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Polydiacetylene Nanowires in Ultrathin Films

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Summary: In this paper the results of studies carried out on thin films of new poly[bis(carbazol-9-ylmethyl)diacetylene]s (PCDAs) are reported. The preparation of the films has required clever synthesis to make processable the conjugated polymers without degrading their optoelectronic properties. To this end, the parent poly(diacetylene), (polyDCHD), has been modified by introducing long alkyl or acyl chains in the 3 and 6 positions of the carbazole rings. Electronic absorption spectra and linear and nonlinear optical characterization of three types of PCDAs are reported and compared.

Keywords: electronic spectra; NLO properties; polycarbazolyldiacetylenes; thin films

Introduction

The formation of ultrathin films of conjugated polymers with nanometer control over thickness is an area of intense study, as these films have desirable electronic, linear and nonlinear optical properties. In recent years we have been involved in the preparation of symmetrical derivatives of poly(carbazolyldiacetylene)s $(-CCz{=}CCz{-}C{\equiv}C-)_n$ by topochemical polymerization of alkyl- and acyl-substituted diacetylenes homologous to 1,6-di(carbazol-9-yl)hexa-2,4-diyne (DCHD). Because of its outstanding properties[1], polyDCHD is one of the most studied polydiacetylenes (PDAs). Among the poly[bis(carbazol-9-ylmethyl)diacetylene]s (PCDAs) prepared in our laboratory, polyDCHD-HS and polyDPCHD have shown a more interesting behavior. PolyDCHD-HS, with long hexadecyl chains in the 3 and 6 positions of carbazolyl substituents, in microcrystalline powder of the red form, is self-assembled into cylindrical shapes producing a two-dimensional columnar structure with hexagonal symmetry Col_{ho}, which undergoes a transition to a less ordered one (Col_{hd}) around 85 °C[2]. This structure differs from the ordered one by a reduced correlation between the repeat units inside the columns. The alkyl chains in a liquid-

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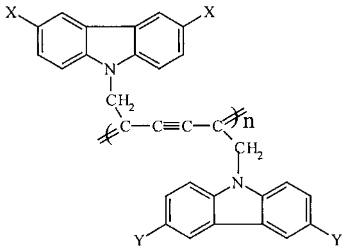
like state fill the space between the columns and are responsible for a large separation of polymer molecules (3.8 nm). The quasi-one-dimensional behavior and good processability of this polymer, which allows the preparation of homogeneous films by standard spin coating technique, has stimulated full investigation of its linear and nonlinear optical properties and so far very interesting results have been obtained[3]. Although the third-order susceptibility $\chi^{(3)}$ of polyDCHD-HS, measured in the telecommunication window either in the solid state by third harmonic generation (THG) technique[4] or in solution by Z-scan[5] is of the same order as that measured for other PDAs (10^{-11} esu), the low absorption in the same spectral region together with the polymer sub-picosecond response time provides a rather nice figure of merit, which makes it promising for applications. On the other hand, the measurement of $\chi^{(3)}$ performed by surface plasmon spectroscopy (SPS) with ps pulses on quasi-monomolecular layers of the polymer spun on silver-coated plates has given a surprisingly large off-resonance nonlinearity $|\chi^{(3)}| > 10^{-9}$ esu at 1064 nm. The giant nonlinearity observed has been related to the nanostructured surface of the silver film that provides an electromagnetic mechanism for the enhancement of the nonlinearity through local field effects[6], and makes these hybrid structures interesting for applications in nanostructural devices having photonic bandgap properties[7].

PolyDPCHD has palmitoyl chains in the 3 and 6 positions of the carbazoles designed to investigate the effects of the decreased electrondonor properties of the carbazole rings on optical and electronic properties of the polymer. Powder X-ray diffraction studies have revealed also in this polymer the formation at room temperature of a Col_{hd} supramolecular structure characterized by an intercolumnar distance of 3.9 nm, equal to that found for the high-temperature mesophase of polyDCHD-HS. PolyDPCHD is poorly soluble at room temperature in common organic solvents, but red films of good optical quality can be obtained by spin-coating or casting of monomer solutions followed by thermal polymerization. Only preliminary data on the characterization of the polymer and its films have so far been reported[8].

In order to exploit the effect of asymmetrical substitution of the carbazole rings on the polymer optoelectronic properties, we have synthesized a novel diacetylene (*a*-DCHD) carrying the hexadecyl substituents only on one of the rings. The resulting polymer, named poly*a*-DCHD (*a* = asymmetric) has been obtained by thermal topochemical polymerization and carefully purified according to the procedure reported in Ref. 2.

Results and Discussion

The chemical structures of the repeat units of the polymers described in the present paper are in Figure 1.



X=Y= *n*-$C_{16}H_{33}$	polyDCHD-HS
X=Y= *n*-$C_{15}H_{31}CO$	polyDPCHD
X= *n*-$C_{16}H_{33}$, Y=H	poly*a*-DCHD

Figure 1. Chemical structures of the PCDAs.

Poly*a*-DCHD and polyDCHD-HS are soluble in common organic solvents so that thin films of optical quality can be prepared by standard spin-coating techniques. The room-temperature absorption spectra of thin films spun on glass substrates from toluene solutions of both polymers are reported in Figure 2 and compared with the solution spectra.

