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The effects of liquid environments on the optical properties of linear carbon chains prepared by laser ablation generated plasmas

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ABSTRACT

Linear carbon chains (LCCs) were successfully produced by laser generated plasmas in different solvents starting from graphite rods. An identification of the prepared carbon structures was carried out from the analysis of the UV–vis spectra. Moreover, a systematic analysis of the DFT computed structural and electronic response of both polyynic and cumulenic model molecules, as a function of the solvents with different polarity, was carried out. The comparison between the calculated UV–vis spectra of polyynes series with the experimental ones clearly indicates that polyynes are the dominant species produced by the ablation process. The optical limiting properties were investigated by the Z-scan method, using a nanosecond pulsed laser. Both the different solvents and the carbon chain length distribution have a driving role in the nonlinear optical response. Hence, the effect of the solvent polarity and acidity was taken into account to explain the nature of the optical limiting behaviour.

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1. Introduction

In the last decade optical limiting phenomena have attracted much research interest for their promising applications such as the production of nonlinear transmission materials able to minimize the potential hazard to eyes and optical sensitive devices in the visible spectra region and in the nanosecond time scale. Among different optical limiting materials, carbon nanostructures such as carbon nanotube and colloids of carbon-based nanomaterials exhibit strong optical limiting properties [1,2]. The advantage of using carbon colloids with respect to those in solid phase is their ability to self-repair and reshape. However, the prepared solutions are not chemically and morphological stable [3]. The one-dimensional structures represent excellent candidates in molecular electronics field applications, thanks to their high electrons density. In this frame, the nonlinear optical properties of linear carbon chains (LCCs) have been widely theoretically explored. These systems are characterized by a high π conjugation and, therefore, they are promising one dimensional conducting materials [4–7]. Polyynes are also the precursors in carbon nanotubes and fullerenes formation. At present, polyynes are successfully synthesized and their long-term stability was checked [8]. However, the results in

terms of photo-stability of the produced carbon mixture are not yet fully satisfactory for the study of their third-order nonlinear optical properties.

Moreover, as already reported in literature [8,9], pulsed laser ablation in a confining liquid is a chemically simple and clean synthesis to obtain size controlled carbon based materials dispersed in different solvents, usually in a one step top–down procedure. The intrinsic ability to produce stable species without the a priori need for any aggressive chemicals, like reducing or capping agents, makes laser ablation in liquids particularly attractive as an eco-compatible technique.

The role of solvents on the formation of sp-hybridized molecules produced by plasma ignition techniques was deeply discussed by Cataldo. Electronic absorption spectra and HPLC analysis clearly show that polyynes are the unique products [10].

In this frame, here we discuss about the formation of sp-hybridized molecules produced by laser ablation in solvents with different polarity, starting from graphite rods.

In order to identify the species which contribute to the linear optical properties, DFT calculations were performed to both polyynic series (HC_{2n}H , $3 \leq n \leq 6$) and cumulenic series ($\text{H}_2\text{C}_{2n}\text{H}_2$, $3 \leq n \leq 6$) in the different solvents, and monocyano HC_{2n+1}N ($3 \leq n \leq 5$) and dicyano NC_{2n}N ($4 \leq n \leq 5$) series in acetonitrile. To the best of our knowledge, no systematic studies on the correlation between linear and nonlinear optical properties of LCC prepared in different solvents has been performed. Therefore, Ultraviolet–visible (UV–vis) results were correlated with the nonlinear optical response of produced carbon species. Moreover, the

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effect of the solvent polarity and acidity was taken into account to explain the nature of the optical limiting behaviour.

