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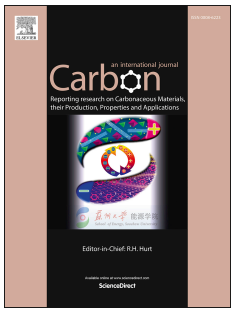

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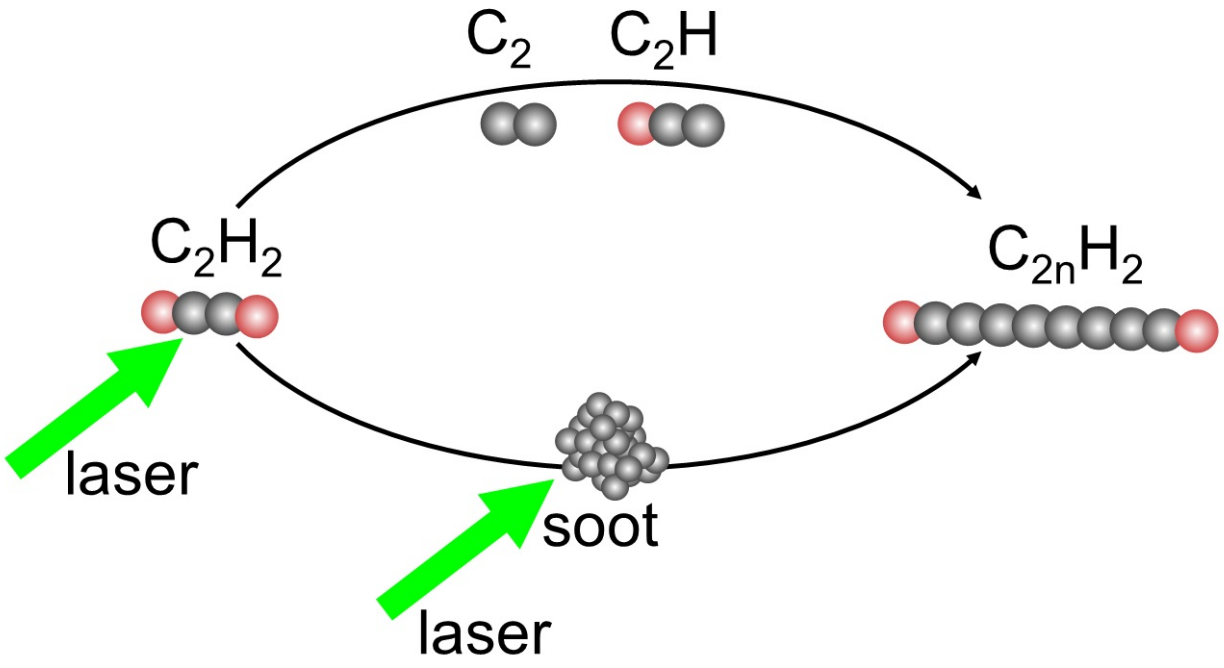

Efficient polyyne formation by ns and fs laser-induced breakdown in ethylene and acetylene gas flow

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Abstract

We studied polyyne formation by gas phase laser-induced breakdown in ethylene and acetylene gas flow using ns and fs lasers. The results show that acetylene is the most efficient target molecule for generating polyynes with high selectivity. Of the two lasers, the fs laser achieved higher selectivity for the production of hydrogen-capped polyynes. We also confirmed strong correlations between C_2 radical and polyyne production, which have already been observed for larger hydrocarbon targets. In terms of the polyyne formation mechanism, we suggest decomposition of irradiated soot to be a possible pathway, in addition to carbon chain growth by binary collisions.

