The spin signature of charged photoexcitations in carbazolyl substituted polydiacetylene

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In this article, photoinduced infrared absorption (PIA-FTIR) and light induced electron spin resonance (LESR) measurements on an asymmetric carbazolyl substituted polydiacetylene (PDA), the poly{1-(N-carbazolyl) penta-1,3-diyn-5-ol} (polyCPDO) are presented. Results from both experimental techniques imply that contrary to other well-known polydiacetylene derivatives, in polyCPDO there exist only long-living, highly localized charged photoexcitations with spin 1/2 (g value~2.0026), indicative for polaronic excitations. PolyCPDO also shows a strong dark ESR signal with the same g value as the LESR signal and with a Curie susceptibility of approximately 10^{-3} spins per CPDO monomer unit. This unusually high number of defects may come from intermediates of the polymerization. Furthermore, the photoexcited states of composites from polyCPDO mixed with a special solubilized methano-fullerene [6,6]-Phenyl C_{61}–butyric acid methyl ester (PCBM) with excellent acceptor properties are investigated and compared with those of the pristine polymer. No enhancement of PIA-FTIR and LESR signals is found for these composites. It is therefore concluded, that even polyCPDO, which shows charged spin 1/2 photoexcitations, does not exhibit a photoexcited charge transfer to fullerenes as observed in other nondegenerate ground state conjugated polymer fullerene composites. © *1999 American Institute of Physics.* [S0021-9606(99)50846-5]

I. INTRODUCTION

Polydiacetylenes (PDAs) differ from other conjugated polymers like polythiophenes (PTs) or polyphenylenevinylenes (PPVs) due to their comparatively large exciton binding energy which is around 0.4–0.5 eV.[1] The fact that the $2\,^1A_g$ state has lower energy than the $1\,^1B_u$ state explains some of the photophysical properties found for PDAs, like their weak luminescence. Moreover, the $2\,^1A_g$ state seems to play an important role in the generation of triplet excitons,[2] which are usually reported as the main long-lived photoexcited state in PDAs.[3] This picture has been questioned in the last few years by systematic cw-PIA and PIA-FTIR studies on several PDAs and in particular on carbazolyl substituted PDAs (PCzDAs).[4–13] Especially PCzDAs are an interesting model system for the photoexcitation processes in PDAs, as they show photoexcited charged states. The photoexcitation scheme for long-lived charged states in PCzDAs can be summarized in the following way. The blue form of PCzDAs, which corresponds to more extended electronic delocalization and presumably to a lower number of conformational defects, always supports charged states.[4–9] In the asymmetrically substituted carbazolyl diacetlylenes with the carbazolyl group attached directly to the PDA backbone, only charged photoexcited states[6,10,11] were detected. On the contrary, both charged and neutral photoexcited states are observed when at least one methylene spacer is inserted between the carbazolyl group and the backbone.[4–9] The photogeneration process of the charged stages in blue PCzDAs seems to depend on the interchain separation.[9] Few evidences of photoexcited charged states in the blue form of different, noncarbazolyl substituted PDAs have also been reported by other groups.[12,13] However, the red form of PCzDAs, which shows a lower effective conjugation length relative to the blue form, exhibits long-lived triplet excitons as dominant photoexcited species.[4]

The nature of the charged states in PDAs is still not fully resolved. While the excited state PA pattern of asymmetrically substituted PCzDAs resembles the one predicted for polarons (two absorption peaks within the band gap), the absence of photoinduced spins argues in favor of bipolarons.[12] Since the theoretical models reported in the literature[14,15] do not give clear assignment of the charged states in PDAs, we decided to look for the experimental determination of both the photoinduced spin signature and the charged character of the photoexcitations to distinguish between polarons and bipolarons.

The motivation of efficient photogeneration of charged excited states is driven by potential applications of these materials in photovoltaic cells or photodetectors. A great effort was done in recent years to increase the photoinduced charge generation efficiency of conjugated polymers.[16,17] Utilizing a
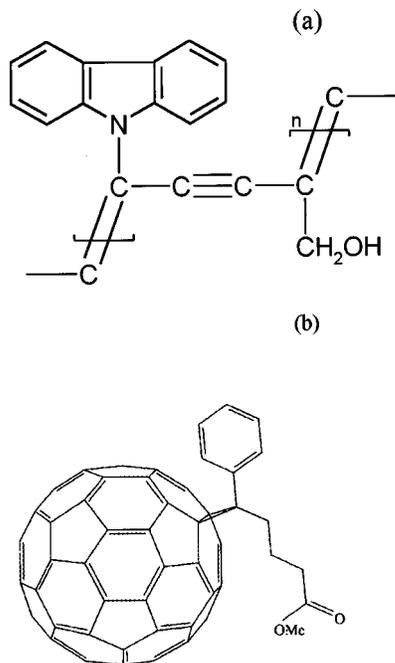
FIG. 1. Chemical structure of (a) polyCPDO and (b) PCBM.

