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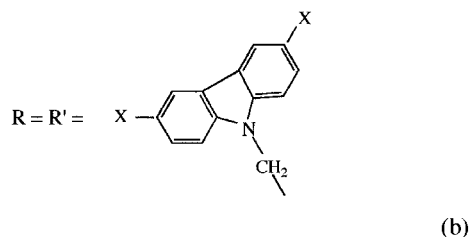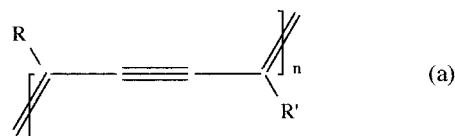Via Dodecaneso 31, I-16146 Genova, Italy

The synthesis of the monomer 1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne, its polymerization and the purification of the polymer, which is soluble in common organic solvents, are reported. Results from powder X-ray diffraction studies carried out on the red form of the polymer are discussed. The red polymer chains self-assemble into cylindrical shapes which produce hexagonal columnar mesophases with a transition from a more ($Col_{h\,o}$) to a less ordered ($Col_{h\,d}$) structure around 85°C. The role played by the long alkyl chains in the formation of the supramolecular hexagonal mesophase is emphasized by comparing these results with those obtained from an analogous polymer with dodecyl substituents which exhibits only the $Col_{h\,d}$ structure over the whole range of temperature explored.

1. Introduction

Among the many conjugated polymers, the polydiacetylenes (PDAs), figure 1 (*a*), are particularly promising non-linear optical materials since they show the largest known non-resonant, sub-picosecond refractive non-linearities [1]. Significant advances have been made towards evaluating polydiacetylenes in prototype optical device formats. For example, waveguiding [2, 3], the fabrication of channel waveguides and optical switching phenomena [4] in thin films could be explored after soluble polydiacetylenes were synthesized. Most of these studies concern the PDAs with $R = R' = (CH_2)_n OCONHCH_2 COOC_4 H_9$ called P*n*BCMU whose solubility in various organic solvents allows the fabrication of large area films suitable for applications [5]. Other soluble PDAs have been synthesized [6, 7], but certainly the most extensive investigations have been carried out on P4BCMU because of its higher solubility.

In the last decade we have become interested in the study of another class of PDAs, having the carbazolyl group directly or indirectly attached to the polymer backbone. The reason for this choice has been dictated by two facts: among PDAs, the asymmetrically substituted PCPDO, poly[1-(*N*-carbazolyl)penta-1,3-diyn-5-ol],

(a)

(b)

X= $(CH_2)_{11}CH_3$ PDCHD-S

X= $(CH_2)_{15}CH_3$ PDCHD-HS

Figure 1. Chemical structures of the polydiacetylene chains: (*a*) structural unit; (*b*) R, R' substituents.

shows one of the lowest observed electronic absorption edges [8] and the symmetrical PDCHD, poly-[1,6-bis(*N*-carbazolyl)-2,4-hexadiyne], exhibits a very

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large third order susceptibility and photocurrent signal [9]. A variety of symmetrically and asymmetrically substituted polycarbazolyldiacetylenes (PCDAs) have been prepared by topochemical polymerization of the crystalline monomers, and have been characterized by spectroscopic techniques. Optical transitions, photo-induced absorptions in the millisecond–second time regime and pump and probe spectroscopy in the femtosecond–picosecond regime have been analysed for selected PCDA samples. These studies have allowed us to reach the following results.

(i) PCDAs having one carbazolyl group directly attached to the polymer backbone are insoluble, show unresolved absorption spectra extending from 1.8 eV to the near-UV and carry only long-lived charged photoexcitations (presumably polarons) [10]. Monomers with the two carbazolyl groups directly bonded to the diacetylenic backbone do not polymerize.

(ii) PCDAs having the carbazolyl groups attached to the backbone through at least one methylene spacer are insoluble, show well resolved electronic absorption spectra typical of the more extended conformation (blue form) consisting of a singlet excitonic peak around 2 eV, followed by its vibrational progression and carry both charged and neutral (triplet excitons) long-lived photoexcitations.

(iii) PDCHD-S, having dodecyl chains on the 3 and 6 positions of the carbazolyl groups attached to the backbone through one methylene spacer, is soluble in common organic solvents, see figure 1 (*b*). This polymer shows in its microcrystalline form an extended conformation (blue form) with an electronic spectrum practically identical to that of the corresponding polymer PDCHD with unsubstituted carbazole rings. In this case neutral triplet excitons are preferentially photogenerated. PDCHD-S in solution or in films cast from solutions exhibits the red form typical of these polymers in a twisted conformation. The electronic absorption spectrum shows an excitonic transition around 2.3 eV similar in shape to, but broader than the spectrum of the blue form. Also Raman spectra agree with the presence of shorter conjugation lengths in the red form. The polymer in the red solid state supports only long-lived photogenerated triplet excitons. No hint of bands due to charged states is found [11].

