

Optical properties and long-lived charged photoexcitations in polydiacetylenes

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We have studied the vibrational and electronic structure and the elementary excitations of poly [1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD), poly[1-(*N*-carbazolyl)penta-1,3-diyne-5-ol] (polyCPDO), and poly[1-(*N*-carbazolyl)penta-1,3-diyne-5-acetoxy] (polyCPDA) by electronic absorption, Raman scattering, and photoinduced absorption in the infrared region. The long-lived photoexcitations are charged bipolarons with associated infrared-active vibrational (IRAV) modes. The results are also discussed in relation to the degree of chain order of the different polydiacetylenes as evidenced by the electronic spectra. Only poly(DCHD) shows an absorption spectrum dominated by a single exciton, suggesting a one-dimensional ordered structure. Consequently, for this polymer only, triplet excitons with a lifetime of the order of ms are photogenerated in addition to bipolarons. Among polydiacetylenes, only poly(CPDA) shows photoinduced IRAV modes not affected by Fano coupling between electronic and vibrational states.

I. INTRODUCTION

The properties of materials with reduced dimensionality and quantum confinement of electrons are of increasing interest in fundamental condensed-matter science. In the field of conjugated polymers, much effort has been devoted to the study of the influence of reduced dimensionality on electronic excitations. Among these organic materials, the polydiacetylenes (PDA's) $(CR-C\equiv C-CR')_n$ are particularly attractive as quasi-one-dimensional model systems. In fact, these polymers, obtained through topochemical polymerization of diacetylene single crystals, originate a highly ordered sequence of conjugated triple and double bonds. Each repeat unit carries two substituents to the C atoms at the double bond, which practically isolate one chain from the others, giving rise to a molecular quantum wire. The low-dimensional character of the π electrons in ordered PDA's is apparent in the optical spectra (whose shape exhibits the inverse-square-root singularity of the joint density of states typical of monodimensional arrays), which are dominated by strong excitons and their vibronic progression. Excitonic states of polydiacetylenes are localized along the polymer backbone as shown by the polarization properties of their absorption spectra and by electric-field-modulated reflectivity measurements.^{1,2} These studies show that the excitons respond to an electric field parallel to the polymer backbone, but are insensitive to fields orthogonal to the main chain.

Low-dimensional structures seem to play an important role in nonlinear optical and electro-optical studies providing unusually large values for the third-order susceptibility $\chi^{(3)}$.³⁻⁸ In particular, the polydiacetylenes with highly polarizable carbazolyl side groups directly or indirectly attached to the polymer backbone are expected to exhibit very large optical nonlinearities.⁹⁻¹¹ As a matter of fact, the magnitude of $\chi^{(3)}$ very recently mea-

sured in poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD) [$R=R'=-CH_2(\text{carbazolyl})$] single crystal for polarization along the polymer backbone was found to be exceedingly high, of the order of 10^{-6} esu on resonance and 10^{-7} esu near resonance.¹² Even higher values could be expected for PDA with the carbazolyl group directly attached to the main chain.

Information on the nature and dynamics of the excited electronic states, which are responsible for the interesting properties of the polycarbazolyldiacetylenes, can be obtained through photoexcitation studies. The photoinduced absorption (PA) spectra of polyDCHD and of the unsymmetrically substituted poly[1-(*N*-carbazolyl) penta-1,3-diyne-5-ol] (polyCPDO) [$R=-N(\text{carbazolyl})$, $R'=-CH_2OH$] and poly[1-(*N*-carbazolyl)penta-1,3-diyne-5-acetoxy] (polyCPDA) [$R=-N(\text{carbazolyl})$, $R'=-CH_2OCOCH_3$], measured on polycrystalline samples in the visible-near infrared (NIR) by the cw modulation technique, are found to be consistent with photogeneration of long-lived bipolarons (BP's).^{13,14} For polyDCHD, in addition to the BP defects, the PA spectrum provides evidence on photogeneration of triplet excitons.¹³

To gain a better understanding of the nature and dynamics of the photogenerated defects in polycarbazolyldiacetylenes, further measurements in the NIR and medium-infrared regions have been carried out, using a Fourier-transform spectrometer. It is the purpose of the present paper to analyze these data and also to discuss them in relation to the degree of order of these polymers as revealed by their electronic and Raman spectra.

