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RAMAN SPECTRA AND THERMAL ANALYSIS ON POLYNYNE AND POLYENE-YNE CHAIN SEGMENTS

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Key Words: Chlorinated Paraffin, Dehydrohalogenation, Carbyne, Polyynne, Polyene-yne, Raman Spectroscopy, Thermal Analysis

ABSTRACT

Chlorinated paraffin and its derivative, dehydrohalogenated paraffin were studied by laser-Raman spectroscopy. It is shown that the dehydrohalogenation reaction leads to almost complete elimination of chlorine from the chain backbone with formation of polyynne segments of 3 to 10 acetylenic units as can be deduced from the triple bond stretching band at 2170 cm^{-1} for the sample having shorter polyynne segments and 2095 cm^{-1} for the sample with longer polyynne segments. The presence of polyene segments is underlined by the intense band at 1500 cm^{-1} in both samples studied.

The thermogravimetric analysis of dehydrohalogenated paraffin as well as the differential thermal analysis has been performed in comparison to carbyne and graphite samples used as references.

INTRODUCTION

As part of our research program on the synthesis of carbyne and polyynes (1-7), we have recently shown that it is possible to prepare stable and soluble polyynes and polyene-yne chain segments by dehydrohalogenating a commercially available chlorinated paraffin wax (8) or chlorinated polyethylene wax and chlorinated docosane synthesized on purpose (9). Previously, this approach concerning the dehydrohalogenation or dehalogenation reaction of halogenated polymers has been reported only on high polymers often leading to insoluble and intractable products (10-14).

Polyynes and polyene-yne molecules which could have potential applications in non-linear optics (15, 16), in electroluminescent devices (17), and in solution they show solvatochromism and thermochromism (18, 19). For quite a while, in the totally different field of pharmaceuticals, polyene-yne molecules are known to have antibiotic activity (20). Surprisingly, we have discovered that the electronic spectrum of dehydrohalogenated paraffin wax resembles that of isomycomycin (8), an isomer of the mycomycin antibiotic produced by *Nocardia acidophilus* (21).

Another exciting aspect connected with polyynes and, with polyene-yne molecules, it may be the possible existence of carbyne together with fullerene in the interstellar dust and in circumstellar envelopes of carbon stars (22). Indirect evidence about the validity of this hypothesis is the fact that cyanopolyynes which are end-capped carbyne oligomers, with $-CN$ groups, have already been detected in the space (22). Additionally, it has already been demonstrated on a lab scale that under the same conditions in which fullerene is formed, cyanopolyynes can also be formed, provided that a suitable source of $-CN$ group is available in the reaction environment to end-cap the polyynes chains (23, 24).

In the present work, we will discuss the Raman spectrum of the dehydrohalogenation product of chlorinated paraffin wax together with the electronic spectra and thermal analysis.

EXPERIMENTAL

Chlorinated wax used in this work was a commercial sample obtained from ICI; trade name Cereclor 70. This product is used as compounding ingredient in the manufacture of fireproof rubber and plastic goods. The sample used in this study had a softening point of 90°-100°C and 70% chlorine content. It

consisted of a mixture of chlorinated normal- and iso-paraffins having from 22 up to 30 carbon atoms in their chains, hence, the molecular weight was in the range of 1000-1320 Dalton. Calculated minimal formula for C_{22} chloroparaffin was $C_{22}H_{26}Cl_{20}$ and for C_{30} chloroparaffin $C_{30}H_{26}Cl_{36}$.

Dehydrochlorination reactions were performed by reacting a base like KOH or LiOH on a suspension of chlorinated wax in methanol or ethanol, as fully detailed in our previous work (8) and will not be repeated here. We have selected two samples for the present study, one having abundant and long polyynes and another with medium segments as judged from the intensity of the FT-IR band due to triple bond stretching (8).

The Raman spectrum of the selected samples has been recorded by using a Renishaw System 2000 (with integral microscope, a modified Olympus BH2) using a laser excitation at 514 nm (Ar⁺ laser from Spectraphysics model 236C), and a CCD (385x578 pixel) detector cooled at -70°C by a double Peltier effect.

Thermogravimetric curves and differential thermal analysis have been recorded on a Linseis apparatus model L81/1000+DTA using a heating rate of 20°C/min, under a nitrogen flow of about 100 ml/min. The sample of carbyne used for comparison was synthesized from dicopper acetylide oxidation through a Glaser coupling reaction as detailed in previous works (1-7).

