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Optical and Spectroscopic Properties of a Novel Polycarbazolyldiacetylene

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Some unsymmetrical diacetylenic monomers containing a carbazolyl group directly attached to the diacetylene skeleton as well as a flexible polar side group were synthesized. Thermal polymerization of the monomers was followed by means of electronic and infrared absorptions and reasonably high monomer-to-polymer conversion was observed in all cases. A detailed study of the evolution of the electronic, infrared and Raman spectra during the polymerization process is here reported for the monomer 6-(*N*-carbazolyl)hexa-3,5-diynil-*N*-[(ethoxycarbonyl)methyl]carbamate (2U1E) which shows the highest polymerization rate. The results are consistent with the formation of two polymeric forms. At short polymerization time, a form associated with an excitonic band at 660 nm is observed which evolves into another polymer structure with the excitonic peak shifted to 620 nm.

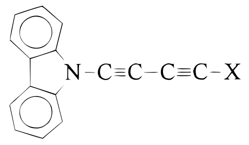
Introduction

Because of their quasi one-dimensional electronic structure, polydiacetylenes (PDAs) can be regarded as molecular "quantum wires". In fact, these polymers, obtained through topochemical polymerization of diacetylenes (DAs), originate highly ordered sequences of conjugated triple and double bonds. Each repeat unit carries two substituents to the sp^2 C atoms which practically isolate one chain from the others. Their delocalized π electrons, which are easily polarizable by electric fields parallel to the polymer backbone, produce fast and large optical nonlinearities[1] as well as very fast photoconduction.[2]

Among PDAs, those with highly polarizable carbazolyl side groups directly or indirectly attached to the polymer backbone show unusually large values of the third-order susceptibility.[3,4] For this reason polycarbazolyldiacetylenes seem to be very attractive for practical applications in nonlinear optical devices.

We report here the synthesis of three novel unsymmetrical model diacetylene compounds, containing a rigid carbazolyl group as well as a flexible polar group bonded to carbons 1 and 4, respectively, of the diacetylenic system (Figure 1).

Our previous experience on other carbazolyldiacetylenes[5] has suggested that thermal polymerization of the polycrystalline samples in KBr pellets produces quite ordered polymers, while more disordered materials are obtained by bulk polymerizing the monomers either thermally or with UV light. Thus, thermal solid-state polymerization has been performed in KBr pellets and followed by means of electronic and infrared absorptions and Raman scattering. For the monomer 2U1E (Figure 1) which exhibits the fastest polymerization we will here present in detailed form the electronic and vibrational spectral changes during polymerization.



(1) $X = -CH_2{\cdot}O{-}CO{-}NH{-}CH_2{\cdot}COOC_2H_5$ 1U1E

(2) $X = -CH_2{\cdot}O{-}CO{-}NH{-}(CH_2)_3{\cdot}CH_3$ 1U3M

(3) $X = -(CH_2)_2{-}O{-}CO{-}NH{-}CH_2{\cdot}COOC_2H_5$ 2U1E

Figure 1. Chemical structures of the diacetylenic monomers synthesized in this work.

Experimental Section

(A) Synthesis of the Diacetylenic Monomers. The synthetic routes to the diacetylenic monomers **1**−**3** are shown in Scheme 1.

N-Acetylcarbazole (**4**),[6] *N*-(α,β-dichloroethenyl)carbazole (**5**),[7] the cuprous salt of *N*-ethynylcarbazole (**7**),[8] 3-bromoprop-2-yn-1-ol,[9] and 4-bromobut-3-yn-1-ol[10] were prepared according

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[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) *Organic Materials for Non-linear Optics*, Hann, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989.

(2) Donovan, K. J.; Sudiwala, R. V.; Wilson, E. G. *Thin Solid Films* **1992**, *210/211*, 271. See also references therein.

(3) Molyneaux, S.; Matsuda, H.; Kar, A. K.; Wherrett, B. S.; Okada, S.; Nakanishi, H. *Nonlinear Opt.* **1993**, *4*, 299.

(4) Nisoli, M.; Pruneri, V.; Magni, V.; De Silvestri, S.; Dellepiane, G.; Comoretto, D.; Cuniberti, C.; Le Moigne, J. *Appl. Phys. Lett.* **1994**, *65*, 590.

(5) Dellepiane, G.; Comoretto, D.; Cuniberti, C.; Musso, G. F.; Piaggi, A.; Speroni, F.; Botta, C.; Luzzati, S. *Synth. Met.* **1994**, *68*, 33.