II. EXPERIMENT

The symmetrical 1,6-di(*N*-carbazolyl)-2,4-hexadiyne (DCHD) has been prepared as described in the literature.¹⁵ The unsymmetrical 1-(*N*-carbazolyl)penta-1,3-

diyn-5-ol (CPDO) and its acetoxy derivative (CPDA) have been synthesized according to the procedure reported in Ref. 14. All the monomers were characterized by IR and ^1H NMR spectroscopies and by elemental analysis. Thermal polymerization was carried out in microcrystalline samples dispersed in KBr pellets at 175°C for DCHD and 78°C for the other two monomers following the time evolution of the visible and infrared absorptions and of the Raman spectra. For DCHD, no evidence of the formation of oligomers has been obtained by solvent extracting a microcrystalline sample bulk polymerized in the same experimental conditions. For the other two systems, oligomers soluble in dichloromethane have been found present also in the final stage of polymerization.

Room-temperature electronic absorption spectra were recorded on a Perkin-Elmer spectrophotometer model Lambda 9, equipped with the integrating sphere accessory. Infrared spectra were obtained on a Bruker Fourier-transform spectrometer (FTIR) (IFS66). Raman spectra in the visible region were recorded with a Jasco spectrophotometer exciting with an Ar^+ laser. In the NIR region, Raman measurements were performed with a Bruker FTIR spectrometer (FRA 106), working with a Nd-YAG (yttrium aluminum garnet) laser (1064 nm).

Steady-state pump and probe photoinduced absorption measurements, described in detail in Ref. 14, were performed at 80 K using the 488-nm line of a cw Ar^+ laser as a pump. For the long-time PA measurements, a Bruker FTIR spectrophotometer (IFS66), modified to allow access for the external pumping source (Ar^+ or He-Ne laser) was used to cover the frequency range between 400 cm^{-1} (0.05 eV) and 15000 cm^{-1} (1.85 eV) with mercury cadmium telluride (MCT), Ge, and Si detectors. Fractional changes in the infrared transmission with the sample at 80 K were measured in response to the external laser incident on the sample for 9 s (70 mW/cm^2 with $\lambda_{\text{exc}}=488\text{ nm}$, and 65 mW/cm^2 with $\lambda_{\text{exc}}=633\text{ nm}$). Successive light-on and -off 9 s cycles were signal averaged until the signal-to-noise ratio was sufficient to obtain the net change in transmission. Long-time signal averaging was necessary to resolve all the details of the infrared-active vibrational (IRAV) modes above the noise level (typically 8–16 h). The resolution in the range of MCT, Ge, and Si detectors was, respectively, 4, 8, and 8 cm^{-1} .

III. RESULTS

A. Optical spectra

Figure 1 shows the room-temperature electronic absorption spectra of polyDCHD, polyCPDO, and polyCPDA. The spectrum for polyDCHD in Fig. 1(a) shows a strong excitonic absorption peak at 1.92 eV, accompanied by vibrational satellites, similar to that seen in the same polymer as a single crystal.^{1,2} The presence of this sharp peak in our sample is certainly to be related to an ordered structure. The spectra for polyCPDO [Fig. 1(b)] and polyCPDA [Fig. 1(c)] exhibit broad absorptions in the visible with no clear evidence of the single excitonic peak. These spectra are typical of disordered samples, because

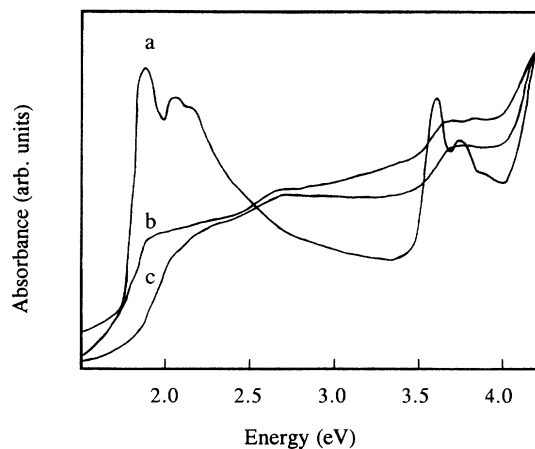


FIG. 1. Room-temperature electronic absorption spectra of (a) polyDCHD, (b) polyCPDO, and (c) polyCPDA.

disorder-induced broadening of the conduction and valence bands leads to the weakening and broadening of the exciton peak accompanied by a small shift towards lower energies.¹⁶ Moreover, notice that, unlike polyDCHD, the electronic spectra of both polyCPDO and polyCPDA maintain large absorptions through the whole visible region from around 2 eV to the near-UV, where the allowed transitions of the carbazolyl groups dominate the spectrum. This behavior can be ascribed to the presence of either oligomeric chains and/or conformational defects in the long polymer backbones.