Even though soluble, PDCHD-S is not suitable for the preparation of films with the homogeneity required for applications. For this reason we have prepared PDCHD-HS carrying the longer hexadecyl substituents

on the carbazole rings, see figure 1 (*b*). In this way a higher solubility is obtained. Moreover special care has been taken to eliminate from the polymerization product even the smallest amounts of residual monomer as well as oligomers which prevent highly homogeneous films from being obtained. In fact, when separate domains of the monomer and polymer are present in the film, a rough surface unsuitable for optical measurements is observed [12]. Further problems may arise if monomer present polymerizes during deposition. The blue forms of both PDCHD-HS and PDCHD-S show similar electronic and Raman spectra, thus indicating that the effective conjugation length is not affected by the length of the alkyl substituents.

During studies of PDCHD-HS in solution, electronic spectra strongly dependent on the solvent were observed. In several organic solvents including toluene, spectra typical of red PDAs with a more or less resolved excitonic peak were obtained. Benzene solutions show instead an excitonic peak at 538 nm (2.3 eV) of remarkable sharpness [3], strongly resembling those of tailored oligomeric systems [13] or of low temperature blue form single crystals [14]. The importance of this finding, never reported before for PDA solutions, as well as the observed influence of both the molecular and the supramolecular structures, on the nature of the long-lived photoexcited states [11] spurred a more extensive investigation of the structural properties of the red form of PDCHD-HS.

In this paper, after a brief description of the synthetic and preparative procedures for obtaining PDCHD-HS, and of the electronic and vibrational properties of its red form in the solid state, results from powder X-ray diffraction studies, for this polymer as well as for monomer-free PDCHD-S, are reported.

The formation of supramolecular hexagonal arrays of long polydiacetylenic columns in both PDCHD-HS and PDCHD-S has been observed. The role played by the long aliphatic chains is emphasized by the observation of a transition from a more to a less ordered mesophase in PDCHD-HS upon increasing the temperature, while only the less ordered mesophase is found in PDCHD-S in the temperature range explored.

2. Experimental

2.1. *Synthesis and characterization of the monomers*

The synthesis of DCHD-S, 1,6-bis(3,6-didodecyl-*N*-carbazolyl)-2,4-hexadiyne, has already been described [14]. The synthetic route to DCHD-HS, 1,6-bis-(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne (1), is shown in the scheme.

Carbazole was a commercial sample used after crystallization; palmitoyl chloride and propargyl bromide (80 wt % in toluene) were commercial samples used
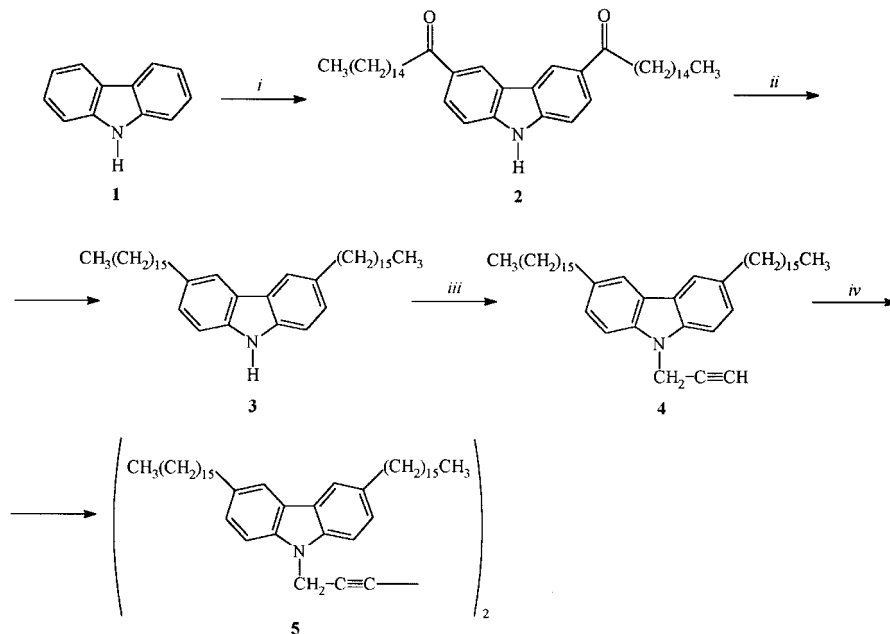
i: CH$_3$(CH$_2$)$_{14}$COCl, AlCl$_3$, CS$_2$; ii: ZnHg/HCl, Tol; iii: Br–CH$_2$–C≡CH, (n-C$_4$H$_9$)$_4$NBr, NaOH, H$_2$O/Tol, sonication; iv: (MeCO$_2$)$_2$Cu, Py/MeOH.

