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Synthesis of polyynes (and ene-ynes) segments by dechlorination reactions of chlorinated polyethylene wax and chlorinated docosane

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High density polyethylene oligomers and docosane ($C_{22}H_{46}$) were subjected to a photochlorination reaction to a chlorine content above 70% as checked by thermogravimetry. The resulting chlorinated materials were dehydrohalogenated by potassium hydroxide in different conditions with simple reaction routes. It is shown by FT-IR, C^{13}-NMR and electronic spectroscopy that soluble low molecular weight polymers were formed having polyyne-ene and polyene-yne segments. These new soluble polymeric materials are of potential interest both in the field of optics and electronics as well as in the understanding the cosmochemical problem of the molecules in interstellar space. © *2000 Kluwer Academic Publishers*

1. Introduction

In recent years there has been a re-flourishing interest on carbyne, another carbon allotrope in addition to diamond, graphite, fullerenes and nanotubes, which to date has never been isolated in pure form. This interest is testified by a book [1] and several reviews on the subject [2–5]. Probably this renewed interest is also linked to the discovery of fullerenes [6] and other exotic forms of carbon such as nanotubes [7] and fullerene polymers [8].

The research on carbyne and carbynoid carbon has many implications in very different fields of science [1–5], but one of the most fascinating aspects involves the possible existence of carbyne together with fullerene in interstellar dust and in circumstellar envelopes of carbon stars [9]. Indirect evidence about the reasonability of this hypothesis is the fact that cyanopolyynes which are end-capped carbyne oligomers with −CN groups have already been detected in space [9]. Additionally, it has already demonstrated on the lab scale that under the same conditions in which fullerene is formed also cyanopolyynes can be formed provided that a suitable source of −CN groups is available in the reaction environment [5, 10]. Since cyanopolyyne exists in space, could polyene-yne or polyyne-ene also exist. A related aspect in connection to carbyne and its oligomers is the source of the so-called "diffuse interstellar bands" whose origin is still a mystery [6]. The most commonly accepted hypothesis is that these bands are due to gas-phase organic molecules, mainly polycyclic aromatic hydrocarbons [11], but also other molecules like the less known polyene-yne and carbon dust could play a role [12].

As part of our research program on the synthesis of carbyne and related materials [13–21] recently we have shown that it is possible to prepare soluble oligomers having segments with acetylenic and ethylenic bonds in their backbone, by a simple dehydrochlorination reaction of chlorinated paraffin wax [20]. Earlier works have shown that polyyne segments can be produced from halogenated polymers by dehydrohalogenation and dehalogenation reactions [22]. One of the most successful works on this matter involved the action of a first group metal such as Na or K on polytetrafluroethylene [23], although in this case the resulting reaction product was unstable.

Our approach on the dehydrohalogenation reaction of halogenated substrates presents the advantage of easy handling, since it can be conducted in current glassware, and has the significant advantage of giving a reaction product which is stable in air and solvent-soluble [20].

As already discussed elsewhere [20] chlorinated paraffin wax has 70% chlorine content but it is a low molecular weight product and it contains a significant fraction of methyl and chloromethyl groups attached to the main backbone. During dechlorination the methyl and chloromethyl groups may interfere in the reaction leading to chain defects and may cause conjugation interruption, limiting the length of the polyyne chains formed. To overcome this problem, a previous approach followed by us [24] and by other researchers [25], was to start from a completely linear precursor of polyyne such as chlorinated polyacetylene. However chlorinated polyacetylene was rather thermally unstable and it was not soluble in any solvent because the starting polymer was already insoluble and chlorination caused additional crosslinking [24].

The new approach reported in this paper involves the photochlorination of a soluble hydrocarbon: docosane.