FIG. 2. Absorption spectrum of polyCPDO, polymerized by UV light.

high quantum efficiency photoinduced electron transfer (t_{et} <1 ps) from the PPVs as well as poly(3-alkyl-thiophene) (P3ATs) composites to C_{60} or substituted fullerenes, the photoinduced charge generation efficiency has been increased by several orders-of-magnitude.[18] However, contrary to other conjugated polymers, there is no photoinduced interaction between fullerenes and red form PDAs.[19] This unusual exception of PDAs in regard of the photoinduced interactions with fullerenes has not been fully understood yet. The structure and morphology of the composite films might be substantial to account for this absence of the photoinduced electron transfer. Lower solubility of fullerenes in PDAs compared with other conjugated polymers might be relevant. Functionalized derivatives of C_{60} like, for example, [6,6]PCBCa (phenyl C_{61} butyric acid cholestanyl ester) again yielded no photoinduced interaction with red form PDA.[17] On the other hand, in the PPV and P3AT films heavily loaded with C_{60}, a partial phase segregation due to the lower solubility of the C_{60} component occurs. Nevertheless, ultrafast photoinduced electron transfer onto fullerenes is unambiguously observed even in these inhomogeneous mixtures. Therefore, the complete absence of the electron transfer observed in red form PDA/C_{60} composites[19] cannot be attributed to sample morphology effects alone. However, all these charge transfer studies have been performed so far only on red form PDAs, whose dominant photoexcitations are neutral triplet excitons. In the discussion above it was already pointed out that the photoexcitation pattern and the occurrence of photoexcited charges in PCzDAs is dominated by the conformation of the polymer, i.e., the red or blue form. We therefore decided to study the effect of fullerenes on the photoexcited states of one of the blue form PCzDAs.

In this article we report the investigation of the photoinduced absorption (PIA) as well as light induced electron spin resonance (LESR) in an unsymmetrical substituted carba-
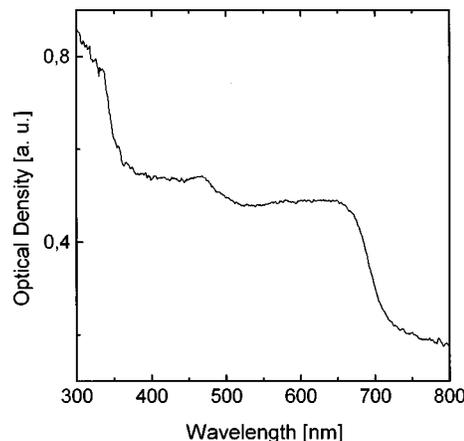
zolyl PDA with aromatic rings directly attached to the backbone, the poly[1-(N-carbazolyl)penta-1,3-diyne-5-o1] (poly-CPDO) both for the pristine polymer and mixed with the methanofullerene [6,6]-Phenyl C_{61}–butyric acid methyl ester (PCBM).[20] We used PCBM as electron acceptor with properties similar to, but with superior solubility compared to pristine C_{60}.[21]

II. EXPERIMENT

Figure 1 shows the chemical structure of polyCPDO and the PCBM molecule. CPDO monomer was synthesized as reported in literature earlier.[10] As reference microcrystalline polyCPDO pellets were prepared by mixing the monomer with micro size KBr powder and subsequent pressing. The solid state topochemical polymerization of the monomers was obtained by heating or UV light exposure .

In order to investigate the occurrence of charge transfer between blue form polyCPDO and PCBM, additional samples were prepared by dropcasting CPDO monomer solution in o-dichlorobenzene (ODCB) with or without equal weight amounts of PCBM onto KBr pellets. These samples were again polymerized by heating or UV light exposure. Even though it is not possible to give a quantitative polymerization yield, the successful polymerization process was observed and qualitatively monitored by UV/Vis, Fourier transformed (FT)-Raman and Fourier transformed infrared (FTIR) spectroscopy. Comparison with the reference pellets proves that CPDO monomer also polymerizes in the composite with PCBM. Partial phase segregation of the two components was observed.

