site. The decrease in θ down the half-met-halide series may contribute somewhat to the increase in delocalization from Cl^- to Br^- to I^-; however, increasing metal–ligand covalency probably dominates. Thus for a superexchange pathway delocalization should correlate with LMCT mixing. α can be expressed in terms of charge-transfer mixing through second-order perturbation theory as given in eq 33.[50]

$$\alpha = \frac{\langle G|H|N(LMCT)\rangle\langle N(LMCT)|H|IT\rangle}{(E_{IT} - E_G)(E_N - E_G)} \qquad (33)$$

From eq 33, α and thus delocalization increases with increasing LMCT state mixing into both the ground and IT states and with decreasing LMCT energy. This is in qualitative agreement with the LMCT energies and intensities for the half-met series as given at the bottom of Table VIII.

These results provide insight into the active site of the multicopper oxidase laccase, which couples four one-electron substrate oxidations to the four-electron reduction of O_2 to H_2O. The native enzyme contains a blue copper site (Type 1), a "normal" copper site (Type 2), and a coupled binuclear copper site (Type 3). A derivative has been prepared in which the Type 2 copper has been removed (the Type 2 depleted, T2D, derivative) and the Type 3 site has been oxidized to the half-met form.[8] This half-met T2D site exhibits properties very different from those of the half-met hemocyanins (and tyrosinases). Exogenous ligands can bind to the site, but *without* the high affinities displayed in hemocyanin. Further, the optical absorption spectra of these derivatives show no IT bands and the EPR spectra exhibit no hyperfine features attributable to delocalization within the binuclear site, even for L = Br^-, I^-, or N_3^-. Based on the analysis above, this lack of both mixed-valent features and high affinity ligand binding suggests that exogenous ligands do not bridge the coppers in half-met T2D laccase. Thus, the Type 3 site in laccase is fundamentally different from the coupled binuclear sites in hemocyanin and tyrosinase, and this difference appears to be important in understanding the differences in reactivity between these active sites. For the T2D derivatives of laccase, in contrast to hemocyanin, the half-met site is a thermodynamically stable one-electron reduced site, and the deoxy Type 3 site does not react with dioxygen in the absence of the Type 2 copper.

Acknowledgment. The authors gratefully acknowledge Dr. Mark Crowder, IBM Almaden Research Center, for obtaining the S-band spectra. NIH Grant DK 31450 is also acknowledged for support of this research.

Supplementary Material Available: Tables S1–S4 containing complete parameters for the EPR simulations in Figure 5 (4 pages). Ordering information is given on any current masthead page.

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Chromatic Properties of Polydiacetylene Films

M. Wenzel and G. H. Atkinson*

Contribution from the Department of Chemistry and Optical Sciences Center, University of Arizona, Tucson, Arizona 85721.

Received December 7, 1988

Abstract: The thermochromic and proposed visible photochromic properties of PDA-12,8 are examined by resonance Raman (RR) and Fourier transform infrared (FTIR) spectroscopies. The chromatic properties are derived from the conversion of a blue-colored PDA-12,8 material (produced upon ultraviolet-induced polymerization) to a red-colored material. Experiments are performed under well-controlled thermal conditions which aid in separating the ultraviolet polymerization used to generate the blue-colored polymeric material from its well-known thermochromic process and from photochromism proposed to be induced by visible radiation. For example, irradiation at 532 nm of water-cooled (0.5 °C) samples of the blue-colored material produces no chromatic changes. A chromatic change to the red-colored material is induced by 532-nm radiation, however, when the PDA-12,8 is not cooled. No evidence supporting a visible photochromic change in PDA-12,8 is found, and it is proposed that the previously reported chromatic properties derive from thermal effects. RR and FTIR data are presented which demonstrate that separate structural changes in the polydiacetylene backbone and in the hydrocarbon side chains of PDA-12,8 accompany the chromatic changes. RR results also show that no change occurs in the distribution of electron density along the PDA-12,8 backbone when chromatic effects are induced.