1. Introduction

Among the huge variety of hydrocarbons, polyynes are regarded as a unique family of molecules because of their fully sp-hybridized CC bonds, leading to long and rigid linear structures that cannot be realized by others [1–3]. In addition to the mass spectrometric detection of polyyne ions (for example [4]), which does not promise polyyne formation in macroscopic quantities, various methods for fabricating polyynes have been developed, such as organic synthesis (firstly by [5]), ns laser ablation (LA) to graphite in organic solvents (first proposed by [6]) or in gas [7], and fs laser irradiation to organic molecules [8]. The formation of sp-carbon-rich materials by laser irradiation is also a hot topic in material science (for example, [9–11]). Importance of the gas-phase reactions in forming such materials is pointed out [12].

In our previous study, we showed that laser-induced breakdown (LIB) in gaseous hydrocarbon molecules (saturated hydrocarbons, benzene, and toluene) yields macroscopic quantities of hydrogen-terminated polyynes ($C_{2n}H_2$, hereafter H-polyynes) [13]. Among these hydrocarbons, benzene achieved the highest polyyne yield. On the other hand, the lowest yield was obtained when just one of the hydrogens of benzene was substituted by a methyl group (toluene). The variance in yields among target molecules indicates that other, more efficient target molecules for H-polyyne formation must exist. Identification of such a molecule may in turn give a clue to elucidation of the H-polyyne-forming reactions. The efficiency of H-polyyne production was conveniently measured by the index χ_p, the ratio of absorption attributed to the H-polyynes and that to the unresolved hydrocarbons. The χ_p values were obtained by comparing the spectrum of the irradiated sample with those from the size-separated H-polyynes [7, 13]. It should be noted that χ_p does not have a quantitative physical meaning, except in terms of being 0 (no H-polyynes) and 1 (H-polyynes only), but this indicates the H-polyyne production preference; higher χ_p corresponds to stronger preference.

A guide for seeking efficient molecules in polyyne formation is available, based on crossed molecular beam experiments and theoretical calculations, which show that reactions between $C_{2n}H$ radicals and acetylene lead to the formation of longer polyynes [14–16]. Polyyne yields should be enhanced by enhancing the density of C_2 and C_2H. The previous LIB study also indicated the importance of these radicals [13], on the basis of the fact that the polyyne yield correlates with the intensity of the Swan band of C_2 radicals in the optical emission from the LIB spot. Although emission from C_2H was not identified, probably due to the broad emission profile, the presence of C_2 represents strong evidence for the presence of C_2H.

In the present study, we employed ethylene and acetylene as target molecules, which are expected to be efficient sources of C_2 and C_2H. The rate constants of the reac-

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tions $C_2H + C_2H_2$ and $C_2H + C_2H_4$ were reported to be nearly equal, about 1×10^{-10} cm^3 s^{-1} [17]. That study generated C_2H by photo-excitation of C_2H_2 seeded in a carrier gas flow, and observed decay of the chemiluminescence (A-X transition) of the CH radical, as induced by the reaction of $C_2H + O_2$. Although information on the growth products is not available, a reasonable guess is that the reaction with acetylene mainly yields C_4H_2, whereas that with ethylene does not. In the molecular beam experiments, C_4H_2 does not react further. On the other hand, in the laser-induced plasma, hydrogen loss of C_4H_2 may occur and C_4H radical can be a source of C_6H_2 allowing further growth of polyynes. If polyyne growth via binary collisions is the main pathway even at under high pressure, most of the soluble products of LIB in acetylene should be H-polyynes, with very small amount of sp^2 carbons, resulting in $\chi_p \simeq 1$.

The previous study also showed that yields vary when induced by nanosecond versus femtosecond lasers (hereafter, ns- and fs-LIB, respectively). Generally speaking, fs-LIB offers better conditions for H-polyynes. This is most likely due to the higher degree of fragmentation in fs-LIB. As in ref. [13], we carried out both ns- and fs-LIB studies to confirm this propensity.

As will be shown later, highest χ_p was obtained for LIB in acetylene, while the value was considerably lower than 1. In other words, formation of soluble products other than H-polyynes were suppressed but still not excluded, suggesting an additional pathway to polyynes.