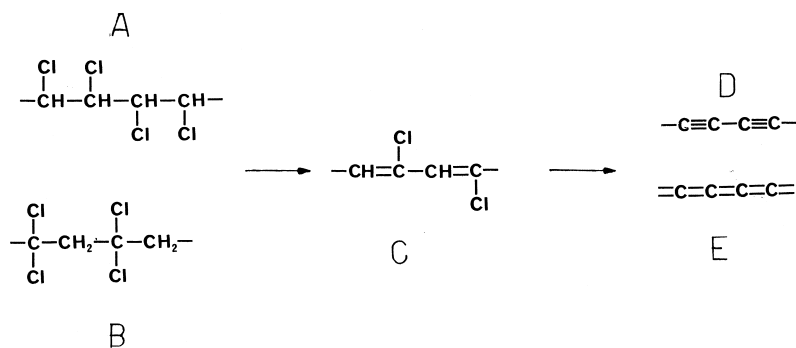
RESULTS AND DISCUSSION

Raman Spectroscopy

Raman spectroscopy is a very sensitive and complementary tool to study the structure of molecules and polymers (25-27). In the previous works on the dehydrohalogenation of chlorinated paraffin and polyethylene wax (8, 9), we have used FT-IR, electronic, and NMR spectroscopy. To complete the characterization of the dehydrohalogenation products, here we are reporting an investigation with Raman spectroscopy.

As shown in Scheme 1, the dehydrohalogenation reaction involves the formation of a chlorinated polyene chain which subsequently could form polyynes and cumulene chain segments. Our previous investigations (8, 9) have already shown that conjugated polyynes and polyene segments are formed.

The Raman spectrum of chlorinated paraffin wax is shown in Figure 1 and is characterized by the aliphatic C-H stretching at 2955 and 2970 cm^{-1} . Other features of the spectrum of the chlorinated paraffin wax are the broad band at 690 cm^{-1} with a shoulder at 635 cm^{-1} which are due to the C-Cl stretching. The



Scheme 1.

Raman resonance at 690 cm^{-1} can be assigned to the asymmetric CCl_2 stretching, while the shoulder at 635 cm^{-1} is due to the symmetric stretching (25). However in the same spectral region lie the stretching modes of the $-\text{CHCl}-$ groups and these probably overlap with the CCl_2 modes leading to the broad band observed in Figure 1.

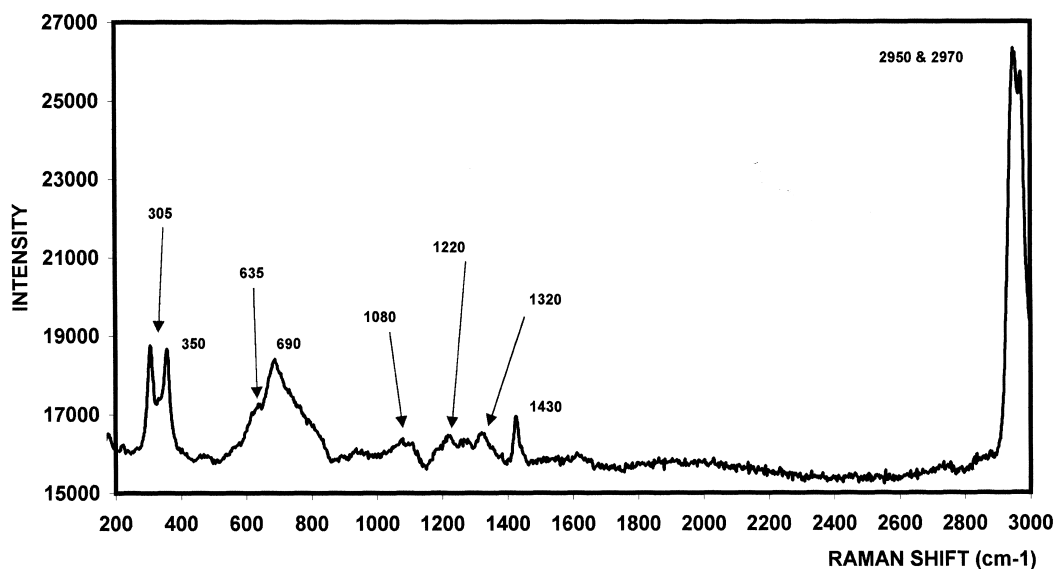


Figure 1. Pure Chlorinated Paraffin.