The chromatic properties of organic molecules, long of interest in fundamental studies,[1] have recently become important elements in applications directed toward the optical processing of information.[2] For example, there are numerous suggestions for optical data storage based on chromatic changes in organic films or solids with optical bistability being one process of major interest.[3] When such chromatic changes occur rapidly (i.e., $<10^{-8}$ s), the material becomes a candidate for optical switching applications.

Polydiacetylenes (PDA), a class of organic molecules which is well known for its nonlinear optical properties,[4] have now also been considered for potential applications in the areas mentioned above. In the cases of PDA having urethane substituents in the side group and of polymerized Langmuir–Blodgett films of PDA formed by long-chain aliphatic substituted diacetylene carbonic acids and their salts, chromatic behavior in solution and in the solid state is well known.[5-7] There also are numerous reports of color changes caused by the addition of a nonsolvent to a polydiacetylene solution[6] or in conjunction with heat treatment in the case of the solid state.[8] A recent series of publications,[9-12]

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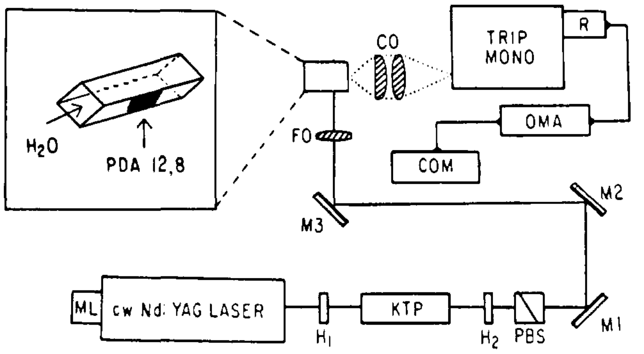

Figure 1. The instrumentation used in the resonance Raman (RR) experiments: ML, mode-locker; H1, half-wave plate (1064 nm); H2, half-wave plate (1064 nm); H2, half-wave plate (532 nm); M1-M5, front-surface, dielectrically coated mirrors; PBS, polarizing beam splitter; FO, optics used for focusing the beam; SR, sample region showing glass tube coated with sample; CO, collecting optics for scattered light; TRIP MONO, triple monochromator; R, intensified reticon; OMA, optical multichannel analyzer; COM, computer.

however, report photochromic properties of PDA films which are prepared by vacuum deposition and ultraviolet solid-state polymerization of pentacosa-10,12-diynoic acid {R—C≡C—C≡C—R′, with R = $-(CH_2)_{11}CH_3$ and R′ = $-(CH_2)_8COOH$}. The resultant blue-colored polymer (PDA-12,8) undergoes an irreversible color change to red when heated to temperatures above 70 °C. The same change in color is reported to be induced by high-energy (78 mJ/cm^2) 488-nm radiation from an argon ion laser.[9-12] The authors characterize the mechanism underlying this color change as purely photochromic (i.e., derived from excited electronic state properties).[9-12] To date, PDA-12,8 is the first polydiacetylene in which photochromism has been reported and, therefore, would have significant value for optical processing.

In this paper, the chromatic properties of PDA-12,8 films are examined under experimental conditions designed to more precisely separate and characterize thermochromism and photochromism. Specifically, (i) the temperature of the polymer is controlled when it is exposed to the low-intensity visible laser radiation in the form of picosecond pulses used to photolytically induce chromatic changes, and (ii) vibrational spectroscopy is utilized to measure the structural changes in the polymer backbone and in the hydrocarbon side chain that may accompany the color changes. These data address both the existence of a photochromic effect in PDA-12,8 films and the molecular model used to describe observed chromatic properties.[10-12] Raman scattering recorded by excitation resonant with the ^1A_g–^1B_u transition of the polydiacetylene is used to analyze the vibrational modes of the polymer backbone while Fourier transform infrared (FTIR) absorption spectroscopy is used to characterize the side-chain structure. These vibrational measurements characterize the molecular structure of different parts of the polymer and thus provide information on whether the same structural forms are produced by the two methods (temperature increase, or visible irradiation) for inducing chromatic changes.