2. Material and methods

Pulsed laser ablation of a graphite target (99.9% of purity) has been carried out in different solvents (i.e. water, acetonitrile, methanol and cyclohexane) using pulses from the second harmonic (532 nm, 5 ns) of a Nd:YAG laser operating at 10 Hz repetition rate. The target was irradiated, at room temperature, with a power density of 0.5 J/cm² for typical irradiation times of 20 min. More details about the preparation procedure are reported in Ref. [8]. The UV–vis spectral characterizations allowed the identifications of the linear carbon chains. The optical absorbance measurements were carried out by a PerkinElmer LAMBDA 2 spectrophotometer, in the 190–900 nm range. The nonlinear optical properties have been determined by the Z-scan method [11] using a pulsed Nd:YAG laser (wavelength 532 nm, 5 ns pulse duration, 10 Hz repetition rate). The incident laser beam was divided by a beamsplitter: the reflected part was taken as reference beam, the transmitted one was focused, with a 300 mm focusing lens, into a 1 cm length quartz cuvette. The sample and the reference beam intensities were detected simultaneously with a dual channel energy meter. The optical limiting efficiency of all the produced samples was investigated by means of nonlinear transmittance measurements as a function of the input fluence. After the nonlinear optical limiting measurements, the optical absorbance of the samples was again carried out in order to test the degree of the LCC photo-stability.

3. Theory/calculation

The equilibrium geometry of cumulene H₂C_{2n}H₂ (3 ≤ n ≤ 6) and polyynes HC_{2n}H (3 < n < 6), monocyano HC_{2n+1}N (3 ≤ n ≤ 5) and dicyano NC_{2n}N (4 ≤ n ≤ 5) chains were calculated, in different solvents, e.g., water, methanol, acetonitrile and cyclohexane, using the Becke's three parameters exchange functional supplemented with the Lee–Yang–Parr correlation functional, B3LYP [12–14]. The conductor-like Polarizable Continuum Model (CPCM) [15–17] was adopted for calculating the solvent effect. In this approach the solute molecule is embedded into a cavity surrounded by a dielectric continuum of a given permittivity and interacts with the solvent represented by a dielectric continuum model.

UV–vis spectra were investigated by using the single excitation configuration interactions (CIS) [18] whose results are in good agreement with experimental data. The simulation of the UV–vis spectra was conducted via configuration interaction that involves 20 excited states starting from the optimized geometries.

Eventually, geometry optimization and UV–vis spectra were performed by using the 6-311+** basis set [19–23], while D95 (d) basis set [24] was adopted to evaluate atomic charges.

4. Results and discussion

4.1. Linear optical properties

In Fig. 1a–d absorption spectra of as prepared LCCs in cyclohexane, methanol, water and acetonitrile are reported together with those recorded after every Z-scan analysis. Features of sp-hybridized carbon chains dominate in the ultraviolet region because of electronic transitions peaking between 190 and 300 nm, with increasing wavelengths as the chain length increases. As reported in a previous work [25] when a carbon target is laser ablated in water (see Fig. 1a), carbon chains C_{2n}H₂ with mainly n = 3–4 are produced. Carbon species with n = 6 have been identified by a prominent absorption feature at 200 nm (with a shoulder at

207 nm), while carbon chains with n = 8 produce two weak signals at 216 and 226 nm. Both features (C₆H₂ and C₈H₂) are clearly visible in Fig. 1a. Otherwise, longer polyynes from C₆H₂ to C₁₂H₂ have been found to be the dominant species in methanol and cyclohexane solution with a similar chain distribution (see Fig. 1b, c). During the nonlinear optical measurements (see the following paragraph), samples are subjected to prolonged 532 nm irradiations, as a consequence the UV–vis LCC features gradually disappear. Moreover, depending on the ablation liquid medium, a different degradation behaviour was detected. While a gradual decreasing in intensity of the overall polyyne peaks together with a light red shift was detected in water, in cyclohexane and methanol, the C₆H₂ chain was the main polyyne molecule that continued to exist. The detected red-shift can be ascribed to the degradation products resulting from chain interactions that tend to evolve toward sp²-like structures [8]. Moreover, when laser ablation is carried out in acetonitrile in addition to H-terminated polyynes, monocyano and dicyano carbon chains are also present in solution as already reported by Cataldo [10,26]. In this case electronic transitions of NC_{2n+1}H and NC_{2n}N were also considered for peak assignments and for the relative concentration calculation. In particular, additionally to hydrogenated polyynes with 6–14 carbon atoms/chain, HC₇N, HC₉N, HC₁₁N, C₆N₂ and C₈N₂ were also detected. Regarding the LCC behaviour in acetonitrile after repeated Z-scan measures, we observed that the absorbance features of shorter chain molecules disappeared and only C₁₂H₂ and C₁₄H₂ were detected in solution. For all the produced systems, the complete LCC photodegradation was observed after 4–5 cycles of Z-scan measures.