Scheme.

as received. Column chromatography was performed on ICN Biomedicals 60–200 silica gel. The solvents employed as eluents were distilled before use. Petroleum ether was the fraction with b.p. 40–70°C. CS$_2$ was distilled over P$_2$O$_5$; pyridine was distilled over KOH pellets and then over CaH$_2$. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Differential scanning calorimetry was also used for obtaining melting points and enthalphies of the monomers. ^{1}H NMR spectra were taken on a Varian Gemini 200 spectrometer; tetramethylsilane (TMS) was used as internal standard and chemical shifts are reported as δ values (ppm).

2.1.1. *3,6-Dihexadecanoylcarbazole (2)*

A mixture of carbazole (15.0 g, 90 mmol) and AlCl$_3$ (23.8 g, 185 mmol) in 100 ml of anhydrous CS$_2$ was heated with stirring at reflux temperature, and palmitoyl chloride (54.6 ml, 180 mmol) was added dropwise. The reaction mixture was heated until cessation of HCl evolution (30 h) and then the solvent was removed by distillation. The subsequent work-up involved treatment of the residue obtained with conc. HCl in crushed ice, further dilution with water, filtration of the solid product and careful washing of the latter on the filter with water and then with a small volume of ethanol. After drying in air, the crude product was crystallized from ethanol/dioxan to give 18.0 g (30.8%) of pure colourless **2**, m.p. 168–169°C. ^{1}H NMR (CDCl$_3$): δ 0.89 (6 H, t,

J 6.4 Hz); 1.26 (48 H, m); 1.82 (4 H, m); 3.12 (4 H, t, J 7.5 Hz); 7.50 (2 H, d, J 8.5 Hz); 8.15 (2 H, dd, J 2.0 and 8.5 Hz); 8.51 (1 H, s); 8.79 (2 H, d, J 2.0 Hz).

2.1.2. *3,6-Dihexadecylcarbazole (3)*

A mixture of amalgamated zinc (prepared by a standard procedure from 121.8 g of granular zinc and 240 ml of 5% aqueous HgCl$_2$), **2** (12.0 g, 18.63 mmol) and conc. HCl (80 ml) was vigorously stirred for 5 min and left to stand overnight. After addition of toluene (15 ml) the mixture was heated at reflux with stirring for 30 h, 10 ml of toluene being added each 10 h. After cooling, the liquid phase was decanted and repeatedly shaken with Et$_2$O. The solid residue was washed with Et$_2$O and the combined organic extracts were washed with 4% HCl, water, and saturated aqueous NaHCO$_3$ and then dried over Na$_2$SO$_4$. The residue obtained from roto-evaporation of the solvent was triturated with ethanol which was then separated by filtration and the solid residue dried under vacuum. The crude material was purified by column chromatography on silica gel (CH$_2$Cl$_2$/petroleum ether 2:5 as eluent), yielding 4.17 g (36.3%) of pure colourless **3**, m.p. 76–77°C. ^{1}H NMR (CDCl$_3$): δ 0.88 (6 H, t, J 6.7 Hz); 1.25 (52 H, m); 1.70 (4 H, m); 2.76 (4 H, t, J 7.8 Hz); 7.21 (2 H, dd, J 1.6 and 8.3 Hz); 7.31 (2 H, d, J 8.3 Hz); 7.85 (3 H, br s).

2.1.3. *N-Propargyl-3,6-dihexadecylcarbazole (4)*

To a solution of **3** (3.31 g, 5.38 mmol) in toluene (30 ml), 3-bromopropyne (0.93 ml of an 80 wt % solution

in toluene, 8.06 mmol) and tetrabutylammonium bromide (0.087 g, 0.27 mmol) were added, followed by 3.3 ml of 50% aqueous NaOH. The flask was stoppered and sonicated for 9 h in a common ultrasonic cleaner, maintaining the temperature of the water bath at 50°C. The mixture was diluted with Et_2O and the organic layer separated. The inorganic layer was again shaken with Et_2O. The combined organic extracts were washed with water, dried (Na_2SO_4) and roto-evaporated. The crude residue (3.32 g, pale yellow solid) was chromatographed on a silica gel column (CH_2Cl_2/petroleum ether 1:10 as initial eluent and then CH_2Cl_2/petroleum ether 1:6 as eluent) to give 3.12 g (88.8%) of pure colourless **4**, m.p. 68.0–68.8°C. ^{1}H NMR (CDCl$_3$): δ 0.88 (6 H, t, J 6.5 Hz); 1.25 (52 H, m); 2.23 (1 H, t, J 2.4 Hz); 2.77 (4 H, t, J 7.6 Hz); 5.00 (2 H, d, J 2.4 Hz); 7.35 (4 H, m); 7.87 (2 H, br s).