Experimental Section

Films of the monomer, pentacosa-10,12-diynoic acid,[13] are prepared by slow evaporation of a chloroform solution at room temperature. For the measurement of the RR scattering, the monomer is deposited on the outer surface of a rectangular, Pyrex tube, the inside walls of which are thermostated by the circulation of cooled water (Figure 1). Solid-state polymerization is initiated by using ultraviolet (UV) radiation from a low-pressure mercury lamp (Ultraviolet Products Inc., Model SCT-1). In case of the FTIR measurements, the films are prepared on a potassium bromide plate of 5-mm thickness. FTIR spectra are measured in a transmission mode using a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer for a sample which is not thermostated.

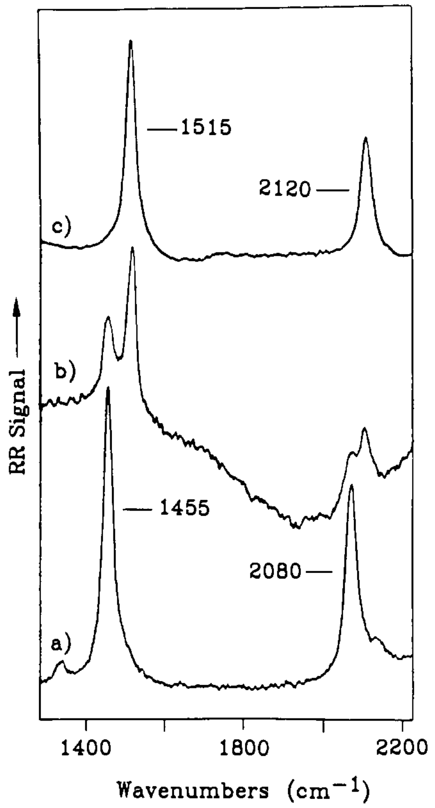

Figure 2. Resonance Raman (RR) spectra of PDA-12,8. All spectra were recorded with 532-nm excitation (7 mW), RR signal in arbitrary units and wavenumber displacement (cm^{-1}) from the 532-nm excitation wavelength: (a) blue polymer prepared with 10 min of UV irradiation and 18 °C water cooling; (b) mixture of blue and red polymer prepared with 10 min of UV irradiation without water cooling; (c) red polymer prepared by convectively heating the blue sample used in (a) to 80 °C for 2 min.

The instrumentation used for recording resonance Raman (RR) spectra is shown schematically in Figure 1. The 532-nm exciting radiation is obtained from a mode-locked Nd:YAG laser (Quantronix, Model 416) operating at 76 MHz. The second harmonic of the Nd:YAG output is obtained from a KTP crystal (Quantronix, Model 324) in the form of a train of 70-ps (fwhm) pulses. A polarizing beam splitter composed of two half-wave plates and a polarizing cube is used to control continuously the power of the exciting radiation reaching the PDA sample. The polarization of the 532-nm beam is oriented perpendicular to the entrance slit of the spectrometer (i.e., parallel to the table) in order to generate RR scattering.

The surface of the substrate on which the PDA-12,8 is deposited is oriented at a 45° angle with respect to the laser beam. The laser beam is focused upon an area of about 0.1 mm^2 on the PDA film. The RR signal is collected by a quartz lens (Melles Griot, Model CMP 119) before being focused onto the entrance slit of a 0.75-m triple monochromator (Spex Triplemate) comprised of a filter stage (incorporating two 600-groove/mm gratings) and a concave grating spectrograph stage fitted with a 600-groove/mm grating. The RR scattering is detected by an intensified reticon (EG&G, Model 1463). The reticon signal is processed by an optical multichannel analyzer (EG&G OMA, Model 1461) before being analyzed on a computer. Typically, a RR spectrum is recorded in 1 min.

