

## Power Dependence on Formation of Polyynes by Laser Ablation in Water

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Polyynes were prepared by liquid laser ablation of a graphite target in deionized water at various physical conditions such as laser power (20 and 40 mJ/pulse) and ablation wavelengths (355, 532, and 1064 nm). The effects of physical parameters on the linear carbon chain length were examined by analyzing the densities of polyynes with different carbon numbers ( $C_6H_2$ ,  $C_8H_2$ , and  $C_{10}H_2$ ) as well as their branching ratios. We concluded the photophysical processes turned out to play a more significant role than thermal ones in the formation of polyynes.

**Key Words** : Polyynes, Laser ablation, Graphite, Photophysical

### Introduction

Polyne molecules are *sp*-hybridized linear carbon chain compound connected by a sequence of alternating carbon-carbon single and triple bonds.<sup>1</sup> They are typically terminated by capping hydrogen atoms or groups to give  $H-(C\equiv C)_n-H$  ( $n \geq 2$ ). Polyynes are of significance in astrophysics and materials science; they are known to exist in the interstellar medium and their one-dimensional electronic structures have attracted attention because of their size-dependent band gaps and nonlinear optical properties.<sup>2-7</sup>

Laser irradiation in liquid phase has been known to be an effective method for generation of materials such as polyynes and metal nanoparticles as it does not require a high-vacuum apparatus and the ablation media can be easily changed. A widely employed synthesis technique uses the interaction of nanosecond laser pulses with suspended carbon particles in organic solvents to produce polyynes.<sup>8,9</sup> This simple method proved to be highly interesting as it produces a high concentration of polyynes.

When a solid graphite target is irradiated by nanosecond lasers in liquid phase, polyynes as well as carbon clusters are produced. Matsutani *et al.* reported the formation of polyynes by liquid-phase laser ablation from powder and pellets of graphite and PTCDA (Perylene-3,4,9,10-tetracarboxylic dianhydride) in *n*-hexane and they could obtain polyynes up to  $C_{22}H_2$  and  $C_{18}H_2$  from pellets of graphite and PTCDA, respectively. And the amount of polyynes generated was greater for powder than pellets.<sup>11,12</sup> Tsuji *et al.* reported that polyynes up to  $C_{14}H_2$  were obtained from graphite pellets in *n*-hexane using 355 or 532 nm laser while the amount of linear carbon chain molecules was small at 1064 nm.<sup>8,10</sup> Compagnini *et al.* reported the preparation of polyynes by laser ablation of a carbon rod in water reaction.<sup>13</sup> They claimed that hydrogen-capped polyynes were formed by polymerization and hydrogenation of  $C_2$  and  $C_2H$  radicals through a chain reaction. Therefore, it is considered that the concentration of hydrogen and  $C_2$  radicals in the plume plays an importance role in the formation of

hydrogen-capped molecules.

In this work, polyynes are formed by laser ablation of a graphite target at several wavelengths (355, 532, and 1064 nm) in deionized water and they were identified by UV-Vis absorption spectra. We discuss the effects of laser power and wavelength on the size of polyynes by laser ablation in liquid.