2.1.4. *1,6-Bis(3,6-dihexadecyl-N-carbazolyl)-2,4-hexadiyne (1)*

With magnetic stirring at room temperature, anhydrous (MeCOO)$_2$Cu (4.16 g, 45.8 mmol) was added to a round bottomed flask shielded with aluminum foil and equipped with a condenser and a silica gel guard tube, to a solution of **4** (1.50 g, 2.29 mmol) in 60 ml of a 1:1 (v/v) mixture of dry pyridine and absolute methanol. The reaction mixture was heated with stirring for 2 h in an oil bath at 70°C, cooled and then poured into an excess of 4% HCl. The resulting acidic mixture was filtered and the solid material was triturated with 4% HCl; the solid obtained on filtration was washed with water on the filter and finally with a little ethanol. The solid product was stored in the dark and dried under vacuum. The crude product (1.43 g) was purified by column chromatography on silica gel (gradient from CH_2Cl_2/petroleum ether 1:10 to pure CH_2Cl_2 as eluent) to give 1.32 g (88.0%) of pure **1**, m.p. 82–83°C, whose pale blue colour indicated the presence of traces of polymer. In dark-room conditions, 222 mg of **1** were dissolved by heating in ethyl acetate. After filtration, a large excess of ethanol was added and the solution was dry ice cooled to -40°C. After a few minutes the product crystallized and was filtered off and then dried under vacuum to give 195 mg of very light pink **1**, m.p. 83–84°C. ^{1}H NMR (CDCl$_3$): δ 0.88 (12 H, t, J 6.4 Hz); 1.26 (104 H, m); 1.68 (8 H, m); 2.75 (8 H, t, J 6.7 Hz); 4.98 (4 H, s); 7.26 (8 H, br s); 7.83 (4 H, br s). DSC: m.p. = 84.5°C; $\Delta H_m = 114.1$ J g^{-1}.

2.2. *Solid-state polymerization of DCHD-HS and purification of the polymer*

The monomer DCHD-HS was bulk polymerized thermally at 10°C below its melting point. The progress of the reaction was followed by spectroscopic techniques.

The polymer is soluble in several organic solvents at higher concentrations than those found for PDCHD-S. In order to extract residual monomer fully from the samples the procedure outlined below has been found the most appropriate.

The thermally polymerized (75°C, 720 h) material (100 mg) was completely dissolved in toluene, by heating and stirring to accelerate the process. Silica gel (1 g) was added to the solution. The material adsorbed onto the silica gel after roto-evaporation of the solvent was placed onto a short silica gel column prepared with 4:1 CH_2Cl_2/petroleum ether. A small volume of the same mixture was used to obtain the quantitative elution of the unreacted monomer. By roto-evaporation of the eluate, 32 mg of monomer were recovered. The red silica gel layer on the top of the column, and containing the adsorbed pure polymer, was recovered by extrusion and the organic matter extracted with toluene with vigorous stirring at reflux temperature. After three extractions (each one requiring a few hours), the extracts were combined, concentrated to 10 ml, dried over Na_2SO_4 and then filtered. A large excess of petroleum ether (b.p. 30–50°C) was added to the solution in a 100 ml conical flask which was stoppered and stored at 4°C. Precipitation of the polymer rapidly occurred and the solid was separated by centrifugation (4500 rpm, 30 min) and then dried under vacuum. By this procedure 52 mg (76.5% based on the reacted monomer) of monomer-free, deep red solid with a metallic lustre were obtained.

2.3. *Characterization methods*

Electronic absorption spectra of the polymer in KBr pellets were recorded on a Perkin-Elmer spectrophotometer, model Lambda 9, equipped with an integrating sphere accessory. Raman measurements were performed on powders with a Bruker FT spectrometer (FRS 100) working with a Nd-YAG laser (1064 nm). Thermal analysis experiments were performed on monomer and polymer powders using a DSC Mettler type TC 10 A using a heating rate of 20°C min^{-1}.