Results

Exposure of a film of pentacosa-10,12-diynoic acid to UV radiation not only initiates solid-state polymerization, but also may heat the resultant PDA-12,8 film to temperatures at which thermochromism occurs. As a consequence, UV polymerization is performed here under experimental conditions that control the temperature of the film sample and, thereby, permit the photolytic polymerization process to be separated from the thermal process

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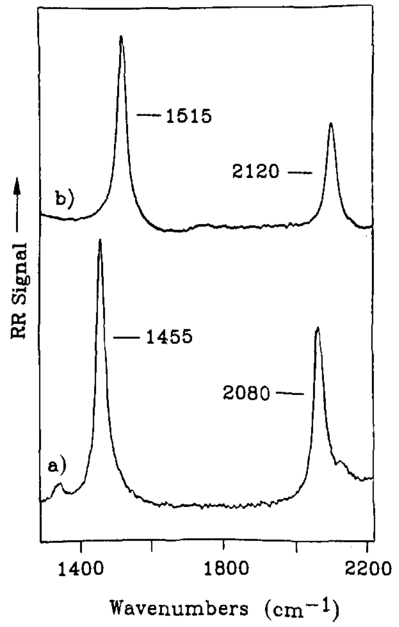

Figure 3. Resonance Raman (RR) spectra of PDA-12,8 exposed to 532-nm radiation. All spectra were recorded with 532-nm excitation (30 mW), RR signal in arbitrary units and wavenumber displacement (cm^{-1}) from the 532-nm excitation wavelength: (a) blue sample exposed for 3 min to 532-nm (30 mW) radiation with water (0.5 °C) cooling (RR bands identical with those shown in Figure 2a—blue sample); (b) the same blue sample used in (a) exposed for an additional 3 min to 532 nm without water cooling (RR bands identical with those shown in Figure 2c—red sample).

which might occur in the resultant polymer. For example, only a blue polymer is formed after 10 min of UV irradiation with 18 °C water running continuously through the sample tube. The RR spectrum of this material, presented in Figure 2a, has two major bands at 1455 and 2080 cm^{-1} which may be assigned respectively to the stretching modes of the double and triple carbon–carbon bonds in the polymer backbone. To illustrate the importance of temperature control, a second PDA-12,8 sample is prepared without water cooling (the experimental conditions are the same otherwise). This sample has a slight reddish color. The RR spectrum (Figure 2b) of this material contains four major bands at 1455, 1515, 2080, and 2120 cm^{-1} of which two (at 1455 and 2080 cm^{-1}) are attributable to the blue material. A third PDA-12,8 sample is prepared by convectively heating a blue polymer (prepared by UV irradiation with water cooling) to 80 °C for 2 min. The RR spectrum of the resulting red-colored material (Figure 2c) contains two major features at 1515 and 2120 cm^{-1} which can be assigned respectively to double and triple carbon–carbon bond stretching modes. Comparisons of the three RR spectra in Figure 2 demonstrate that (i) these cooling conditions ensure that no thermochromism occurs during the UV polymerization and (ii), without cooling, both polymerization of the monomer and thermochromism of the resultant polymer occur with UV irradiation leading to a mixture of the blue and red polymeric material (Figure 2b).

The blue polymer prepared by UV irradiation with water cooling and having the RR spectrum presented in Figure 2a is utilized to study the proposed photochromism. The sample is exposed to 532-nm laser radiation (30 mW) for 3 min with water cooling (0.5 °C) without any observable change in its blue color. The RR spectrum of this material (Figure 3a) is identical with that shown in Figure 2a, demonstrating that the vibrational properties of the polymer backbone remain unchanged. When the same sample is irradiated at 532 nm for an additional 3-min period, but without water cooling, the sample turns red immediately and the RR spectrum shown in Figure 3b is obtained. This latter spectrum is identical with the spectrum in Figure 2c which is measured for the thermally generated red polymer.

The FTIR spectra of the hydrocarbon side chain groups for each of these materials are presented in Figures 4 and 5. The FTIR spectra of a monomer film and of a blue-colored polymer film prepared under thermally controlled conditions are presented in Figure 4. The infrared bands between 3000 and 2800 cm^{-1} derive from the symmetric and asymmetric stretching vibrational modes of CH_2 and CH_3, while the bands between 1450 and 1200 cm^{-1} can be assigned to bending and wagging vibrational modes. It can be seen clearly that the polymer spectrum can be distinguished from the monomer spectrum. For example, both the shoulder at 2937.5 cm^{-1} and the broad band between 1300 and 1310 cm^{-1} in the monomer spectrum have vanished in the polymer spectrum, whereas a new shoulder at 2931 cm^{-1} can be easily detected. The importance of temperature control during the polymerization also can be seen in these data. The FTIR spectrum of a sample polymerized without cooling is shown in Figure 5. In general, its features are similar to the spectrum of a sample prepared under temperature-controlled conditions although measurable changes can be detected (e.g., the change in the intensity ratios of the bands at 1260 and 1250 cm^{-1}). These differences become clearer when a blue sample prepared with

