Solution spectroscopic properties of polyDCHD-HS: a novel highly soluble polydiacetylene

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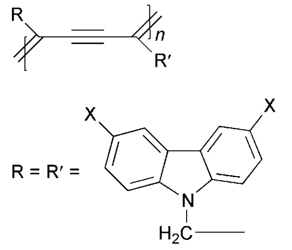
The solution properties of a novel soluble polydiacetylene, poly[1,6-bis(3,6-dihexadecyl-9*H*-carbazol-9-yl)hexa-2,4-diyne] (polyDCHD-HS), have been investigated by using UV–Vis absorption, fluorescence, and FT-Raman spectroscopies. The polymer gives rise to stable, brilliant red solutions in aromatic solvents and in chloroform at room temperature with no evidence of the colour transition to yellow that usually takes place by increasing the temperature with other soluble polydiacetylenes. A particular role appears to be played by benzene–polyDCHD-HS interactions, because in this solvent a very narrow and intense excitonic peak is observed at room temperature in the electronic spectrum. Interestingly, these solutions show also a well-resolved fluorescence spectrum, with a very small Stokes shift and a rather high quantum yield ($\cong 10^{-2}$). Furthermore, a very efficient transfer of the excitation energy from the carbazolyl substituents to the conjugated backbone is found to take place. On account of the observation that by increasing the temperature of the benzene solutions up to 75 °C the excitonic feature in both the absorption and the emission spectra undergoes fully reversible broadening and intensity reduction accompanied by the increase of the Stokes shift, without any dramatic colour change, it is likely that the rates of torsional motions in the polymer chains are thermally activated without modifying the average conjugation length of the polymer chains. FT-Raman measurements in benzene solutions in the same temperature range have confirmed this conclusion. The photophysical properties of polyDCHD-HS in benzene around 60 °C are quite similar to those observed in other aromatic solvents at room temperature. By heating up the red solutions in toluene or in chlorobenzene, no spectral shift is observed but only a limited increase of the absorption band broadening. All these findings strongly suggest that by the appropriate choice of the substituents it is possible to obtain stable solutions of the red form of polydiacetylenes.

Introduction

Carbazolyldiacetylenes with long alkyl chains in the 3 and 6 positions of the carbazolyl groups of the DCHD monomer (1,6-di-9*H*-carbazol-9-ylhexa-2,4-diyne) have been synthesized[1] and found to polymerize yielding the poly(carbazolyldiacetylene)s (PCDAs), soluble in common organic solvents. The alkyl-substituted polymers poly[1,6-bis(3,6-didodecyl-9*H*-carbazol-9-yl)hexa-2,4-diyne] (polyDCHD-S) and poly[1,6-bis(3,6-dihexadecyl-9*H*-carbazol-9-yl)hexa-2,4-diyne] (polyDCHD-HS), obtained by thermal polymerization of the bulk microcrystalline monomers still contain large amounts of monomer. Since both the polymers are readily soluble in various solvents, with the solubility of polyDCHD-HS substantially higher than that of polyDCHD-S, monomer-free polymers can be obtained by removing the residual monomers by the particular procedure whose details are described in ref. 1.

The blue forms of both polyDCHD-S and polyDCHD-HS, prepared by polymerizing the microcrystalline powders in pressed KBr pellets, have been found to have electronic and Raman spectra very similar to those of the unsubstituted intractable polyDCHD, thus showing that they have similar conjugation lengths.[2,3] In contrast, the nature of their photoexcitations is strongly affected by the substitution[2,3] and can be considered as an indication of the important role that the supramolecular structure of PCDAs plays in the relaxation kinetics from the excited states. This effect is even more evident in thin films of the alkyl-substituted polymers, either cast from solutions or obtained by embedding the polymer in a polyethylene matrix, which look red and show electronic and Raman spectra typical of the red polydiacetylenes (PDAs). In fact, photoexcitation studies carried out on these films revealed that only intramolecular triplet excitons were photogenerated, presumably because both the large distance between the conjugated backbones and the twisted chain conformation typical of red PDAs prevent the formation of charged species.



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

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

Interesting information on the red form of both these novel PCDAs has been derived from powder X-ray diffraction studies.[1] The results of these studies are consistent with the presence of two-dimensional hexagonal columnar structures that represent a new architecture for polydiacetylenes in the solid state. The columns in the hexagonal structures, with a diameter of 1.8 nm and a distance of 0.47 nm between the disk-like elements that form the columns, correspond to the PDA backbones with the carbazolyl substituents and to the length of the chain structural units, respectively. The distance between the column axes, which are kept together by the interdigitation of the long alkyl side chains on the carbazolyl rings, increases

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with the length of these chains from 3.25 nm for polyDCHD-S to 3.84 nm for polyDCHD-HS. It is noteworthy that the hexagonal structures have been found to exist in the whole temperature range explored, from about 20 up to 250 °C, the maximum temperature reached in the experiment. The low-temperature hexagonal structure of polyDCHD-S differs, however, from that of polyDCHD-HS as it possesses a lower correlation between the disc-type units inside the columns. In polyDCHD-HS, instead, some loss of the correlation occurs only above 85 °C.