This hydrocarbon has a completely linear and saturated molecule having 22 carbon atoms. It is soluble in common solvents. As shown in the present paper also its chlorinated derivative is soluble in common solvents and the resulting polyyne prepared by dehydrohalogenation reaction still shows good solubility in suitable solvents so that uniform films can be spin cast onto suitable substrates for the measurements of their electronic and optical properties. In addition to photochlorinated docosane in this paper we describe also the preparation of photochlorinated polyethylene wax. Chlorinated polyethylene is a commercial elastomer available for a long time [26]. Since the chlorine content of this material largely affects its softening point and brittleness temperature as well as its mechanical properties [27], it is commercially available only as a grade with 40% chlorine content which is the optimum compromise between low temperature flexibility and mechanical properties. However this grade is not suitable for our purpose of obtaining long unsaturated chains. In this paper we show how to prepare a soluble and oligomeric chlorinated polyethylene starting from a polyethylene wax and photochlorinating it up to 70% chlorine content. Also this intermediate is then used as precursor for the preparation of polyyne segments by a dehydrohalogenation reaction.

2. Experimental

The solvents used were of analytical grade from Fluka. Chlorine was generated and purified on laboratory scale as described in literature [28].

Polyethylene wax (PEW) was high density type produced by Repsol Quimica (Spain) and used as finishing for textiles and surfaces as well as to increase the softening point of paraffin wax. Being high density type, the polyethylene wax used was mostly linear with a molecular weight of 6000 Daltons, a softening point of 98–108°C, and a Brookfield viscosity at 140°C of 350 mPas.

Docosane, a saturated linear paraffin having the formula $C_{22}H_{46}$, was obtained from Merck.

UV irradiation was performed by a water-cooled high pressure mercury lamp Helios Italquartz model 125 W. The chlorine amount of the chlorinated intermediates prepared in this work was measured by a thermobalance from Linseis at a heating rate of 10°C/min under nitrogen flow up to 525°C. Then the residual char was burned by admitting oxygen in place of nitrogen into the thermobalance. FT-IR spectra were recorded on a Perkin Elmer 1710 spectrometer. The samples were dissolved in chloroform or dichloromethane and film of polymers were grown onto KBr plates by solvent evaporation. C^{13}-NMR spectra were recorded in $CDCl_3$ at Istituto di Strutturistica Chimica, Area della Ricerca del CNR, Monterotondo Stazione, 000 16 Rome, Italy.

2.1. Photochlorination of polvethylene wax

Polyethylene wax (4,1 g) was dissolved in 200×10^{-6} m^3 of CCl_4 by heating the granules in CCl_4 at the refluxing temperature. The cooled solution appeared opalescent and was charged in a quartz reactor. A stream of dry chlorine was then bubbled into the solution until it became green. At this stage UV irradiation was switched on and chlorine bubbling was prolonged for all the irradiation time (2 hours). The photochlorination reaction was exothermal but the UV lamp used was a water-cooled type. Then the lamp was switched off and a stream of air was bubbled through the solution for 25 minutes to strip off residual chlorine and hydrochloric acid formed during chlorination. Chlorinated polyethylene wax (Cl-PEW) was isolated as a glassy and spongy mass by distilling off CCl_4 under reduced pressure. The yield was 15,6 g with a chlorine uptake estimated from weight increase of about 73,7%.

2.2. Photochlorination of Docosane ($C_{22}H_{46}$)

Docosane (4,5 g) was readily dissolved in 130×10^{-6} m^3 of CCl_4. It was irradiated for two hours with the UV lamp under a stream of dry chlorine continuously bubbled into the solution. Then residual chlorine and hydrochloric acid present in the solution were stripped off by a stream of dry air. Chlorinated docosane (Cl-DOC) was isolated by steam distillation of the CCl_4 solution leaving a glassy mass. If CCl_4 was eliminated by distillation under reduced pressure, the resulting Cl-DOC appears as a highly viscous mass because of the incomplete elimination of CCl_4 which then acts as a plasticizer. The yield was about 16,5 g with a chlorine uptake estimated from weight increase of 72,7%.

2.3. Dehydrochlorination of Cl-PEW with KOH and crown-ether (run 1)

Cl-PEW (1,3 g) was dissolved in a mixture of 80×10^{-6} m^3 of dioxane and 20×10^{-6} m^3 of tetrahydrofurane. Solid KOH (6,1 g) was added with slight darkening of the solution. Then 0,15 g of crown ether (18-crown-6) was added and the solution started to darken quickly. The mixture was stirred for 24 hours at room temperature and then it was poured into 400×10^{-6} m^3 of a 12% HCl solution. The black precipitate was collected by filtration, washed abundantly with water and dried in air. The yield was 0,65 g (about 50%).