As reported in the next section, a simulation of the UV–vis spectra was conducted via DFT calculations in order to confirm the previous absorbance assignments and to clarify the effects of the different solvents, in terms of polarity and acidity, on the LCC optical properties.

In Table 1 the amount (in terms of relative abundance expressed in %) of the different species, estimated on the basis of the simulated and the experimental data, are shown. We outline that the calculations were made by fitting the most intense observed peaks and assuming the same extinction coefficient for the calculated and experimental spectra. The resulting percentage, reported in Table 1, is in good agreement with the literature data [10,27]. It is necessary to point out an uncertainty in the identification of the NC₆N and NC₈N absorption wavelengths, being the experimental positions in agreement with data reported by Cataldo [10] but partially different from our DFT calculated values.

4.2. DFT calculations

All the calculations were carried out respectively in water, methanol, acetonitrile and cyclohexane but no significant difference is observed among the polar solvents. Therefore, henceforth we will report the data in methanol (M, polar solvent, 1.70 debye) and cyclohexane (C, apolar solvent) in order to evidence the effect of polarity solvents on LCCs electronic transitions.

Atomic charges, evaluated by means of B3LYP/D95(d), are symmetrically distributed in all the analyzed systems. It was found that the polar solvent increases the negative charge along the chain leaving a more marked positive charge onto hydrogen atoms, see Tables A.1 and A.2 reported in the Appendix. The net charge tends to become neutral in the central region of the molecules with increasing of the chain length. In cumulenes the net positive charge of hydrogen atoms is mainly balanced by the next carbon atom while in polyynes the two carbon atoms next to hydrogen are principally involved in the charge balance.

Calculated values for the main electronic transitions of D_{∞h} polyynes (1Σ_u⁺ ← X¹Σ_g⁺) and D_{2h} cumulenes (¹B_{1u} ← X¹A_{1g}) are reported in Table 2 together with the oscillator strength.