Photoinduced FTIR (PIA FTIR), ESR (electron spin resonance), and LESR (light induced ESR) spectra have been measured from these pellets. The LESR experimental procedure consisted of the following sequence:

(i) scan the ESR spectrum of the nonilluminated sample (referred to as dark signal);

(ii) scan the ESR spectrum under illumination (referred to as illuminated signal);

(iii) scan the ESR spectrum after turning off the illumination (referred to as light-off signal);
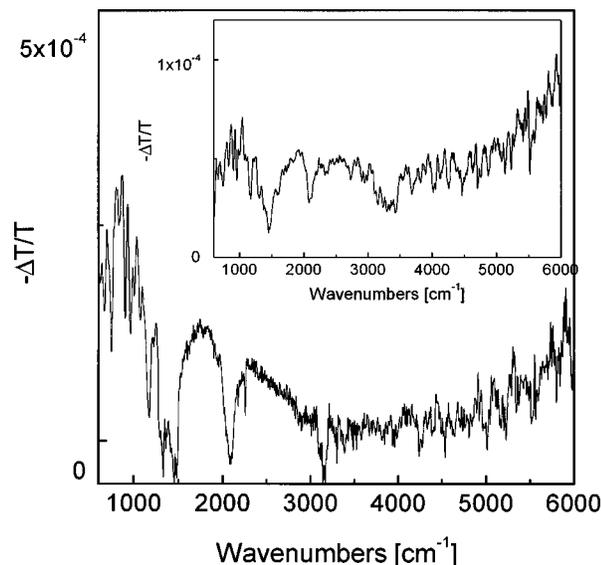
FIG. 3. $-\Delta T/T$ for microcrystalline polyCPDO in pressed KBr pellets. The inset shows $-\Delta T/T$ for a polyCPDO/PCBM composite, produced by drop casting of monomer solution onto KBr pellets and UV polymerization.

FIG. 4. Raman spectrum (a), IR absorption (b), and IRAV (c) of polyCPDO after UV polymerization.

(iv) warm up the sample (over 200 K), cool down to working temperature, and scan the ESR spectrum again (referred to as annealed signal).

As definition for this work the LESR signal is calculated as the difference between the illuminated and the light-off signal, thereby being indicative for the *prompt* photoinduced spins.[22] Additionally a persistent LESR signal is defined as the difference between the light-off signal and the dark signal. This signal, observed at temperatures below 200 K, is indicative for trapped, long-living photoinduced spins.[22] LESR measurements were performed on a Bruker EMX spectrometer with a 200 MHz broadband bridge using an Ar$^+$ laser at 488 nm as a pump. Samples were placed in a rectangular high Q cavity with a 50% grid for illumination. ESR and LESR spectra have also been taken from samples where the monomer and a composite mixture have been poured into a 3 mm ESR tube. After evaporation of the solvents samples have been polymerized. The tubes were evacuated up to 10^{-5} Torr and sealed. For consistency, some LESR and FTIR-PIA measurements presented in this work were taken from the same samples. After the PIA measurements samples were crushed and filled into ESR tubes and sealed under vacuum.

FTIR-PIA spectra were recorded on a Bruker IFS 66S spectrometer with a liquid nitrogen cooled MCT detector to cover the frequency range from 600 to 7000 cm^{-1} with a resolution of 4 cm^{-1}. The pellets were mounted on the cold finger of an evacuated liquid nitrogen bath cryostat with ZnSe windows. The vacuum during all measurements was better than 10^{-5} Torr. The samples were illuminated through a 90° geometry quartz window of the cryostat with the 488 nm line of an Ar$^+$ laser. Spectra were recorded by 200 accumulations of ten dark and ten illuminated cycles of 10 s each to increase the signal-to-noise ratio. Increasing cycle times to intervals longer than 10 s resulted for polyCPDO in stronger photoinduced signals which indicate the long life-
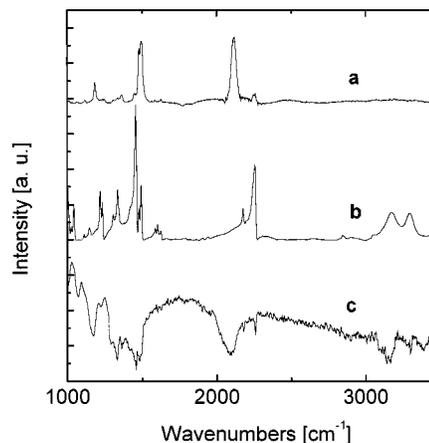
time of the carriers. All the measurements were, however, carried out with the 10 s intervals.