2.4. Dehydrochlorination of Cl-PEW with KOH/MeOH (run 2)

Cl-PEW (1,2 g) was dissolved in 55×10^{-6} m^3 of dioxane. An homogeneous solution of 6,0 g of KOH (85% active) in 50×10^{-6} m^3 of methanol was quickly added to the dioxane solution under stirring at room temperature. Instantaneously the solution became dark and after 2 minutes from the addition the separation of a black precipitate can be observed. The mixture was stirred for 20 minutes at room temperature and then it was treated with a large excess of aqueous 12% HCl solution, it was then filtered, washed with water and dried in air, 0,54 g of a dark-brown material was collected (yield 45%).

2.5. Low temperature dehydrochlorination of Cl-DOC with KOH/EtOH (run 3)

Cl-DOC (1,5 g) was dissolved in 45×10^{-6} m^3 of tetrahydrofuran (THF) and cooled at $-78°$C into an acetone/dry ice bath. A solution of 6,5 g of KOH (85%) in 50×10^{-6} m^3 of aqueous ethanol (95%) was cooled at $-30°$C and then was added to the THF solution. Darkening of the mixture was observed. The mixture was stirred and kept at $-78°$C for 10 minutes and then it was poured into an excess of 12% HCl solution cooled at $+1°$C. After neutralization the mixture was filtered but the reaction product collected was a tarry mass soluble in acetone and in CH_2Cl_2.

2.6. Low temperature dehydrochlorination of Cl-DOC (run 4)

All the following operations were conducted just above the congealing point of dioxane at $+10°$ to $+12°$C. Cl-DOC (1,0 g) was dissolved in 55×10^{-6} m^3 of dioxane and treated with a cooled solution of KOH (6,0 g) in 50×10^{-6} m^3 of aq. ethanol. After 10 minutes the reaction mixture was poured into a cooled solution of 12% HCl. By filtration a red-brown powder was collected. Yield 0,58 g (58%).

2.7. Dehydrochlorination fo Cl-DOC in dioxane (run 5)

Cl-DOC (1,0 g) was dissolved in dioxane (40×10^{-6} m^3). A solution of 4,0 g of KOH in 40×10^{-6} m^3 of absolute ethanol was then added. The solution was stirred at 80°C for 20 minutes and then it was quenched in an excess of a 12% HCl aqueous solution. The brown black material collected by filtration and washing with water once dried was 0,4 g (40%).

2.8. Dehydrochlorination of Cl-DOC in toluene (run 6)

Cl-DOC (4,5 g) was dissolved in 45×10^{-6} m^3 of toluene. A solution of 6,5 g KOH (85%) in 60×10^{-6} m^3 absolute ethanol was then added under stirring. The mixture was heated to the refluxing temperature for 30 minutes and then it was cooled and poured into an excess of 12% HCl solution. The dark-brown precipitate was collected by filtration, washed with acetone and dried in air. Yield 2,2 g (48.9%).

3. Results and discussion

3.1. General aspects about photochlorination of paraffins

When a saturated hydrocarbon is subjected to UV irradiation in the presence of chlorine, a substitution reaction takes place and a large fraction of the hydrogen atoms present in the paraffin chain are replaced by chlorine atoms and eliminated under the form of hydrochloric acid [29]. The initial reaction step involves the light-induced dissociation of chlorine molecules to chlorine radicals. There radicals are responsible for the attack on the hydrogen atoms of the paraffin chain. Tertiary carbon atoms, are attacked preferentially then the secondary and finally the primary atoms because of the difference in stability of tertiary, secondary and primary carbon atoms. All the chemistry in this field is well understood also from the reaction mechanism involved [29, 30].

When a low molecular weight paraffin like docosane ($C_{22}H_{46}$) as well as the higher molecular weight polyethylene are subjected to photochlorination, by using an excess of chlorine. It is possible to prepare products having more than 70% of chlorine content. Under these conditions on average one chlorine atom is attached to each carbon atom.

3.2. Thermogravimetric analysis of Cl-PEW and Cl-DOC

The thermogram shown in Fig. 1 confirms that chlorinated polyethylene wax (Cl-PEW) prepared in this work have more than 70% of chlorine content. Also for chlorinated docosane (Cl-DOC) a similar thermogram can be obtained, but it is complicated by the weight loss of the residual solvent.