(6) Stevens, T. S.; Tucker, S. H. *J. Chem. Soc.* **1923**, *123*, 2140.

(7) Okamoto, Y.; Kundu, S. K. *J. Org. Chem.* **1970**, *35*, 4250.

(8) Atkinson, R. E.; Curtis, R. F.; Taylor, J. A. *J. Chem. Soc. C* **1967**, 578.

(9) Ando, T.; Shioi, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *45* (8), 2611.

(10) Chodkiewicz, W. *Ann. Chim.* **1957**, *2*, 819.

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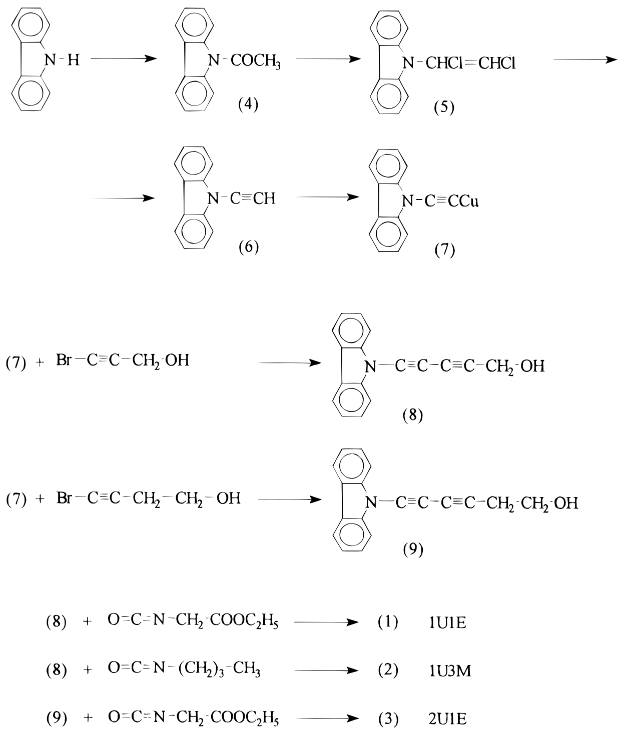
Scheme 1



to literature methods. Carbazole, butylisocyanate, and ethyl isocyanatoacetate were commercial products.

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm). The monomers were also characterized by differential scanning calorimetry on a Perkin Elmer DSC-7 apparatus.

***N*-Ethynylcarbazole (6).** A solution of 11 g (0.042 mol) of **5** in 80 mL of dry ether was added dropwise at −10 °C to a stirred solution of BuLi 1.6 M in hexane (54 mL; 0.0864 mol). After the addition, the reaction mixture was left at room temperature for 2 h. The temperature was then lowered to −10 °C, and a saturated acqueous solution of NaCl (80 mL) was added as rapidly as possible. The ether layer was separated, washed with water, dried (Na_2SO_4), and filtered, and the solvent evaporated. The residue obtained was extracted with petroleum ether and the solution treated with activated charcoal. After filtration, evaporation of the solvent yielded 7.15 g (89%) of **6** melting at 57−58 °C as reported in literature.[7]

5-(*N*-Carbazolyl)penta-2,4-diyn-1-ol (8). The synthesis was performed following the method of Curtis and Taylor.[11]

The copper(I) salt **7** (6.5 g, 0.026 mol), suspended in pyridine (100 mL), was thoroughly purged with argon, and then a solution of 3-bromo-prop-2-yn-1-ol[9] (3.5 g, 0.026 mol) in pyridine (10 mL) was added dropwise with stirring under argon, maintaining the temperature at 40 °C. The solution obtained was then poured into 4 N hydrochloric acid (1500 mL) and extracted with ether. The ether layer was washed with 4 N HCl, saturated sodium hydrogen carbonate, and water and dried over Na_2SO_4. Evaporation of the solvent gave a dark oil; the pure product was isolated by chromatography on a silica gel column using dichloromethane as eluent. Crystallization from benzene gave 2.55 g (40%) of pure **8** melting at 131−132 °C as reported in literature.[12]

6-(*N*-Carbazolyl)hexa-3,5-diyn-1-ol (9). This compound was prepared by a procedure similar to that described for **8**, starting from **7** and 4-bromobut-3-yn-1-ol. Mp after crystallization from benzine 80−100 °C/benzene mixture: 123−125 °C (yield 30%). Elemental Anal. Calcd for $C_{18}H_{13}NO$: C, 83.40; H, 5.02; N, 5.40%. Found: C, 83.07; H, 4.94; N, 5.30%. ^{1}H NMR ($CDCl_3$) δ 8.0 (d, 2H), 7.67 (d, 2H), 7.5 (t, 2H), 7.34 (t, 2H), 3.85 (m, 2H, CH_2−OH), 2.71 (t, 2H).