The band gap of polyDCHD is 2.335 eV as determined by electroreflectivity^{1,2} or 2.35 eV by electroabsorption data.¹⁷ The location of the band edge in our PDA's with the aromatic ring directly bonded to the main chain is unknown. Unfortunately, the optical data presented here do not allow us to obtain this information, which could be of great help in understanding the role of the carbazolyl substituent in extending the delocalization of the π electrons.¹⁸ However, polyCPDO appears to have an absorption edge redshifted about 0.1 eV with respect to polyCPDA, which may suggest a corresponding decrease in the band gap.

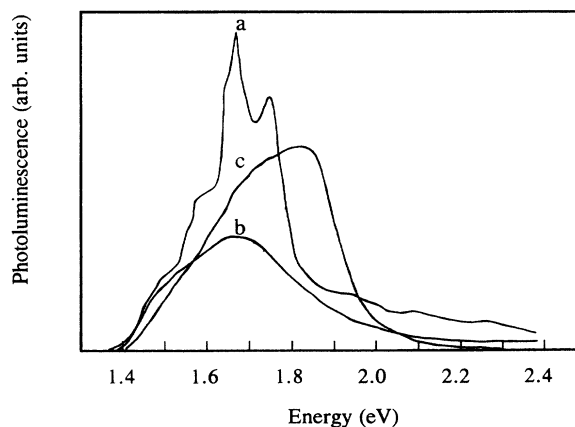


FIG. 2. Photoluminescence spectra of (a) polyDCHD, (b) polyCPDO, and (c) polyCPDA at 80 K, $\lambda_{\text{exc}}=488\text{ nm}$.

B. Photoluminescence spectra

Figure 2 presents the photoluminescence spectra of the polymers studied in the present paper. The main emission peak falls for both polyDCHD and polyCPDO around 1.7 eV while at 1.8 eV for polyCPDA, in agreement with the different thresholds shown in the absorption spectra (Fig. 1). Only polyDCHD exhibits a vibrational structure in the luminescence, probably related to its more ordered structure. We note that the energy difference between the two main peaks in Fig. 2(a) (1.76 and 1.68 eV) coincides with the difference between the vibrational frequencies of the triple and double bonds. From these data, one can obtain a value of 1.92 eV for the 0-0 line to which corresponds a shoulder in the emission spectrum. This energy falls at the position of the excitonic absorption peak. On this basis, also the low-energy shoulders at 1.58 and 1.5 eV can be assigned to the first overtone of the C=C stretching and to the combination mode of the C=C and C≡C stretchings, respectively. For the unsymmetrical PDA's, the vibrational structure is blurred out by the mainly disordered nature of the samples.

C. Raman spectra

The present interpretation of the optical data in terms of the degree of order of the polymer structure is further supported by Raman investigations. Indeed, the Raman spectra for polyDCHD reported in Fig. 3 do not show underlying luminescence emission typical of disordered PDA's. On the contrary, the Raman spectra of both polyCPDO and polyCPDA at 1064 nm exhibit broad, laser-induced emissions, with superimposed typical Raman bands due to the C≡C and C=C stretching modes. The Raman spectra of polyCPDO and polyCPDA reveal triple-bond stretchings at 2125 and 2127 cm^{-1} , and double-bond stretchings at 1495 and 1500 cm^{-1} , respectively.¹⁹ For these samples, Raman spectra at higher excitation energy could not be observed because of their strong luminescence.

The room-temperature Raman spectra of polyDCHD (Fig. 3) display features very similar to those observed in

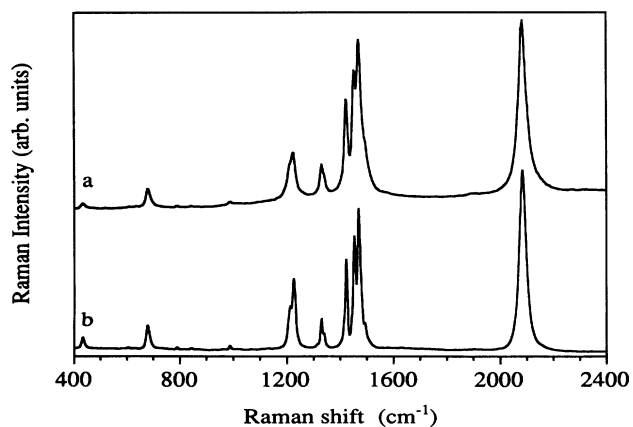


FIG. 3. Room-temperature Raman spectra of polyDCHD for excitations at (a) 488 nm (spectral resolution 5 cm^{-1}) and (b) 1064 nm (spectral resolution 2 cm^{-1}).

the single crystal, with the exception of the different relative intensity exhibited by the bands associated with the triple- and double-bond stretchings.²⁰ In addition to the Raman lines discussed in Ref. 20, we observe very weak features at 989, 843, 790, and 605 cm^{-1} , which are also present in the spectrum of the single crystal. The presence of the 989- cm^{-1} line has been pointed out previously and attributed to a fundamental mode,²¹ while the origin of the other three peaks is still unknown. Moreover, we observe a weak peak at 434 cm^{-1} , which could be related to the 460- cm^{-1} structure observed in electroreflectance spectra.²