The maximum decomposition rate occurs at 366°C, as shown by the first derivative of the thermogram curve of Fig. 1. It is interesting to note the difference in stability with chlorinated polyacetylene which we studied previously [10]. In fact, chlorinated polyacetylene with about 60% chlorine content reaches its maximum decomposition rate at only about 170°C. Thus it has a considerably lower stability than Cl-PEW and even than PVC [10].

3.3. FT-IR spectroscopy on Cl-PEW and Cl-DOC

The FT-IR spectrum of polyethylene wax (Fig. 2A) and of docosane (Fig. 3A) are typical spectra of hydrocarbons dominated by the strong C-H stretching of CH_3 and CH_2 groups at 2966–2850 cm^{-1}, by the C-H bending at 1470, 1450 and 1375 cm^{-1} and by the CH_2 rocking at 720 cm^{-1} [31]. The introduction of chlorine atoms by photochlorination is testified by the development of an intense multiplet band between 800 and 650 cm^{-1} (see Figs 2B and 3B) due to C-Cl stretching [31] and by the consequent reduction in intensity of the bands due to C-H stretching at 2966–2850 cm^{-1}. If we compare the C-Cl stretching region of the spectrum of Fig. 2B recorded on Cl-PEW with Fig. 3B obtained on Cl-DOC, we can immediately see that Cl-PEW has two groups of bands of different intensity while Cl-DOC has a unique group of bands having approximately the same intensity. These numerous bands in the C-Cl stretching region are essentially due to the different conformation of the $-$CH(Cl)-CH(Cl)- units in the paraffin chain which could be both anti and gauche [32, 33]. Based on the intensity of the IR bands due to anti conformers which always absorb at higher wavenumbers than the gauche conformers [32, 33], we may deduce that Cl-PEW is richer than Cl-DOC in anti conformers because of its higher molecular weight and the presence of side alkyl substituents which introduce some additional steric hindrance. Concerning the presence of geminal