FT-Raman spectra were recorded with a Bruker FT spectrometer (FRS100) working with a Nd-YAG laser (λ_{exc} = 1064 nm), at room temperature.

UV-Vis absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer with an integrating sphere at room temperature.

III. RESULTS

Figure 2 shows the typical absorption spectrum of UV polymerized polyCPDO. The microcrystalline polyCPDO samples dispersed in KBr exhibited a broad absorption in the visible with a smooth onset around 770 nm,[11] typically of disordered samples.[23] The strong absorption of polyCPDO through the whole visible region from 2 eV to the near-UV can also be ascribed to the presence of oligomeric chains and/or conformational defects in the polymer backbone.

In Fig. 3 the PIA-FTIR spectra of a microcrystalline polyCPDO and polyCPDO/PCBM (Fig. 3 inset) are reported. The two spectra, which were taken from samples with comparable optical density, are similar. No significant enhancement of infrared activated vibrations (IRAV) by the addition of PCBM to polyCPDO can be detected.

The PIA-FTIR spectrum of polyCPDO presented here is in good agreement with recent reports.[6] This spectrum, if analyzed according to the interpretation of experimental work on other PDAs suggest the presence of a very broad absorption band centered around 800 cm^{-1} with superimposed windows arising from Fano resonance.[6,13] At about 5000 cm^{-1} the onset of higher energy electronic transition is observed in agreement with the photoinduced absorption band at about 8000 cm^{-1} previously reported,[6] which is outside our experimentally available spectral range. From these studies it is safe to conclude that two photoinduced bands are the fingerprint of the electronic excited states of polyCPDO.

For a detailed discussion of the low energy PIA band of polyCPDO, the Raman, IR, and PIA-FTIR spectra are collected in Fig. 4. The bands recorded below 1200 cm^{-1}, where no assignment of the vibrational spectrum is given, will not be discussed here.
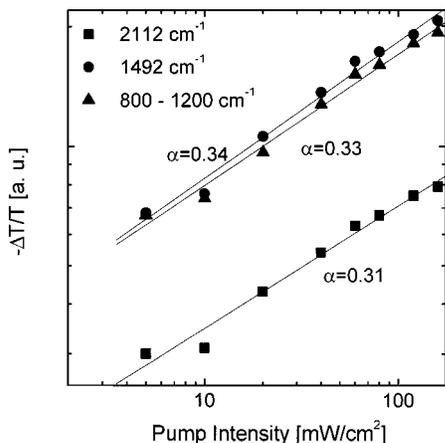
FIG. 5. Intensity dependence of $-\Delta T/T$ for excitation power at 488 nm at 2112 cm^{-1} (C≡C, full squares ■), 1492 cm^{-1} (C=C, full circles ●) and for the integral over 800–1200 cm^{-1} (full triangles ▲). The lines are fits with a power law $-\Delta T/T \sim I_{488}^{\alpha}$, where the exponent α turns out to be ~0.31, ~0.33, and ~0.34 for the three spectral regions.

FIG. 6. Rise (open squares □) and decay (open circles ○) behavior of the photoinduced absorption $-\Delta T/T$ at 100 K during and after illumination with laser light at 488 nm with 25 mW/cm^2. Fits with exponential growth and decay behavior yielded 41 s for the rise time τ_1 and 71 s for the relaxation time τ_2, respectively. For the relaxation behavior the $-\Delta T/T$ signal was evaluated by integrating over the IRAV region between 800 and 1200 cm^{-1}. Similar time constants were obtained from the C≡C IRAV band.

The Raman spectrum of the polymer shows two strong bands due to the C=C (1500 cm^{-1}) and C≡C (2120 cm^{-1}) stretching vibrations of the polymer together with a weak feature due to the C≡C (2250 cm^{-1}) stretching vibration of the residual monomer present in the sample. Small monomer residuals are indeed present in the polymerized sample when no extraction can be applied. In polyCPDO we have found rather large variations of the C≡C stretching vibrating (from 2096 to 2130 cm^{-1}) even under nonresonant excitation with $\lambda_{exc} = 1064$ nm depending on the polymerization conditions used. The IR absorption spectrum shows two bands at 2256 and 2176 cm^{-1} assigned to the symmetric and antisymmetric vibration of the C≡C bond of the monomer.[24] No features related to the C≡C stretching mode of the polymer could be detected because of the low dipole moment changes associated with this motion. In the 2800–3100 cm^{-1} and 3100–3500 cm^{-1} the complex pattern of the Ch and OH stretching modes, respectively, is observed.[25]

The PIA-FTIR spectrum shows features at 1332 cm^{-1}, a doublet at 1454–1480 cm^{-1}, at 2101, and at 3150 cm^{-1}. Very sharp negative peaks are also detected at 2179 and at 2258 cm^{-1}. By comparing the IR absorption with the PIA-FTIR spectrum, these last two bands can be interpreted as laser induced thermo-modulation of the ground state C≡C monomer bands. In a similar way the window at 3150 cm^{-1}, assigned to the CH stretching modes of both the monomer and the polymer, can be interpreted.