Table 1

monomer	melting point (°C)	ΔH_m (kJ/mol)	ΔS_m (J/mol K)	half-conversion time (h)
1U1E	112 ± 1	3.1	8	450
2U1E	145 ± 0.5	5.3	12.7	30
1U3M	125 ± 1	12.1	30.4	110

5-(*N*-Carbazolyl)penta-2,4-diynyl *N*-[(ethoxycarbonyl)methyl]carbamate (1). To a solution of 0.9 g of **8** (0.0037 mol) in dry benzene (15 mL) 4.11 mL of ethyl isocyanatoacetate (0.037 mol) was added, and the mixture was stirred under reflux for 70 h. The reaction mixture was then poured into 150 mL of water and extracted with ether. The solvent was evaporated, and the residue purified by chromatography on a silica gel column with dichloromethane as eluent. After crystallization from ethanol 0.3 g (22%) of pure **1** melting at 111 °C was obtained.

Elemental Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.59; H, 4.81; N, 7.49. Found: C, 70.72; H, 4.78; N, 7.45. ^{1}H NMR ($CDCl_3$) δ 8.0 (d, 2H), 7.67 (d, 2H), 7.51 (t, 2H), 7.35 (t, 2H), 5.35 (br, 1H, NH), 4.95 (s, 2H), 4.25 (q, 2H), 4.0 (d, 2H), 1.3 (t, 3H).

5-(*N*-Carbazolyl)penta-2,4-diynyl *N*-Butylcarbamate (2). A procedure similar to that described for **1** was employed to prepare **2** starting from **8** and butylisocyanate. Mp after crystallization from ethanol: 124 °C (yield 52%). Elemental Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.74; H, 5.81; N, 8.14%. Found: C, 76.83; H, 5.75; N, 8.09%. ^{1}H NMR ($CDCl_3$) δ 8.0 (d, 2H), 7.67 (d, 2H), 7.51 (t, 2H), 7.36 (t, 2H), 4.95 (s, 2H), 4.8 (br, 1H, NH), 3.25 (q, 2H, NH−CH_2), 1.7−1.2 (m, 4H), 0.95 (t, 3H).

6-(*N*-Carbazolyl)hexa-3,5-diynyl *N*-[(Ethoxycarbonyl)methyl]carbamate (3). A procedure similar to that described for **1** was used to prepare **3** starting from **9** and ethyl isocyanatoacetate. Mp after crystallization from ethanol: 144−145 °C (yield 69%). Elemental Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.13; H, 5.15; N, 7.22%. Found: C, 71.30; H, 4.95; N, 7.10%. ^{1}H NMR ($CDCl_3$) δ 8.0 (d, 2H), 7.68 (d, 2H), 7.51 (t, 2H), 7.35 (t, 2H), 5.3 (br, 1H, NH), 4.25 (q, 2H), 4.20 (t, 2H), 4.0 (d, 2H, NH−CH_2), 2.8 (t, 2H), 1.3 (t, 3H).

(B) Monomer Polymerization. Polymerization was carried out in microcrystalline samples dispersed in KBr pellets at temperatures 20 °C below the monomer melting points. The monomer into polymer conversion curves were evaluated by infrared measurements according to the procedure outlined in the following.

(C) UV−Visible, FT-IR, and FT-Raman Spectroscopies. Room-temperature electronic absorption spectra were recorded on a Perkin-Elmer Model Lambda 9 spectrophotometer, equipped with the integrating sphere accessory.

Infrared spectra were obtained on a Bruker Fourier-transform spectrometer (FTIR, IFS66). Raman spectra were recorded with a Bruker FT spectrometer (FRS 100), working with a Nd:YAG laser (1064 nm).

The monomer into polymer conversion curves were evaluated by measuring the time decrease of the C≡C IR bands, A_t, of the monomer during polymerization and using the relation $(A_0 - A_t)/A_0$ where A_0 is the initial peak height. On the contrary, the polymerization kinetics could not be followed by Raman measurements because of the low response of the monomer to the NIR excitation light, as will be discussed later on.