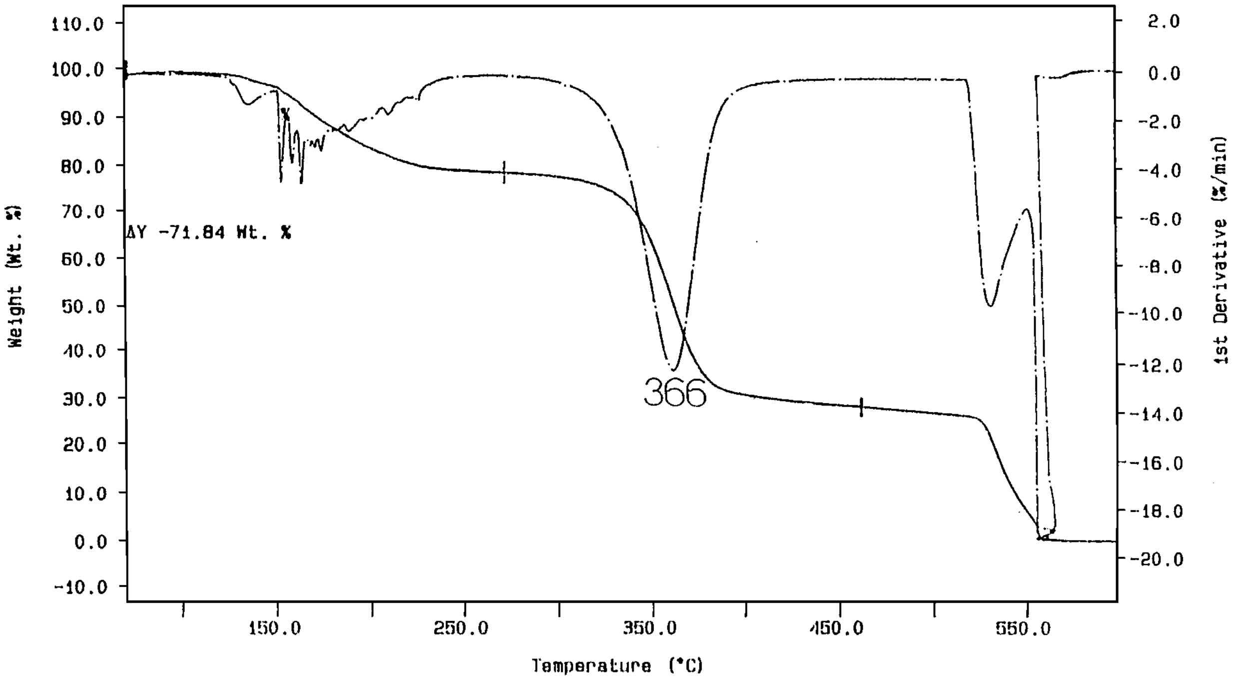

Figure 1 Thermogravimetric curve (with its first derivative) of photochlorinated polyethylene wax (Cl-PEW). Heating rate 10°C/min, under nitrogen flow. At about 525°C the gas was switched to oxygen.

chlorine atoms attached to the same carbon atom of the chain, from the spectra of Fig. 2B and 3B, we may deduce that their concentration is low as suggested by the weak shoulders at 578 cm^{-1}, which can be assigned to the symmetric stretching of $-C(Cl)_2-$groups [20].

3.4. FT-IR spectra on dehydrohalogenated Cl-PEW and Cl-DOC

Cl-PEW is soluble in dioxane. If solid KOH is added to this solution in presence of a crown ether like 18-crown-6 which is able to solubilize a small fraction of KOH, then a dehydrohalogenation reaction takes place. Fig. 2C shows the spectrum of the dehydrohalogenated product which is stable in air and which displays the triple bonds stretching at 2177 cm^{-1}, while the strong band due to C-Cl stretching is now weak and due to residual chlorine. Similarly when a Cl-PEW in dioxane solution is treated in a methanolic solution of KOH, then a stronger triple bond stretching band can be observed in the infrared spectrum (Fig. 2D) and consequently the C-Cl stretching band is almost completely disappeared.

Completely analogous spectra are obtained by working with Cl-DOC instead of Cl-PEW as can be seen in Fig. 3C and 3D. Dehydrohalogenation at low temperature (Run 4 at +10°C) does seem to improve the concentration of the polyyne segments, as can inferred from Fig. 3C, where still significant residual C-Cl stretching bands can be observed in comparison to the good intensity of the triple bonds stretching band at 2181 cm^{-1} which in this case shows also an additional smaller band at 2100 cm^{-1}. However, by working at a temperature below 0°C (see Run3), there are no advantages since the dehydrohalogenation reaction is too slow and a very small amount of polyyne segments are obtained. Therefore reasonable lower temperatures favour the formation of polyyne segments and limit its crosslinking reaction while at too low a temperature the dehydrohalogenation reaction is too slow that no polyyne segments are produced in a reasonable time.

Other features of the spectra of all the dehydrohalogenated products are the bands at 3440 and 1720 cm^{-1} respectively due to hydroxyl and ketonic groups while the bands at 1620–1565 cm^{-1} are due to double bonds stretching (sometimes the =C-H stretching at about 3030 cm^{-1} is observed also) confirming that together with acetylenic segments also polyenic segments are formed. Thus in our conditions the dehydrohalogenation reaction leads to at least 4 different products in the main chain. Elsewhere we have already discussed the fact that the polyenic moiety may be partially chlorine-substituted [20]. The FT-IR spectra of Figs 2C and D and 3C and D which refer respectively to the materials prepared by Run 4 and Run 5 at higher temperatures, are impressively similar to those of dehydrochlorinated paraffin wax [20] and also dehydrochlorinated polyvinylidene chloride [34], confirming the presence of polyene-yne segments in their chain.