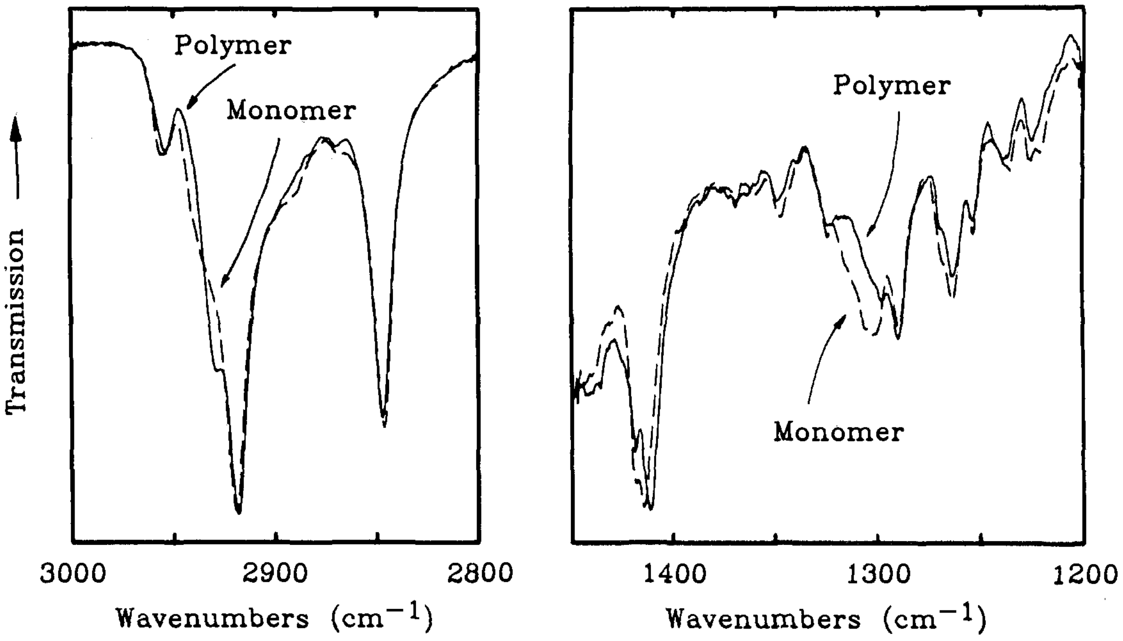

Figure 4. FTIR spectra of the monomer (– –) and the blue polymer (—) prepared with 10 min of UV irradiation and 18 °C water cooling.