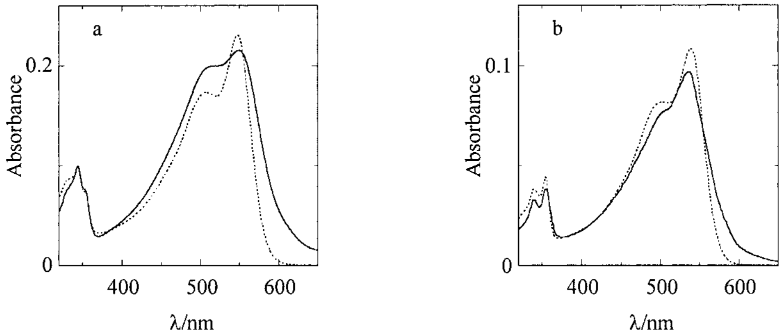


Figure 2. Absorption spectra of the films on glass (full line) and toluene solutions (dotted line) of (a) poly*a*-DCHD and (b) polyDCHD-HS.

The correspondence of the solution and film spectra shows that also in the solid state the polymer backbones are isolated. At this point it is interesting to notice that the absorption spectrum of a thin film of polyDPCHD (Figure 3), cast on glass as reported in Ref. 8, shows a strong and extremely narrow exciton band similar to those observed in PDA single crystals, and a well resolved fluorescence emission. These properties appear quite different from those reported in Figure 2 for the other polymers, which, as films, do not give appreciable emission at room temperature. However, both poly*a*-DCHD and polyDCHD-HS in benzene solution show absorption and emission profiles practically identical to those of Figure 3[9,10]. These results indicate that isolated red PDA chains with ordered conformations show measurable fluorescence. This finding is in agreement with the observation of a very high fluorescence yield for red chains of poly4BCMU isolated in the monomer matrix at very low temperature[11]. Unfortunately, at present, we cannot quantify the fluorescence yield for our film.

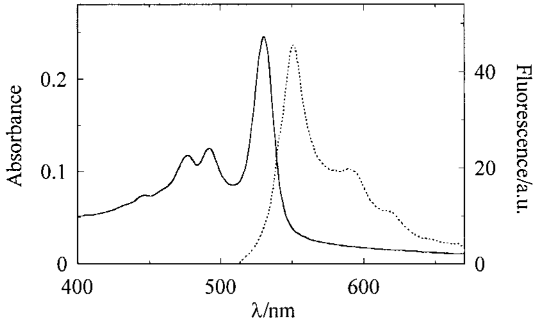


Figure 3. Absorption (full line) and emission (dotted line) spectra of a polyDPCHD film on glass. Excitation wavelength 480 nm, T = 20 °C.

Since these polymers have been designed for application in photonic devices, their thermal and photochemical stability have been checked. PolyDPCHD films are the most stable because they do not undergo changes up to 180 °C and after six hours of UV irradiation with 35 W lamp. All the polymers, however, are completely stable at a conventional temperature of 75 °C.

The optical linear characterization so far performed on these polymers has provided the refractive index values reported in Table 1. For the first two polymers, measurements have been carried out with thicker guided films, which have permitted the determination of both transverse electric (TE) and transverse magnetic (TM) refractive indices (n_{TE} and n_{TM}). It is interesting to notice negligible film birefrigence evidenced by these values. We believe that this insensitivity to polarization may also hold for the nonlinearity, thus making these polymers very interesting for telecommunications. The only slightly lower value of n_{TM} found for the thinner film of polyDCHD-HS spun on a silver layer indicates that different substrates and film thickness do not substantially affect the refractive index. The refractive index of polyDPCHD has been measured by ellipsometry[12] with unpolarized light. The higher values found for this polymer are probably due to a different chemical nature of the substituents in the carbazole rings.

Table 1. Linear optical properties of poly*a*-DCHD, polyDCHD-HS and polyDPCHD.

PCDA	λ nm	Thickness μm	n_{TM} 1)	n_{TE} 1)	n 2)
Poly*a*-DCHD	632.8	2.0	1.583	1.589	-
PolyDCHD-HS	1321	2.4	1.567	1.548	-
	849	2.4	1.585	1.563	-
	849	0.02 3)	1.550	-	-
PolyDPCHD	1321	0.032	-	-	1.648
	849	0.032	-	-	1.663
	632.8	0.032	-	-	1.702

1) From m-line spectroscopy measurements, Ref. 3

2) From ellipsometry measurements, Ref. 12

3) Film spun on silver-coated plate

So far the third-order nonlinear polarizability coefficient $\chi^{(3)}$ has been measured on thin films of polyDCHD-HS and polyDPCHD by employing two different techniques. THG technique has been applied[4,12] to study films spun on glass. Surface plasmon spectroscopy (SPS) has been used to study thin films of polyDCHD-HS spun on silver-coated plates[6].

Table 2. Nonlinear optical properties of polyDCHD-HS and polyDPCHD.

PCDA	λ nm	Thickness nm	$\chi^{(3)}$ 1) esu	$\chi^{(3)}$ 2) esu
PolyDCHD-HS	1500	140	4.0×10^{-11}	-
	1800	140	2.9×10^{-11}	-
	1064	157	-	$\sim10^{-9}$
	1064	43	-	$\sim10^{-8}$
PolyDPCHD	1600	32	4.5×10^{-11}	

1) From THG measurements, Refs. 4,12

2) From SPS measurements, Ref. 6

Table 2 collects all the obtained data. As already noted, very different values have been obtained by the two methods for polyDCHD-HS, while similar data are observed for the two polymers by using the THG technique. However, we would like to stress that the THG dispersion curves of $\chi^{(3)}$ for the two polymers are quite different as a result of different contributions of multiphotonic processes[4,12].

Conclusions

We have shown that in thin red films the conjugated backbones of our PCDAs are isolated and of polyDPCHD also in ordered conformations. The presence of ordered chains in organized nanostructured particles enhances the fluorescence emission. The $\chi^{(3)}$ values from THG are of the same order of magnitude at fixed wavelength and seem to be unaffected by detailed chemical structure of substituents. However, the $\chi^{(3)}$ dispersion evidences different contributions of multiphoton processes[4,12], which deserves further investigations.

Acknowledgments

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