3.5. C^{13}-NMR spectra of dehydrohalogenated products

Generally carbonaceous matter containing carbyne and cabynoid structures is insoluble in all common solvents, even if we have demonstrated that some soluble oligomeric fraction can be extracted from these materials (14, 16–18). For C^{13}-NMR characterization of the mentioned carbonaceous solids only solid-state CP-MAS system was found to be effective [34–36]. Since in this work we are showing how to prepare a material containing polyyne and polyene segments, which is soluble in common solvents, we have used solution C^{13}-NMR spectral technique to characterize

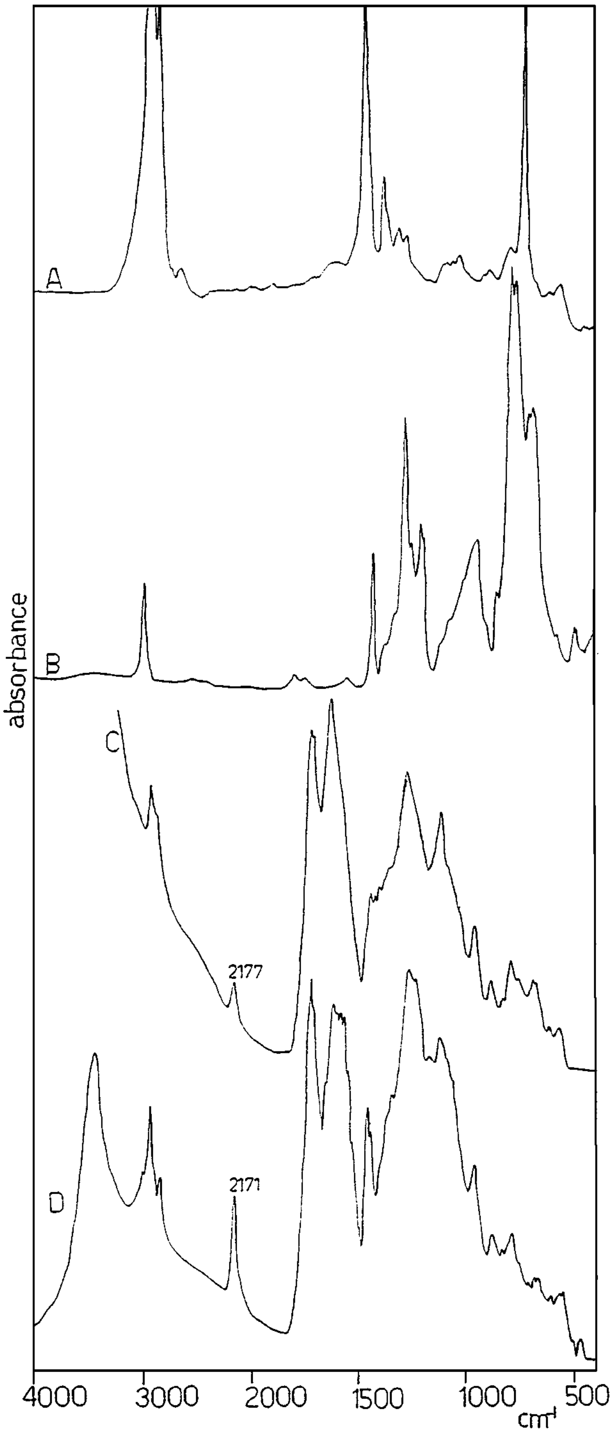

Figure 2 FT-IR spectra (films grown on KBr plates) of: [2A] pure polyethylene wax; [2B] chlorinated polyethylene wax (Cl-PEW); [2C] Cl-PEW dehydrochlorinated with KOH and crown ether (Run 1); [2D] Cl-PEW dehydrochlorinated with KOH/MeOH (Run 2).