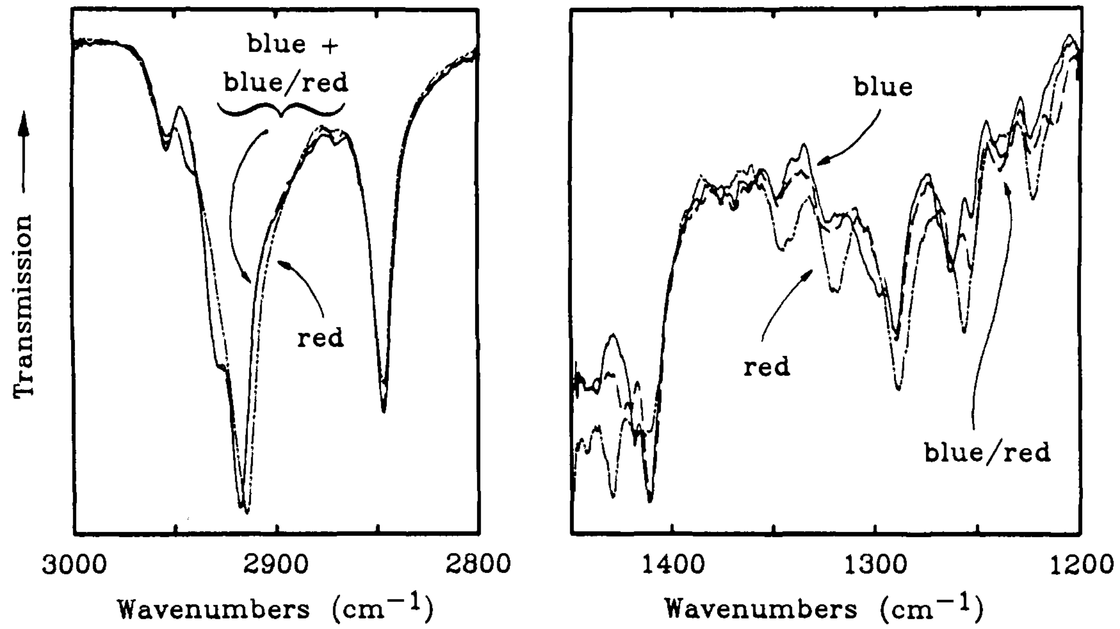

Figure 5. FTIR spectra of PDA-12,8: (i) blue polymer prepared with 10 min of UV irradiation and 18°C water cooling (—data); (ii) blue/red polymer prepared with 10 min of UV irradiation without water cooling (- - -data); (iii) red polymer prepared by convectively heating the blue polymer to 80 °C for 2 min (—··—··—data).

water cooling is heated to temperatures above 70 °C where the color completely changes from blue to red. By comparing the corresponding FTIR spectrum (also shown in Figure 5) with that of the blue material, it is evident that the shoulder at 2931 cm^{-1} has vanished and that the band at 2923 cm^{-1} has shifted toward lower wavenumbers. In addition, new bands at 1425 and 1252 cm^{-1} become visible while the bands near 1410 cm^{-1} and at 1260 and 1250 cm^{-1} have disappeared. The data in Figure 5 demonstrate that the pure blue and pure red material have distinctively different FTIR spectra. The third spectrum in Figure 5 is of a material polymerized by UV irradiation without cooling and represents a mixture of blue and red material.

Discussion

It is evident from the data presented here that chromatic properties of polydiacetylenes need to be measured under experimental conditions which control the temperature of the material. Such temperature control makes it feasible to separate thermochromism from those phenomena related only to the optical population of the excited electronic states (i.e., photochromism). The significance of this experimental criterion is illustrated by the data from Figures 2, 4, and 5 which clearly demonstrate that, without temperature control during the UV polymerization, the resulting polymer attains temperatures high enough to initiate thermochromism. For example, the material formed when the monomer is polymerized without cooling is not the same material formed by UV polymerization of the monomer at room temperature as evidenced by the RR and FTIR spectra presented in Figures 2 and 5, respectively. The intensities of the new RR bands (1515 and 2020 cm^{-1}) appearing in Figure 2b increase as a function of UV polymerization time (without cooling), while the relative intensities of the RR bands assigned to the blue material (Figure 2a) decrease. Thus, the relative amounts of the two materials in the mixture change as a function of UV irradiation time. By comparison with the spectrum in Figure 2c, the two new RR bands are assignable to the red material produced by thermochromism. The same type of conclusions can be reached from the FTIR data (Figure 5). Thus, the UV irradiation initiating the solid-state polymerization of the monomer is accompanied by a thermochromatic color change of the resulting polymer from blue to red when the temperature of the sample is permitted to rise. Analogously,thermochromism can be induced by the temperatures reached when the PDA-12,8 sample is exposed to visible radiation. With cooling, no change in the color, RR spectrum (Figure 3), or FTIR absorption spectrum (Figure 5) occurs even for extended irradiation times. When the sample temperature is permitted to rise by removing the cooling, changes in color, the RR spectrum (Figure 3) and the FTIR absorption spectrum (Figure 5) appear instantly. It is evident from these data that visible irradiation of the blue polymer without cooling leads to a red-colored material which is characterized by RR and FTIR spectra identical with those obtained from the red polymer produced by convective heating of the blue polymer. Thus, there is no evidence from these data to suggest that photochromism occurs in PDA-12,8.