Of particular interest is the IRAV window observed at 2087 cm^{-1}. A strong Raman band due to the C≡C stretching mode is observed at a frequency very close to 2120 cm^{-1}, while no correlating bands are found in the IR spectrum. This suggests a Raman mode, which becomes IR activated due to the photoexcitation process (IRAV). Similar conclusions are valid for the PIA-FTIR window around 1480 cm^{-1}. By comparison with the Raman spectrum of poly-CPDO this mode can be assigned to the IRAV mode of the C=C stretching. According to the standard theories for the
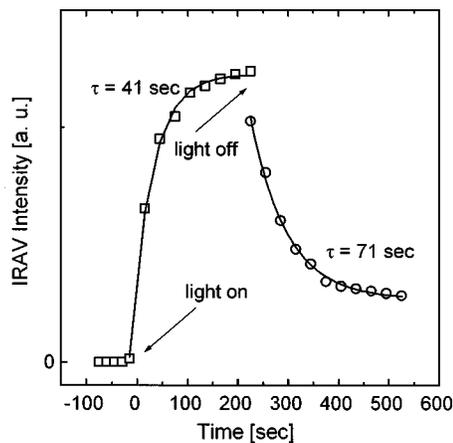
IRAV modes in conjugated polymers,[26–28] these data indicate the photogeneration of charged states.

The intensity dependence of the low energy PIA feature on the excitation power is shown in Fig. 5. The region at 800 cm^{-1}, and the IRAV modes at 2112 and 1492 cm^{-1} yield a $\sim I^{0.3}$ scaling behavior. The same scaling exponent in the intensity dependence of the electronic and IRAV bands further confirms the coupling between the vibrational and electronic photoexcited properties. Similar scaling exponents have been reported for the charged states of other blue from PDAs like PDA-4BCMU (Ref. 7) and PDA-DCHD (Refs. 5, 29, 30). The sublinear intensity dependence of the PIA-FTIR spectra discussed here has also been observed for other conjugated polymers[31,32] and is usually interpreted in terms of saturation kinetics if the scaling exponent is smaller than 0.5. The saturation of the available localization sites due to the presence of traps for the photogenerated excitations dominates the intensity scaling exponent. Examples of monomolecular relaxation behavior with similar intensity scaling exponents were discussed recently for PDA-4BCMU (Ref. 7) but also for oligothiophenes[33] and multiple quantum wells,[34] while examples of bimolecular relaxation behavior with intensity scaling exponents between 0.25 and 0.5 were discussed, for instance, for poly(p-phenylenevinylene).[32]

The rise and decay of the PIA signal was measured over a time scale of several minutes and is plotted in Fig. 6. Spectra are taken within 30 s intervals during the illumination and after switching off the light. The data were tentatively fitted by exponential functions, which gave for the rise and the relaxation time $\tau_1 = 41$ s and with $\tau_2 = 71$ s, respectively. At liquid N$_2$ temperature even after long times some residual IRAV intensity is present which only can be quenched by warming up of the sample (persistent signal). A similar relaxation behavior for trapped charges has been observed for various asymmetrical substituted PDAs[12,13] by other groups but also for different conjugated polymers.[31]
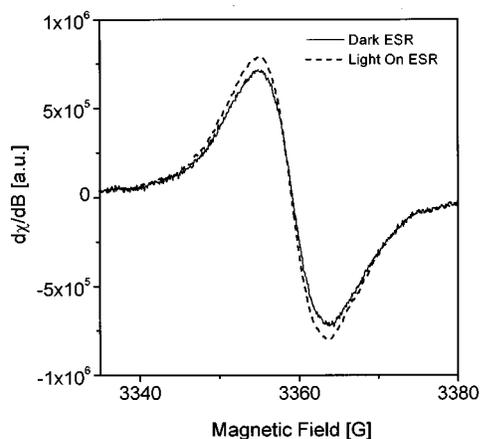
FIG. 7. Dark ESR (—) and light-on ESR (···) signal of polyCPDO at 100 K and 2 mW microwave power.