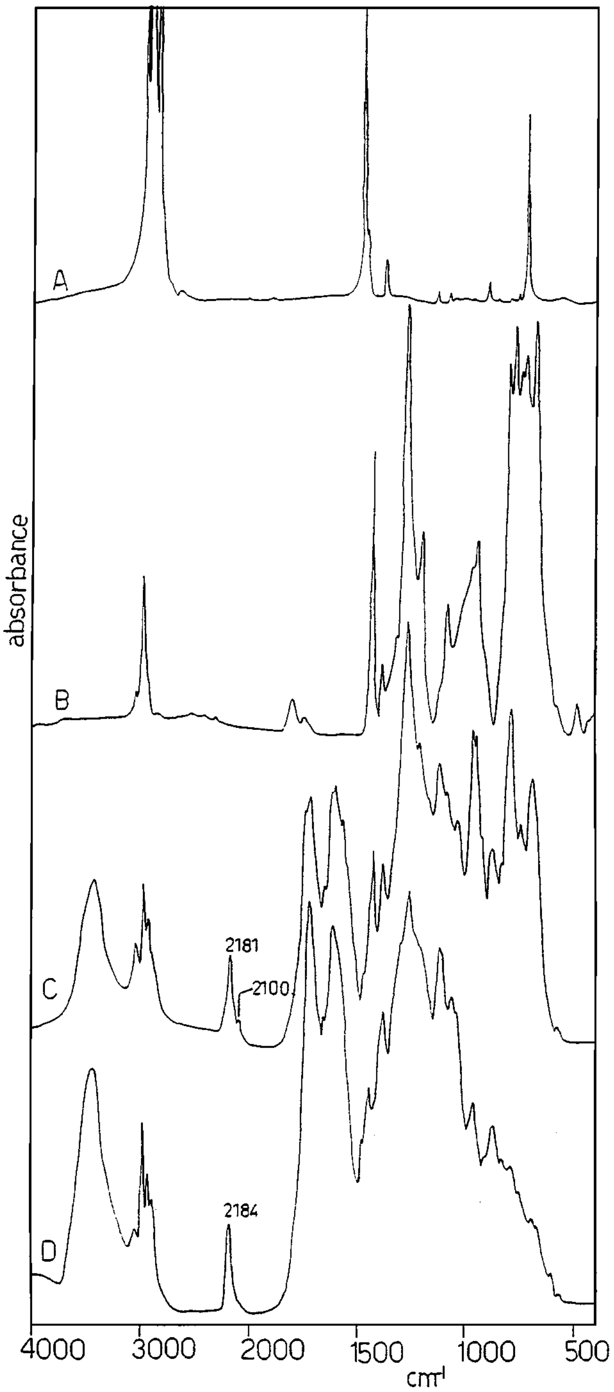

Figure 3 FT-IR spectra (films grown on KBr plates) of: [3A] pure docosane; [3B] chlorinated docosane (Cl-DOC); [3C] Cl-DOC dehydrochlorinated with KOH at low temperature (Run 3); [3D] Cl-DOC dehydrochlorinated at room temperature (Run 5 and 6).

these products. In terms of solubility, the best results are achieved by utilizing Cl-DOC or chlorinated wax [20] rather than Cl-PEW as starting substrate. In fact Cl-PEW was found only partially soluble.

C^{13}-NMR spectrum of dehydrohalogenated Cl-DOC is shown in Fig. 4A and is characterized by four groups of different bands. Based on the previous studies and NMR signal assignments made on carbyne and carbynoid structures [34–36], we can assign the signals at about 125–135 ppm to sp^2 hybridized carbon which constitutes essentially the polyene fraction. Acetylenic carbon is typically observed in the range of 65–90 ppm but the range widens to 25–95 if polar groups are attached to a sp-hybridized carbon atom [37]. The chemical shift of acetylene appears at 71.9 ppm but in conjugated 2,4-hexadiyne the chemical shift appears at upper fields (respectively at 72 and 64.7 ppm in this case) [38]. In the case of 1,2-pentadiyne, the terminal acetylenic carbon atom shows its chemical shift at 64.7 ppm [39]. Longer conjugation of several acetylenic units should give a C^{13}-NMR signal even at higher fields. Thus the NMR broad band in the range of 45–70 ppm, centred at about 60 ppm can be assigned to long polyyne chains. The band is large due to the different polyyne segments length occurring in the material. Additionally

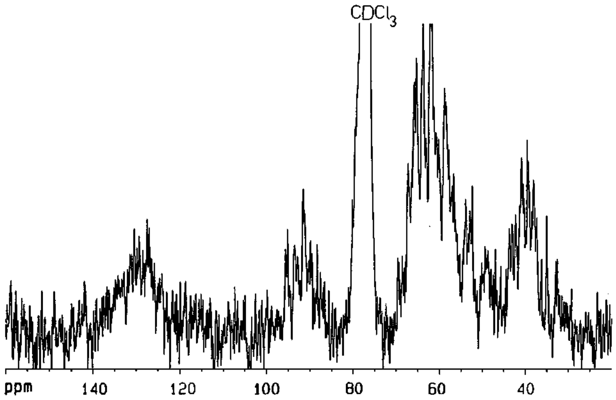

Figure 4 C^{13}-NMR spectrum of dehydrohalogenated docosane (solvent: $CDCl_3$).

some terminal acetylenic group (whose concentration is indeed negligible based on the FT-IR spectrum), if present could contribute to this band. Other acetylenic groups, for instance those conjugated with ethylenic units (ene-yne moiety), those attached to polar groups (hydroxyl, aldheyde groups) and those isolated are responsible for the chemical shift in the range of 85–95 ppm [38, 39].