X-ray diffraction experiments were performed with a home made pinhole camera designed to operate with either powders or oriented samples under vacuum with a Ni filtered Cu beam ($\lambda = 1.54$ Å). The apparatus was equipped with a device for recording the diffraction patterns between room temperature and 350°C with an accuracy of 1°C. Powder samples in copper cells with mylar windows were used. Several exposures were used in order to measure the strongest as well as the weakest reflections. Intensities and widths of the reflections were measured with a laboratory built microdensitometer designed to analyse the X-ray diagrams provided by the pinhole camera.

3. Results and discussion

3.1. *Spectroscopic characterization of the polymer*

The room temperature electronic spectrum of PDCHD-HS in KBr pellets is shown in figure 2. This spectrum, typical of the red form, exhibits the excitonic peak and its vibronic structure at around 540 nm (2.30 eV) and 500 nm (2.48 eV). The absorptions around 350 nm (3.54 eV) originate from the carbazole groups. The presence of the excitonic absorptions is typical of structurally ordered polydiacetylenic chains.

The Raman spectrum of PDCHD-HS (figure 3) shows the most intense peaks originating from the stretching vibrations of the triple and double bonds of the polymer red form at 2115 and 1514 cm^{-1}, respectively. These results are in agreement with the presence of chains with effective conjugation lengths shorter than those of the blue form, but the sharp features are indicative of a narrow distribution of the conjugation lengths.

3.2. *X-ray diffraction studies*

X-ray diffraction measurements were made on PDCHD-HS as well as on PDCHD-S. The two polymers were studied in the red form between room temperature and 250°C (limit of stability for the mylar windows). Below 250°C, the X-ray diagrams of the two polymers exhibit in the low-angle domain two or three sharp Bragg reflections with reciprocal spacings in the ratio 1 : $\sqrt{3}$: $\sqrt{9}$. On the contrary, the aspect of the wide angle domain varies with both the temperature and the chemical nature of the polymer, thus allowing the classification of the X-ray diagrams into two different sets: the first is characterized by the superposition of a rather
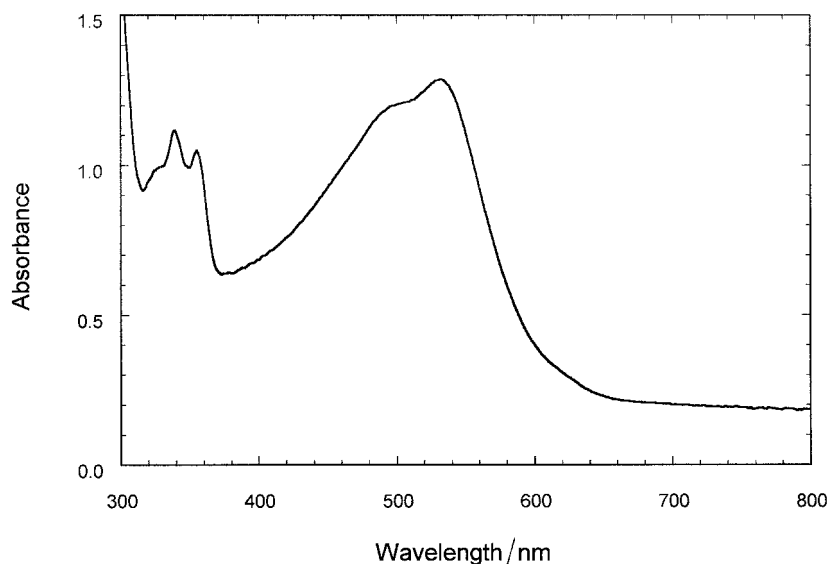

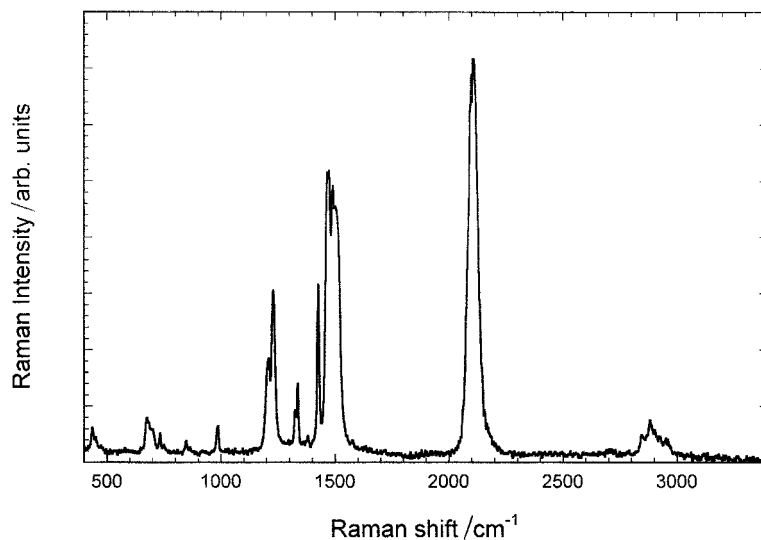Figure 2. Absorption spectrum of red PDCHD-HS in KBr pellets.

