman spectra of the C=C and C≡C stretching resonances for spin-cast poly(4BCMU) on an FEP substrate for ω_p = 2.141 eV. Stretch-alignment ratios and experimental signal magnitudes are as indicated.

Table 1. Cross Sections for Ground State Vibration-to-Excited Electronic State Transitions in Poly(4BCMU)

	crystal ω_X = 1.96 eV	spin-cast on quartz ω_X = 2.29 eV	spin cast on modified FEP substrate ($1 \leq l/l_0 \leq 5$)	
			ω_X = 2.02 eV	ω_X = 2.29 eV
$\sigma_{C=C}$ (eV)	0.15	0.26	0.45	0.25
$\sigma_{C≡C}$ (eV)	0.07	0.15	0.25	0.15

centered at 2.29 eV ($\gamma_x \cong 50$ meV). The second excitonic resonance, required to achieve agreement with the data, appears at 2.02 eV ($\gamma_v \cong 50$ meV). There are two possible reasons for the presence of this additional electronic resonance, and based on the information at hand, we cannot unambiguously determine which explanation is correct. One possibility is that the modification of the FEP copolymer substrate has introduced sites that interact strongly with the poly(4BCMU) backbone chromophore. The removal of fluorine and introduction of C=C and C≡C bonds onto the substrate surface presents an opportunity for strong $\pi-\pi$ interaction between the two polymers. It is also possible that other types of chemical interaction could be present in this polymer system. Bening and McCarthy[15] have shown that oxygen is introduced during rinsing of the FEP copolymer to form C=O moieties. Our previous work on the polydiacetylene PTS demonstrates the important role that oxygen interactions with the polydiacetylene backbone can have on the inverse Raman response.[23] For PTS, a resonance at ~2.39 eV, 400 meV higher in energy than the excitonic resonance, is associated with molecular oxygen adsorbed onto the conjugated backbone. The 2.02 eV electronic resonance we observe in poly(4BCMU) film could have a similar origin, with some oxygen-containing moiety (likely C=O) existing at the interface between the substrate and the poly(4BCMU), although the energy of the additional resonance we observe in this work is ~270 meV below that of the 2.29 eV exciton. It is also possible, given the energy of the additional excitonic resonance, that small crystalline domains of poly(4BCMU) could be re-established in the films as a result of the annealing and stretching processes. The energy of this additional electronic resonance (2.02 eV) is within approximately one line width of the ~1.96 eV excitonic resonance seen in blue phase crystalline poly(4BCMU). The transition cross sections for the electronic-to-vibrational transitions we have measured provide some insight into the origin of this additional resonance (Table 1). Our work on adsorption of oxygen to PTS showed transition cross sections of $\sigma \sim 1$ eV for the adsorbate-induced electronic state-to-polymer backbone C=C stretch.[23] For the stretch-aligned films reported here, we observe $\sigma_{C≡C} \cong 0.15$ eV and $\sigma_{C=C} \cong 0.25$ eV for coupling to the 2.29 eV exciton. For the 2.02 eV electronic transition we detect in the stretch-aligned films, we obtain best-fit values of $\sigma_{C=C} \cong 0.45$ eV and $\sigma_{C≡C} \cong 0.25$ eV. On the basis of these data, it appears that the 2.02 eV electronic transition seen in stretch-aligned films arises from an interaction of the poly(4BCMU) backbone with the substrate, where the interacting substrate moiety is not molecular oxygen.

It is also possible that the additional excitonic resonance at 2.02 eV is intrinsic to poly(4BCMU) and its relative contribution to the nonlinear response depends on the annealing history of the polymer. To evaluate this possibility, we have examined the inverse Raman scattering response of both freshly deposited and annealed samples of poly(4BCMU) cast on quartz substrates. The observed agreement between theory and experiment for calculations with two excitonic resonances (2.02, 2.29 eV) is poor. The corresponding calculation, where only the 2.29 eV resonance is included, provides excellent agreement with the experimental data, demonstrating that the 2.02 eV excitonic

experimental and calculated responses results from two factors. First, in the development of the theory, Lorentzian line shape functions were used,[21] and this is likely not an accurate representation of the experimental line shapes. Our previous stimulated inverse Raman scattering data on crystalline polydiacetylenes show that, even for these highly ordered materials, a Lorentzian line shape does not respresent the actual resonances accurately.[13,14,23] In addition, the uniform background signal we observe, only for the poly(4BCMU) films on FEP substrates, is due either to a coherent response from the substrate or from an induced spectroscopic feature arising from interactions between the substrate and the poly(4BCMU). Spontaneous Raman scattering from the substrate shows a vibrational resonance at 1560 cm^{-1} superimposed on a broad background. We believe the background signal in our inverse Raman spectra of the poly(4BCMU)/FEP system is of the same origin as that of the broad background observed in spontaneous Raman scattering data on the modified FEP substrate.