2. Experimental

The experimental procedure was essentially the same as that reported in the previous paper [13], except for a few modifications necessary for acetylene. The ns-LIB study was conducted at Tokyo Metropolitan University, employing the second harmonics (532 nm) of a Nd:YAG laser (Spectra Physics PRO-290, 150 mJ/pulse) with a repetition rate of 30 Hz. The laser was tightly focused onto the center of the irradiation cell using a lens with a focal length of 70 mm. The fs-LIB study was conducted at the University of Waterloo. A focused beam of a Ti:Sapphire laser (35 fs pulses, 800 nm, 1 kHz, 2.0 mJ/pulse) was introduced to the irradiation cell. The focal length was 80 mm. A schematic drawing of the apparatus, which was the same for the ns- and fs-LIB experiments, is shown in Fig. 1. It comprises a gas transport line with a flow meter, a laser irradiation cell, and a vessel for collecting irradiation products. A cooled organic solvent (5 mL) was set in the vessel, which was stored at about -80 C° in the case of ethylene, and at about -40 C° in the case of acetylene (to avoid condensation for safety reasons). The neat (undiluted) target gases were introduced at a flow rate of 50 mL/min. Pure ethylene (99.9%) and dissolved acetylene were used.

Soot generation was noticed during irradiation, especially in the case of ns-LIB in acetylene. The soot may lower the effective laser fluence, leading to a reduction in the polyyne yield. On the other hand, irradiated soot may be an additional source of polyynes, pushing the yield in the opposite direction.

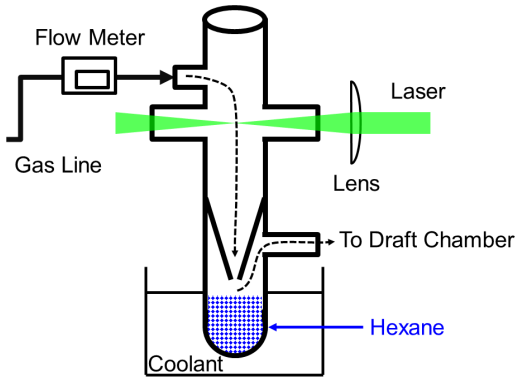

Figure 1: Schematic drawing of the apparatus employed in the present laser-induced breakdown (LIB) study

After irradiation, the temperature of the hexane solution of the product was gently elevated to room temperature and filtered. Then, the solutions were diluted by 5 mL volumetric flask for UV-vis absorption measurement. The polyynes yields were evaluated by convolution of the established absorption spectrum of each size H-polyyne. In case of necessity, the solutions were further analyzed with high-performance liquid chromatography (HPLC) combined with a spectrometer at Kindai University.

Visible photon emission from the ns-LIB spot was observed using a fiber spectrometer (Ocean Optics USB4000) with a 1,064 nm laser (460 mJ/pulse), to avoid excessive enhancement of the background due to scattering of the incident laser. The emission of the fs-LIB spot was also measured using the USB4000.

3. Results and Discussion

Ultraviolet (UV) spectra of the samples obtained by ns-LIB (blue curves) and fs-LIB (red curves) are shown in Figs. 2(a) and (b), for ethylene and acetylene targets, respectively. For comparison, the spectra of those obtained previously by LIB in hexane [13], and by graphite LA in propane gas flow [7], are also shown in (c) and (d), respectively. As shown in (a) and (b), longer polyynes are more prominent in the case of fs-LIB. We discuss this tendency quantitatively below.

Most of the peaks are assigned to H-polyynes, whereas the structureless absorption is due to various other hydrocarbons. The prominent feature of the spectra in (a) and (b) is the peak-to-valley contrast, which is much sharper than that obtained previously (Fig. 2(c)), indicating that the ratios of H-polyynes among all the soluble products are higher. These data look rather similar to the case of

graphite LA under propane flow, as shown in Fig. 2(d), which was reported to be a method of highly selective production of H-polyynes [7].