Figure 3. Raman spectrum of red PDCHD-HS in powder form.

sharp reflection on a diffuse band, figure 4 (*a*); the second is characterized only by a diffuse band, figure 4 (*b*).

The set of sharp Bragg reflections with reciprocal spacings in the ratio $1 : \sqrt{3} : \sqrt{9}$ is characteristic of a bidimensional hexagonal array of long rods that can slide in a direction parallel to their axis. The lattice parameter *d* of the hexagonal array is different for the two polymers: $d = 38.4$ Å for PDCHD-HS and $d = 32.5$ Å for PDCHD-S. The diffuse band at wide angles which corresponds to a periodicity $a = 4.5$ Å, independently of temperature, is characteristic of melted paraffinic chains [15]. The reflection at wide angles corresponds to a periodicity $c = 4.7$ Å and is independent of temperature in its domain of existence.

Taking into account that the polymers studied are formed by diacetylenic units bearing carbazolyl side groups substituted on C3 and C6 of the aromatic ring by two long paraffinic chains, the two types of X-ray

diagram can be interpreted by the model reported in figure 5 (*a*). The solid state structure of the polymers is of the columnar type, with the columns formed by the polydiacetylene chains assembled in a hexagonal bidimensional lattice of parameter *d* and separated by the paraffinic chains in a liquid-like state, figure 5 (*b*).

The two sets of X-ray diagrams correspond to two types of hexagonal columnar structures: one is of the hexagonal ordered Col_{ho} type, the other of the hexagonal disordered Col_{hd} type [16]. In the hexagonal ordered structure, Col_{ho}, the reflection at $c = 4.7$ Å corresponds to the distance *c* along the column axis between the parallel, rigid, disc-like repeating units with the connected carbazolyl groups. The paraffinic chains in a liquid-like conformation (as shown by the diffuse band at $a = 4.5$ Å) fill the space between the columns and ensure the decorrelation between adjacent columns. The hexagonal disordered columnar structure Col_{hd} differs
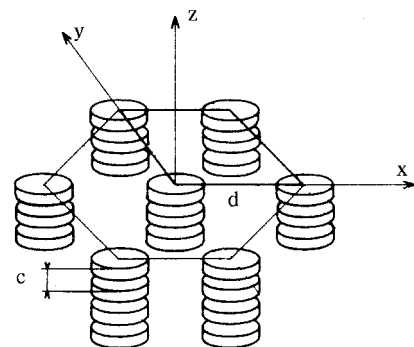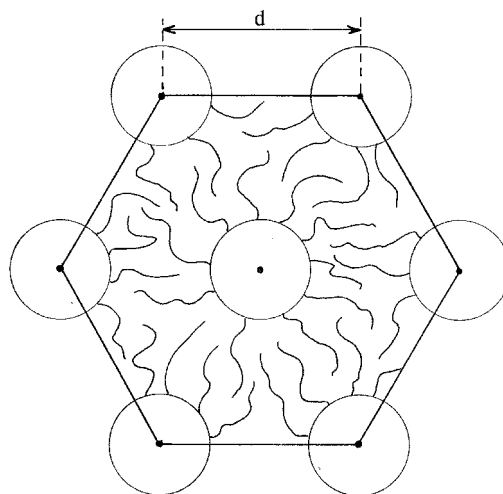

(*a*)
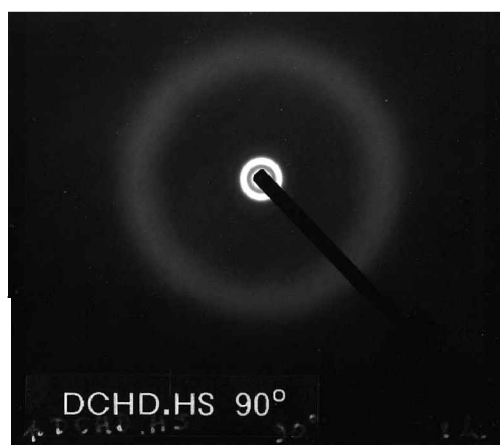
(*b*)

Figure 4. Pinhole camera X-ray diagrams of red PDCHD-HS: (*a*) Col_{ho} columnar phase at 25°C; (*b*) Col_{hd} columnar phase at 90°C.