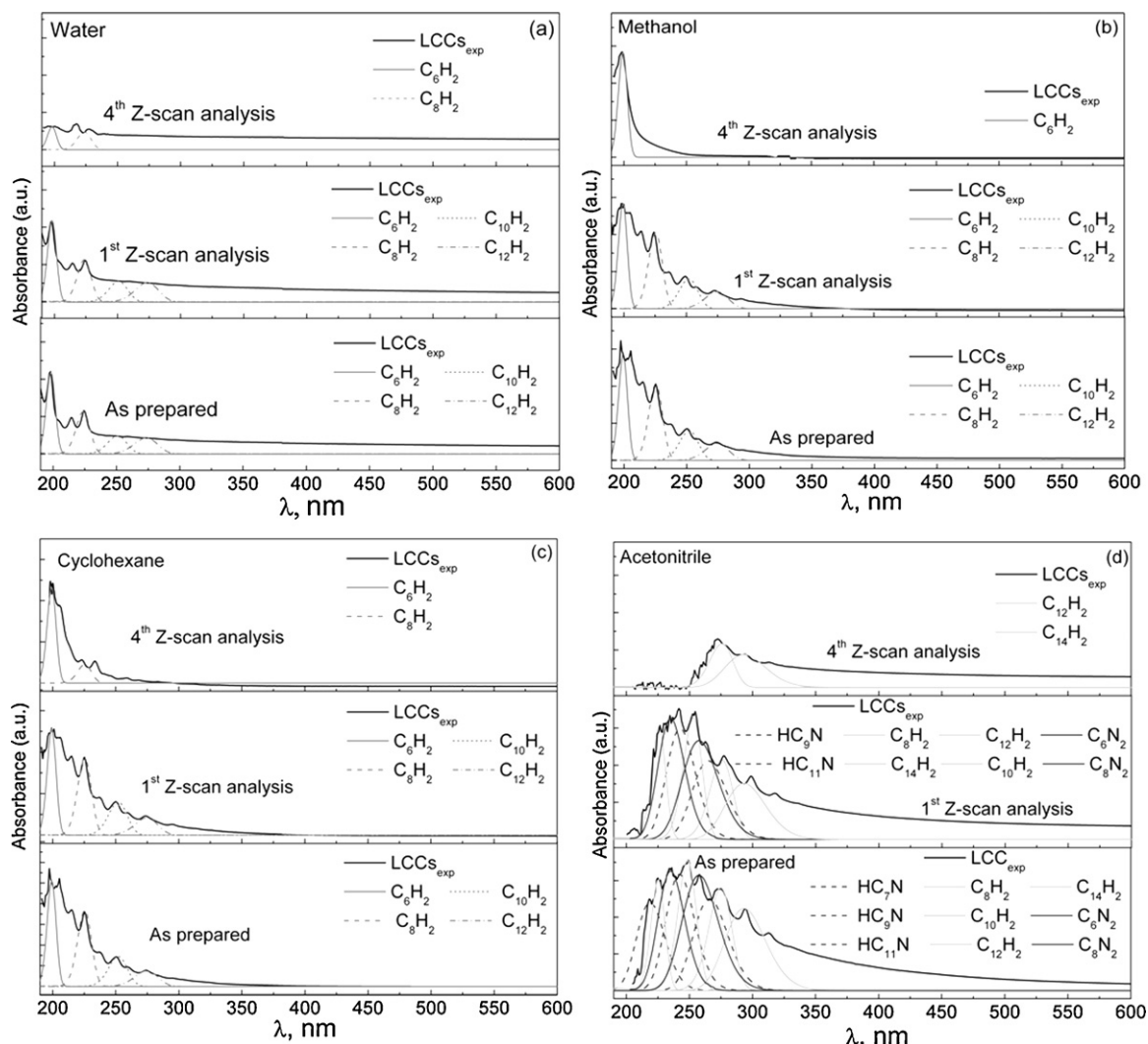


Fig. 1. UV-vis absorption spectra of LCCs produced in water (a), methanol (b), cyclohexane (c) and acetonitrile (d), before and after Z-scan analysis.

Polynes analyzed in this study, containing an even number of carbon atoms, possess a ground state arising from an electronic configuration π_g^4 , where the last two occupied levels are degenerate. Transition $\pi_g \rightarrow \pi_u^*$ shows a red shift with increasing chain

length due to the extent of π electron delocalization which move the electronic energetic levels closer together. In cumulenes the ground state derives from a π_g^2 electronic configuration; for these systems we observe a principal transition at higher wavelength,

Table 1

Relative abundance of the observed polyyne series in the different solvents, obtained by fitting the most intense peaks and assuming the same extinction coefficient for the calculated and experimental spectra.

Solvents	C ₆ H ₂ %	C ₈ H ₂ %	C ₁₀ H ₂ %	C ₁₂ H ₂ %	C ₁₄ H ₂ %	HC ₇ N%	HC ₉ N%	HC ₁₁ N%	C ₆ N ₂ %	C ₈ N ₂ %
Cyclohexane	65	24	8	3	–					
Methanol	66	23	7.5	3.5	–					
Water	75	23	Traces	Traces	–					
Acetonitrile	–	8	9	13	23	10	10	15	5	7

Table 2

Wavelengths (nm) and oscillator strengths of: (i) the first ($^1B_{1u} \leftarrow X^1A_{1g}$) transitions of the H₂C_{2n}H₂ series in methanol (M) and cyclohexane (C); (ii) the first ($1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) transitions in the HC_{2n}H series in methanol (M) and cyclohexane (C); (iii) in the HC_{2n+1}N series in acetonitrile.

