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Solid state films of two urethane polycarbazoldiacetylenes with methylene spacers between the urethane moiety and the diacetylene backbone

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Summary

Two urethane carbazolyldiacetylenes, 6-(N-Carbazolyl)hexa-2,4-diyn-1-ol-1acetate buthyl urethane and 9-(N-carbazolyl)nona-5,7-diyn-1-ol-acetate buthyl urethane (hereafter named CHBU and CNBU, respectively), which present methylene spacers with different length between the urethane and diacetylene moieties, have been synthesized in order to obtain a conjugated polymer for non linear optics. The UV polymerization is studied by UV-Vis spectroscopy in polymeric films prepared by mechanical alignment of the monomer powder on hot substrates followed by UV polymerization. PolyCHBU films containing residual monomer exhibit thermochromic properties from blue to red form while no spectroscopic changes are observed for the polyCNBU films upon temperature. For polyCHBU, both blue and red films present also optical dichroism as observed by polarized UV-Vis spectroscopy, polarized microscopy and AFM.

Introduction

Since the discovery in 1969 by G. Wegner [1] that diacetylene monomers could polymerize in very colored polymers, the interest in the study of polydiacetylenes (PDAs) has increased due to the following properties which make PDA unique conjugated systems: 1) they can be obtained by topochemical polymerization of their corresponding monomers (RC≡C-C≡CR’). This solid state polymerization allows preparing polymer single crystals, thin films or polycrystalline powders by irradiation or by heating the corresponding monomer in single crystals, thin films or polycrystalline powders. Neither catalyst nor solvents, as in usual chemical polymerizations, are necessary thus purification consists only in the extraction of residual monomer or oligomers which exhibit a higher solubility with respect to the polymer. 2) The physicochemical properties of the polymers can be defined by a proper choice of the lateral substituents R, R’. 3) The extended electronic delocalization through the conjugated chain gives high third order susceptibilities, which can be enhanced by the substitution with high polarizable group and by orientation.

Among the most studied PDAs, two classes are to be mentioned. First, the carbazolyl-substituted PDAs for which at least one substituent is the highly polarizable carbazole directly or undirectly bonded to the diacetylenic backbone. As an example, poly(di-N-carbazolyl-2,4-hexadyine) (polyDCHD) single crystals and epitaxial films present one of the higher $\chi^{(3)}$ measured in PDAs [2, 3]. The second class corresponds to the urethane substituted PDAs. One of the most reported urethane PDA is poly4BCMU, R=R'= $-(CH_2)_4OCONHCH_2COOC_4H_9$. For this polymer, good values for the non linear response have been obtained. Moreover, it presents thermochromic and solvatochromic properties which make it candidate for sensoring devices [4-6]. With the purpose to obtaining a high non linear optical polymer which could resemble the aforementioned properties for the two PDAs classes, we synthesized two diacetylenes bearing as substituents the polarizable carbazolyl ring and an urethane group and with mehylene spacers of different length between the urethane and diacetylene moeities. In this paper we report on the synthesis of the two diacetylenes and the preparation of oriented films by mechanical alignment of the monomer powder.

Experimental

Materials and instruments

Melting points were determined on an Electrothermal apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Brücker AC-200F spectrometer (200 MHz), using TMS as internal standard. The chemical shifts are reported as δ in ppm. IR spectra were obtained on a Bomem MB 155 FT-IR spectrometer in thin films deposited on KBr pellets. UV polymerization was performed in ambient condition with a MineralLight UV lamp (λexc=254 nm, 6W). The DSC analysis was performed on a Perkin-Elmer DSC7 apparatus at a scanning rate of 10 °C/min. Polarized optical microscopy was carried out on an Olympus microscope coupled with image analyzer Optomex and Mettler heating plate at a scanning rate of 5 °C/min. UV-Vis absorption spectra were realized with a Shimadzu 2401 spectrophotometer equipped with polarizer. The optical dichroism R is obtained as $\frac{A_{//}}{A_{\perp}}$, where $A_{//}$ and $A_{\perp}$ are the absorbance at the excitonic peak with polarization parallel and perpendicular with respect to the aligning direction. Molecular models were obtained by using the ACD Labs ChemSketch program. Corning glass and SPI quartz slides were used as substrates. The film morphologies were studied at ambient conditions with an AFM microscope Nanoscope III Dimension^{TM} 3100 from Digital Instruments. Films were analyzed using the tapping mode at scanning rates of 0.3 Hz. The roughness of the surface topography (R_q) is given by the root mean square average (RMS) of height deviation and is taken from the mean data plane, and expressed as: $R_q = [1/N\ \Sigma(Z_i)^2]^{1/2}$, where Z_i is the current Z value, and N is the number of points within the box.