(*a*)

(*b*)

Figure 5. Schematic representation of the hexagonal columnar structures: (*a*) lattice parameters of the Col_{ho} hexagonal phase; (*b*) top view of the hexagonal packing of the columns.

from the Col_{ho} structure by the absence of correlation between discs inside the columns.

The polymer PDCHD-HS exhibits both types of columnar structure as a function of temperature. For temperatures lower than about 85°C, the structure is the hexagonal ordered Col_{ho} type, while for temperatures higher than 85°C the hexagonal disordered Col_{hd} structure is observed. For the first type of columnar structure, Col_{ho}, the lattice parameter $d = 38.4$ Å is independent of temperature. The transition from the Col_{ho} columnar structure to the Col_{hd} structure is accompanied by a small increase of the lattice parameter to $d = 39.0$ Å and is reversible. For the second columnar structure, Col_{hd}, the lattice parameter d decreases from 39.0 to 36.8 Å when the temperature increases from 90 to 250°C according to a contraction coefficient $k = - \Delta d/[\bar{d}(\Delta T)] = 4.1 \times 10^{-4}$ K^{-1} where $\bar{d}$ is the average lattice parameter. The red polymer was also investigated by DSC. Figure 6 illustrates its behaviour during heating (*a*) and cooling (*b*) cycles in the 0–350°C temperature range. The endothermic peak ($\Delta H = 30.8$ kJ mol^{-1}) at 69.5°C in figure 6(*a*), and the exothermic peak ($\Delta H = - 34.5$ kJ mol^{-1}) at 59°C in figure 6(*b*), can be correlated with the phase transition from Col_{ho} to Col_{hd} columnar structures. The small endothermic peak ($\Delta H = 3.6$ kJ mol^{-1}) at 131.3°C, figure 6(*a*), could be tentatively assigned to a small increase of disorder in the Col_{hd} columnar phase since no transition is observed by X-ray diffraction. The corresponding small exothermic peak ($\Delta H = - 4.6$ kJ mol^{-1}) at 107.1°C in the cooling thermogram, figure 6(*b*), appears to confirm the reversible nature of this change.

For red PDCHD-S only the hexagonal disordered Col_{hd} columnar structure is observed over the whole temperature range explored. The lower value of the lattice parameter found in this case, $d = 32.5$ Å, reflects the shorter length of the paraffinic substituents on the carbazolyl ring. No significant features are observed in its DSC thermogram.

In conclusion, polycarbazolyldiacetylenes with long aliphatic chains in the carbazole ring exhibit from room temperature to 250°C columnar mesophases whose degree of order depends on the alkyl chain length. In particular, the polymer with dodecyl substituents exhibits only one mesophase of the hexagonal disordered Col_{hd} type in the temperature range explored. Two different mesophases are instead observed as a function of temperature in the polymer with longer alkyl chains. For temperatures lower than 85°C, a columnar hexagonal ordered Col_{ho} phase is observed, while at higher temperatures a columnar hexagonal disordered Col_{hd} phase occurs. The two types of columnar phase are characterized by a phase separation at the molecular level between the conducting columns and the alkyl substituents in a melted state.

Finally we would like to stress that the supramolecular structures here discussed, and due to the long alkyl groups on the aromatic substituents of polydiacetylene chains, represent a novel solid state organization for this class of polymers. Besides giving rise to soluble polymers the presence of these substituents determines a supramolecular assembly that could strongly influence the non-linear optical properties of the material. The microphase separation prevents interactions between the polydiacetylene backbones. The higher intercolumnar distance in PDCHD-HS with respect to PDCHD-S would involve a better quenching of the interchain decay route of the photoexcitations and therefore a stronger inhibition of the formation of charged states. Indeed the importance of the interchain distance in the dynamics of
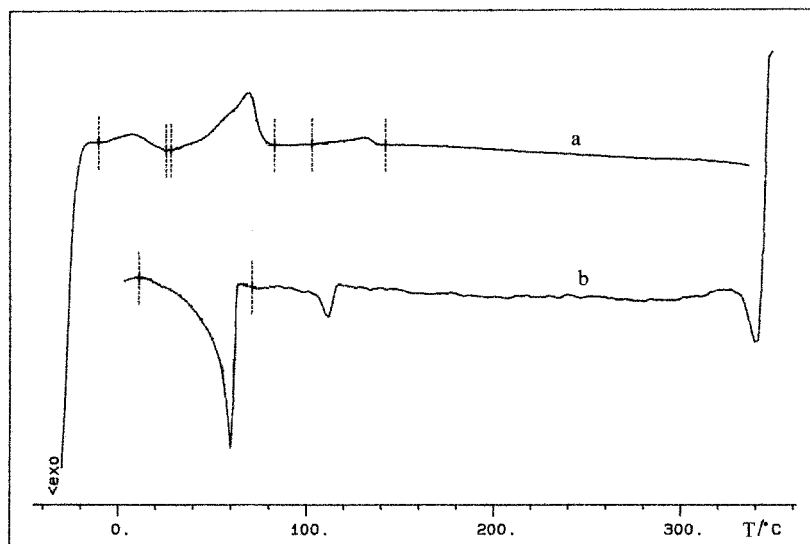