For a further discussion of the Raman data, let us concentrate on the bands due to the C≡C stretching [2084 cm^{-1} , half-width at half maximum (HWHM) = 34 cm^{-1} , at 1064 nm] and to the region where four sharp lines (1493, 1468, 1452, and 1421 cm^{-1} , at 1064 nm) are originated by a Fermi resonance, which involves the C=C bond and the methylene and carbazolyl groups. These two regions are known to be sensitive to the effective conjugation length and/or to the environmental properties connected with the sample structures in polydiacetylenes as revealed by the spectral changes observed with different exciting wavelengths.^{21,22} For this reason, the analysis of the resonant Raman scattering of these spectral regions is a very sensitive tool for testing the quality of PDA samples. As can be seen from Fig. 3, by varying the excitation from 1064 to 488 nm, no dispersion is observed for our polyDCHD. These results indicate a large degree of order in the structure of this polymer.

D. Photoinduced absorption spectra

Figure 4 shows the PA spectra of polyDCHD in the NIR region observed (a) with the cw photomodulation technique by exciting at 488 nm (2.54 eV), and (b) with the FTIR equipment by exciting at 488 and 633 nm (1.96 eV).

An interpretation of the spectral features of Fig. 4(a) has been already proposed¹³ The three signals observed at 0.81, 0.96, and 1.04 eV have been assigned to the high-energy peak associated with a long-lived BP defect and to its vibrational structure. The 1.26-eV peak, whose intensity is strongly enhanced at low temperature [see inset in Fig. 4(a)], has been instead associated with photoexcited triplet excitons characterized by a lifetime of the order of ms. The long-time PA spectra reported in Fig. 4(b) still show the peaks associated with the BP, but no evidence of the 1.26-eV signal. This is in agreement with its lifetime value inferred from the steady-state measurements. The same features are present for 1.96-eV pumping as for 2.54-eV pumping, suggesting that the same type of defect states are formed, though with different efficiency, by exciting above or below the band gap.

Figure 5 shows the corresponding spectrum in the medium-infrared region for excitation at 2.54 eV. This spectrum, if analyzed according to the interpretation of the existing experimental work on other PDA's,^{23,24} suggests the presence of a very broad absorption band centered around 0.1 eV ($\sim 800 \text{ cm}^{-1}$) with superimposed windows at ~ 2000 , ~ 1400 , and $\sim 1200 \text{ cm}^{-1}$ associated