### Experiment

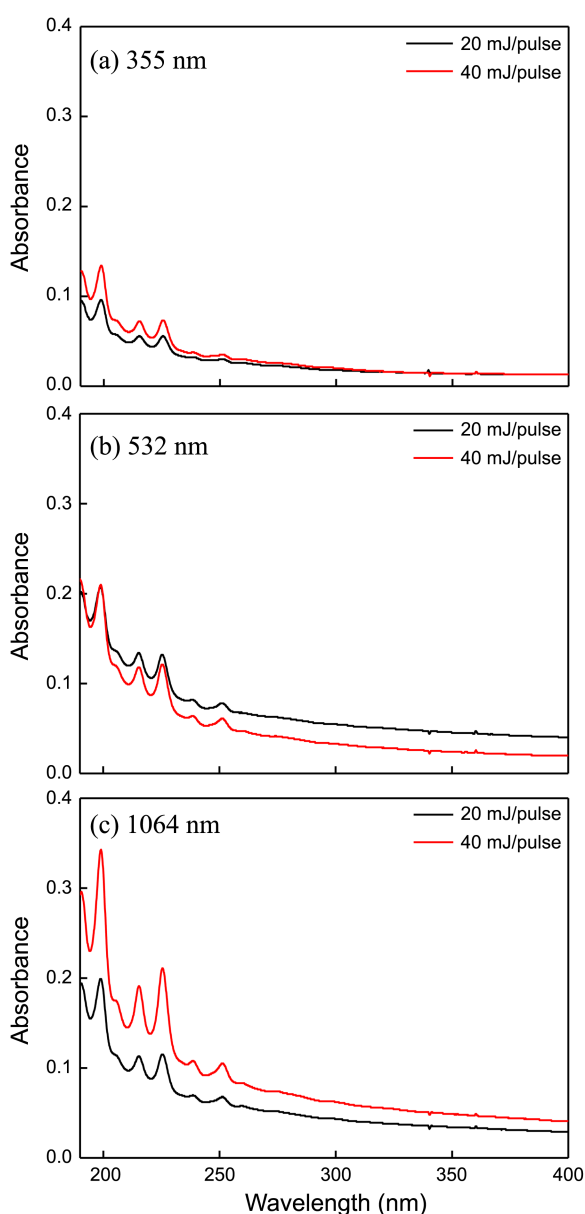
Polyynes were produced by laser ablation of a graphite target (99.99%) in a stainless steel vessel filled with 30 mL of deionized water. The laser wavelengths employed in the experiment were 355, 532, and 1064 nm. The surface of the graphite target was polished with 1200-grade emery paper prior to laser irradiation by a Q-switched Nd:YAG laser (Continuum, Surelite I, pulse duration = 5 ns) operated at 10 Hz. In order to avoid the generation of splashes, the maximum energy of the Nd:YAG laser was 40 mJ/pulse and the experiments were performed at two different laser energies, 20 and 40 mJ/pulse. The laser beam was loosely focused using a lens with a focal length of 300 mm. The spot size of the focused laser beam was 2.0 mm in diameter and the typical irradiation time was 20 min. The solution was stirred using a magnetic stirrer during laser ablation. The target was also continuously rotated to minimize the effect of target aging and to provide some stirring effect. The optical properties of the nascent polyynes solutions were examined at room temperature by a UV-Vis absorption spectrophotometer (Shimadzu UV1800). We focused on polyynes with carbon numbers more than 5 due to instrumental limitation; for polyynes with the number of carbon atoms less than 6, the corresponding absorption peaks are observed below 190 nm, which is out of range for typical spectrometers.

### Results and Discussion

Previous works by other groups reported so far were

performed with the optimized ablation laser power and ablation time at different wavelengths.<sup>8,12</sup> Here, however, we present the effects of carbon nanoparticle concentrations on the formation of polyynes by varying not only the laser wavelength but also the laser power.

Figure 1 shows the UV-Vis spectra of polyynes solutions prepared by laser ablation in deionized water at different laser powers (20 and 40 mJ/pulse) and wavelengths (355 (a), 532 (b), and 1064 nm (c)). Characteristic absorption peaks of polyynes were displayed in the wavelength region of 190–300 nm. We could assign the peaks of polyynes prepared at several wavelength and power after base correction according to the number of carbon atoms in the polyynes; C<sub>6</sub>H<sub>2</sub> (199.0 nm), C<sub>8</sub>H<sub>2</sub> (215.0 nm), and C<sub>10</sub>H<sub>2</sub> (255.0 nm). As displayed in Figure 1, the peak intensities of polyynes were