Results and Discussion

In Table I the melting points of the monomers are reported together with the correspondent melting enthalpy (DH$_m$) obtained by differential scanning calorimetry. Scan rates of 20 °C/min were used in order to avoid polymerization during heating. The observation of melting points practically coincident with those

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(11) Curtis, R. F.; Taylor, J. A. *J. Chem. Soc. C* **1971**, 186.

(12) Matsuda, H.; Nakanishi, H.; Hosomi, T.; Kato, M. *Macromolecules* **1988**, *21*, 1238.

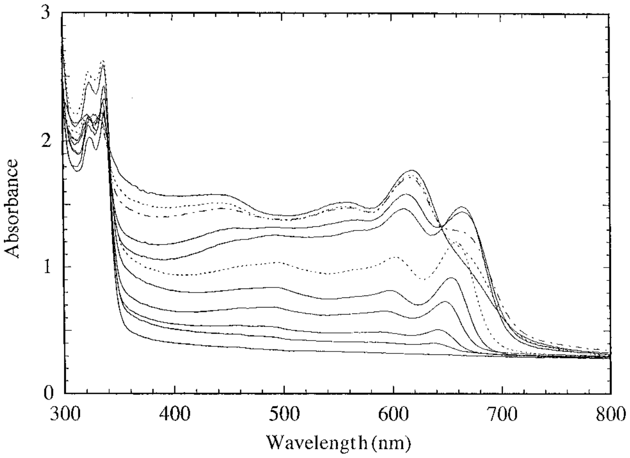

Figure 2. Evolution of the electronic spectra of 2U1E during polymerization at 120 °C. Heating times from bottom to top around 400 nm: 0, 1, 3, 5, 8, 11, 20, 24, 40, 50, and 220 h.

determined on the Büchi apparatus and of sharp melting endotherms was considered evidence of the absence of any polymerization effect.

The DH$_m$ values appear to be much smaller than those of other unsymmetrical carbazolyldiacetylenes prepared in our laboratory[13] as well as of other diacetylenes reported in the literature.[14] Due to the melting point values, the melting entropies (DS$_m$) of these urethane monomers are also quite low. This fact seems to indicate that extensive hydrogen bonding is present in the melt phase. In Table 1 the thermal polymerizability of the monomers determined by the infrared conversion curves is also shown. Among these samples, 2U1E exhibits the fastest and most complete conversion into polymer. Moreover, during the polymerization processes poly(2U1E) presents in the visible region a well-resolved electronic spectrum with excitonic features. On the contrary, broad structureless features are observed for the other two polymers. For all these reasons a detailed optical analysis during polymerization has been performed only on monomer 2U1E.

Electronic Absorption Spectra. Figure 2 shows the absorption spectra of 2U1E during thermal polymerization at 120 °C. The monomer spectrum exhibits, in addition to the strong absorption below 300 nm related to the high-energy transitions of the carbazolyldiacetylene chromophor, the doublet at 325 and 340 nm characteristic of the carbazolyl group.[15] At the initial stages of the polymerization, two additional absorption maxima start to appear at 645 and 600 nm, indicating the formation of a system with highly delocalized π electrons. As the polymerization proceeds, a uniform increase of absorbance is observed for both peaks that are slightly red shifted to 660 and 610 nm, respectively. At longer heating times (>20 h) the intensity of the lower energy peak decreases while the higher energy maximum gains intensity until the 660 nm peak becomes a very weak shoulder. Finally, for reaction times longer then 65 h, the spectrum of the polymer, which consists of a main absorption at 620 nm and of weaker bands at 550 and 450 nm, remains unchanged. However, as will be discussed later on, total conversion is reached only after heating for 220 h. The presence of an isosbestic point at 645 nm suggests that in the range 20–220 h a transformation occurs from a low-energy to a high-energy "blue" phase.

The presence of phase transitions during the thermal polymerization of diacetylenic single crystals has been pointed out by several authors.[16–19] However, usually, these phase transitions appear to be associated with the "red" and "blue" forms of the polymer. The observed changes of the electronic spectra during these transformations have been interpreted in terms of the mismatch of the polymer crystal structure relative to that of the monomer. This interpretation could also account for the spectral shifts observed in Figure 2. In this picture the initial "blue" form could represent the electronic transitions of the diluted polymer chains surrounded by the monomer sea. The loss of the monomer and of the monomer–polymer interactions as the polymerization proceeds could lead to a modified local environment of the polydiacetylene backbone responsible for the appearance of the final "blue" form. Alternatively, since the high-energy form seems to originate from the low-energy one, as indicated by the isosbestic point, a change in the hydrogen- bonding architectures could be responsible for this transformation. X-ray diffraction measurements on the monomer and on partially polymerized samples could allow to settle this point. Unfortunately this analysis was inhibited by poor crystal quality of the bulk samples.