Figure 6. DSC thermograms of red PDCHD-HS: (*a*) heating; (*b*) cooling traces.

long-lived photoexcitations has been recently discussed for the blue forms of the alkyl substituted polymers with respect to the unsubstituted PDCHD [11, 17].

References

[1] CHEMLA, D. S., and ZYSS, J. (editors), 1987, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols 1 and 2 (Academic Press).

[2] TOWNSEND, P. D., BAKER, G. L., SCHLOTTER, N. E., KLAUSER, C. F., and ETEMAD, S., 1988, *Appl. Phys. Lett.*, **53**, 1782 and references therein.

[3] CRAVINO, A., MOGGIO, I., DELL'ERBA, C., COMORETTO, D., CUNIBERTI, C., DELLEPIANE, G., GIORGETTI, E., GRANDO, D., and SOTTINI, S., *Synth. Met* (in the press).

[4] TOWNSEND, P. D., JACKEL, J. L., BAKER, G. L., SHELBURNE III, J. A., and ETEMAD, S., 1989, *Appl. Phys. Lett.*, **55**, 1829.

[5] CHU, B., and XU, R., 1991, *Acc. chem. Res.*, **24**, 384.

[6] MÜLLER, M. A., and WEGNER, G., 1984, *Makromol. Chem.*, **185**, 1727.

[7] RAU, N. O., and SCHULTZ, R. C., 1984, *Makromol. Chem. Rapid Commun.*, **5,** 725; BLOOR, D., and WORBOYS, M. R., 1998, *J. mater. Chem.*, **8,** 903; KIM, W. H., KODALI, N. B., KUMAR, J., and TRIPATHY, S. K., 1994, *Macromolecules,* **27,** 1819.

[8] MATSUDA, H., NAKANISHI, H., HOSOMI, T., and KATO, M., 1988, *Macromolecules*, **21,** 1238.

[9] MATSUDA, H., NAKANISHI, H., MINAMI, N., and KATO, M., 1988, *Mol. Cryst. liq. Cryst.*, **160,** 241.

[10] DELLEPIANE, G., CUNIBERTI, C., PIAGGIO, P., MUSSO, G. F., COMORETTO, D., LANZANI, G., PIAGGI, A., and BORGHESI, A., 1992, *Synth. Met.*, **51,** 239; COMORETTO, D., CUNIBERTI, C., MUSSO, G. F., DELLEPIANE, G., SPERONI, F., BOTTA, C., and LUZZATI, S., 1994, *Phys. Rev. B*, **49,** 8059.

[11] COMORETTO, D., MOGGIO, I., CUNIBERTI, C., DELLEPIANE, G., GIARDINI, M. E., and BORGHESI, A., 1997, *Phys. Rev. B*, **56,** 10 264.

[12] CRAVINO, A., MOGGIO, I., DELL'ERBA, C., COMORETTO, D., CUNIBERTI, C., DELLEPIANE, G., GIORGETTI, E., GRANDO, D., MARGHERI, M., and SOTTINI, S., *Opt. Mater.* (submitted).

[13] WUDL, F., and BITLER, S. P., 1986, *J. Am. chem. Soc.*, **108,** 4685; KHOLER, B. E., and SCHILKE, D. E., 1987, *J. chem. Phys.*, **86,** 5214.

[14] WEISER, G., 1992, *Phys. Rev. B*, **45,** 14 076.

[15] COLOMBI, C., COMORETTO, D., CUNIBERTI, C., MUSSO, G. F., PIAGGIO, P., DELLEPIANE, G., NOVI, M., DELL'ERBA, C., and BOLOGNESI, A., 1996, *Macromol. Chem. Phys.*, **197,** 1241.

[16] LEVELUT, A. M., 1983, *J. Chim. phys.*, **80,** 149; DESTRADE, C., FOUCHER, P., GASPAROUX, H., NGUYEN, H. T., LEVELUT, A. M., and MALTHETE, J., 1984, *Mol. Cryst. liq. Cryst.*, **106,** 121.

[17] DELLEPIANE, G., COMORETTO, D., CUNIBERTI, C. (in preparation).