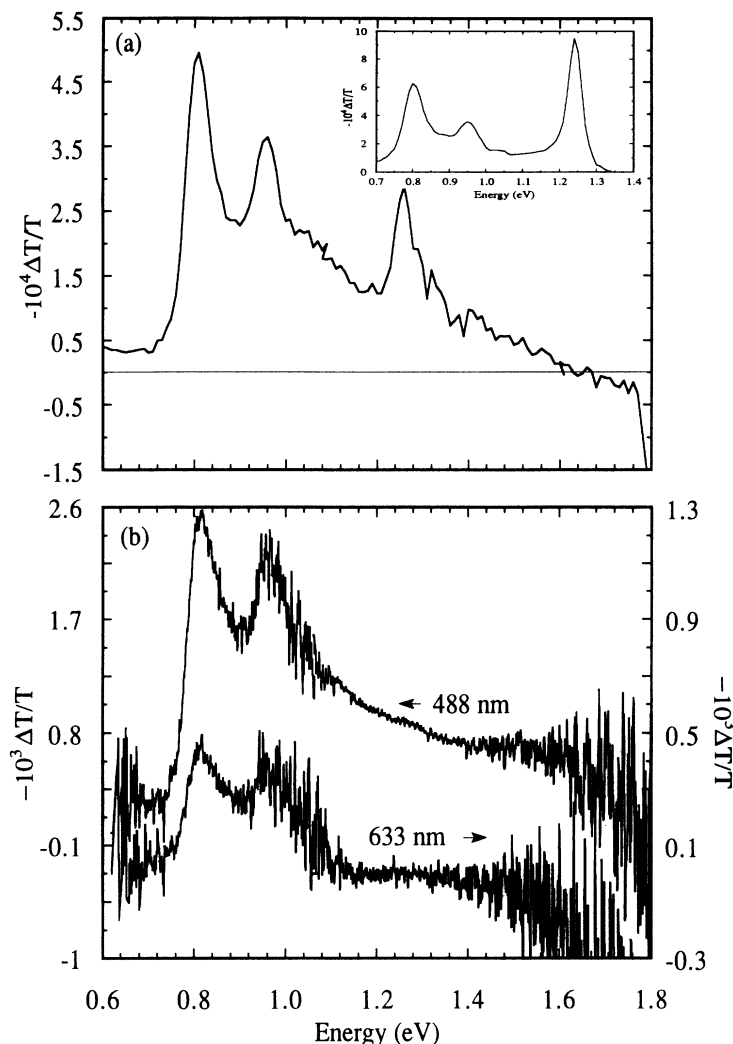


FIG. 4. Photoinduced absorption spectra of polyDCHD in the NIR-UV region. (a) cw photomodulation technique (chopper frequency = 13 Hz, $\lambda_{\text{exc}}=488$ nm, $T=77$ K). Inset: $T=20$ K. (b) FTIR apparatus, $\lambda_{\text{exc}}=633$ nm, $T=80$ K, Ge detector 18 000 scans, Si detector 18 000 scans; $\lambda_{\text{exc}}=488$ nm, $T=80$ K, Ge detector 18 000 scans, Si detector 24 000 scans.

with the IRAV modes of the $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, and $\text{C}-\text{C}$ bond stretchings, respectively. The apparent bleachings arise from Fano resonances as observed in other organic solids [doped C_{60} ,²⁵ tetrathiafulvalene-tetracyanoquinodimethane,²⁶ triethylammonium-tetracyanoquinodimethane,²⁷ and intercalated graphite²⁸]. We cannot, however, discard the possibility of interpreting this spectrum on the basis of the presence of two relatively broad bands around 0.1 eV (~ 800 cm^{-1}) and 0.23 eV (~ 1850 cm^{-1}), which could be originated by the low-energy counterpart of the BP state. In this latter case, several IRAV modes are observed as absorptions while only the $\text{C}\equiv\text{C}$ -induced mode is observed as bleaching. These different interpretations, while providing different values for the frequencies of the IRAV modes, do not substantially affect the information on the energy position of the photogenerated electronic defects. On the other hand, this ambiguity in the assignment of the medium-infrared region in terms of a single- or a double-peak structure also exists for poly(*p*-phenylene vinylene) derivatives²⁹ and for poly(3-hexylthienylene).³⁰

The same features, although with reduced intensity, are observed for 1.96-eV pumping. Moreover, we would like to stress that the thermal modulation of the infrared

modes may somewhat affect the shapes of both bands and windows. Additional bands arising from shape modes or from ring modes could add further complications.^{31–33}

The steady-state PA spectra of both polyCPDO and polyCPDA in the visible-NIR region have been reported in a previous paper. For polyCPDA, the long-time spectrum exhibits two broad and asymmetrical bands at 1.14

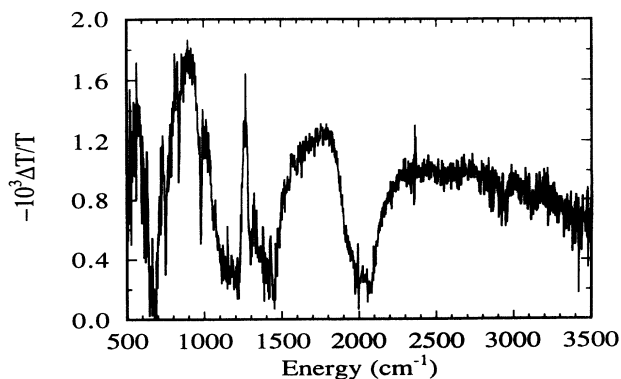


FIG. 5. Photoinduced absorption spectrum of polyDCHD in the infrared region by the FTIR apparatus; $\lambda_{\text{exc}}=488$ nm, $T=80$ K, 26 500 scans.