On the basis of these results and also because solutions of our polymers are used for the preparation of thin films for waveguiding tests,[4] we planned to gain further information from the study of their solution properties. In this paper only the results for polyDCHD-HS will be reported because on account of its solid state properties and high solubility it seemed to be more interesting for a detailed characterization. The electronic absorption spectra of red solutions in several solvents will be presented and discussed. Of particular interest is the behaviour of the polymer in benzene solutions where the room temperature spectra exhibit at the wavelength of 535 nm excitonic features with a sharpness never observed before in solutions of red PDAs at this temperature. Moreover, well-resolved fluorescence spectra and emission intensities remarkably high for a polydiacetylene in solution have also been observed. By increasing the temperature these features are gradually lost, but without any evidence of the transition from the red to the yellow form, as usually happens for other PDA solutions.[5–7]

Experimental

The monomer DCHD-HS, synthesized as described in a previous paper,[1] was bulk-polymerized thermally at 75 °C (10 °C below its melting point). The unrefined polyDCHD-HS, soluble in several organic solvents, had to be purified in order to fully extract the residual monomer and short oligomers that could interfere with the measurements of its properties. To this end we applied a particular purification procedure whose details are fully described in ref. 1. From the weight average molecular weight (M_w) determined by static light scattering,[8] an average number of repeat units in the range 125–130 was evaluated for the monomer-free polymer.

All the solvents used were spectroscopic grade commercial products from Merck.

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer and on a Kontron UVIKON 941 instrument for measurements as a function of temperature. The linewidth (FWHH) of the exciton peak was measured and, in spectra at temperatures where this peak was not well resolved from the exciton vibronic replica, a symmetric shape of the absorption band relative to its low-energy half was conventionally assumed in the deconvolution procedure.

Emission spectra were obtained with a Perkin-Elmer MPF-44A spectrofluorometer. The spectra were corrected for the wavelength dependence of the detector response, as well as for inner filter and re-absorption effects when necessary. Emission intensities from excitation at different wavelengths were normalized at a constant value of the source intensity.

The temperature dependence of the absorption and emission spectra was studied in the range from 20 to 75 °C.

The Raman spectra were recorded by using a Bruker-FT spectrometer Model FRS 100 working with a Nd-YAG laser (1064 nm). Benzene solutions in the temperature range from 25 to 60 °C were studied by means of a home-made thermostatic unit.

Results and discussion

PolyDCHD-HS has been found to be highly soluble in aromatic solvents, such as benzene, toluene, chloro- and *o*-dichlorobenzene, *o*-, *m*-, or *p*-xylene, and in chloroform. It is, however, sparingly soluble in other organic solvents, like dichloromethane and tetrahydrofuran, and fully insoluble in the more polar *N*,*N*-dimethylformamide and dimethyl sulfoxide solvents. The polymer forms red solutions in all the solvents considered, independently of its degree of solubility. This finding contrasts with the formation of yellow solutions usually found for other soluble PDAs in good solvents[5–7] as well as with the current opinion that red solutions always appear as a result of aggregation.[6] Indeed, while dilute red solutions of polyDCHD-HS in aromatic solvents do not give any evidence of aggregation, aggregated red phases have been observed either in these solvents at high concentrations or in the solvents where the polymer solubility is low. To distinguish true solutions from aggregated ones, the effects on the UV–Vis absorption spectra of concentration, time and filtration have been examined. A comparison of the results obtained for polyDCHD-HS with those from dilute red solutions of poly(4-BCMU)† ($R = R' = -(CH_2)_4-OCONHCH_2COOC_4H_9$) in toluene has also been made.

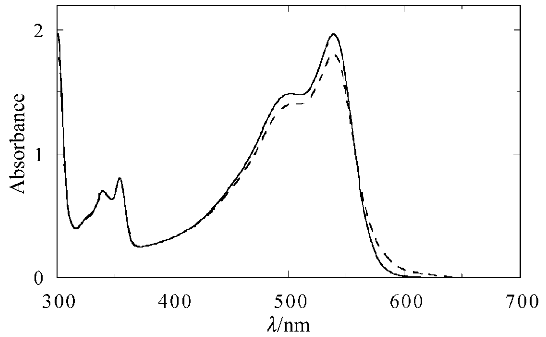

Fig. 1 Room-temperature absorption spectrum of polyDCHD-HS in toluene; fresh solution (full line), after two months (dashed line).

In Fig. 1, the room-temperature electronic absorption spectrum of monomer-free polyDCHD-HS in toluene is presented. The purple–red solution gives rise to an evident excitonic peak at 538 nm (2.30 eV) followed by its unresolved vibronic features around 500 nm (2.48 eV). Notice the low absorption of the doublet around 350 nm (3.54 eV), due to the carbazolyl substituents, relative to that of the main chain peaks that is characteristic of the absence of any contribution from the monomer. In the same figure is also shown how the spectrum of the solution changed after two months under laboratory conditions: a small intensity increase in the high wavelength tail has taken place at the expense of the excitonic absorbance without shift in the absorption maximum. No further change was observed with time if the solution was kept in the dark. Also filtration through a 0.2 µm PTFE filter leaves the absorbance profile unchanged. Similar spectral behaviour has been observed for the xylenes and the chloro-substituted benzenes.