(a)	λ	f_{calc}	(b)	λ	f_{calc}	(c)	λ	f_{calc}
C ₆ H ₄ (C)	313.3	1.92	C ₆ H ₂ (C)	193.8	4.24	C ₆ N ₂	214.64	3.623
C ₆ H ₄ (M)	297.8	1.73	C ₆ H ₂ (M)	186.7	4.32	C ₈ N ₂	265.08	9.147
C ₈ H ₄ (C)	371.0	2.63	C ₈ H ₂ (C)	222.1	5.67	HC ₇ N	205.69	3.914
C ₈ H ₄ (M)	352.4	2.27	C ₈ H ₂ (M)	213.6	5.84	HC ₉ N	223.47	6.652
C ₁₀ H ₄ (C)	426.4	3.52	C ₁₀ H ₂ (C)	248.5	6.88	HC ₁₁ N	244.11	7.739
C ₁₀ H ₄ (M)	401.9	3.00	C ₁₀ H ₂ (M)	238.9	7.12			
C ₁₂ H ₄ (C)	478.4	4.47	C ₁₂ H ₂ (C)	248.4	8.11			
C ₁₂ H ₄ (M)	453.6	4.04	C ₁₂ H ₂ (M)	272.5	7.97			

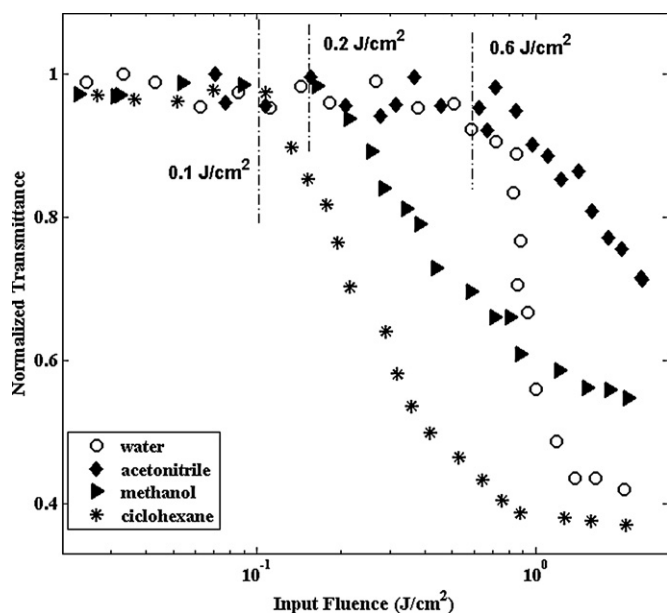


Fig. 2. Normalized non-linear transmittance as a function of the incident pulse energy density, for all the samples.

characterized by the promotion of an electron from HOMO to LUMO ($B_{2g} \rightarrow B_{3u}$), and a secondary transition involving the HOMO $-1 \rightarrow$ LUMO $+1$ electron promotion ($B_{2u} \rightarrow B_{3g}$), see Table 2.

Calculated UV–vis spectra in methanol and cyclohexane show a slightly difference in wavelength absorption values. Peaks in cumulenes occur at lower frequency with respect to polyynes because the energy levels are closer in the former, see Table 2. Such finding is confirmed by the lower gap values calculated in cumulenes. From comparison with experimental data, see Fig. 1, it results that HC_{2n}H ($3 \leq n \leq 6$) are the species mainly present in solution. We point out that the absence of cumulene species in plasma produced LCCs was already experimentally evidenced by Cataldo [10]. The trend of the peaks calculated for polyynes is in strong agreement with the experimental data, such values, in fact, differ by a constant from the experimental values (assignments are highlighted in Fig. 1).

UV–vis spectra of monocyano and dicyano carbon chains are also evaluated in acetonitrile since the presence of such species has been detected in this solvent. The first ($1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) transition for the series HC_{2n+1}N ($3 \leq n \leq 5$) and NC_{2n}N ($3 \leq n \leq 4$) are also reported in Table 2. For these compounds, calculated absorption wavelengths are partially in agreement with experimental values reported by Scemama et al. [28], while differ, as mentioned before, from the data reported by Cataldo [10].