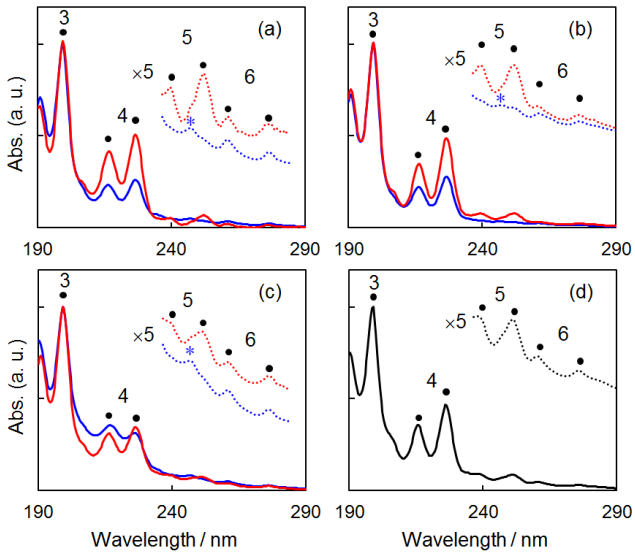

Figure 2: Ultraviolet (UV) spectra of the products obtained by ns-LIB (blue curves) and by fs-LIB (red curves); (a) LIB in ethylene, (b) LIB in acetylene, (c) LIB in hexane (the same data were presented in ref. [13]), and (d) graphite laser ablation (LA) in propane gas flow (the same data were presented in ref. [7]). The peak assignment is indicated by the dots and the numbers n in $C_{2n}H_2$. The asterisk indicates the peak of a polyyne derivative. All of the spectra were normalized at the first peak of C_6H_2. The spectra in the wavelength region of longer polyynes are plotted at a magnified scale and vertically shifted for better separation. Filled dots indicate H-polyynes with the carbon numbers $2n$.

The inset shows the spectra around 260 nm in more detail. The peak at 247 nm in ns-LIB (indicated by *) does not match the H-polyynes. According to the previous studies of in-solvent LA, various polyyne derivatives give peaks in this wavelength region [18, 19]. It is natural to guess that the 247 nm peak is due to some unknown polyyne derivative(s), while the known derivatives do not give a peak at 247 nm. On the other hand, H-polyynes (252 nm for $C_{10}H_2$) is dominant in fs-LIB. The preference for the formation of H-polyynes was also observed previously for LIB in larger hydrocarbons, as shown in Fig. 2(c). As mentioned in ref. [13], the higher degree of hydrogen loss in fs-LIB is probably due to the higher laser field.

The preference in forming H-polyynes is visualized by comparing the aforementioned index of χ_P. The values of χ_P obtained by ns- and fs-LIB in ethylene and acetylene gas flow are shown in Fig. 3, together with those obtained previously for comparison. Among these LIB target molecules, the χ_P value reached the highest in LIB with acetylene for both ns and fs lasers. Between the two lasers, the fs laser yielded higher values, consistent with previous results. In other words, fs-LIB in acetylene results in the highest selectivity of H-polyynes. The χ_P value was approximately 0.65, which was comparable

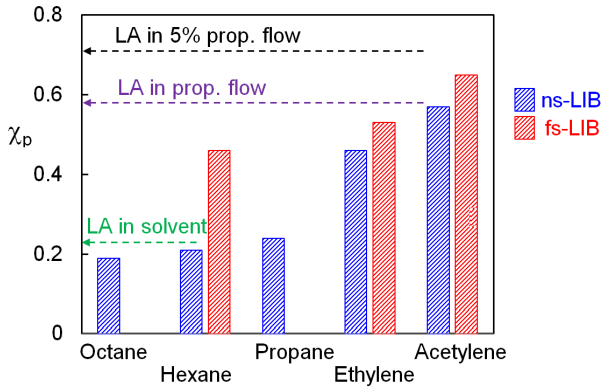

Figure 3: χ_P values obtained in the present study (ethylene and acetylene), and those of the previous LIB study (octane, hexane, propane, [13]). χ_P values reported for graphite LA in hexane (LA in solvent) and in propane gas flow (LA in prop. flow, neat and Ar diluted) [7] are indicated by arrows.