A final remark concerns the possibility of interpreting the observed spectra in terms of two "blue" excitonic bands accompanied by their vibronic structures. Indeed the separation of the two absorption maxima found at early stages of the polymerization is 1160–1240 cm^{-1}, not much different from the value expected for a double-bond stretching. Furthermore, the difference of the two absorption maxima of the final blue form is about 2050 cm^{-1}, close to a triple bond stretching frequency. On the other hand, we cannot disregard the possibility that the 550 nm absorption is due to short or disordered conjugated chains, as it is certainly the case for the band at 450 nm.

Vibrational Spectra. Infrared and Raman spectra are here discussed together as they provide complementary information on the polymerization reaction. FT-infrared spectra measured on the same sample used for the electronic spectra measurements of Figure 2 are reported in Figures 3 and 4.

The monomer spectrum (Figure 3) shows two strong infrared bands at 2255 and 2175 cm^{-1} originated by the stretching modes of the two $C\equiv C$ bonds. Note that no $C\equiv C$ infrared band is observed in symmetrically substituted diacetylenes while only a weak infrared band is present around 2250 cm^{-1} in those asymmetrically substituted diacetylenes having a CH_2 spacer between the carbazole group and the diacetylene skeleton.[13] The 2175 cm^{-1} band can be assigned to the triple bond stretching of the $-C\equiv C-N=$ group, since a band very

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(13) Piaggio, P.; et al., unpublished results.

(14) Strohriegl, P. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 437.

(15) Grasselli, J. C. *Atlas of Spectral Data and Physical Constants for Organic Compounds*; Chemical Rubber Co.: Cleveland, 1973; p B40.

(16) For references see: *Polydiacetylenes*; Bloor, D., Chance, R. R., Eds.; Martinus Hijhoff: Dordrecht, 1985.

(17) Enkelmann, V. In *Polydiacetylenes*; Cantow, H. J., Ed.; *Advances in Polymer Science*; Springer: Berlin, 1984; Vol. 63, p 91.

(18) Batchelder, D. N.; Bloor, D. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: New York, 1984; Vol. 11, p 133.

(19) Sandman, D. J.; Chen, Y. J. *Synth. Met.* **1989**, *28*, D613.

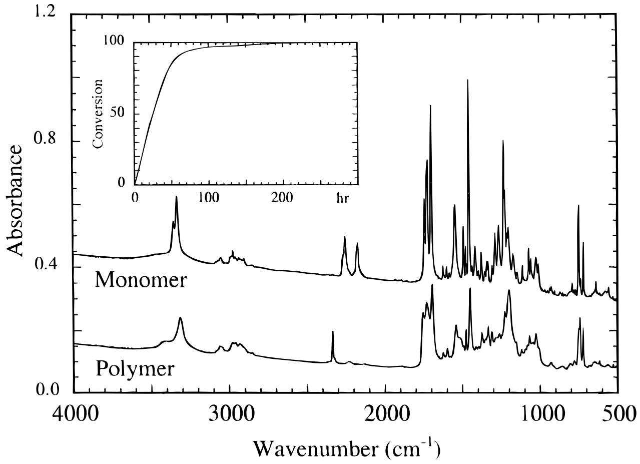

Figure 3. FT infrared spectra of 2U1E and final poly(2U1E). Insert: infrared conversion curve at 120 °C from the 2255 cm^{-1} band.