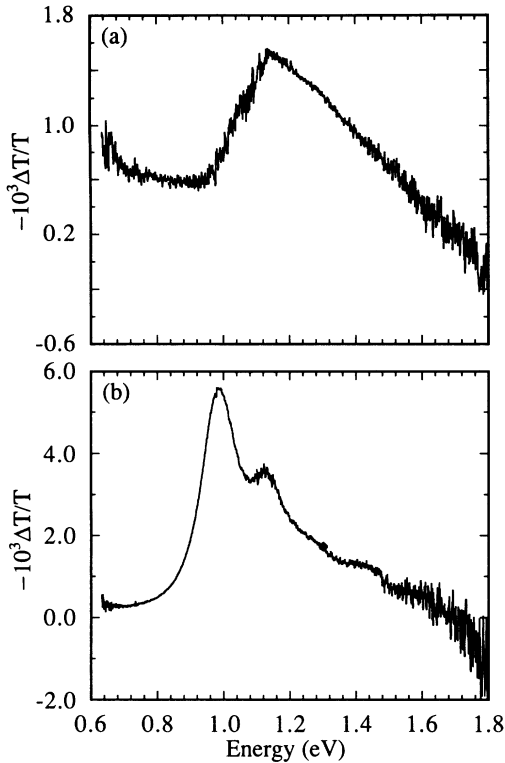


FIG. 6. Long-time high-energy BP band. (a) PolyCPDA $\lambda_{\text{exc}}=488$ nm, $T=80$ K, Ge detector 22 000 scans, Si detector 22 000 scans. (b) PolyCPDO $\lambda_{\text{exc}}=488$ nm, $T=80$ K, Ge detector 18 000 scans, Si detector 24 000 scans.

[Fig. 6(a)] and 0.46 eV similar to those already observed for the cw experiments. On the contrary, for polyCPDO, the high-energy broad signal around 1.1 eV in Fig. 1(b) of Ref. 14 is here resolved into a structure consisting of a main peak at 0.98 eV followed by a lower-intensity and well-defined signal at 1.11 eV as shown in Fig. 6(b). This result, which is due to a better resolution of the FTIR apparatus with respect to that used for the photomodulation technique, can be considered as evidence of the contribution of the vibrational states of the bipolarons in case of sufficiently well-organized crystalline systems as already observed for polyDCHD.

Figures 7 and 8 present the photoinduced infrared

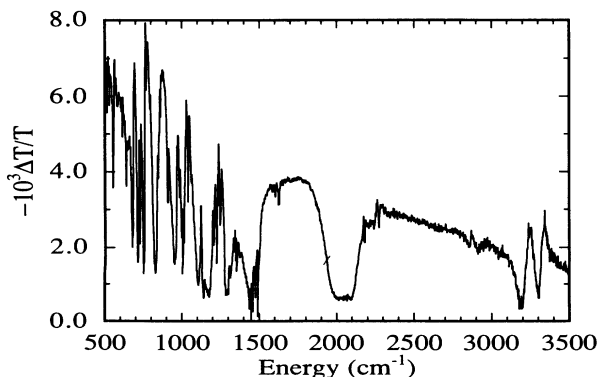


FIG. 7. Photoinduced infrared spectrum of polyCPDO. $\lambda_{\text{exc}}=488$ nm, $T=80$ K, 21 000 scans.

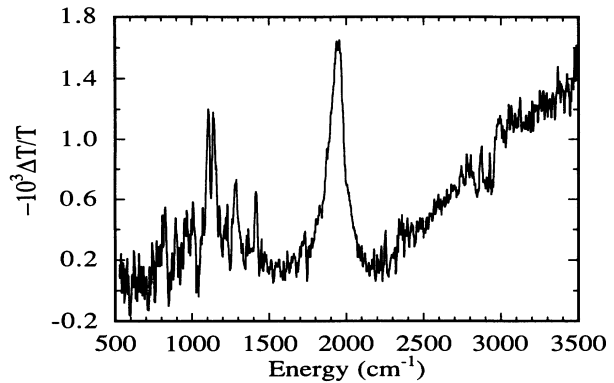


FIG. 8. Photoinduced infrared spectrum of polyCPDA. $\lambda_{\text{exc}}=488$ nm, $T=80$ K, 27 450 scans.

spectra for both the unsymmetrical polymers. The spectrum of polyCPDO shows features quite similar to those exhibited by polyDCHD. Accordingly, a twofold interpretation can be proposed in this case as for polyDCHD, i.e., the PA spectrum can be again interpreted either in terms of a single electronic peak at ~ 0.1 eV with transmission windows associated with the IRAV modes, or in terms of two electronic peaks at about ~ 0.1 (~ 800 cm^{-1}) and ~ 0.2 eV (~ 1600 cm^{-1}) followed by a number of infrared-induced vibrations.

Instead, a quite different behavior is shown by polyCPDA (Fig. 8). In this case, the low-energy bipolaronic signal whose maximum falls at 0.46 eV (~ 3711 cm^{-1}) does not extend into the infrared region below 2500 cm^{-1} . Therefore, unlike polyDCHD and polyCPDO, no interaction between the electronic and vibrational states occurs, and no Fano interference effects are observed. Thus, the photoinduced infrared spectrum of polyCPDA shows features similar to those found for other conjugated polymers for which the low-energy BP band falls in the NIR, as occurs, for instance, in polyacetylene. Notice, in fact, the relatively strong absorption at 1950 cm^{-1} due to the $\text{C}\equiv\text{C}$ mode, which is redshifted 165 cm^{-1} from its Raman frequency. This large frequency shift is indicative of a large electron-phonon coupling in this system. More uncertain is the assignment of the $\text{C}=\text{C}$ IRAV mode to the 1415 cm^{-1} weak signal. If this assignment were correct, a frequency shift of 80 cm^{-1} would be inferred. In addition to these two vibrations, several other photogenerated signals appear at 1284, 1136, 1106, and 827 cm^{-1} , whose origin is still obscure.