to the value in LA of graphite in hydrocarbon gas flow (about 0.6); this was the highest value among the various methods utilizing pulsed laser excitation (more precisely, the highest χ_P was 0.71, obtained by LA in Ar-diluted 5% propane) [7]. The high χ_P values in LA are intuitive because sufficient chain-form carbon clusters are produced by LA, and polyyne-forming reactions are merely terminated by hydrogen. That is, growth processes are completed before the molecule is surrounded by hydrocarbons. On the other hand, the LIB process requires chain growth, for example by the previously proposed reactions [14–16]. The highly efficient, and selective, polyyne production by LIB suggests that such reactions may occur easily, and compete well with others, for example the sp^2-carbon-forming processes.

The presence of the building blocks, C_2 and C_2H, was then evaluated based on optical emission of the LIB spot. The emission spectra of the ns- and fs-LIB spots in ethylene and acetylene are shown in Fig. 4, which illustrates strong C_2 swan bands. This provides additional evidence that efficient C_2, and most likely C_2H, formation results in efficient polyyne production.

Although the abovementioned results are consistent with the growth process of $C_{2n}H + C_2H_2 \rightarrow C_{2n+2}H + H_2$, they also suggest an alternative interpretation. Figure 3 shows that the χ_P values for acetylene are highest, and differ from ethylene by only approximately 0.1, which is smaller than the difference between ethylene and propane for ns-LIB. Binary collision of $C_{2n}H$ and ethylene may yield various soluble hydrocarbons, leading to considerably lower χ_P values. The correlation between C_2 (and C_2H) density (Fig. 4) and polyyne yield indicates the importance of these radicals, while C_2 can be simply used for the growth of pure carbon clusters, as in the case of graphite LA.

To fully consider the polyyne-growth mechanism, it would be informative to compare the size distributions obtained using various methods. Plots of the relative ab-

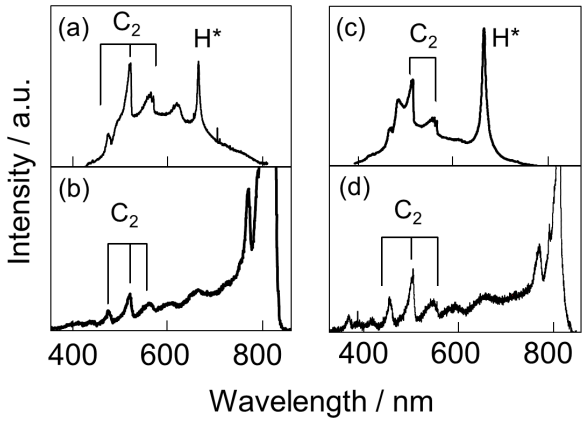

Figure 4: Optical emission spectra of the LIB spots; (a) ns-LIB in ethylene, (b) fs-LIB in ethylene, (c) ns-LIB in acetylene, (d) fs-LIB in acetylene. "C_2" and "H*" indicate C_2 swan bands and the hydrogen Balmer line, respectively, which are considerably broadened by the Stark effect. The Balmer line is observed only for ns-LIB, probably due to the lack of reaction $H^+ + e^- \rightarrow H + h\nu$ in fs-LIB ($H^+ + C_2H_2 \rightarrow H + C_2H_2^+ + h\nu$ is endothermic).