FIG. 9. Saturation behavior of the LESR signal (full squares ■) and of the light-off ESR signal (full circles ●) at 295 K and of the LESR signal (open squares □) and of the light-off ESR signal (open circles ○) at 100 K. Light-off signal was taken after LESR measurement switching off illumination.

PolyCPDO shows a strong dark ESR signal at $g = 2.0026$, which gains intensity under illumination (Fig. 7). The temperature dependence of the permanent radicals follows a $1/T$ Curie-type behavior (Fig. 8). Also a $1/T$ scaling behavior is observed for the photoinduced radicals. The integrated intensity referenced to a weak pitch standard[35] gives approximately one spin for every 10^3 monomer units for the dark signal. Estimation of the LESR signal yields an approximate creation of one spin for every 10^4 monomer units upon photoexcitation. From the complete reversible generation of the photoinduced spins, further photoinduced polymerization can be excluded as the origin for the photoinduced spins. Both, the "light-off" and the "light-induced" signal have similar microwave saturation behavior (Fig. 9). At $T = 100$ K the LESR signal reaches its maximum at a microwave power around 5 mW. At $T = 295$ K the maximum is shifted to slightly higher microwave powers around 20 mW. Figure 10 shows the dependence of the LESR signal on the light intensity with a scaling exponent $\alpha = 0.54$ at 295 K and $\alpha = 0.67$ at 100 K. These measurements were performed at the conditions where the magnetic resonance signals are in a nonsaturated regime, i.e., 64 μW. The occurrence of light

intensity dependent saturation is in agreement with the occurrence of more efficient trapping of the spins at lower temperatures.

The time behavior of the ESR signal under illumination was recorded at four different temperatures: at $T = 100$ K, $T = 170$ K, $T = 240$ K, and $T = 295$ K [Figs. 11(a)–11(d)]. Figures 11(a) and 11(b) show the slow dynamics of the photoinduced spins under illumination and after switching off the illumination at 100 K and 170 K, respectively. After switching of the light, approximately 30% or less of the spins (prompt signal) relax, while the rest remains nearly constant. These permanent spins were then annealed by heating the sample to room temperature. After cooling down in the dark, the ESR signal is on the same level as before the illumination cycle, proving that the persistent photoinduced spins were quenched completely. This reversibility also proves that photoinduced polymerization cannot be a reason for the LESR signal. The photoinduced ESR signal is therefore a superposition of two spin components with different relaxation behaviors, a *prompt* and a *persistent* component.[22] At
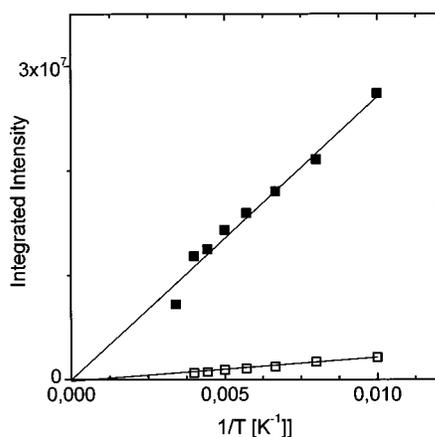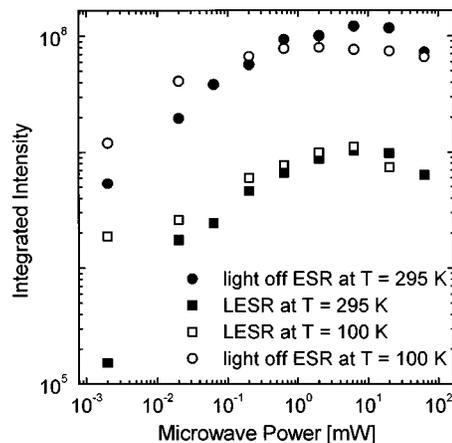

FIG. 8. Temperature dependence of the integrated intensity of the microwave absorption of the dark signal (full squares ■) and of the LESR signal (open squares □). Lines are extrapolations to a $1/T$ fit.
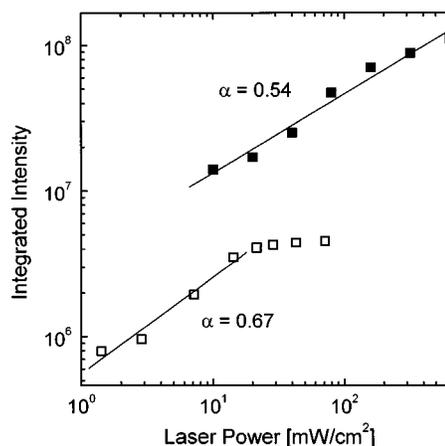