In contrast, substantially different results have been found in solvents like tetrahydrofuran (THF) and dichloromethane (DCM). As shown in Fig. 2, fresh solutions in THF are clear and exhibit absorption spectra similar to those observed in toluene, though with a less evident excitonic peak at 539 nm. However, after 15 days under laboratory conditions the spectrum is modified, showing a small shoulder around 610 nm, while the solution appears slightly opalescent. After filtration through a 0.2 µm-membrane filter, an orange liquid is left that shows a blue-shifted broad band around 495 nm with strongly reduced absorbance. A deep-red solid remains on the membrane. Dilute red solutions of polyDCHD-HS in DCM behave similarly but, after filtration only a pale yellow liquid is left and practically the whole red solid remains on the filter.

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† 4-BCMU = 8,25-diaza-5,10,23,28-tetraoxa-6,9,24,27-tetraoxodotriaconta-15,17-diyne.

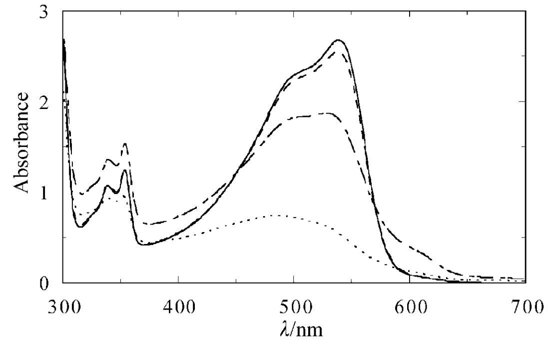

Fig. 2 Room-temperature absorption spectrum of polyDCHD-HS in tetrahydrofuran; fresh solution (full line); after 5 days (dashed line), 15 days (dashed-dotted line); after filtration (dotted line).

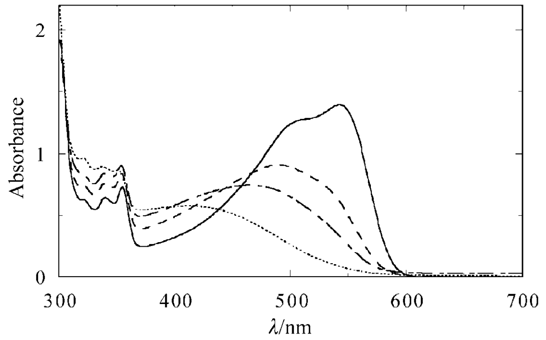

Fig. 3 Room-temperature absorption spectrum of polyDCHD-HS in carbon tetrachloride; fresh solution (full line); after 6 days (dashed line), 10 days (dashed-dotted line), 2 months (dotted line).

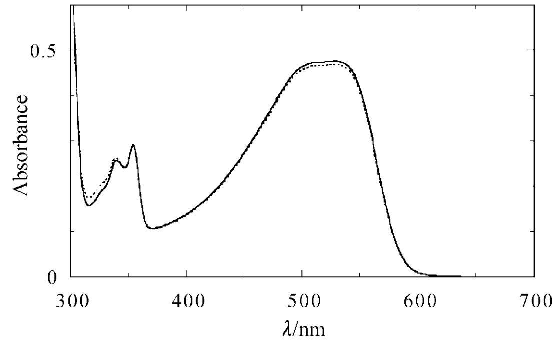

Fig. 4 Absorption spectra of polyDCHD-HS in chloroform at 20 °C; fresh solution (full line), after filtration through a 0.2 µm membrane (dotted line).

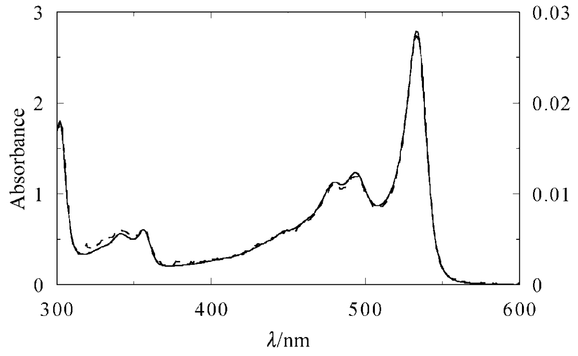

Fig. 5 Absorption spectra of polyDCHD-HS in benzene at 20 °C. Polymer concentration: 5.5×10^{-5} M (full line, left scale), 5×10^{-7} M (dashed line, right scale).

In carbon tetrachloride, where the polymer dissolves quite well, the excitonic peak of fresh solutions falls at 542 nm, but a relevant and fast chromatic change takes place and the solution colour changes from red to deep orange and then to yellow as shown by the time evolution of the electronic spectra in Fig. 3. After only 10 days in the laboratory conditions the dramatic blue-shift and the broadening of the main band are clearly evident. The changes become even more evident after 60 days, but in this case the filtration procedure had no effect on the solution. Moreover, a fresh solution kept in the dark did not undergo these ageing effects, thus showing that they must be related to a damaging process taking place in the polymer chains due to the combined action of oxygen and light. Notice also the concomitant relative increase in the absorbance of the carbazole doublet, presumably due to the contribution of short oligomers generated in the photodegradation process. Indeed, the photochemical degradation of conjugated systems in carbon tetrachloride, accompanied also by photooxidation in the presence of dissolved air, is a well-known process.[9] Moreover, the presence of a C=O peak at 1740 $\mathrm{cm^{-1}}$ and of an OH band at 3420 $\mathrm{cm^{-1}}$ detected in the IR spectra of the photodegraded samples of polyDCHD-HS[10] confirms these observations.