The energetic threshold for the photolytic induction of thermochromism in PDA-12,8 films can be characterized by the visible laser energies and cooling conditions used to record the data in Figures 3 and 5. Each of the 532-nm laser pulses used to generate the mixtures of blue and red polymers (Figures 3 and 5) have an irradiance of about 400 nJ/cm^2. This irradiance is smaller by a factor of $\sim 10^5$ than that used (78 mJ/cm^2) in earlier studies to induce a chromatic change from the blue to the red polymer.[12] The temperatures of the polymeric samples, however, are also different. The samples examined here are cooled to temperatures near 273 K (i.e., about 20–25 K below room temperature), while the samples from earlier studies were held at 80 K.[11] It is evident from the results presented in Figure 4 that the low irradiance (i.e., 400 nJ/cm^2) pulses effectively induce the blue to red chromatic change in PDA 12,8. It is equally clear that the small (20 K) decrease in sample temperature is effective in preventing any chromatic change. The increased cooling efficiency offsets the radiative heating from the laser pulses effectively enough to hold the sample temperature below the thermochromic threshold. The energetic threshold for thermochromism in PDA-12,8 is more precisely established by the data presented in Figure 6. The RR spectra of PDA-12,8 samples that have been exposed to 532-nm laser energies between 15 and 20 mW are shown. No cooling is used to control the sample temperature as the irradiance is increased (200 to 267 nJ/cm^2). Only the blue polymer is present following 5 min of irradiation by 15 mW, but RR bands from a mixture of blue and red material are observed following 17-mW irradiation for the same period. Exposure of the blue polymer to 20 mW of 532-nm laser radiation converts the sample immediately to red. The radiative heating of PDA-12,8 caused by picosecond pulses must increase the localized temperature above the thermochromic threshold (i.e., above 70 °C). The same type of radiative heating apparently occurs when the 80 K blue polymer is exposed to 60-mJ/cm^2 laser radiation.[11] The much larger (10^5) irradiance must increase the local temperature of PDA-12,8 above

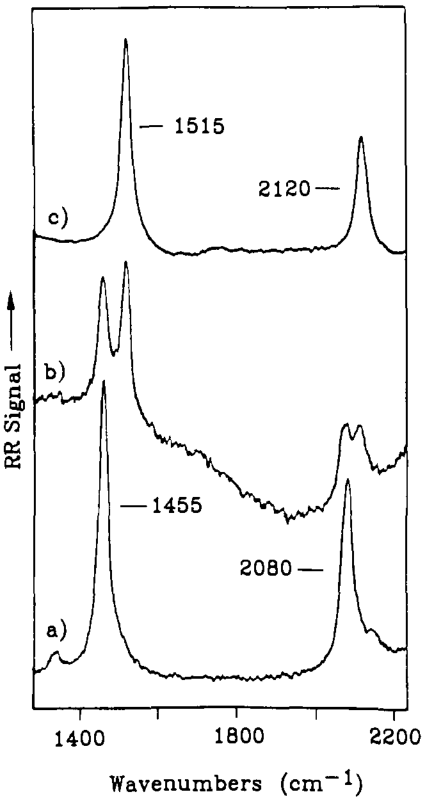

Figure 6. Resonance Raman (RR) spectra of three blue-colored PDA-12,8 samples exposed to 532-nm radiation of varying average power without water cooling (RR signal in arbitrary units and wavenumber displacement (cm^{-1}) from the 532-nm excitation wavelength): (a) exposed for 3 min to 532-nm (15 mW) radiation, RR bands identical with those shown in Figure 2a (blue sample); (b) exposed for 3 min to 532-nm (17 mW) radiation, RR bands similar to those shown in Figure 2b; (c) exposed for 1 min to 532-nm (20 mW) radiation, RR bands identical with those shown in Figure 2c.

the thermochromic threshold in spite of the initial 80 K sample temperature. Such a temperature increase of several hundred degrees is not unexpected since substantially larger temperature changes (1000 K) have been reported for polyatomic molecules in room-temperature solutions that are exposed to similar pulsed laser energies.[14,15] The reduced sample temperature which was intended to eliminate thermal effects may not be effective given the high laser energies used.