Monomer synthesis

The synthetic route to obtain the two diacetylenes is depicted in Scheme 1. 3-bromoprop-2-yin-1-ol and 6-bromohex-5-yin-1-ol were prepared according to literature [7]. Carbazole and 4-butylisocynatoacetate were commercial products.

3-(N-carbazolyl)prop-1-yin (1). In a three-necked flask, under Ar atmosphere, 10.06 g (60.0 mmol) of degassed carbazole was dissolved in 70 ml of fresh-distilled THF. After lowering the temperature to 0°C, 38 ml (60.8 mmol) of a 1.6 mol/l hexane solution of BuLi were added drop-wise. After 30 min of magnetic agitation, the mixture was allowed to reach room temperature and then 4.6 ml (60.9 mmol) of 3-bromopropyne was added drop-wise. After one night under agitation at room temperature, THF is evaporated. A brownish product is obtained, washed several times with heptane and then crystallized in CH_2Cl_2/heptane. Orange-brownish crystals (Yield 71 %). M.p.: 104-106 °C. ^{1}H RMN ($CDCl_3$): 8.09 (d, 2H); 7.48 (m, 4H); 7.28 (m, 2H); 5.06 (d, 2H, N-CH_2); 2.27 (t, 1H, ≡CH); E.A. %. Calculated C: 87.78; H: 5.40; N: 6.82. Experimental: C: 87.73; H: 5.45; N: 6.89.

6-(N-carbazolyl)hexa-2,4-diyn-1-ol (2). In a two-necked flask, under Ar atmosphere, 2.56 g (12.4 mmol) of 3-(N-carbazolyl)prop-1-yne, 0.092 g of $NH_2OH{\cdot}HCl$, 0.163 g (1.65 mmol) of CuCl, 2.1 ml of water, 2.1 ml (37.1 mmol) of ethylamine (70% w/V), and 11.9 ml of DMF were introduced. After dissolution, a solution of 2.60 g (19.2 mmol) of 3-bromoprop-2-yin-1-ol in 0.60 ml of DMF was added drop-wise. The reaction is strongly exothermic thus the temperature is controlled and kept <40°C. After 1h30 min, the reaction is allowed to reach room temperature and then 5 g of NaOH in 50 ml of water is added. The organic phase is separated by extraction with ethyl ether, washed first with HCl 0.6M and then with a saturated solution of $NaHCO_3$ and finally dried on Na_2SO_4. After evaporation of the solvent, the residue is washed with hexane and then crystallized with CH_2Cl_2/hexane.

White crystals (Yield 71 %). M.p.: 119-120 °C. ^{1}H RMN (acetone-d6): 8.13 (d, 2H); 7.63 (d, 2H); 7.50 (t, 2H); 7.25 (t, 2H); 5.41 (s, 2H, CH_2-N); 4.31 (m, 1H, OH); 4.20 (d, 2H, CH_2OH); E.A. %. Calculated C: 83.37; H: 5.05; N: 5.40. Experimental: C: 82.31; H: 4.99; N: 5.02.

9-(N-carbazolyl)nona-5,7-diyn-1-ol (3). The same procedure and reactives molar proportion to obtain **2** was used to obtain **3**, starting from 6-bromohex-5-yin-1-ol. White-beige crystals (Yield 45 %). M.p.: 103-105 °C. ^{1}H RMN (acetone-d6): 8.12 (d, 2H); 7.63 (d, 2H); 7.49 (t, 2H); 7.24 (t, 2H); 5.37 (s, 2H, CH_2-N); 3.48 (t, 3H, CH_2OH+OH); 2.26 (t, 2H, ≡C-CH_2); 1.51 (m, 4H, $(CH_2)_2$); E.A. %. Calculated C: 83.69; H: 6.35; N: 4.65. Experimental: C: 83.91; H: 6.53; N: 4.56.