There are two distinct classes of stimulated inverse Raman scattering data that we present here. The first set of data is for spin-cast poly(4BCMU) on a quartz substrate annealed at room temperature for more than four years (Figure 4) and for a freshly prepared poly(4BCMU) spin cast on a FEP substrate (Figure 5). The data shown in Figure 4 are consistent with the poly(4BCMU) film not interacting significantly with the substrate, and only one electronic resonance (2.29 eV) is required to achieve excellent agreement between experiment and calculation. We note that, for these data, there is no anomalous offset of the signal, indicating that there is no detectable response attributable to interactions between the polymer nonlinear chromophore and the silica substrate. The second set of data is for poly(4BCMU) spin cast on the modified FEP copolymer substrate (Figure 5). For these data, in addition to the constant offset to the signal discussed above, the agreement between experiment and theory is achieved only when two excitonic resonances are included in the calculation. In correspondence with the quartz substrate data, one excitonic resonance is

(23) Blanchard, G. J.; Heritage, J. P. *Chem. Phys. Lett.* **1991**, *177*, 287.

Table 2. Excitation Energy Dependence (eV) of Vibrational Resonance Frequencies of Spin-Cast and Aligned Poly(4BCMU) Films

	$l/l_0 = 1$		$l/l_0 = 1.5$		$l/l_0 = 3$		$l/l_0 = 5$	
ω_p	$\omega_{C=C}$	$\omega_{C\equiv C}$	$\omega_{C=C}$	$\omega_{C\equiv C}$	$\omega_{C=C}$	$\omega_{C\equiv C}$	$\omega_{C=C}$	$\omega_{C\equiv C}$
1.978	0.213	0.245	0.196	0.244	0.182	0.254	0.200	0.249
2.077	0.197	0.265	0.186	0.264	0.187	0.264	0.189	0.265
2.109	0.186	0.260	0.186	0.264	0.191	0.260	0.192	0.265
2.142	0.208	0.263	0.190	0.254	0.178	0.250	0.208	0.254

Table 3. Comparison of Elongation Ratio and Optical Dichroism at 2.29 eV

elongation ratio (l/l_0)	dichroism ($\alpha_\parallel/\alpha_\perp$)
1	1
1.5	1.9
3	2.2
5	2.5

resonance for poly(4BCMU) spin cast on FEP arises from the interaction between the two polymers and is not intrinsic to poly-(4BCMU).

The data we present in Figure 5 contain information similar to that obtained from spontaneous resonance Raman scattering measurements.[24] The polydiacetylene backbone C=C and C≡C stretching resonance frequencies are sensitive to the disorder present in the stretch-aligned films. The positions of both resonances depend on the excitation frequency (Table 2), but the relationship between these two quantities is not direct. We concur with the previous interpretation that the excitation energy dependence of the vibrational resonances comes about because different excitation frequencies access different regions of the stretch-aligned film that possess a characteristic type or extent of disorder. Exactly analogous behavior has been measured in spin-cast, unstretched films of poly(4BCMU).

Stretch alignment of poly(4BCMU) introduces some amount of macroscopic orientation into a material that is, before processing, isotropic in two dimensions. We have compared the linear response of the stretch-aligned films parallel and perpendicular to the stretch-alignment axis. We report these results in terms of the anisotropy ratio $\alpha_\parallel/\alpha_\perp$ for the supported poly(4BCMU) films stretched to different elongation ratios (Table 3). For the different elongation ratios, $\alpha_\parallel/\alpha_\perp$ increases with elongation, but comparison of these values with the experimental value of $\alpha_\parallel/\alpha_\perp \sim 50$ for crystalline poly(4BCMU) demonstrates that the extent of alignment is modest when the modified FEP substrate is used. For the elongation ratio, l/l_0, spanning the range of 1 (unstretched) to $\sim$5, we measure a corresponding variation in $\alpha_\parallel/\alpha_\perp$ from 1 to 2.5. To put these values in perspective, disordering a single crystal with $\alpha_\parallel/\alpha_\perp \sim 50$ by exposure to solvent vapor reduces $\alpha_\parallel/\alpha_\perp$ to 5.[20] Larger values of $\alpha_\parallel/\alpha_\perp$ in the stretch-aligned films require a significantly larger elongation ratio, although the exact value of l/l_0 required to achieve $\alpha_\parallel/\alpha_\perp > 10$ cannot be predicted because of the mechanical strain and stress limitations inherent to both the modified FEP substrate and poly(4BCMU) materials. We recognize that the limiting factor to attaining a higher elongation ratio in this work lies with the FEP copolymer substrate. While other polymers possessing greater deformability can be used, stress-induced crystallinity precludes their use because of significant Rayleigh scattering losses and interference. These anisotropic linear response experiments serve to demonstrate that, with the appropriate substrate, a dichroism close to that of a crystalline material could ultimately be obtained.