As illustrated in Fig. 4, in chloroform in which the polymer is highly soluble red solutions are also formed. The spectral profile shows in fact a broad maximum at 538 nm and poorly resolved vibronic peaks that do not change in the concentration range $\approx 10^{-7}$–10^{-4} (mol of repeat units $\mathrm{l^{-1}}$) on prolonged storage or on filtration through a 0.2 µm membrane filter.

In Fig. 5 the electronic absorption spectra of two red solutions of polyDCHD-HS in benzene are shown. These spectra, of two dilute solutions that differ in concentration by two orders of magnitude, are time independent and what is most interesting is that they show an excitonic peak of remarkable sharpness (FWHM = 532 $\mathrm{cm^{-1}}$) and height. The large ratio of the intensity of the purely excitonic transition at 534 nm (2.32 eV) relative to the vibronic replica at 494 (2.51 eV) and 479.5 nm (2.57 eV) indicates that a small electron–phonon coupling is present. Spectra of this type have been observed in PDAs only at low temperature in single crystals[11] or in oligomers in glassy solvents[12] and at room temperature for poly(4-BCMU) chains diluted in their monomer matrix.[13] It is worth noting in Fig. 5 that the two spectra, which represent solutions with concentration 5.0×10^{-7} and 5.5×10^{-5} (mol of repeat units $\mathrm{l^{-1}}$), respectively, are fully superimposed. Filtration of the red solutions through 0.2 µm filters does not affect the spectral profile or the absorbance of the polymer. These results lead us to believe that also in these solutions no significant interchain interactions take place. The vibronic bands, shifted by 1516 and 2129 $\mathrm{cm^{-1}}$ from the excitonic peak, correspond to the excited state carbon–carbon double and triple bond stretching modes, respectively. Data from FT-Raman scattering analysis of polyDCHD-HS in the same solvent (discussed later) have provided the corresponding ground state vibrational frequencies of 1519 and 2118 $\mathrm{cm^{-1}}$, close to the values derived from the absorption spectra. The similarity of these frequencies obtained by the two techniques further confirms that the geometry of the excited polymer is not substantially different from that in the ground state. The absence of broadening effects observed in benzene solutions suggests that the intramolecular motions in the polydiacetylene chains are hindered by interactions with the solvent and that homogeneously ordered conformations, characterized by a narrow distribution of conjugation lengths, are consequently stabilized.

In order to gain more information on the polyDCHD-HS–benzene system, we have studied the temperature dependence of the absorption spectrum. The results at 25, 40 and 60 °C, compared in Fig. 6, show that by increasing the temperature no shift of the excitonic peak is observed, while appreciable changes in both the spectral broadening and the electron–phonon coupling take place. It is a relevant fact that, unlike other soluble PDAs whose solutions become yellow upon increasing the temperature owing to a rod-to-coil transition,[5–7]

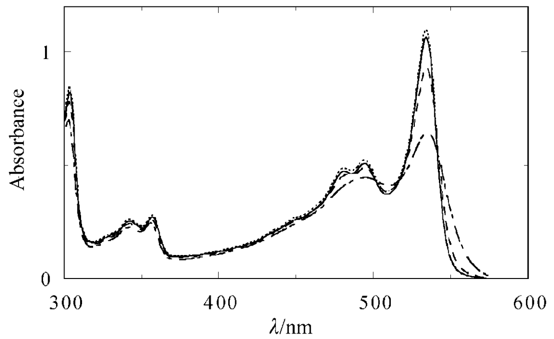

Fig. 6 Temperature dependence of the absorption spectrum of polyDCHD-HS in benzene at $T = 25$ (full line), 40 (dashed line), and 60 °C (dashed-dotted line); spectrum after returning to 25 °C (dotted line).

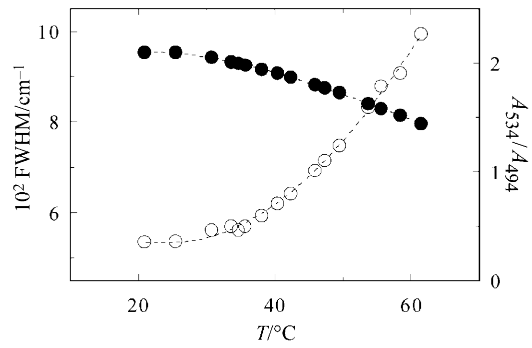

Fig. 7 Temperature dependence of the width, FWHM (empty circles) of the excitonic peak and of the ratio of its absorbance relative to its nearest vibronic band, A_{534}/A_{494} (filled circles).