Another factor in such an analysis is the pulse repetition rate of the laser excitation. The interval between laser pulses (70-ps duration) in the low-energy experiments described here is about 13 ns, while earlier studies use a single pulse of 10-ns duration. The peak powers in these two experiments differ by approximately 10^4, with the 70-ps excitation being lower. There is no evidence to suggest that nonlinear optical phenomena are involved in the blue to red polymer transformation described in this work. The third-order dependence of the amount of red polymer formed with the pulse energies reported previously[11] has been interpreted in terms of long-lived (5 ms) intermediate clusters formed during the chromatic processes.[16] The data presented here suggest that, in such a model, the lifetime of intermediates must be substantially shorter (13 ns).

The results of the vibrational measurements also provide some information about the structural changes that occur with the observed thermochromic effects (initiated by both convective heating and photolytic heating). The FTIR data show that the three-dimensional arrangement of the side chains in the red polymer is different from that in the blue-colored starting material. This is consistent with the results of published X-ray measurements of this compound where heating to temperatures above 60 °C caused a change in the side-chain packing from an orthorhombic to a triclinic subcell.[17] These same types of conclusions have been reached from high-resolution X-ray studies of disubstituted diacetylenes prepared as Langmuir–Blodgett (LB) films.[18] In these X-ray,[18] the contributions of different side chain groups (carbonyl versus methyl) to changes in the long-range order of the multilayer LB films could be identified. Analogously, the thermochromic properties of urethane-substituted polymers have been associated with the breaking of hydrogen bonds in the side chains resulting in a more flexible chain and a reduction in conjugation lengths.[19] The RR spectra of the blue and red polymer both contain two major bands which can be assigned to stretching modes of double and triple carbon–carbon bonds in the polymer backbone. In case of the red polymer, both of these bands are simultaneously shifted to higher wavenumbers, related to their positions in the RR spectrum of the blue polymer (Figures 2 and 3). These results show that in PDA-12,8 the electronic structure in the polymer backbone does not change from an acetylenic to a butatriene form when the blue to red chromatic transformation occurs. In other studies of PDA, including PDA-12,8, such an electronic change has been thought to be responsible for the observed thermochromic transformations.[8,9,20] The shift of the RR bands toward higher wavenumbers in the spectrum of the red polymer can be explained in terms of a simultaneous increase in double- and triple-bond character caused by (i) different nonbonding interactions of the polymer backbone induced by the change in the side-chain packing, (ii) altered electron densities in the backbone of the blue and red polymer, or (iii) both.

Concluding Remarks

The results described above give no evidence for the existence of a photochromic effect in PDA-12,8, but clearly demonstrate photoinduced thermochromism. Neither is any changed in the electronic structure of the polymer backbone observed (e.g., a transition from an acetylenic to a butatriene form). The FTIR data presented indicate a reorganization of the three-dimensional side-chain structure which explains the shift of RR band frequencies measured and is consistent with earlier findings for cases of thermochromism.[17] Localized heating of the microstructure can occur during laser irradiation to the extent that the material exceeds the thermochromic threshold even for low-temperature samples (i.e., 80 K and 78-mJ/cm2 excitation). The picosecond laser data presented here demonstrate that this thermochromic threshold can lie within a 20 K gap. In general, these results indicate that the control of the sample temperature is essential for the identification of photochromic effects. Finally, it should be emphasized that photoinduced thermochromism (as described here) can be controlled in PDA-12,8 over a very narrow thermal gap (20 K) when laser pulse energies are carefully controlled and, therefore, PDA-12,8 remains an important material to be considered for optical data storage and processing.

Acknowledgment. The authors wish to gratefully acknowledge the assistance of Professor E. Hanamura, Professor Y. Tokura, and Dr. A. Itsubo for obtaining the PDA-12,8 sample and Dr. R. Sperline for recording FTIR spectra.

Registry No. Pentacosa-10,12-diynoic acid (homopolymer), 66990-33-8.

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