The Raman spectrum of Figure 1 shows the C-Cl bending at 350 cm^{-1} due to $-\text{CCl}_2-$ moieties and at 305 cm^{-1} due to $-\text{CHCl}-$ groups (25). The Raman line at 1430 cm^{-1} is due to $-\text{CH}_2-$ bending and methyl asymmetrical bending (25).

Figure 2 shows the Raman spectrum of a dehydrohalogenated paraffin wax whose IR spectrum suggested a medium content of acetylenic segments. The Raman spectrum in Figure 2 confirms the presence of conjugated acetylenic segments with two bands at 2170 and 2350 cm^{-1} . The presence of two bands is due to Fermi resonance (26) rather than to the asymmetric and symmetric stretching. In fact, the band at 2350 is just an overtone of the Raman line at 1188 cm^{-1} which in its turn is due to $\equiv\text{C}-\text{C}$ stretching overlapped with other types of C-C stretching vibrations (25). The band at 2670 cm^{-1} should be a combination band ($1188 + 1500\text{ cm}^{-1}$). The very intense Raman resonance at 1500 cm^{-1} can be assigned to conjugated double bonds (vide infra for further discussion). The medium Raman line at 1295 cm^{-1} is due to bending vibration of double bonds (19). It is interesting to note that all the C-Cl stretching and bending bands are no longer present in the spectrum of Figure 2, suggesting that all chlorine of the starting substrate has been eliminated. Moreover the chlorinated polyene reported in Scheme 1 as a possible intermediate, is present only in minute amount as suggested by the weak line at 715 cm^{-1} typical of C-Cl stretching. Also, in Figure 2, the C-H stretching (at about 2900 cm^{-1}) is weak and broad

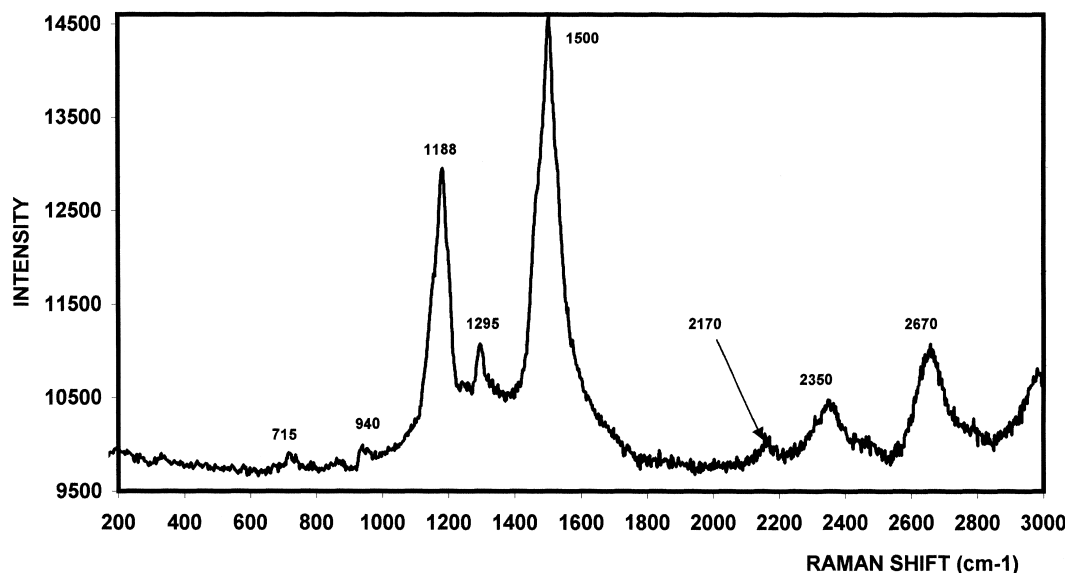


Figure 2. Dehydrohalogenated Paraffin.

while it was very intense in the starting product. Allene groups should not be present for the absence of the out-of-phase and in-phase C=C=C stretch.