the polyDCHD-HS–benzene solutions change their colour from orange–red to deep red. This change in colour is due to the broadening of the main band that causes a small increase of absorbance at the high wavelength tail of the spectrum, which at high temperature becomes similar to that in toluene at room temperature as shown in Fig. 1. The temperature dependence of the linewidth of the excitonic peak, FWHM, and of the ratio A_{534}/A_{494} of the exciton to the nearest vibronic replica are illustrated in Fig. 7, where it is evident that both these quantities undergo substantial changes only at temperatures higher than about 35 °C. We want to stress at this point that these effects are completely reversible as may be observed in Fig. 6, where the spectrum recorded at 25 °C after the heating process is also presented. Indeed, the small absorbance increase that occurs in the whole spectral range relative to the original spectrum at the same temperature can be reasonably attributed to some solvent evaporation, notwithstanding the precautions taken to avoid it, during the heating process. That the observed temperature effects do not derive from reduction of the conjugation length has been confirmed by the results of FT-Raman measurements on benzene solutions of polyDCHD-HS in the range from 30 up to 60 °C. In fact, as may be seen in Fig. 8, the Raman bands of the conjugation dependent C≡C and C=C modes that at 25 °C peak at 2118 and 1519 cm^{-1}, respectively, appear to undergo only reversible marginal shifts towards lower frequencies that, however, do not go beyond the limits of the experimental resolution (2 cm^{-1}) when the temperature reaches 60 °C. Note that in order to get appreciably good signals from the polymer solutions in the FT-Raman spectra we had to use concentrations in the range from 15 to 20 mg ml^{-1}, *i.e.* much larger than those employed in the other spectroscopic measurements. We believe that this concentration difference should not impair the kind of information that has been derived from the Raman experiments because also in these conditions no phase separation was observed upon prolonged storage.

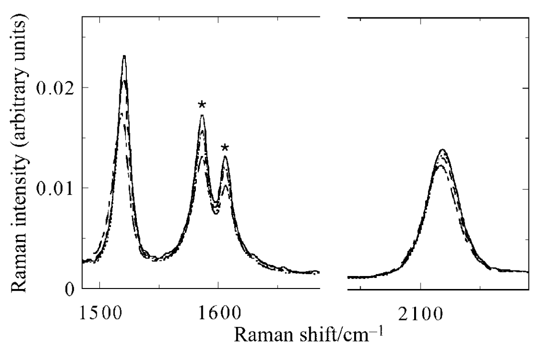

Fig. 8 FT-Raman spectra of a benzene solution of polyDCHD-HS at different temperatures in the regions of the C≡C and C=C stretching modes: $T = 30$ (full line), 40 (dashed line), 60 °C (dashed-dotted line); spectrum after returning to 30 °C (dotted line). Benzene lines (*).

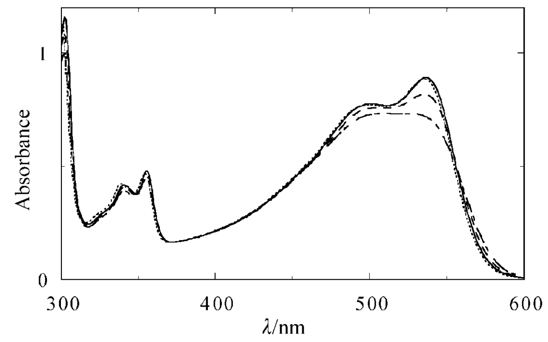

Fig. 9 Temperature dependence of the absorption spectrum of polyDCHD-HS in toluene: $T = 25$ (full line), 40 (dashed line), 77 °C (dashed-dotted line); spectrum after returning to 25 °C (dotted line).

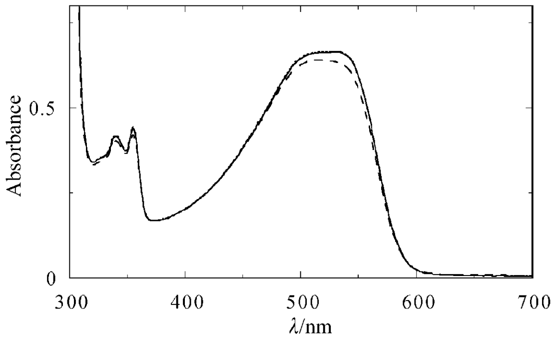

Fig. 10 Absorption spectra of polyDCHD-HS in chloroform at different temperatures: $T = 25$ (full line), 55 °C (dashed line); spectrum after returning to 25 °C (dotted line).