4.3. Z-scan analysis

The optical limiting efficiency of the sp-hybridized linear carbon chains was investigated by means of nonlinear transmittance measurements as a function of the input fluence. First, the optical limiting measurements were carried out keeping the sample at the focal point, varying the input energy and recording the output energy without placing an aperture in front of the detector. Fig. 2 shows the nonlinear limiting performance of the samples when repetitively irradiated by a visible laser pulse lasting a few nanoseconds. The normalized transmittance (i.e. the ratio between the incident and reference beam intensities) begins to decrease at a fluence of $0.6 \text{ J}/\text{cm}^2$, $0.2 \text{ J}/\text{cm}^2$ and $0.1 \text{ J}/\text{cm}^2$, respectively for the samples prepared in water/acetonitrile, methanol and cyclohexane. The dashed lines in figure indicate the threshold values at which the

nonlinear mechanisms are activated. No contribution to the optical limiting response can be attributed to the solvents since their normalized transmittance remains unchanged around 1, when the Z-scan measurements were carried out on the solvents alone. The threshold values seem to depend both on the LCC chain length distribution and on the solute–solvent interaction, due to the different solvent polarity.

The lower threshold values observed in LCCs/methanol and cyclohexane dispersions can be ascribed to the presence of longer chains, as already discussed above. LCCs in water and acetonitrile showed the same threshold fluence. Really, in acetonitrile a threshold value comparable to those obtained for LCCs prepared in methanol and cyclohexane was expected since, also in this case, longer polyyne chains were detected. The presence of monocyano and dicyano polyynes and the highest acetonitrile polarity strongly affect the nonlinear response.

Using the procedure described by Sheik-Bahae et al. [29] the nonlinear refraction index n_2 and the nonlinear absorption coefficient β are estimated from the Z-scan data, acquired in the open and closed aperture configurations. More details about the procedure adopted to analyze the Z-scan data are reported in a previous work [11]. Fig. 3 shows the normalized transmittance curves as a function of polyynes sample position in the open and closed/open aperture, respectively.

For the LCCs prepared in water, methanol and acetonitrile, the normalized open transmittance curves show an almost symmetrical transmittance valley profile respect to the focus (reverse saturable absorption behaviour, RSA). This indicates that the samples have a nonlinear absorption behaviour. The observed differences among the three samples may indicate a nonlinear scattering contribution, stemming from an ablative mechanism and ascribed to a laser induced breakdown occurring at $F \approx 1 \text{ J}/\text{cm}^2$. However, no scattering measurements have been performed in our case, hence we cannot confirm the occurrence of any possible scattering effect dependent on the specific carbon specie. The peak-to-valley of the closed/open aperture configuration (see Fig. 3) satisfied the condition $\Delta Z_{p-v} \approx 1.7z_0$, where $z_0 = kw_0^2/2$ is the diffraction length of the beam; $k = 2\pi/\lambda$ is the wave vector; w_0 is the beam waist radius and λ is the laser wavelength. The above condition on ΔZ_{p-v} confirms the presence of a cubic nonlinearity [29]. In both cases, the peak/valley shape indicates a negative signature (the so called self-defocusing effect). Being the measured n_2 value negative, the situation is characteristic of a classical thermal effect in the solvent [29]. At the focal point a local heating, caused by the conversion of part of the polyynes absorbed energy into heat, occurs. This leads to a heat transfer from the absorbers to the liquid which, in turn, induces a local density reduction with a refractive index change. Such finding is a common dispersive process occurring above a certain radiation intensity threshold.

The LCC samples prepared in cyclohexane show a quite different behaviour: a peak (increased transmittance) can be observed indicating a saturable absorption (SA) mechanism (see Fig. 3c). The open and closed/open-aperture Z-scan measurements are similar, (see Fig. 3c, d) hence, the contribution of the nonlinear refraction to the optical limiting response is negligible. The saturable absorption mechanism could be explained considering that, in the focus region, the high energy density is able to promote the formation of carbon chain anions, C_{2n}^- [30]. These species absorb in the 400–800 nm wavelength range and cannot be observed in the UV/VIS optical measurement because of their lifetime that is barely limited to the time of the laser action. The same effect cannot be observed in the samples grown in a polar solvent. In this case, the negative species are promptly neutralized by means of a proton transfer due to the acidity of polar solvent and the saturable absorption phenomena cannot take place.