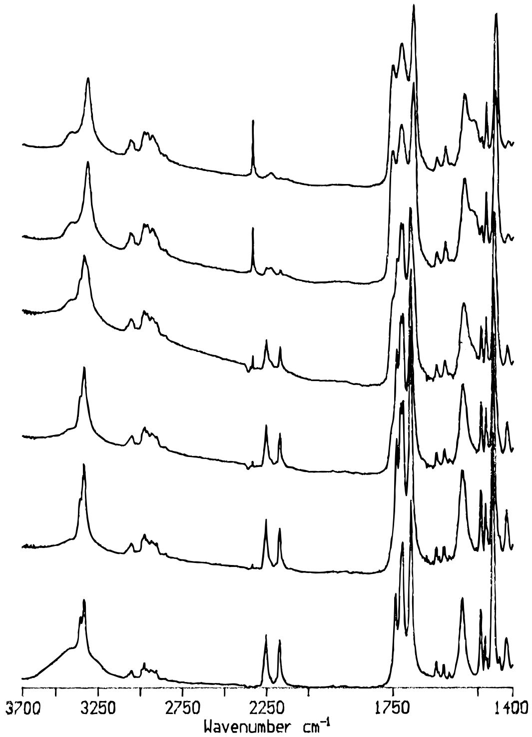

Figure 4. FT infrared spectra of 2U1E and of partially polymerized poly(2U1E). Heating times from bottom to top: 0, 20, 25, 40, 100, 254 h.

close to it has been observed in all the diacetylenes with the carbazole directly bonded to the acetylenic group.[12,13] Hence the assignment of the 2255 cm^{-1} band to the triple bond stretching of the $-C{\equiv}C-CH_2R$ group is straightforward. The lower frequency observed for the $-C{\equiv}C-N{=}$ group indicates that some delocalization of the π electrons of the aromatic system takes place with the acetylenic backbone. The intensity of these bands decreases due to polymerization but, as shown in Figure 4, it becomes negligible only after heating longer than 220 h. The quantitative evaluation of the monomer conversion derived from these bands as described in the Experimental Section, is reported for the 2255 cm^{-1} band in the insert of Figure 3. It is seen that a 50% conversion is reached after heating for 30 h and that only after 100 h practically full polymerization is achieved. In the same region the polymer does not present any C≡C stretching band due to the small dipole moment change expected for this mode. The fairly sharp infrared band at 2335 cm^{-1} (Figure 4), that gains intensity as the polymerization proceeds, cannot be assigned to this mode. In fact we vere able to assign it to the stretching vibration of carbon dioxide trapped in the KBr pellet,[13] deriving from a slow decomposition of the urethane side groups at the high temperatures required for the polymerization. It seems also likely that some water formed in the same decomposition gives rise to the feature around 3400 cm^{-1}. We believe however that this decomposition involves only a very small number of urethane groups and that the observation of the 2335 cm^{-1} band is possible because of the large absorption coefficient of carbon dioxide. In fact the strong absorptions of the urethane carbonyls do not seem to be affected by this reaction. On this basis we think that the urethane decomposition should not have any influence on the present discussion which is mainly devoted to the analysis of the vibrational modes of the conjugated backbone.

In addition to these spectral changes which accompany the polymerization process, other appreciable variations are observed in the infrared spectra. We will discuss here only those observed in the NH and CO stretching regions because they can be related to hydrogen bonding between the side groups. The NH stretching band of the monomer appears as a doublet (3354, 3332 cm^{-1}) on top of a broad absorption (which can be assigned to the presence of water in KBr and which disappears upon heating). This doublet indicates the presence of either a crystal splitting or two types of hydrogen bonds. Within the first 30 h the NH stretching doublet, altough not so well resolved, is still present. For longer polymerization time, a new broad band appears at about 3312 cm^{-1} which gains intensity and sharpness as the reaction proceeds. The shift toward lower frequency of the NH band can be related to the formation of stronger H-bonding in the polymer relative to the monomer. This finding is further confirmed by the behavior of the amide II band, which in the monomer appears as a single peak at 1546 cm^{-1} and evolves toward a doublet feature with the maximum at 1541 cm^{-1} and a shoulder around 1520 cm^{-1} in the polymer.

In the C=O stretching region the monomer spectrum exhibits three sharp bands around 1700−1750 cm^{-1}. Several interpretations of this spectral region have been reported for other diacetylenes with urethane side groups.[20−22] In agreement with the conclusions reached in ref 22, we assign the sharp peak at 1699 cm^{-1} to the C=O stretching mode of the urethane group involved in strong H-bonding and the sharp peak at 1743 cm^{-1} to the C=O stretching of the ester carbonyl. The intermediate asymmetric band at 1725 cm^{-1} may be due to the C=O stretching of either the free or non-H-bonded urethane or of the H-bonded ester carbonyls. This multiplet structure modifies upon heating along with the modification of the NH stretching band discussed above. In other words, we believe that when about half of the monomer has been converted to polymer, the

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(20) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *79*, 4387.

(21) Chang, C.; Hsu, S. L. *Makromol. Chem.* **1985**, *186*, 2557.

(22) Walters, G.; Painter, P.; Ika, P.; Frisch, H. *Macromolecules* **1986**, *19*, 888.