In order to check whether the colour transition from red to yellow, not observed in benzene, could instead take place in toluene solutions of polyDCHD-HS, which at room temperature show absorption spectra similar to those in benzene around 60 °C, we have also studied the temperature dependence of the absorption spectrum in toluene up to 77 °C. Upon increasing the temperature, behaviour qualitatively similar to that seen in benzene was observed, *i.e.* a gradual increase of the excitonic band broadening and a reduction of the relative intensities of the excitonic to vibronic peaks without evidence of spectral shift. The solution maintains its intense red colour, as may be seen in Fig. 9 where some of the spectra at different temperatures are shown, and the temperature-induced changes are fully reversible. Also in other aromatic solvents, like chlorobenzene or xylenes, polyDCHD-HS forms red solutions at room temperature that upon increasing the temperature behave similarly to those in toluene. Furthermore, as illustrated in Fig. 10, where the absorption spectra of a chloroform solution at 25 and 55 °C are shown together with the spectrum

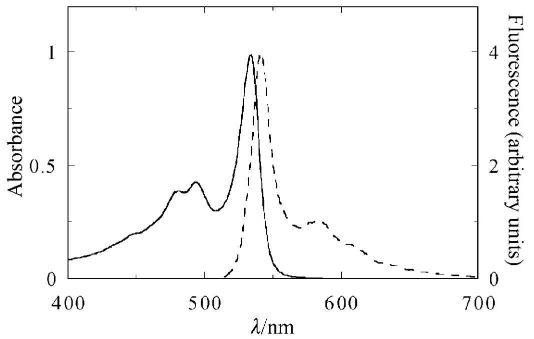

Fig. 11 Comparison of the fluorescence emission spectrum with the electronic absorption in the visible spectral region of polyDCHD-HS in benzene at 20 °C.

recorded after slow cooling of the solution to 25 °C, also in this solvent polyDCHD-HS maintains the red form over the whole temperature range explored.

It is noteworthy that the formation of stable red solutions in chloroform at room temperature has been more recently reported for another polydiacetylene, carrying a rigid pyrimidyl ring on one side and the same flexible side group as in 4-BCMU on the other one.[14]

In order to evaluate how different the behaviour of poly(4-BCMU) in solution could be from that reported for polyDCHD-HS in the present paper, we have recorded the absorption spectra of its dilute toluene solutions starting with the high-temperature yellow form and slowly cooling them down to room temperature. In all the solutions examined, after the evident thermochromic transition to the red colour, we always observed at room temperature phase separation with lag-times dependent on the polymer concentration. Also in solutions as dilute as ≈10^{-7} M (mol of structural units l^{-1}) phase separation was observed after a few days at room temperature, presumably because of a high molecular weight of the sample at our disposal. Indeed, true red solutions of poly(4-BCMU) have been reported to exist only at extremely small concentrations.[15,16]

As pointed out in the introduction, the fluorescence emission of polyDCHD-HS in benzene at room temperature is remarkably higher than usually found in other PDA solutions.[7] The fluorescence spectrum at 20 °C, obtained by excitation at 480 nm of a dilute benzene solution, is shown in Fig. 11 and compared with the low-energy bands of the absorption spectrum. The quasi-mirror image and the very small Stokes shift (about 200 cm^{-1}) indicate that the geometry of the polymer is not strongly affected by the photoexcitation. This result and the accompanying relevant fluorescence intensity suggest that the exciton is the emitting state thus excluding an extrinsic origin of the emission. From the resolved structure of the emission profile we have derived the values of 1403 and 2094 cm^{-1} for the ground state carbon–carbon double and triple bond stretching frequencies, respectively. The fact that these frequencies are significantly lower than the values from Raman scattering reported above, and so in particular for the double bond that is carrying the substituents, suggests that polymer–solvent interactions are involved in the relaxation process from the excited state.

In order to evaluate the fluorescence quantum yield (φ_p) of polyDCHD-HS in benzene, the areas of the corrected emission spectra of the polymer in dilute solutions (A_p) were compared with that (A_r) from a reference molecule. A dilute solution of Rhodamine B (RhB) in poly(methyl methacrylate) (PMMA), whose quantum yield φ_r is 0.80, was used. The value of $\varphi_p = 0.012$ was thus obtained at 25 °C from the relationship in eqn. (1) where I_p and I_r indicate the amounts of incident

$$\varphi_p = \varphi_r \frac{A_p}{A_r} \frac{I_r}{I_p} \left(\frac{n}{n_{PMMA}}\right)^2 \quad (1)$$

light absorbed by the polyDCHD-HS and the RhB solutions, respectively, and the last term accounts for the different refractive index of the two solvent media.[9]

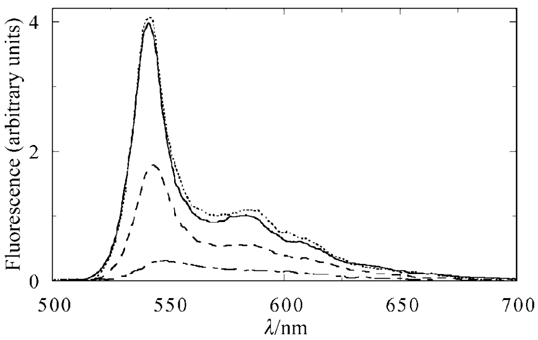

Fig. 12 Fluorescence spectrum of polyDCHD-HS in benzene at $T = 25$ (full line); at 40 (dashed line) and at 60 °C (dashed-dotted line); spectrum after returning to $T = 25$ °C after heating up to 75 °C (dotted line).