(24) Zheng, L. X.; Benner, R. E.; Vardeny, Z. V.; Baker, G. L. *Phys. Rev. B* **1990**, *42*, 3235.

Table 4. $\Delta\alpha$, the Nonlinear Response, Normalized for Sample Thickness and Laser Intensities, for the Various Forms of Poly(4BCMU) Studied

crystalline poly(4BCMU)		poly(4BCMU) spin cast onto modified FEP substrate				
			$\Delta\alpha$ (cm^{-1})			
ω_p (eV)	$\Delta\alpha$ (cm^{-1})	ω_p (eV)	$l/l_0 = 1$	$l/l_0 = 1.5$	$l/l_0 = 3$	$l/l_0 = 5$
1.774	140	2.142	2.5	42	46	130
1.741	4.9	2.109	2.3	21	24	111
1.701	4.1	2.077	3.4	12	28	106
1.653	1.2	1.978	2.7	13	34	58
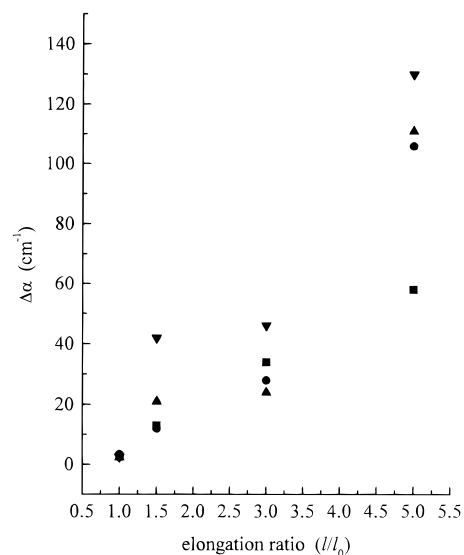
Figure 6. Dependence of $\Delta\alpha$, the normalized nonlinear response, for the C=C stretch on the stretch-alignment ratio of the film. Values are for the four excitation energies, ω_p, indicated in Table 3 for $\omega_p = 1.653$ eV (■), $\omega_p = 1.701$ eV (●), $\omega_p = 1.741$ eV (▲), and $\omega_p = 1.774$ eV (▼).

It is important to quantitate the enhancement in nonlinear response we derive from stretch alignment of these films. Comparison of absolute $\Delta T/T$ quantities is not meaningful because of sample-to-sample variations in the thickness of the poly(4BCMU) films, and because elongation of the polymer/substrate system serves to thin the poly(4BCMU) film. As discussed above, the quantity we determine experimentally is $\Delta T/T \sim \Delta\alpha l$. By normalizing our data for film thickness (l) and laser intensity ($T = I/I_0$), we can obtain the quantity $\Delta\alpha$, which can be compared directly for all of the samples (Table 4) in Figure 6. There is a significant loss of nonlinear response in the spin-cast, non-aligned film compared to that of the crystalline polymer, and this is anticipated, because of misalignment between the polymer backbone and the linearly polarized incident electric fields. Stretch alignment to an elongation ratio of $l/l_0 = 5$ returns the $\Delta\alpha$ value to that seen for the crystalline polymer. We anticipate that greater elongation of the spin-cast films will allow the realization of a nonlinear response in the disordered material that is significantly larger than that for the corresponding crystal. Even at this limited elongation ratio, however, we observe a significant enhancement of the nonlinear response in the spin-cast and stretch-aligned system. Because the nonlinear chromophore is substantially disordered over short (oligomer) length scales, the linear response is comparatively broad. Accordingly, the nonlinear response of the spin-cast and aligned system exhibits a substantially weaker wavelength dependence than that seen for crystalline poly(4BCMU) (Table 4). Thus optical devices based on aligned, spin-cast films of

poly(4BCMU) will exhibit the additional benefit of a comparatively broad operating frequency range.

Conclusions

We have investigated the optical response of poly(4BCMU) thin films supported on a modified FEP copolymer substrate and processed to different elongation ratios. We detect an additional electronic resonance at 2.02 eV, which is due to annealing, stress-induced crystallinity, or a strong interaction between the poly(4BCMU) backbone and the modified FEP substrate. The stretch-oriented, FEP-supported poly-(4BCMU) films are of high optical quality, and the elongation ratio attainable by using the FEP substrate ($l/l_0 \sim 5$) is sufficient to return the nonlinear response of the orientated poly-(4BCMU) films to that of the crystalline polymer. The achievement of higher stretch-alignment ratios with favorable substrates can yield a nonlinear response larger than that of the crystalline material. More significant, we can adjust the magnitude of the $\chi^{(3)}$ response of poly(4BCMU) through macroscopic processing means, and we expect that this approach will prove to be of general utility for processable organic materials.