The interpretation of the Raman spectrum of Figure 2 is in good agreement with that published by Giesa and Schulz (19) on their polyene-yne. In fact, the spectrum of Giesa and Schulz showed only 4 Raman lines, respectively at 2155 (triple bonds stretching), 1551 (double bond stretching), 1286 (bending vibration of double bond) and 908 cm^{-1} (bending of triple bond) (19). Moreover, in their interesting work, Giesa and Schulz (19) have shown that by increasing the chain length of the polyene-yne, a shift is observed toward lower frequencies of the Raman lines due to acetylenic and ethylenic double bond. In fact, they have synthesized different homologues having increasing chain length and have measured the Raman spectrum and then have found the following empirical laws which link the number of conjugated double or triple bonds with the respective Raman lines (for solid):

$$\nu(\text{C}=\text{C}) = 1460 \text{ cm}^{-1} + 238/N$$

$$\nu(\text{C}\equiv\text{C}) = 2083 \text{ cm}^{-1} + 259/N$$

By applying these equations to the Raman lines in Figure 2, we get a polyene length of 6 double bonds and a polyyne of 3 conjugated triple bonds.

The Raman spectrum of the dehydrohalogenated product, having the highest fraction of conjugated triple bonds (by FT-IR), shows substantially the same Raman spectrum of Figure 2. The unique big difference is in the resonance band due to triple bond stretching which in this case, appears at 2095 cm^{-1} and is broader and more intense than in Figure 2. The band at 2095 cm^{-1} suggests a very long chain length of acetylenic bonds involving more than 10 units.

Probably the main difference between the regular ene-yne product made by Giesa and Schulz (19) and our dehydrohalogenation product is the regularity in the sequence of double and triple bonds and in their length; this regularity is extremely high by design in the case of the polyene-yne of the mentioned authors and less regular and quite random in our case.

Thermal Analysis (TGA & DTA)

The evaluation of the thermal behavior of the dehydrohalogenated paraffin is compared in Figures 3 and 4 with that of a chlorinated paraffin, the starting product, and with two carbyne samples having high and low copper content, prepared by the Glaser coupling reaction (1, 3-7). As additional reference material, a sample of graphite has been evaluated.