6-(N-carbazolyl)hexa-2,4-diyn-1-ol-acetate of butyl urethane (4, CHBU). In a two-necked flask, under Ar atmosphere and in dark, 0.43 g (1.67 mmol) of 6-(N-carbazolyl)hexa-2,4-diyn-1-ol, 1.5 ml (14.4 mmol) of 1,2-dimethoxyethane, 0.014 g (0.022 mmol) of dibutyltin dilaurate and 0.14 ml (1.01 mmol) of triethylamine were introduced. A solution of 0.27 g (1.71 mmol) of 4-buthylisocyanatoacetate in 0.6 ml of 1,2-dimethoxyethane (5.77 mmol) was then added drop-wise under strong agitation. After two hours of agitation at 40 °C, the mixture is allowed to get room temperature before to add 40 ml of heptane. The precipitate is recovered by filtration and washed with cold heptane. The product (white-bluish crystals) is then crystallized in CH_2Cl_2/heptane. (Yield 62 %). M.p.: 90-91 °C. ^{1}H RMN (acetone-d6): 8.13 (d, 2H); 7.64 (d, 2H); 7.49 (t, 2H); 7.28 (t, 2H); 6.70 (s, 1H, NH); 5.43 (s, 2H, N-CH_2); 4.70 (s, 2H, ≡C-CH_2O); 4.06 (t, 2H, CH_2-CH_2-O); 3.83 (d, 2H, HN-CH_2);

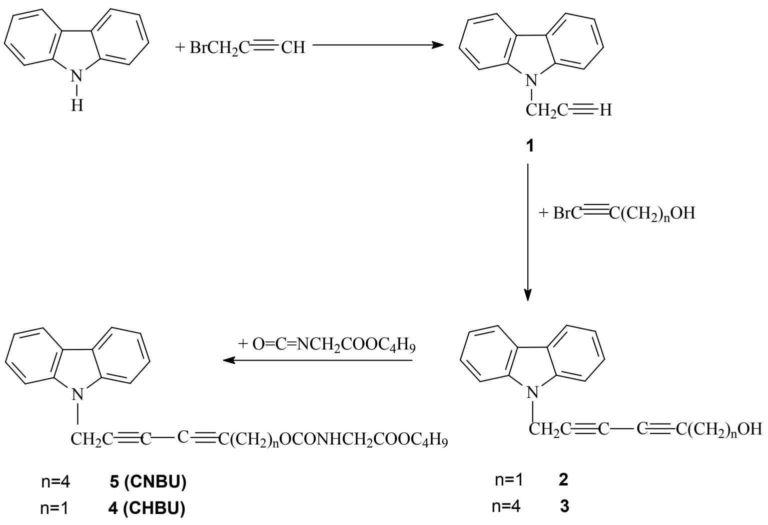
1.56 (m, 2H, CH_2-CH_2-CH_3); 1.37 (m, 2H, CH_2-CH_3); 0.88 (t, 3H, CH_3). E.A. %. Calculated C: 72.10; H: 5.81; N: 6.72. Experimental: C: 72.70; H: 5.78; N: 6.55. IR (cm^{-1}). 3405, 3053, 2959, 2870, 1729, 1454, 1323, 1057, 750, 722.

9-(N-carbazolyl)nona-5,7-diyn-1-ol-acetate of butyl urethane (5, CNBU). The same procedure and reactives molar proportion to obtain **4** was used to obtain **5**, starting from **3**. Pink crystals. (Yield 60 %). M.p.: 83-84 °C. ^{1}H RMN (acetone-d6): 8.14 (d, 2H); 7.65 (d, 2H); 7.50 (t, 2H); 7.25 (t, 2H); 6.50 (s, 1H, NH); 5.37 (s, 2H, N-CH_2); 4.05 (m, 2x2H, CH_2-CH_2-O); 3.82 (d, 2H, HN-CH_2); 2.28 (t, 2H, CH_2-C≡); 1.48 (m, 2x4H, CH_2-CH_2-CH_3); 0.90 (t, 3H, CH_3). E.A. %. Calculated C: 73.34; H: 6.59; N: 6.11. Experimental: C: 72.88; H: 6.52; N: 5.69. IR (cm^{-1}). 3431, 3058, 2956, 2872, 2124, 1715, 1485, 1455, 1324, 1057, 750, 722.

Films preparation

Prior to film deposition, the glass or quartz slides were treated with a sulfochromic solution for at least one day, successively rinsed with distilled water, soaked in an ultrasonic bath for 20 min and finally dried in an oven at 60 °C.

The films were prepared by mechanical unidirectional alignment of the monomer powder with a spatula on hot substrates at a temperature at which the crystalline powder becomes more fluid but not completely melt (55 °C for polyCNBU and 70 °C for polyCHBU). Successively, the monomeric films were UV polymerized until the intensity of the polymeric peak in the UV-Vis spectra stops increasing. Then they were washed with acetone under magnetic agitation for 30’ to extract the residual monomer. The extraction was repeated up that the UV spectra of the extracted solution do not present the carbazolyl bands characteristic of the monomer. Typical values of the absorbance at the excitonic peak for the UV-Vis spectra of monomer free polymer films are around 0.11 and 0.38 for polyCNBU and polyCHBU, respectively. On the basis of the extinction coefficients calculated from the absorption spectra of films of other PDAs [2, 8], the thickness is estimated to be approximately 10 nm for polyCNBU and 30 nm for polyCHBU samples.