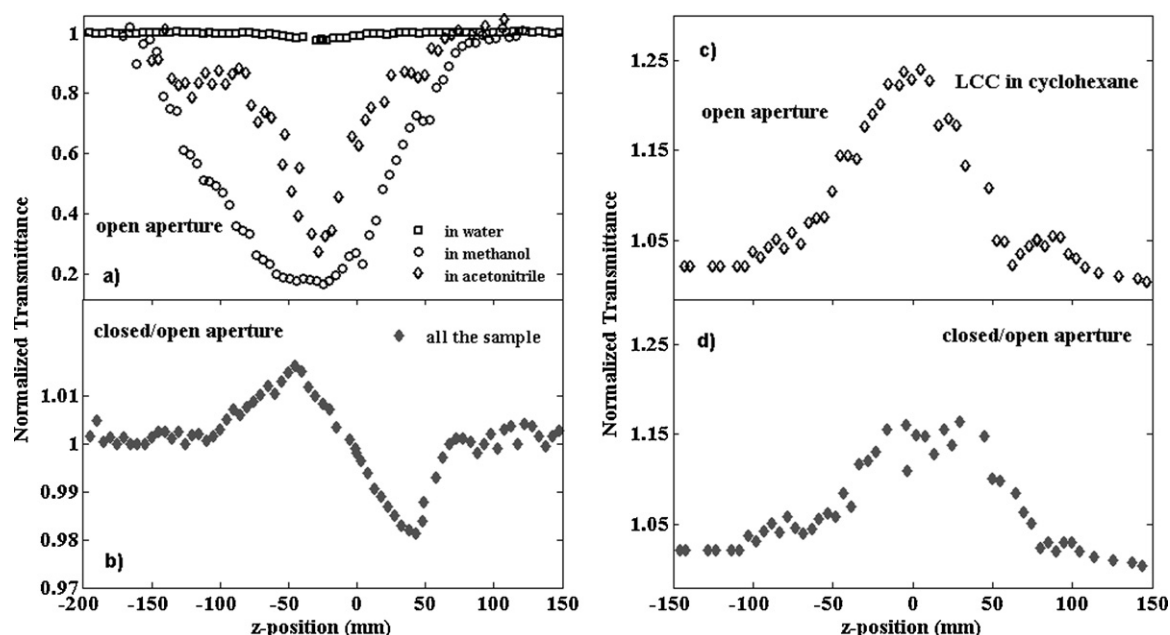


Fig. 3. Normalized transmittance as a function of sample position in (a) open, (b) closed/open aperture configuration of the LCC sample in water, methanol and acetonitrile and (c) open, (d) closed/open aperture configuration of the LCC sample in cyclohexane.

A quantitative evaluation of the nonlinear absorption coefficient β can be made from the normalized open transmittance at the focal point which, in turn, gives the imaginary part of the third order optical susceptibility $\chi^{(3)}$. The nonlinear refraction index n_2 value can be estimated from the difference between the peak and valley transmittance ΔT_{p-v} which, in turn, gives the real part of $\chi^{(3)}$ [29]. The resulting $\chi^{(3)}$ values increases from 3×10^{-11} esu for LCCs in polar solvents to 1.0×10^{-10} esu for LCCs in cyclohexane. These values are comparable to the ones reported for single wall nanotubes

[31], which are considered good optical limiting carbon based materials.

After several irradiation, the optical limiting behaviour is still activated, as shown in Fig. 4. The Z-scan data remain almost unchanged even if the normalized transmittance values are reduced as well as the overall absorbance ones. This indicates a relatively good photo-stability of all the samples under prolonged and focused nanosecond laser irradiation. The transmittance decreasing behaviour is obviously ascribed to the decreased