IV. DISCUSSION

The photoinduced spectra reported here allow us to further support our previous assignments, i.e., the creation of long-lived bipolaronic defects for all the polycarbazolyldiacetylenes examined. The lifetimes of these BP's cannot be exactly determined. We can, however, state that they are of the order of seconds or longer.

For polyCPDA, the interpretation of the PA features appears much simpler than for the other two polymers. Indeed, we observe two strong, asymmetric peaks at 1.14 and 0.46 eV whose evolution with the laser power and the

chopper frequency agree with their bipolaronic nature. In this case, the vibrational structure of the BP's, if present, is hidden beneath the broad and asymmetrical bipolaronic bands. Further indication on the formation of these charged defects is provided by the appearance of the IRAV modes. In this contest we would like to stress that only for this polydiacetylene the photoinduced infrared modes appear as absorptions redshifted from the corresponding Raman modes as expected from the amplitude-mode formalism.³⁴ Indeed the low-energy bipolaronic state of polyCPDA does not interact with the vibrational states, and thus no Fano-like resonance arises as it happens instead in the PA spectra of all the other PDA's.

The PA spectra of polyDCHD and polyCPDO exhibit much more complex features. First of all, a structure in the high-energy bipolaronic signal is evident for both polymers. In the case of polyCPDO, this structure consists of two peaks separated by 0.13 eV, while three peaks are observed for polyDCHD with an energy separation of 0.15 and 0.23 eV from the main signal. The low-energy region does not allow a clear interpretation because of the already mentioned overlap between electronic and vibrational states. Owing to this fact, a precise assignment of the low-energy BP transitions and of the IRAV modes cannot be performed except for the broad transmission window at around 2000 cm^{-1} , which has been observed also in other PDA's and interpreted in terms of a Fano coupling between the electronic state and the $\text{C}\equiv\text{C}$ vibrational mode. Notice that these windows are redshifted with respect to those observed for other noncarbazolyl substituted PDA's. The low- and high-frequency sides of these transmissions fall at ~ 2000 and $\sim 2100\text{ cm}^{-1}$ for polyCPDO and at ~ 1970 and $\sim 2060\text{ cm}^{-1}$ for polyDCHD, respectively. Since the two lowest frequencies are close to the 1950-cm^{-1} value of the absorption peak observed for polyCPDA and assigned to its $\text{C}\equiv\text{C}$ IRAV vibration, we may tentatively assign them to the same mode. The interpretation of the higher frequencies, redshifted about 20 cm^{-1} from the corresponding Raman modes, is a difficult task. First of all we note that no corresponding feature is observed in the photoinduced spectrum of polyCPDA. The explanation offered for an analogous observation in PDA-1OH in terms of the bleaching of the triple-bond absorption,²³ though acceptable for polyCPDO, cannot be valid for the symmetrical polyDCHD where the $\text{C}\equiv\text{C}$ vibration is infrared inactive. For this reason, we believe that the interpretation of the doublets in these transmission windows would require further analysis. This requirement is even more pressing for the interpretation of the $\text{C}=\text{C}$ IRAV modes in the spectral region around 1500 cm^{-1} , which cannot be unambiguously assigned.

So far we have assigned the long-time PA spectra of polycarbazolyldiacetylenes to bipolaronic defects and their vibrational structure. In fact, we believe that the alternative assignments proposed for other conjugated polymers in terms of either the presence of BP's with different confinement degrees³⁰ or of BP's with different charge signs³⁵ cannot be used to explain the whole body of our data. This is particularly true for polyDCHD,

where the two satellite peaks of decreasing intensity associated with the main bipolaronic absorption at 0.8 eV could hardly be interpreted as evidence of different bipolaronic defects.