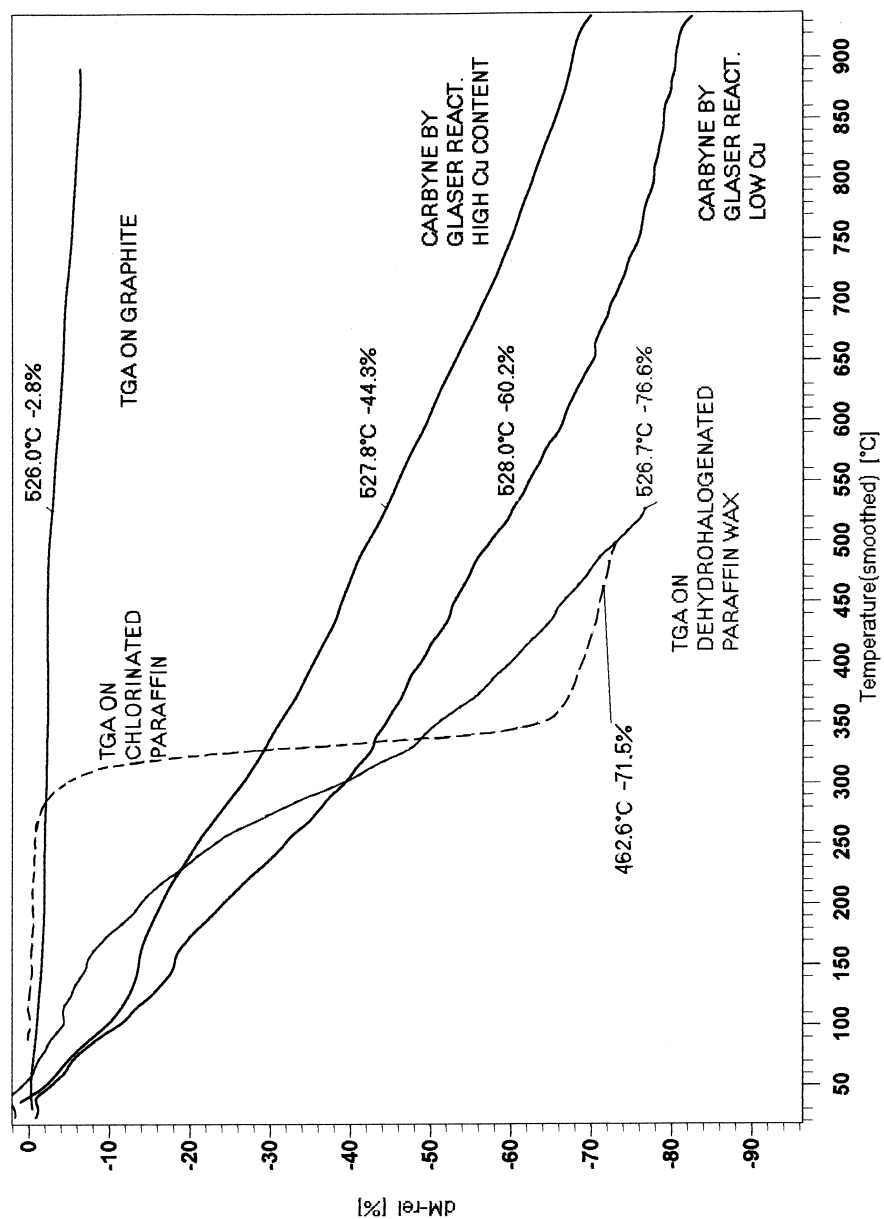


Figure 3. TGA.

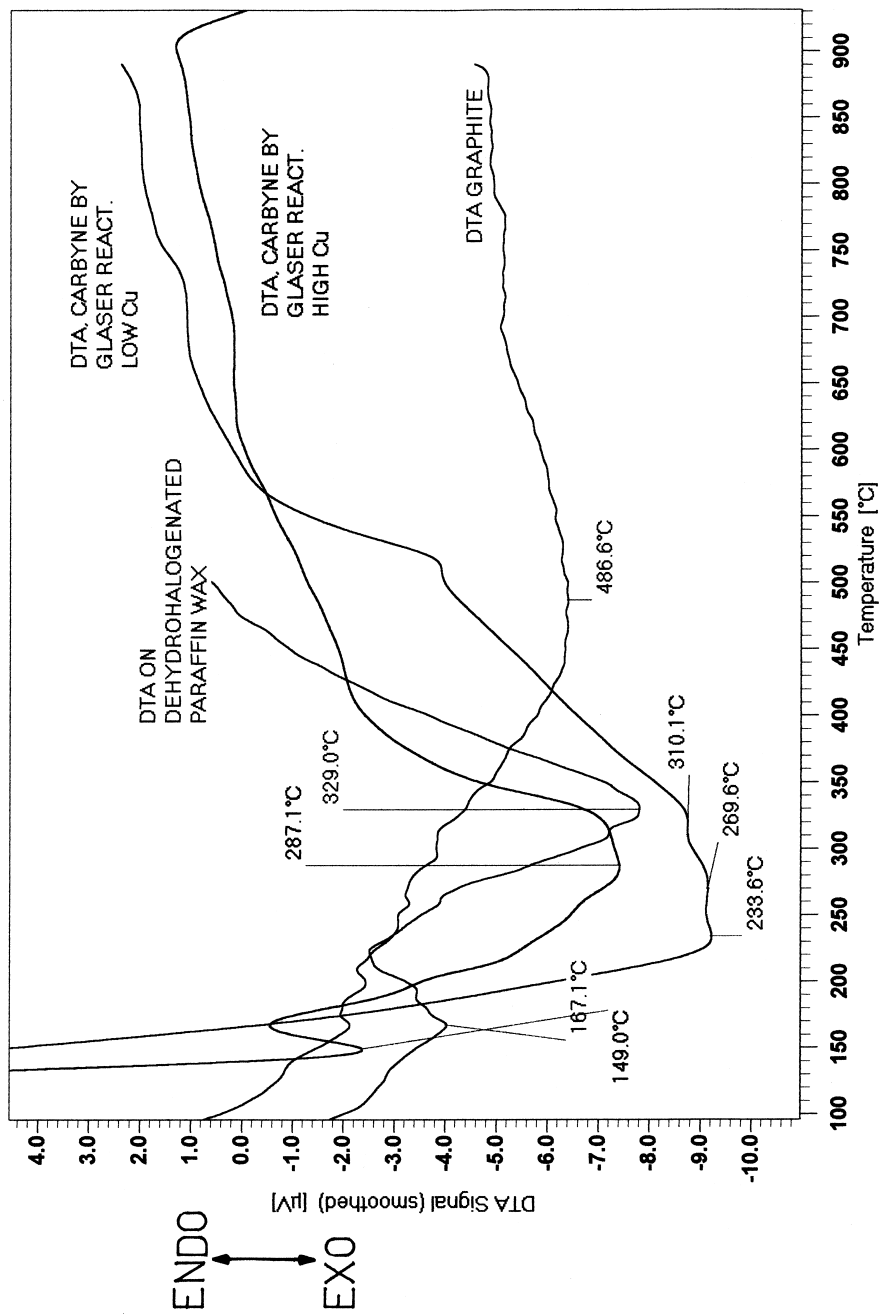


Figure 4. DTA.