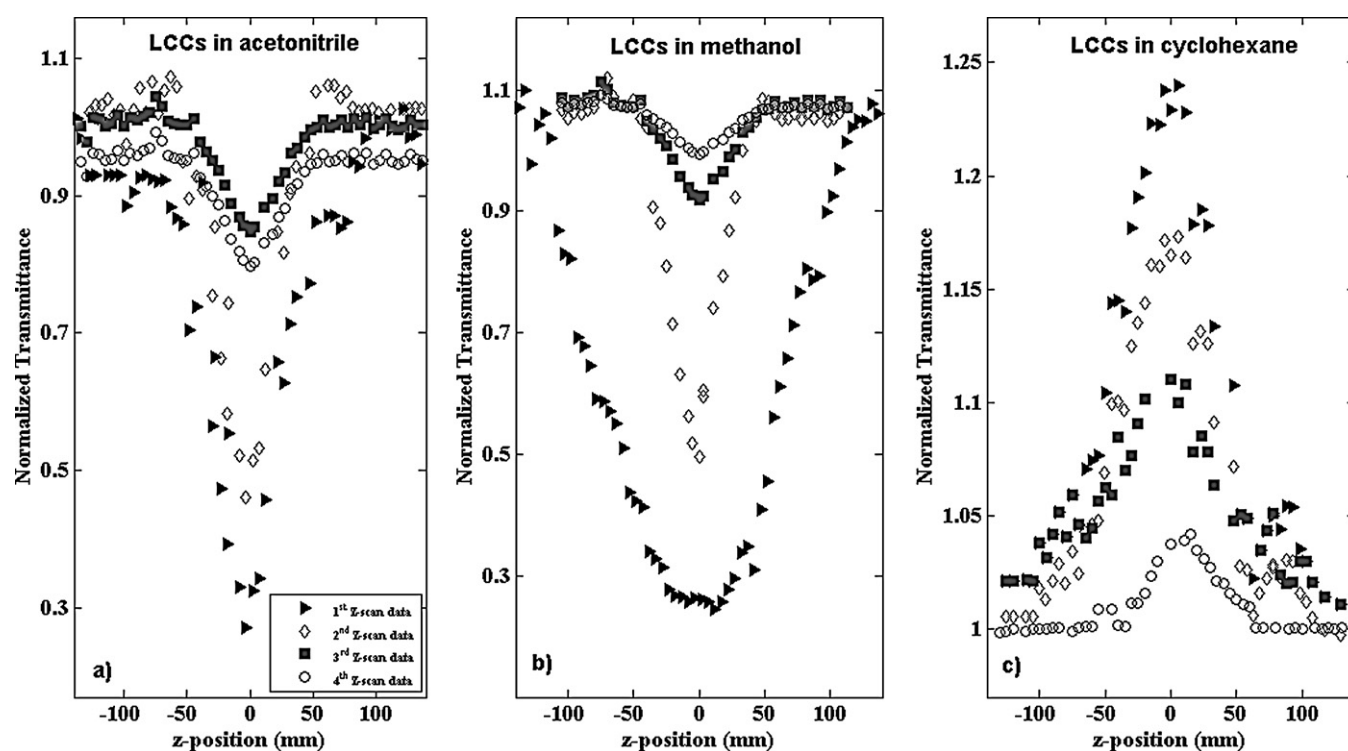


Fig. 4. Normalized transmittance as a function of sample position in the open aperture, after repeated measurements. Similar trends were observed for polyyynes in water.

LCC concentration, independently on the sp^2 degradation products present in the solution.

5. Conclusions

In summary, linear carbon chains were successfully produced by laser ablation in liquid and their linear and nonlinear optical properties were univocally captured by UV–vis and Z-scan measurements as a function of solvents with different polarity.

A systematic analysis of the DFT computed structural and electronic response of both polyyne and cumulenic model molecules, as a function of the solvents with different polarity, was also carried out. The comparison between the calculated UV–vis spectra with the experimental ones clearly indicates that polyynes with different chain length are the dominant species produced by the ablation process and that bathochromic effects are negligible for these carbon species in the different ablation liquids.

Overall, we demonstrated that both solvents with different polarity and chain length distributions have a driving role in the nonlinear optical response. Regarding the nonlinear mechanisms, a change from RSA to SA was observed as function of both solvent polarity and acidity.

We believe that with a better understanding of the fundamental electrostatic interaction between LCCs and the environment, further synthesis improvements for the application of these allotropes, as optical sensitive devices, can be made.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2012.03.156>.

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