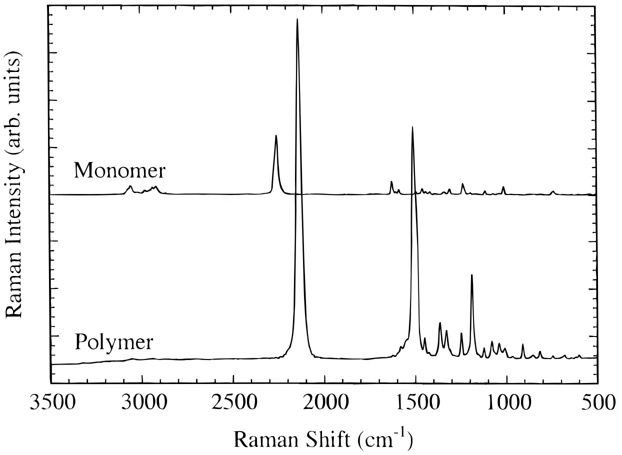

Figure 5. FT Raman spectra of 2U1E and final poly(2U1E).

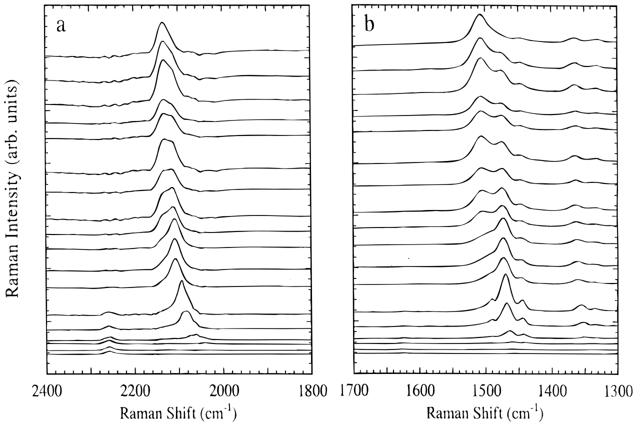

Figure 6. Effect of the polymerization on the FT Raman band of (a) the $C{\equiv}C$ and (b) the $C{=}C$ stretching vibrations. Heating times from bottom to top: 0, 1, 3, 5, 8, 11, 20, 22, 24, 40, 42, 44, 48, 50, 54, 56, 60, 220 h.

crystalline structure undergoes an abrupt modification with a redistribution of the H-bonding lattice. We notice that this change is observed for heating times comparable to those for which the transformation between the two blue phases is detected in the electronic spectra. FT Raman measurements have been performed on the same sample used to follow the whole polymerization process with both electronic and infrared spectra. However, the Raman study of the first stages of the reaction on this sample could not provide any information because of the very low intensity of the polymer bands. To study the early stages of the reaction we have then used a thicker sample after checking that its electronic spectra would show the same behavior displayed in Figure 2. The Raman spectra of both monomer and polymer are reported in Figure 5. Figure 6 collects all the data concerning the evolution during polymerization of (a) the triple-bond stretching and (b) the double-bond stretching vibrations.

The following comments can be made:

(i) The Raman spectrum of the monomer (Figure 5) is dominated by the intense signal at 2260 cm^{-1}, coincident with the higher frequency triple-bond vibration observed in the infrared (the other infrared $C{\equiv}C$ stretching mode at 2175 cm^{-1} does not originate any Raman line). In the same spectrum we observe weaker features due to the vibrations of both the diacetylene backbone and the side groups. The assignment of these modes is however beyond the scope of the present paper.

(ii) The spectrum of polymer (Figure 5) displays features very similar to those observed in other polydiacetylenes.[18,23] In addition to the intense Raman lines originated by the triple-bond stretching at 2136 cm^{-1} and double-bond stretching at 1510 cm^{-1}, we observe other weaker features in the low-energy region whose assignement is still obscure.

(iii) For the study of the evolution of the Raman data during polymerization let us concentrate on the bands due to the $C{\equiv}C$ (Figure 6a) and to the $C{=}C$ stretching vibrations (Figure 6b). With reference to Figure 6a, notice first the very weak $C{\equiv}C$ signal from the polymer which arises within 2 h at about 2030 cm^{-1}. By further heating, the maximum of this line shifts to higher wavenumbers. Notice the rather sharp and symmetric band centered at 2108 cm^{-1} for 20 h heating time corresponding to the decay of the lower energy electronic peak in Figure 2. At this stage, even though the polymer yield as deduced from the infrared conversion curve is still low, the monomer band is no longer present in the FT Raman spectrum.