FIG. 10. Light intensity dependence of LESR signal of polyCPDO at 100 K (□) and 295 K (■). Power law fits of the type $y = x^\alpha$ yield exponents $\alpha = 0.67$ at 100 K and $\alpha = 0.54$ at 295 K.
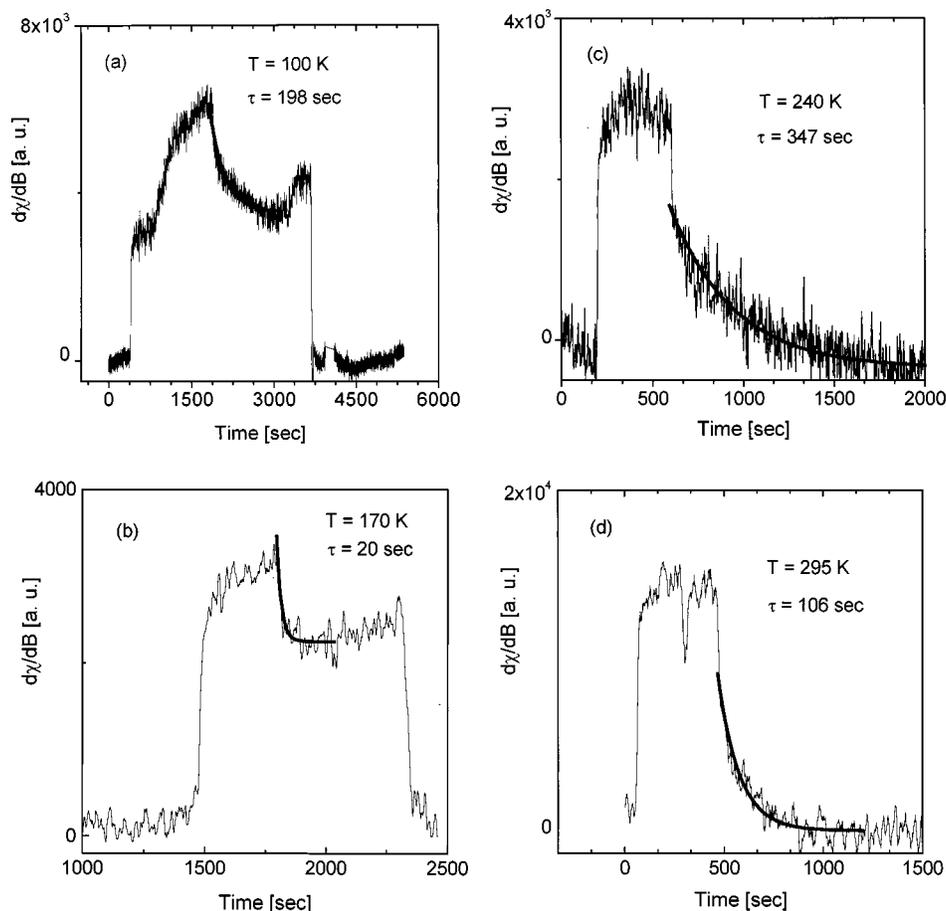
FIG. 11. Slow dynamics of photoexcited spins in polyCPDO for four temperatures: (a) $T=100$ K, (b) $T=170$ K, (c) $T=240$ K, and (d) $T=295$ K. Illumination was provided by the 488 nm line of an argon ion laser at a power of 25 mW/cm^2. Relaxation times were fitted by exponential decay law, fits are drawn as full lines in the figures.

higher temperatures ($T>200$ K) [Figs. 11(c) and 11(d)], the prompt relaxation of the spin follows again an exponential decay, with no permanent spins remained. These data imply an activation energy for the recombination process of persistent spins of $\Delta E < 200$ K (<17 meV).

Again, upon addition of PCBM to polyCPDO the same LESR spin signatures as for pristine polyCPDO were observed without significant enhancement. Moreover, no PCBM radical anion, which is easy to be identified by ESR spectroscopy due to its g value <2, was detected.