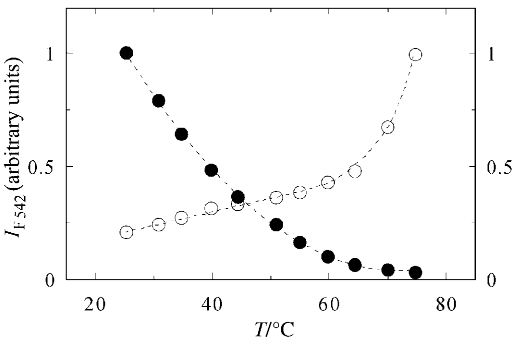

Fig. 13 Temperature dependence of the fluorescence intensity maximum, I_{max} (filled circles) and of the Stokes shift, $\Delta\nu$ (empty circles) of polyDCHD-HS in benzene.

The value φ_p found is about one order of magnitude higher than the largest value reported for other PDA solutions at room temperature.[7] When the temperature is increased, the fluorescence drops to much lower values as illustrated in Fig. 12, where the emission spectra at 25, 40, and 60 °C are reported. The detailed temperature dependence of both the relative fluorescence intensity and the Stokes shift is shown in Fig. 13, where it can be seen that at 75 °C less than 5% of the initial fluorescence intensity is retained and that at the same time the Stokes shift is increased from 200 cm^{-1} up to about 1000 cm^{-1}. As already remarked for the absorption spectra, the temperature effects on fluorescence also disappear when the solution is taken back to 25 °C (see dotted curve in Fig. 12). These results confirm that temperature-activated torsional motions have to be considered responsible for the observed thermal effects since fluorescence quenching and increased Stokes shift are well correlated with intramolecular mobility.[17]

The fluorescence data so far reported refer to excitation of polyDCHD-HS at $\lambda_{ex} = 480$ nm, the wavelength corresponding to the higher-energy vibronic band in the absorption spectrum. However, no change in the shape or the intensity of the emission spectrum has been observed when using other excitation wavelengths, as shown in Fig. 14 where the corrected fluorescence intensities measured at 25 °C at the maxima of the two main peaks in the emission spectrum ($\lambda = 542$ and 487 nm) are plotted against the absorbance values at the excitation wavelengths of 480, 450 and 334 nm, respectively. If fluorescence emission intensities independent of the excitation energy are expected for $\lambda_{ex} = 450$ and 480 nm in view of their vibronic origin, then also worthy of note is the fact that when excitation occurs on the carbazole ring ($\lambda_{ex} = 334$ nm) the fluorescence intensity follows the same curves as the results obtained with the other two wavelengths. Indeed, this result proves that an

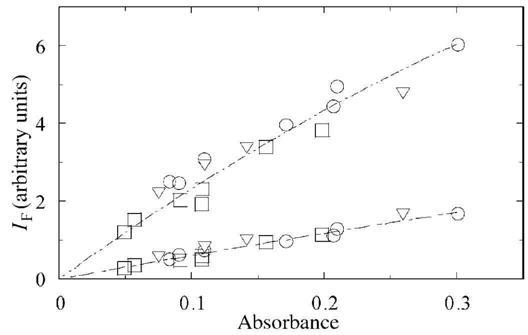

Fig. 14 Fluorescence intensities of polyDCHD-HS in benzene at 25 °C measured at 542 nm (upper curve) and at 587 nm (lower curve) *vs.* absorbance at the excitation wavelengths: 480 nm (circles), 450 nm (squares), 334 nm (triangles).

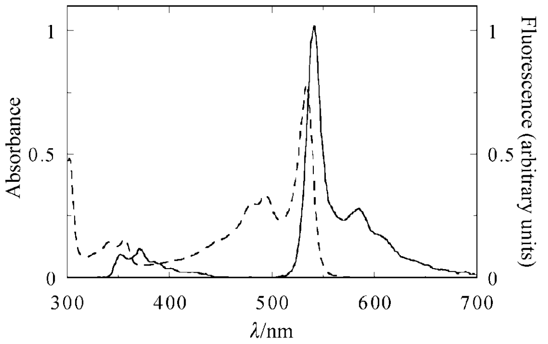

Fig. 15 Absorption (dashed line) and fluorescence (full line) spectra of polyDCHD-HS in benzene at 25 °C for $\lambda_{ex} = 334$ nm. The emission spectrum in the range 340–450 nm is due to the carbazolyl groups.

efficient transfer of the excitation energy takes place from the aromatic substituents to the conjugated polymer backbone. In order to illustrate this effect we refer to the complete fluorescence spectrum in Fig. 15 derived from the excitation at 334 nm where, in addition to the polymer spectrum, the emission of the carbazolyl substituents around 370 nm is reported. In order to quantify the amount of the energy transfer, we have used as reference compound the monomer DCHD-HS whose fluorescence quantum yield in benzene, $(\varphi_{cz})_m$, has been found to equal 0.27. From the corrected areas of the emission bands of the carbazolyl groups of the monomer and of the polymer, respectively, the following value of the quenching ratio has

$$(\varphi_{cz})_p/(\varphi_{cz})_m = 0.019$$

been obtained. Hence, the fluorescence quantum yield of the polyDCHD-HS carbazolyl substituents, $(\varphi_{cz})_p$, amounts to only *ca.* 0.05.