As the polymerization proceeds, the 2108 cm^{-1} line evolves into a two-peak structure whose shape varies smoothly toward the symmetric band at 2136 cm^{-1} observed at the end of the reaction. The complex bandshapes at intermediate reaction times are probably originated by the presence of two different forms of the polymer whose contributions change gradually upon heating.

(iv) Results similar to those just described for the $C{\equiv}C$ spectral region can also be reached by following the behavior of the $C{=}C$ stretching band during the polymerization. Here again, a very weak Raman signal is observed at 1460 cm^{-1} at the very first step of the reaction which evolves toward the 1473 cm^{-1} peak after 20 h. Further heating originates the two-peak structures displayed in Figure 6b which finally ends into the 1510 cm^{-1} peak.

All these results are consistent with the following picture. At the beginning of the polymerization, a few highly delocalized polymeric chains, as revealed by the weak 2030 and 1474 cm^{-1} Raman lines, are formed in the monomer matrix consistently with the initial observation of the electronic band at 645 nm. For heating time up to about 20 h, these bands become broader, probably due to a distribution of different conjugation lengths, and their maxima shift toward higher wavenumbers, thus indicating a gradual shortening of the polymer delocalization. This result is apparently in contrast with the behavior of the electronic spectra in which a shift of the absorption maximum from 645 to 660 nm is observed. We believe that a possible explanation for this discrepancy could lie on the fact that, while Raman spectroscopy is mainly sensitive to the effective conjugation length,[18] electronic absorption is also affected by the polarizability of the environment which is changing during polymerization. At 20 h, when the monomer conversion reaches about 40%, with the subsequent transformation of the crystal structure evidenced in the infrared,the frequency of the $C{\equiv}C$ peak

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(23) Hankin, S. H.; Sandman, D. J. Applications of Raman Spectroscopy to the Study of Polydiacetylenes and Related Materials. In *Structure–Property Relations in Polymers*; Urban, M. W., Craver, C. D., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1993; Vol. 236, p 243.

is shifted to 2108 cm^{-1} and a new band appears as a shoulder at 2136 cm^{-1}. This double structured band is present up to the end of the polymerization process with an intensity enhancement of the high frequency peak. For this reason we associate the 2108 cm^{-1} peak with the blue form of the polymer responsible for the 660 nm electronic maximum and the 2136 peak with the polymeric form absorbing at 620 nm. Analogous conclusions can be reached by the analysis of the spectral feature changes of the C═C mode in Figure 6b.

We would like to stress at this point that though our Raman data are obtained with excitation in the near infrared, yet for the polymer some preresonance enhancement is present which allows to follow the spectral evolution in terms of conjugation length changes. Clearly this effect hides the presence of the monomer with the consequence that FT Raman technique cannot be used in determining conversion curves, as it has been proposed for Resonance Raman experiments with excitations in the visible.[18]

Conclusion

The polymerization of a newly synthesized asymmetrical diacetylene with a carbazolyl group directly attached to the diacetylene skeleton and a urethane-containing polar group as substituents has evidenced the presence of chromic effects. These effects have been related to a modification of the H-bond network associated with the urethane groups. New infrared evidences have been found on some conjugation of the carbazole group with the diacetylenic structure in the monomer, which is probably conserved also in the polymer as indicated by the very low energy of the excitonic peak. Significant π-conjugation between aromatic side groups and polymer backbone[24] would be of great importance for increasing the nonlinear optical properties of PDAs.

At the beginning of the polymerization a few isolated, highly delocalized chains are formed in the monomer crystal lattice. As the number of polymeric chains increases their interactions give rise to a red-shift of the excitonic peak from 645 to 660 nm. As far as the H-bonding architecture in the crystalline structure remains unchanged the excitonic peak does not change. A drastical variation in the optical spectra is observed only when a new H-bonding organization is settled as inferred from the infrared spectra. Along with this modification in H-bonding structure, further monomer polymerization gives rise to broad electronic absorptions at 550 and 450 nm. All together, the vibrational analysis performed is in favor of the interpretation of these absorptions in terms of either conformational defects in long chains deriving from twisting of the backbone or from oligomer formation. Heating time dependence of the Raman spectra gives further support to this view by providing details of the evolution of the conjugation length in the polymer.

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(24) Orchard, B. J.; Tripathy, S. K. *Macromolecules* **1986**, *19*, 1844.