A comparison of the BP transitions determined in this study for the different polycarbazolyldiacetylenes is reported in Table I. Here, we indicate with ω_1 and ω_2 the two BP transitions. In order to analyze these data in terms of the existing theories, we need the value of the band gap. For polyDCHD, $E_g = 2.335\text{ eV}$ has been experimentally determined.² For polyCPDA and polyCPDO, we assume $E_g = 2.4$ (Ref. 36) and 2.3 eV , respectively, in agreement with the difference exhibited by their optical spectra. Notice that the energy separation of the two subgap bipolaronic absorptions, $2\omega_0 = \omega_2 - \omega_1$, amounts to 0.65 eV in polyCPDA. This value is substantially smaller than 1.07 eV reported for PDA-1OH,²³ to our knowledge the only other polydiacetylene for which the two BP bands have been detected. On the other hand, the ratio $2\omega_0/E_g$ is related to the size of the bipolaronic defect by means of the confinement parameter Γ , which can be calculated by considering the superalternant structure of the polydiacetylene backbone according to the model proposed by Choi and Rice.³⁷ The value $\Gamma = 0.85$ estimated for polyCPDA turns out to be much smaller than that corresponding to PDA-1OH ($\Gamma = 1.2$), thus suggesting the existence of a more extended defect.

Correspondingly, for the other two polycarbazolyldiacetylenes slightly larger values of Γ are obtained as shown in Table I. Here the analysis is more uncertain than for polyCPDA, because of the ambiguity in the assignment of the low-energy BP peaks. However, if we assume a single electronic peak around 0.1 eV in this region, the values of Γ derived would become practically identical to that of polyCPDA. In any case, the introduction of carbazolyl substituents appears to reduce the degree of confinement of the photoinduced defects, independently on the details of the chemical structure such as the number of the carbazolyl groups and the mode of attachment to the polymer skeleton. Furthermore, it has to be noted that the values of Γ do not appear to depend on the degree of chain order as evidenced by the differences in the electronic absorption spectra.

Let us finally note in Table I that the frequency of both the bipolaronic bands decreases on going from polyCPDA to polyDCHD. So, by analyzing these data in terms of the effective Coulomb correlation energy³⁷ $2U_{\text{eff}} = E_g - (\omega_1 + \omega_2)$, we find that U_{eff} consequently increases from 0.4 to 0.7 eV, as shown in Table I. The value $U_{\text{eff}} = 0.4\text{ eV}$ reported for polyCPDA is larger than that

TABLE I. Experimental values of the bipolaron energy transitions (ω_1 and ω_2), energy gap E_g , and theoretically derived Coulomb on-site effective energy (U_{eff}) and confinement parameter (Γ) in the Choi-Rice model.

PDA type	ω_1 (eV)	ω_2 (eV)	E_g (eV)	U_{eff} (eV)	Γ
polyCPDA	0.45	1.1	2.4	0.40	0.85
polyCPDO	~ 0.1	0.98	2.3	0.65	0.9
polyDCHD	~ 0.1	0.81	2.335	0.70	0.9

indicated in our previous papers because of the larger band-gap energy assumed here. This choice increases U_{eff} of this polymer to the same value reported for PDA-10H, notwithstanding the difference in their confinement parameters discussed above. The strong Coulomb interactions determined for these polymers should favor the relative stability of polarons with respect to bipolarons unless, as discussed in Ref. 38, a very large electron-phonon coupling is effective. On the other hand, we do not have any evidence for the presence of polarons in polyCPDA, where only two bands are observed with an energy separation of 0.65 eV. The same assignment can be proposed for polyCPDO and polyDCHD, where an even larger value of U_{eff} has been derived. In these systems, in fact, the components of the high-energy subgap band exhibit essentially the same frequency response indicating the same time scale for the associated defects. We are, therefore, left with the problem of explaining the stability of BP's in these polymers with so large U_{eff} . At present, we cannot offer any explanation for this finding. We can, however, note that an indication of a quite large $e-e$ interaction can be inferred for polyDCHD from the energy difference between the singlet and triplet excitonic states.³⁹ We have indeed shown that the PA spectrum of this polymer, for chopper frequency higher than 10 Hz, exhibits the 1.26-eV signal assigned to a triplet-triplet transition. The energy level of the triplet excitonic state has been very recently fixed at 1.1 eV,⁴⁰ which is well below the singlet excitonic state at 1.9 eV. Even if a

quantitative estimation of the $e-e$ interaction cannot be performed, this large energy difference points to a more relevant contribution than in other PDA's.⁴¹

In conclusion, the more ordered structure of polyDCHD with respect to the unsymmetrical polycarbazolyldiacetylenes discussed here is certainly responsible for the variety of electronic excitations (triplet excitons in addition to bipolarons) observed in this polymer. We would like to point out that by increasing the structural order of these polymers, a sharpening of the singlet excitonic absorption bandwidth is obtained, which may be related to the enhancement of the third-order nonlinear optical susceptibility of the material.⁴² On the other hand, the excitonic absorption is a typical feature of polydiacetylenes and it has also been observed in highly ordered PPV.⁴³ Although the presence of excitonic transitions has been proposed to be a general feature of conjugated polymers,⁴⁴ highly ordered polydiacetylenes seem to represent the more appropriate models of organic quantum wires.

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