Figure 3 shows the thermogravimetric (TGA) curves of the tested samples under a nitrogen atmosphere. It can be easily observed that graphite is very stable up to 900°C with negligible weight loss. On the other side, dehydrohalogenated paraffin containing ene-yne segments characterized in the previous section by Raman spectroscopy, shows a weight loss trend similar to carbyne up to 230°C, but after this stage, the weight loss rate becomes more dramatic in comparison to carbyne samples. This can be attributed to the considerably lower molecular weight of the dehydrohalogenated paraffin sample in comparison to carbyne. Moreover, we have already shown (5, 7) that a carbyne sample prepared through Glaser reaction and other reactions, contains a significant fraction of sp^3 hybridized carbon (diamond-like carbon) and sp^2 hybridized carbon (disordered graphite). In those samples, the polyynene fraction or carbyne domains made by sp -hybridized carbon are only a part of the total sample. Thus, the TGA behavior reflects the heterogeneous composition of the carbyne sample with a weight loss attributable to the decomposition and volatilization of the more volatile polyynene fraction, while the residual is graphite and diamond-like carbon. In fact, it is assumed that the polyynene chains in carbyne samples are end-capped by copper atoms at the extremities of the chains, and copper atoms play a stabilization role (1, 3-6). This assumption is confirmed by the TGA curves shown in Figure 3 where we can observe that the weight loss at 528°C of carbyne sample with low copper content is -60.2% versus -44.3% for the sample having higher copper content. The thermal behavior of graphite in comparison to carbyne is completely different, pointing out once again the different structure of these materials. For comparison, the weight loss of chlorinated paraffin is also shown; chlorinated paraffin is the starting material from which we have prepared the polyene-yne by dehydrohalogenation reaction. Above 300°C chlorinated paraffin undergoes a sudden and dramatic weight loss due to the emission of hydrochloric acid. At about 450°C the weight loss corresponds to the total chlorine content of the original sample. The DTA of the decomposition of the chlorinated wax (not shown in Figure 4 for clarity) shows an initial broad endothermic peak due to melting and incipient decomposition followed by an exothermic peak at 341°C due to the catastrophic decomposition. In Figure 4, carbyne sample (low copper) shows a broad exothermic peak between 233° and 350°C which then is prolonged up to 550°C. The carbyne sample with higher copper content shows a narrower exothermic transition with a maximum at 287°C and a completion above 350°C. These exothermic transitions suggest that chemical reactions involving crosslinking of carbyne domains, rearrangements of disordered graphite domains (graphitization) take place as well as a decomposition reaction

(with vaporisation of some component). The DTA behavior of polyene-yne is somewhat similar to that of carbyne and completely different from the original chlorinated paraffin. The exothermal transition is even narrower than that of high copper carbyne with a maximum at 329°C. This fact suggests that, similar decomposition and rearrangement reactions occurring in carbyne samples take also place, at least partially, in the polyene-yne sample.

CONCLUSION

This study confirms, by means of Raman spectroscopy, the previous results on the chemical structure of dehydrohalogenated paraffin made by electronic and infrared spectroscopy (8). The resulting material is a solvent-soluble oligomer having conjugated polyene and polyene chain segments whose length has been estimated by Raman spectroscopy by using an empirical law (19). The thermal analysis confirms that dehydrohalogenated paraffin is less stable than carbyne samples prepared through Glaser coupling reaction, because of its lower molecular weight and its higher tendency to volatilization and decomposition. On the other hand, the carbyne samples appear more stable because of their inhomogeneous nature as shown in a previous work (7). In fact, in addition to acetylenic carbon, they are composed also of sp^2 - and sp^3 -hybridized carbon. However, the DTA shows a certain thermal similitude between dehydrohalogenated paraffin and carbyne.

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