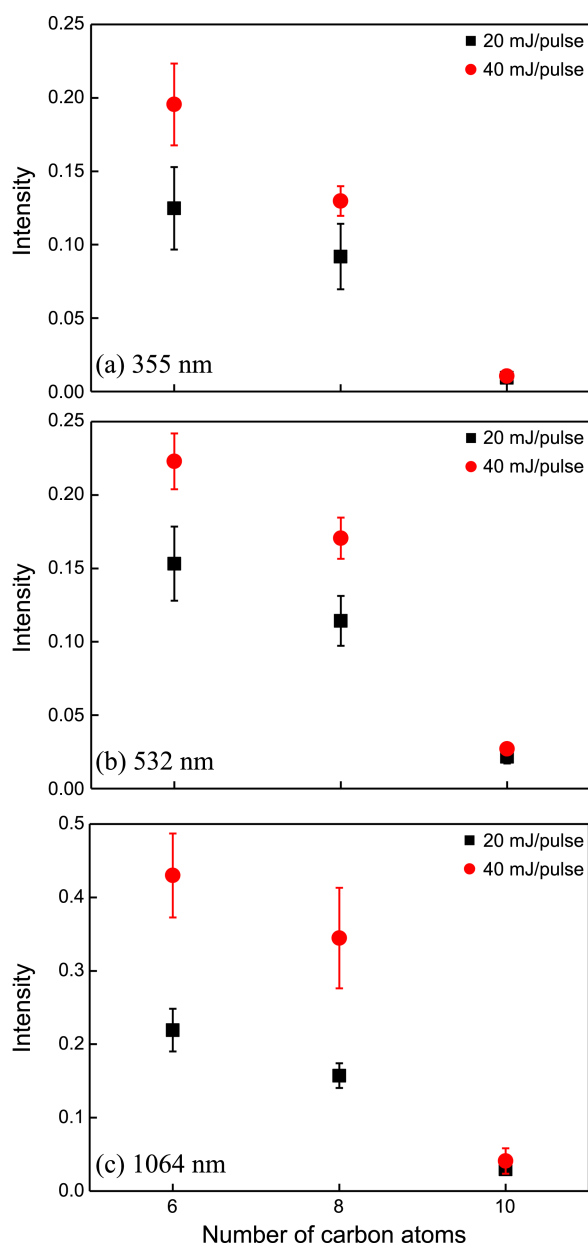


**Figure 1.** Typical UV absorption spectrum of a polyyne solution formed by laser ablation of a graphite target in deionized water at (a) 355, (b) 532, and (c) 1064 nm. The laser powers were 20 and 40 mJ/pulse, respectively.

remarkable at 40 mJ/pulse, which indicates that a large amount of polyynes was generated. The peak intensity of polyynes increased remarkably at 1064 nm compared to other wavelengths, 532 and 355 nm. Our results are consistent with the previous work by Matsutani *et al.*, who showed that the amount of polyynes generated by laser ablation of fullerene and graphite pellet targets in methanol and *n*-hexane was significantly larger at 1064 nm than other wavelength (532 and 355 nm).<sup>11</sup> But they did not report the effects of laser power on the formation rate of polyynes. The formation of polyynes can be explained by the following mechanism. Above all, generation of polyynes requires C<sub>2</sub> radicals.

In general, both insoluble graphite-like carbon (amorphous) and soluble hydrogen-capped polyynes are generated by laser ablation of graphite target in water. The formation of polyynes in gas phase was previously explained by adopting photochemical process.<sup>8</sup> Similarly, in liquid laser ablation, C<sub>2</sub> radicals produced by laser ablation of graphite in water are considered to be polymerized and subsequently hydrogenated to become C<sub>*n*</sub>H<sub>2</sub> (polyynes). Namely, as pointed out by Tsuji *et al.*, the length of linear carbon chains increases *via* successive coupling reaction (or chain reaction) of C<sub>2</sub> radicals.<sup>8,11</sup> In other words, the lengths of polyynes are determined when continuous coupling reaction is interrupted as the polymerized C<sub>2</sub> radicals are capped by hydrogen atoms provided by the solvent and the production of polyynes is dependent on the concentration of C<sub>2</sub> radicals. When the laser power is high or the wavelength is short, the laser beam is more absorbed in liquid before it arrives at the target surface as more impurities which can absorb or scatter the incident photon are formed by interaction of the laser beam and the solvent. As a result, less polyynes are produced at shorter wavelength and the length of polyynes becomes shorter as the chain reaction stops at an early stage due to the deficiency of C<sub>2</sub> radicals.