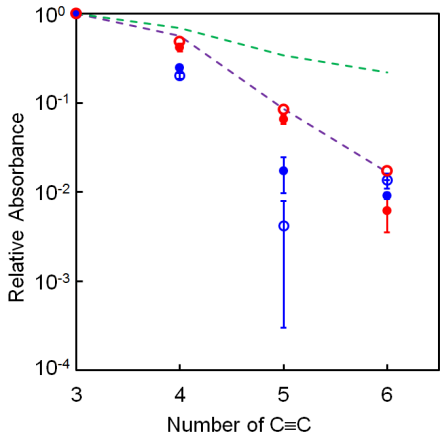

Figure 5: Peak intensities of $C_{2n}H_2$ (n=4-6) relative to C_6H_2 (see text) for ns-LIB in ethylene (○), ns-LIB in acetylene (●), fs-LIB in ethylene (○), fs-LIB in acetylene (●). The results for graphite LA in propane gas flow (purple dashed line) and hexane solution (green dashed line), calculated using data presented previously [7, 13], are shown for comparison. The plots also indicate that the conditions favorable for longer polyynes are not favorable for the selective formation of H-polyynes.

sorbances of the peaks of $C_{2n}H_2$ $(n = 4 - 6)$ with respect to that of C_6H_2 are shown in Fig. 5. It should be noted that the plots do not directly reflect the relative abundance because the absorption coefficients vary between species; they are in fact the fitting parameters employed for determining the χ_p values. In general, the molar absorption coefficient of longer polyynes is larger, leading to some overestimation of longer polyynes, while the scaling factors are common for a given species. In all of the gas-phase reactions, the formation of longer polyynes is suppressed compared to the case of LA in solvent (green dashed line). As shown in the figure, longer polyynes, up to $C_{10}H_2$, are enhanced when fs-LIB is used. For $C_{12}H_2$ and longer, the peaks are too small for us to discuss their abundance. There may be differences between ethylene and acetylene, but the nature of such differences was not identified.

The most striking feature is the close similarity between the plots for fs-LIB and LA under propane flow. As the χ_p values for these processes are also similar, it is intuitive to assume that the irradiated soot may play a role. This leads to the other hypothetical polyyne growth mechanism, in which the chain-form carbon clusters are initially produced, and the role of acetylene is merely as a source of hydrogen. Considering that soot formation is most prominent in the case of ns-LIB in acetylene, in which the production of longer polyynes was suppressed, the contribution of soot should be discussed in quantitative terms at present.

4. Conclusion

We conclude that the most efficient molecule for polyyne production is acetylene, at least among the molecules that have been examined so far. Qualitatively it is consistent with the expectation based on the binary collision scheme, whereas comparison between the results for ethylene and acetylene raised a question whether it is an exclusive mechanism. As mentioned in the experimental section, soot was produced during irradiation, and may enhance the yield by LA, or suppress it by scattering the incident laser. Although soot formation was less prominent in the case of fs-LIB, and in ethylene, it can occur in fs-LIB in ethylene, as reported previously [20]. The contribution of irradiated soot to polyyne formation will be discussed in the future.

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[1] F. Cataldo, Polyynes: Synthesis, Properties, and Applications, CRC Press/Taylor & Francis, Boca Raton, FL, 2005.
[2] R.I. Kaiser, Experimental investigation on the formation of carbon-bearing molecules in the interstellar medium via neutral-neutral reactions, Chem. Rev. 102 (2002) 1309-1358.
[3] C.S. Casari, M. Tommasini, R.R. Tykwinski, A. Milani, Carbon-atom wires: 1-D systems with tunable properties, Nonoscale 8 (2016) 4414-4435.
[4] E.A. Rohlfing, High resolution time-of-flight mass spectrometry of carbon and carbonaceous clusters, J. Chem. Phys. 93 (1990) 7851-7862.
[5] R. Eastmond, T.R. Johnson, D.R.M. Walton, Silylation as a protective method for terminal alkynes in oxidative couplings: a general synthesis of the parent polyynes H(C=C)$_n$H (n = 4-10, 12), Tetrahedron 28 (17) (1972) 4601-4616.
[6] M. Tsuji, T. Tsuji, S. Kuboyama, S.-H. Yoon, Y. Korai, T. Tsujimoto et al., Formation of hydrogen-capped polyynes by laser ablation of graphite particles suspended in solution. Chem. Phys. Lett. 355 (2002) 101-108.