Scheme 1. Synthetic route to the synthesis of the two uretane diacetylenes.

Results and discussion

The two carbazolyl monomers are soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, acetone. The DSC thermogram of both monomers present only one broad band at 91 °C (ΔH=103.93 J/g) for CHBU and at 83 °C (ΔH=51.68 J/g) for CNBU practically coincident with the melting points as found with the Electrothermal apparatus. This temperature is also confirmed by optical microscopy where an isotropic liquid is observed. Both diacetylenes polymerize thermally and by UV irradiation giving blue (polyCHBU) and red (polyCNBU) polymers. Since the polymers are completely insoluble, polymeric films from the monomer have been prepared as reported in the Experimental Section. The UV polymerization of these films has been monitored by UV-Vis spectroscopy. Figures 1a and b present the spectral evolution of CHBU and CNBU films, respectively, during UV irradiation and the corresponding polymerization kinetics (inserted figures).

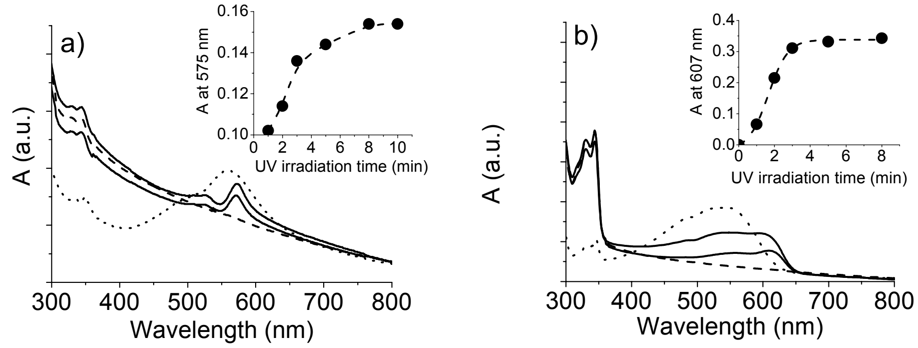


Figure 1. UV-Vis spectral evolution for films of polyCNBU (a) and polyCHBU (b). Dash line: monomer, solid lines: from bottom to top, 3, 8' UV polymerization. Dot line: monomer free film.

For both samples, the monomeric spectra exhibit two peaks at 333 and 343 nm (dash lines). After irradiation (solid lines), new peaks in the visible region appear. For polyCNBU (Figure 1a) the main excitonic peak is located at 575 nm with a vibronic replica at 527 nm, while for polyCHBU (Figure 2b), the excitonic peak, which is located at 610 nm (blue form) after three minutes of UV irradiation, shifts to 598 nm (violet form) with further polymerization. This hypsochromic effect is accompanied by a band broadening. A similar behavior along with polymerization time has been reported by Dellepiane et al. [9] for a diacetylene, bearing an urethane substituent and a carbazolyl ring directly attached to the diacetylenic backbone. In that case, after an exhaustive investigation of the vibrational and electronic spectral changes during polymerization, the authors conclude that the two polymeric forms (red and blue forms) were due to different H bonding organization in the polymeric growing network. In our case, on the basis of the similarity of the urethane moiety, the same explanation could be considered. However, we can not discard that the presence of residual monomer as evidenced by the fact that the excitonic peak intensity is lower than that of the carbazolyl bands, could also contribute to the distortion of the polymeric backbone along with the UV irradiation. After washing with acetone (Figure 1, dot lines), the excitonic/carbazolyl intensity ratio is inverted and a flatter baseline is observed. For the spectra of the monomer free films of both polymers, a blue shift is observed. The excitonic peak shifts for polyCNBU (Figure 1a) from 575 nm to 558 nm and for polyCHBU (Figure 1b) from 598 nm to 546 nm (red form). The same spectral behavior is observed for CHBU films with low polymerization rate (blue form) upon heating. Optical microscopy analysis reveals that the blue to red change corresponds to the formation of drops due to partial melting of the material and which diffuse into the solid infusible film. As the temperature is coincident with the melting point of the monomer, we assume that these drops are formed due to the residual monomer. Among the two diacetylenes, CHBU gives rise to blue, violet or red polymeric forms depending on irradiation time, temperature and monomer extraction by solvent washing. For polyCNBU, polymeric forms with shorter conjugation are always obtained, where a difference of few nanometers in the conjugation is observed when the polymer is submitted to temperature or monomer extraction. The fact that polyCNBU can not assume a more extended blue form could be ascribed to the higher degree of rotational freedom around the longer methylene spacer between the urethane moiety and the diacetylenic backbone with respect to CHBU (see molecular models in Figures 2).