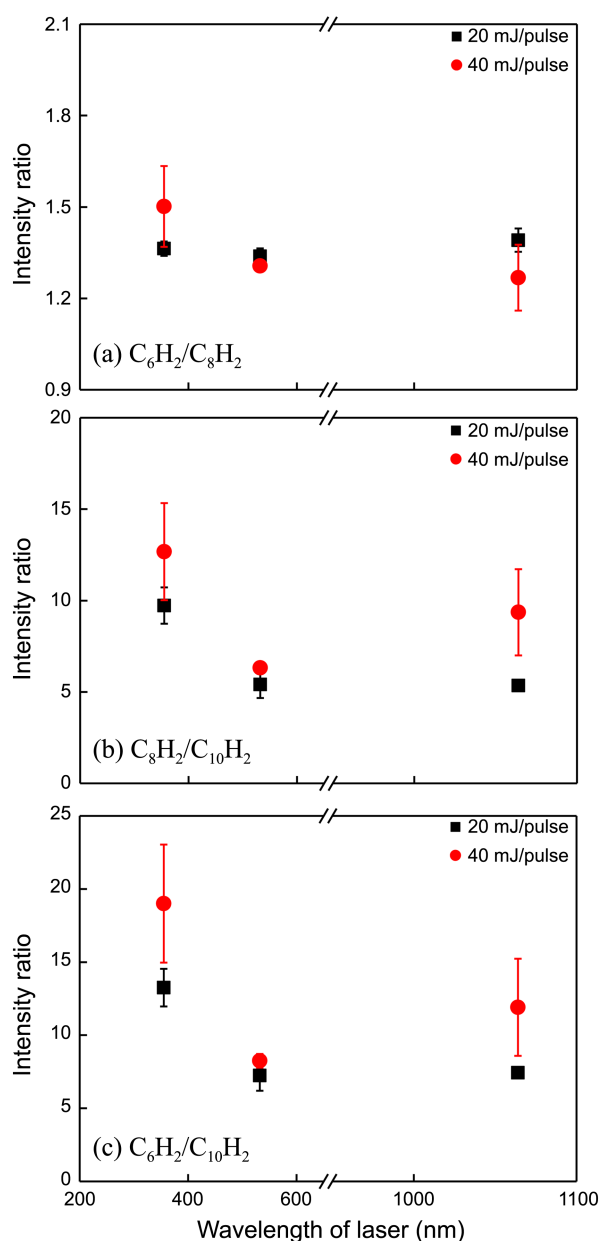
In order to examine the physical effects on the amount of polyynes and carbon chain length in detail, we adopted different laser powers (20 and 40 mJ/pulse) and wavelengths (355, 532, and 1064 nm) and compared the branching ratios of C<sub>6</sub>H<sub>2</sub>/C<sub>8</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>2</sub>/C<sub>10</sub>H<sub>2</sub>, and C<sub>8</sub>H<sub>2</sub>/C<sub>10</sub>H<sub>2</sub> after baseline correction of the UV-Vis spectra. Figure 2 shows peak intensities of three different polyynes produced by laser ablation of a graphite target in water at 20 and 40 mJ/pulse, where Figures 2(a), 2(b), and 2(c) correspond to 355, 532, and 1064 nm, respectively. This indicates that polyynes were produced more at higher laser intensity at all the wavelengths employed. Figure 3 shows the intensity ratios of polyynes peaks, C<sub>6</sub>H<sub>2</sub>/C<sub>8</sub>H<sub>2</sub> (a), C<sub>8</sub>H<sub>2</sub>/C<sub>10</sub>H<sub>2</sub> (b), and C<sub>6</sub>H<sub>2</sub>/C<sub>10</sub>H<sub>2</sub> (c), as a function of the laser wavelength at two different laser intensities. The branching ratio of C<sub>6</sub>H<sub>2</sub>/C<sub>8</sub>H<sub>2</sub> remained nearly the same regardless of the wavelength when the laser intensity was 20 mJ/pulse. However, when the laser intensity was increased up to 40 mJ/pulse, C<sub>8</sub>H<sub>2</sub> was relatively more produced than C<sub>6</sub>H<sub>2</sub> at 1064 nm while C<sub>6</sub>H<sub>2</sub> was more enriched at 355 nm. However, note that longer polyynes, namely C<sub>10</sub>H<sub>2</sub>, were less produced at the higher



**Figure 2.** Relative intensity of polyynes produced by laser ablation of graphite target as a function of the number of carbon atoms.

laser intensity when we consider the branching ratios of  $C_8H_2/C_{10}H_2$  and  $C_6H_2/C_{10}H_2$ . In Figure 3(a), the branching ratios of  $C_6H_2/C_8H_2$  at 355 and 532 nm showed same trends as in 3(b) and 3(c). On the other hand, the trend was slightly different at 1064 nm, which may stem from the low laser fluence at 1064 nm.

In general, photochemical mechanisms are employed to describe chemical reactions caused by absorption of light; photochemical processes offer advantages over thermal methods to produce thermodynamically disfavored products by overcoming large activation barriers in a short period of time and allowing reactivity otherwise inaccessible by thermal methods. Accordingly, the photochemical processes play more important role in formation of polyynes by liquid laser ablation than thermal ones at shorter wavelengths or



**Figure 3.** The branching ratios of (a)  $C_6H_2/C_8H_2$ , (b)  $C_8H_2/C_{10}H_2$ , and (c)  $C_6H_2/C_{10}H_2$  in polyynes prepared by laser ablation of graphite target in water as a function of the laser wavelengths after baseline correction and normalization. The laser powers were 20 and 40 mJ/pulse, respectively.

the higher laser power. In this experimental, when polyynes were produced by laser ablation of graphite target, polyynes were generated by photochemical process more than thermal process. For this reason, polyynes were produced by liquid laser ablation method mainly short-length polyynes than long-length ones.

In conclusion, we observed that both laser intensity and wavelength play an important role in the formation of polyynes by liquid laser ablation. In order to derive the optimum condition for the production of larger polyynes by liquid laser ablation, further investigations related to the ablation time as well as more detailed information on the effects of

laser wave length and intensity are required.

### Summary

We have investigated the absorption spectra of polyynes produced by laser ablation of a graphite target in deionized water at different laser power and wavelength to verify their effects on the formation rate of polyynes and the efficiency of producing longer polyynes. The lower laser intensity and longer wavelength proved to be helpful to produce longer polyynes in general.

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