An efficiency of around 98% is inferred for excitation energy transfer from the carbazolyl substituents to the polymer skeleton from the value of the quenching ratio reported above. Indeed, the overlap of the emission spectrum of the carbazolyl groups on the absorption spectrum of the conjugated backbone observed in Fig. 15 allows us to conclude that of the total emission of the polymer when excited at 334 nm about 65% derives from energy transfer, while the residual 35% is due to the direct excitation of the polymer backbone. We want at this point to remark that also in a photoinduced absorption study carried out on the unsubstituted polyDCHD in the solid state[18] we observed the generation of identical intragap absorptions by laser pumping into the absorption bands of either the carbazolyl substituents or the conjugated backbone, in full agreement with other literature data from measurements of free carrier yields on the same polymer.[19,20] However, the presence of an energy transfer process much faster than the charge transfer found to represent the main route for the efficient quenching of the carbazolyl group fluorescence in the same polymer[20] gives support to our interpretation of the results of excitation of the carbazolyl groups of polyDCHD-HS in benzene solution.

Conclusions

The spectroscopic properties of polyDCHD-HS solutions are unique when compared with the behaviour of other soluble PDAs. Among the several soluble PDAs so far reported in the literature the most extensive solution studies are described for poly(4-BCMU).[5–7,21,22] Although the presence in this polymer of urethane groups in the substituents may affect its organization in solution (because of the possible formation of intra- and intermolecular hydrogen bonds, and so particularly in low polarity solvents) other soluble PDAs without urethane substituents, like PTS12 ($R = R' = –(CH_2)_4OSO_2C_6H_4CH_3$)[6] and 9-PA ($R = R' = –(CH_2)_9OCOCH_2C_6H_5$),[7] have also been found to behave similarly, thus leading to the conclusion that the side groups do not affect significantly the solution behaviour of the soluble polydiacetylenes. All these polymers exhibit a yellow colour in good solvents, like for instance in chloroform at room temperature or in toluene at high temperature. By cooling the toluene solutions down to room temperature, or by adding a very poor solvent to those in chloroform, a yellow to red thermochromic transition is observed, usually followed by phase separation with lag-times depending on both the molecular weight of the polymer and the solution concentration. As previously stated, it has been reported that only at extremely small concentrations may red solutions of poly(4-BCMU) be observed. Quite different behaviour is exhibited by polyDCHD-HS whose solubility at room temperature (driven by the two long alkyl chains on each carbazolyl substituent) is large in aromatic solvents, very low in solvents of medium polarity, and null (also at high temperature) in the highly polar ones.

We believe the particular behaviour shown by polyDCHD-HS in solution to be derived from the coupling of its particular chemical structure with the rather low degree of polymerization of the chains. It is noteworthy that in all solvents in which our polymer is soluble, red solutions are observed independently of the temperature. As already pointed out previously, aromatic solvents are the most suitable to get stable polyDCHD-HS solutions showing absorption spectra with clearly evident excitonic peaks over the range from 534 to 538 nm, but it is noteworthy that only in benzene is this peak very intense and extremely narrow at room temperature. This feature, observed previously in red solid solutions of single poly(4-BCMU) chains diluted in a single crystal monomer matrix at low temperature[13] and in one PDA oligomer dissolved in 2-MeTHF at 77 K,[11] appears to be related to the intramolecular order of the conjugated backbone. On the other hand, the room-temperature fluorescence spectrum of polyDCHD-HS in benzene (well resolved into an intense $S_1 \rightarrow S_0$ peak with a small Stokes shift and weaker associated vibronic features) represents behaviour that may be considered typical of a high degree of order in the conjugated chains.[17] By increasing the temperature both the absorption and emission spectra show broadening effects and a decrease in intensity that are more evident for the purely excitonic peak, and, at the same time, the Stokes shift increases from 200 cm^{-1} at 25 °C to 1000 cm^{-1} at 74 °C. That this behaviour cannot originate from reduced conjugation length is indicated by the observation that neither the position of the excitonic peak in the absorption spectra nor the FT-Raman bands associated with the triple and double bond stretching modes show appreciable changes when the temperature is increased. We believe it to be due rather to the increased effects of torsional motions that reduce the correlation between the repeat units within the rigid polymeric structure.[17,23] The fact that in all the other solvents in which the polymer dissolves well (as shown here for toluene and chloroform) no transition from the red extended chain to the yellow coiled conformation can be induced by increasing the temperature shows that the particular chemical structure of the chain substituents and their interactions with the solvent media keep the conjugated chains in the extended, though torsionally distorted, chain conformation proposed for the red polydiacetylenes.[5,22]

The formation of red solutions in chloroform, stable at room temperature over a wide range of concentrations, which has also been found for another polydiacetylene,[14] has been considered by the authors as proof that single chains of PDAs in the red conformation may be solubilized by the appropriate choice of the substituents.

We believe further that a limited chain contour length of the polymer (evaluated for polyDCHD-HS as ≈62 nm from the average number of structural units) can play an important role in determining the stability of the red form in solution. It is likely that the preferential interactions of the polymer substituents with aromatic solvents, and particularly with benzene molecules that do not have any dipole, act as the key factor in maintaining the highly ordered intrachain structure in these solvents.

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