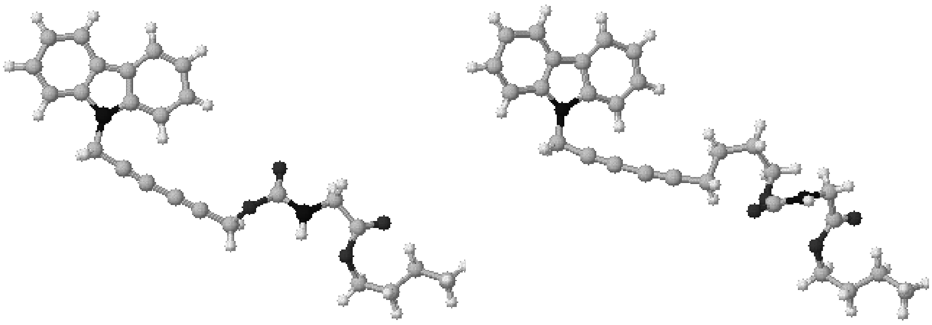


Figure 2. Molecular models of polyCHBU (left) and polyCNBU (right).

For the monomer free films, the polarized micrographs show that both polyCHBU and polyCNBU films are polycrystalline. For polyCHBU both blue and red films present a certain degree of orientation (Figure 3, left) as confirmed by polarized UV-Vis spectroscopy where an optical dichroism R of 1.5 is observed. A detailed analysis by AFM reveals, however, that the film is composed of longer oriented crystals immersed in a sea of tinier unoriented crystals as shown in the image of Figure 3, right. For polyCNBU, the films present crystals aggregation and holes, where no material is deposited. For what concerns the orientation, the dichroism obtained for the polyCHBU films is lower than those that we reported for rubbed PDA films. In ref. [10], we found that the orientation by rubbing seems to be favored for long rod materials and increases with the chain length of the molecules. As a matter of fact, for the PDAs studied in that work, we reported on oriented films prepared by alignment of *polymeric* films. Thus, the lower dichroism observed here could be ascribed to the fact that, due to the insolubility of polyCHBU, we are obliged to align the *monomeric* chains which are obviously shorter than the polymeric ones. On the basis of the results here reported and of our previous works [10], we think that higher dichroisms could be obtained if the mechanical alignment would be applied on the polymer. Thus our actual interest is to synthesize new monomers similar to those here presented but bearing long aliphatic chains on the carbazole, which have been demonstrated to improve the polymer solubility [11].

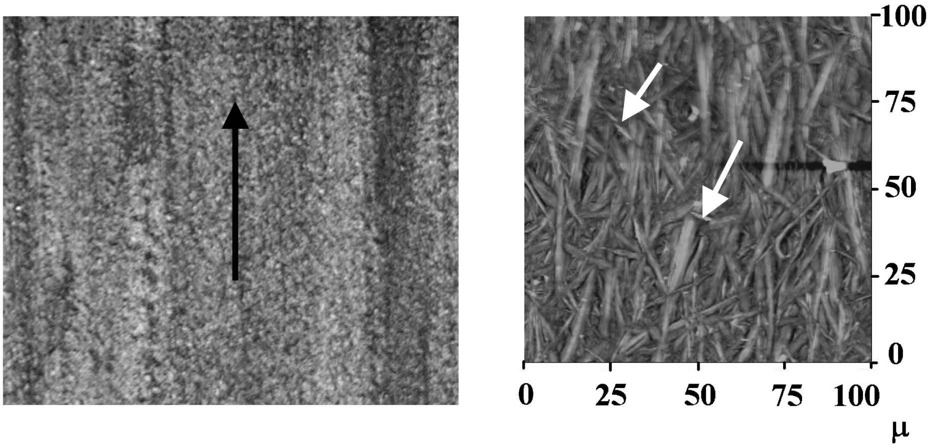


Figure 3. Left: Optical micrograph for red polyCHBU film. Crossed polarizers, 50X, dark field. Right: AFM image.

Conclusions

We reported on the synthesis and solid state films of two carbazolyl urethane diacetylenes bearing different length spacer between the diacetylene and urethane moieties. When the spacer is a simple methylene (polyCHBU), the PDA presents different polymeric forms depending on temperature or irradiation time. On the contrary a shorter conjugation form is always found for the other PDA with a butyl spacer. PolyCHBU films are homogeneous and exhibit a certain degree of orientation.

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