IV. DISCUSSION

In general, PDAs are nonfluorescent conjugated polymers. A possible explanation for this property is given in terms of the existence of a parity forbidden g-state below the $1B_u$ state which acts as an efficient sink for photoexcitations.[36] The dominant photoexcited state has therefore excitonic character. However, in some PDAs such as poly-9PA,[12] poly-4BCMU,[12,37] poly-1OH,[13] and especially PCzDAs, long-lived charged photoexcited states are present. While in poly-DCHD both neutral and charged photoexcited states are found, polyCPDO shows only charged photoexcited states. The PIA-FTIR and LESR investigations on polyCPDO presented in this work prove the presence of photoexcited charged states with spin 1/2 character. Both experimental methods find evidence for long-lived photoexcited states, which are easily saturated at rather low excitation intensities. The different light intensity scaling expo-

nents may be explained by the fact, that PIA-FTIR and LESR test the photoexcited states at a different saturation level. It is important to note, that similar observations were made for the intensity scaling behavior of photoexcited polarons in conjugated polymer/small molecular acceptor composites.[31] Also in these systems, where the correlation between the LESR and the PIA-FTIR signal is definitely established and assigned to polarons on the conjugated polymer, the IRAV bands show different scaling exponents as compared to the LESR signal. Further evidence for the correlation between the LESR and the IRAV signal comes from the long-time behavior of the photoexcited states. Both methods observe two components in the relaxation behavior of the photoexcited states, one prompt and one persistent.

In addition, the PIA of polyCPDO in the full energy range shows only two peaks as usually observed and explained for polaronic species.[38]

The existence of a dark ESR signal indicates the presence of defects on the polymer chain. Chromatographic investigations of polyCPDO prove a high concentration of short chain segments, which may be responsible for these defects. The 1/T behavior for both ESR and LESR signals with similar τ_2 and saturation behavior indicate their similar origin related to defect sites. This is also in agreement with the finding that the IRAV bands of the $C=C$ and $C\equiv C$ vibrations are weakly shifted compared to their Raman frequencies indicating localization. The particular window-like shape of the IRAV modes, recently also reported for

poly-p-phenylene,[39] is attributed to Fano-type quantum interference as previously shown for other PDAs[6,13] and organic crystals.[40] The relation between IR, Raman, and IRAV modes so far discussed for polyCPDO is usually described for conjugated polymers by the amplitude[26] or effective conjugated coordinate[27] formalism. These formalisms are not rigorously valid for PDAs where a triple bond is contributing to the conjugation. However, the amplitude mode model was already successfully to the interpretation of Raman spectra of PDAs (Ref. 41) and should therefore allow to make some qualitative comments on the IRAV modes observed in poly-CPDO. The energy shift between the Raman and the PIA-FTIR peaks of the higher energy mode ($C\equiv C$ stretching) is less than 50 cm^{-1}. Since the Raman and the PIA-FTIR data have been recorded under different experimental conditions, i.e., different temperature and excitation wavelength, this value might be affected by some uncertainties. However, it is important to notice, that in order conjugated polymers higher shifts of the IRAV modes toward lower energies are observed (137 cm^{-1} for polythiophene, 95 cm^{-1} in transpolyacetylene, and 106 cm^{-1} for polyisothianaphtene). The polyCPDO data are therefore qualitatively different when compared to those of other conjugated polymers, where the corresponding IRAV modes are shifted to lower energies from their corresponding Raman modes, as described by the amplitude or effective conjugated coordinate formalism. The small shift between the resonant enhanced Raman and IRAV frequencies implies strongly localized, immobile charged excitations.

No evidence for a photoinduced charge transfer to PCBM was observed by the quasisteady-state measurements. The effect of phase separation, which may occur between CPDO and PCBM during polymerization, cannot be ruled out as a possibility of a very fast forward and back transfer between polyCPDO and the fullerene. Since the generation of photoexcited charged states requires the separation of the electron-hole pair onto different molecules, the absence of charge transfer indicates rather weak interactions between the fullerene and the polyCPDO. The effect of localization of the photogenerated excitations at deep trap sites should be considered as hindrance factor, too.

V. CONCLUSION

In this work the spin nature of the charged photoexcited states of polyCPDO has been investigated. PIA-FTIR and ESR/LESR measurements suggested the correlation between the photoexcited charge states and photoexcited spin 1/2 states, indicative for polaronic excitations. Both methods imply that the photoexcited states are strongly localized. The presence of a dark ESR signal in all samples which shows similar magnetic resonance behavior as the LESR signal further supports the hypothesis that the photoexcited polarons are stabilized by deep traps. No enhancement of IRAV and LESR signals was detected upon addition of PCBM thus suggesting the suppression of the photoinduced charge transfer process between these two molecules.

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