The broad range assigned to polyyne segments accounts for both differences in segment length and also in the different chemical environment where these segments lie. In other words, polyyne segments having different lengths may lay among many different chemical groups like ketonic, hydroxylic, polyenic chloroalkyl and chloroalkene groups. Thus each of those different segments may contribute with its individual chemical shift causing band broadening. Tetrahedrally-hybridized carbon (sp^3) bearing residual chlorine groups accounts for the signal at about 40 ppm. In Fig. 1 the peak at 77 ppm is due to $CDCl_3$, the solvent used to record the NMR spectrum.

The results deduced from the C^{13}-NMR spectrum are in good agreement with the FT-IR data, in fact both suggest the presence of polyene and polyyne segments.

3.6. Optical properties of dehydrohalogenated Cl-DOC

Dehydrohalogenated Cl-DOC shows almost complete solubility in ethanol and in dichlormethane, while this is not the case for dehydrohalogenated Cl-PEW. Elsewhere [20] we have discussed in detail the electronic spectra of non-linear dehydrohalogenated chlorinated paraffin and have noticed the similitude with the electronic spectra of isomycomicyn and other polyene-ynes. In Fig. 5 we are reporting the electronic spectra of low-temperature dehydrohalogenated Cl-DOC in ethanol. These spectra show a better definition than the spectra obtained previously from non-linear chlorinated paraffin wax [20] and are of further support for the polyene-yne nature of the dehydrohalogenated Cl-DOC. It may be that the better spectral definition is linked to a more regular structure of the product because of its linearity which helps in conjugation along the chain without interruptions.

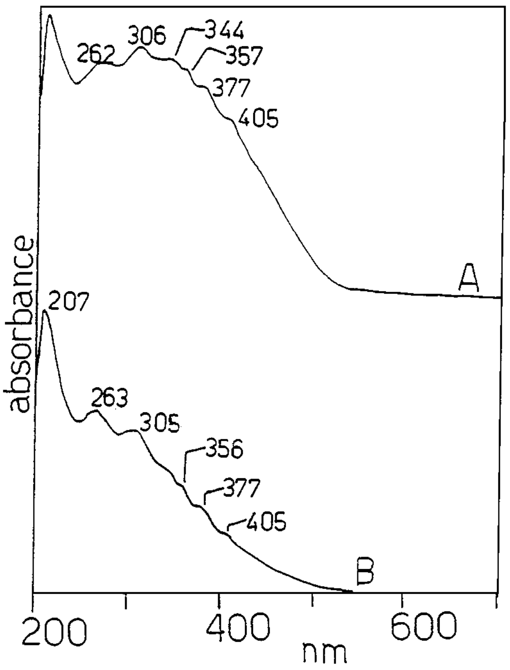

Figure 5 Electronic spectra in ethanol: [5A] Cl-DOC dehydrochlorinated at low temperature (Run 3), [5B] Cl-DOC dehydrochlorinated at room temperature (Run 5 and 6).

4. Conclusions

We have shown that starting from polyethylene or from docosane in two steps it is possible to prepare valuable soluble and film-forming materials having polyene-yne and polyyne-ene segments. The first step involves a photochlorination reaction which leads to the preparation of the chlorinated intermediates having 70% of chlorine content. These intermediates can be easily transformed into the polyene-yne and polyyne-ene chains by a simple dehydrohalogenation reaction route. A completely soluble material having high linearity can be prepared by dehydrohalogenation of Cl-DOC.

The materials described in this paper can find application as films for instance in electronic devices and sensors or in optical devices working with materials having non-linear optical properties [40].

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