[7] Y. Taguchi, H. Endo, Y. Abe, J. Matsumoto, T. Wakabayashi, T. Kodama et al., Polyyne formation by graphite laser ablation in argon and propane mixed gases, Carbon 94 (2015) 124-128.

[8] Y. Sato, T. Kodama, H. Shiromaru, J.H. Sanderson, T. Fujino, Y. Wada et al., Synthesis of polyyne molecules from hexane by irradiation with intense femtosecond laser pulses, Carbon 48 (2010) 1673-1676.

[9] L. Ravagnan, F. Siviero, C.S. Casari, A.L. Bassi, C. Lenardi, C.E. Bottani et al., Photo-induced production of sp-hybridized carbon species from Ag-coated polytetrafluoroethylene (PTFE), Carbon 43 (2005) 1317-1339.

[10] A. Hu, M. Rybachuk, Q.-B. Lu, W.W. Duley, Direct synthesis of sp-bonded carbon chains on graphite surface by femtosecond laser irradiation, Appl. Phys. Lett. 91 (2007) 131906.

[11] C.S. Casari, C.S. Giannuzzi, V. Russo, Carbon-atom wires produced by nanosecond pulsed laser deposition in a background gas, Carbon 104 (2016) 190-195.

[12] M. Bogana, L. Ravagnan, C. S. Casari, A. Zivelonghi, A. Baserga, A. Li Bassi et al., Leaving the fullerene road: presence and stability of sp chains in sp^2 carbon clusters and cluster-assembled solids. New J. Phys. 7 (2005) 81.

[13] Y. Taguchi, H. Endo, T. Kodama, Y. Achiba, H. Shiromaru, T. Wakabayashi et al., Polyyne formation by ns and fs laser induced breakdown in hydrocarbon gas flow, Carbon, 115, (2017) 169-174.

[14] F. Goulay, D.L. Osborn, C.A. Taatjes, P. Zou, G. Meloni, S.R. Leone, Direct detection of polyynes formation from the reaction of ethynyl radical (C_2H) with propyne (CH_3-C≡CH) and allene (CH_2=C=CH_2), Phys. Chem. Chem. Phys. 9 (2007) 4291-4300.

[15] X. Gu, Y.S. Kim, R.I. Kaiser, A.M. Mebel, M.C. Liang, Y.L. Yung, Chemical dynamics of triacetylene formation and implications to the synthesis of polyynes in Titan's atmosphere, Proc. Natl. Acad. Sci. 106 (2009) 16078-16083.

[16] Y.L. Sun, W.J. Huang, S.H. Lee, Formation of polyynes C_4H_2, C_6H_2, C_8H_2, and $C_{10}H_2$ from reactions of C_2H, C_4H, C_6H, and C_8H radicals with C_2H_2, J. Phys. Chem. Lett. 6 (2015) 4117-4122.

[17] D. Chastaing, P. L. James, I. R. Sims, I. W. M. Smith, Neutral-neutral reactions at the temperatures of interstellar clouds: Rate coefficients for reactions of C_2H radicals with O_2, C_2H_2, C_2H_4 and C_3H_6 down to 15 K, Faraday Discuss. 109 (1998) 165-181.

[18] Y. Wada, K. Koma, Y. Ohnishi, Y. Sasaki, T. Wakabayashi, Photoinduced reaction of methylpolyynes $H(C{\equiv}C)_nCH_3$ ($n = 5-7$) and polyyne $H(C{\equiv}C)_5H$ with I_2 molecules, Eur. Phys. J. D 66 (2002) 322.

[19] N. Kitamura, A. Osawa, R. Sata, H. Suzuki, Y. Morisawa, M. Hatanala et al., Laser ablated octatetrayne derivative $C_{12}H_8$, Abstract of The 56th Fullerenes-Nanotubes-Graphene General Symposium, (2019) 84.

[20] A. Matsuda, T. Hayashi, R. Kitaura, A. Hishikawa, Femtosecond laser filamentation in gaseous ethylene: Formation of hydrogenated amorphous carbon, Chem. Lett. 46, (2017) 1426-429.