Preparation of Polyynes by the Laser Ablation of Graphite in Water and Organic Solvents

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Polyynes were formed by laser ablation of a graphite target in deionized water (H_2O and D_2O) and various organic solvents such as acetonitrile, *n*-hexane, and *c*-hexane and were identified by analyzing ultraviolet (UV) absorption and Raman spectra. We assigned the major UV absorption peaks that coincided with the electronic transitions corresponding to linear polyyne chains. The UV absorption peak intensities of a polyyne solution decreased as the holding temperature of the solution increased. Also, the absorption spectra of polyynes obtained by laser ablation of a graphite target at different volume fractions of H_2O and D_2O were examined.

Key Words : Polyynes, Laser ablation, Graphite

Introduction

Polyynes are linear carbon chain compound with alternating carbon-carbon single and triple bonds and are typically terminated by hydrogen atoms to give $H(C\equiv C)_nH$. Polyynes are of significance in astrophysics, molecular science, and nanotechnology[1]; they are known to exist in the interstellar medium[2-4] and their one-dimensional electronic structures have attracted considerable research interest because of their size-dependent band gaps[5] and nonlinear optical properties.[6]

Polyynes were first demonstrated using conventional chemical methods.[7] Laser irradiation of carbon materials in the liquid phase has also been shown to be an effective method for generation of polyynes as it is a simple technique that does not require a high-vacuum apparatus and has easily changeable ablation media. A widely employed synthesis technique uses the interaction of nanosecond laser pulses with suspended carbon particles in organic solvents to produce polyynes.[8,9] Recently, formation of polyynes has been performed with femtosecond laser irradiation, where polyynes are synthesized in an organic liquid even without introduction of any carbon particles.[10-12] This method is very interesting in that it is quite simple and 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. Compagnini *et al.* reported the formation of polyynes by pulsed laser ablation of a carbon rod in water.[13] They claimed that that hydrogen-capped polyynes are formed by polymerization and hydrogenation of C_2 and C_2H radicals through a chain reaction. In addition, they observed that C_2 and C_2H radicals are the major species in the plume when graphite is ablated in liquids.[9] Therefore, it is thought that the hydrogen concentration in the plume, as in the case of ablation in water, is crucial for enhancing the termination step with the formation of shorter hydrogen-capped mole-cules. A similar result has been also reported by Heath *et al.*,[14] who showed that C_8H_2 molecules are found to be particularly stable when laser vaporization of graphite into He carrier gas is performed with traces of H_2 and H_2O.

In the present study, polyynes are formed by laser ablation of a graphite target at 1064 nm and identified by analyzing normal Raman spectra and UV absorption spectra in deionized water (H_2O and D_2O) and various organic solvents such as acetonitrile, *n*-hexane, and *c*-hexane. We discuss the effects of the holding temperature on the formation rate and size of polyynes.

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 (H_2O and D_2O) and various organic solvents such as acetonitrile ($\geq 99.9\%$), *n*-hexane ($\geq 98.5\%$), and *c*-hexane ($\geq 99.9\%$). These solvents were purchased from Sigma-Aldrich and used without further purification. The surface of the graphite target was polished with 1200-grade emery paper prior to laser irradiation using a Q-switched Nd:YAG laser (Continuum, Surelite I, λ = 1064 nm, pulse duration 5 ns) operated at 10 Hz. The energy of the Nd: YAG laser was maintained at 40 mJ/pulse in order to avoid generation of splashes. 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 during the ablation using a magnetic stirrer. 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 polyyne solutions were examined at several different temperatures (including room temperature) by a UV-vis absorption spectrophotometer (Shimadzu UV1800). Normal Raman spectra were recorded by a spectrophotometer (HORIBA T64000).

Results and Discussion

The UV absorption spectra of polyyne solutions prepared by laser ablation of a graphite target in deionized water and organic solvents are shown in Figures 1 and 2. The peak at 198.0 nm belongs to C_6H_2; the peaks at 205.0, 215.5, and 226.0 nm represent C_8H_2; those at 239.5 and 251.5 nm belong to $C_{10}H_2$; and those at 275.0, 297.0, and 318.0 nm represent $C_{12}H_2$, $C_{14}H_2$, and $C_{16}H_2$, respectively.[15,16] Figure 1 shows the positions of the absorption maxima for two different samples: one ablated in H_2O and the other in CH_3CN. Peaks are observed between 200.0 and 340.0 nm, indicating the presence of polyynes with length of up to $C_{16}H_2$.[17] Very small (or short) polyynes (n < 8) are difficult to observe due to the weak intensity of the absorption peak at 200.0 nm. The absorption behavior as a function of polyyne length is obtained by semi-empirical calculations of the electronic absorption of H-polyynes and dicyano polyynes.[18] If the low-energy electronic transitions of $^1\Sigma^+ \leftarrow {}^1\Sigma^+$ (for monocyano polyynes) and $^1\Sigma^+_u \leftarrow {}^1\Sigma^+_g$ (for polyynes and dicyano-polyynes) are allowed, they should contribute at increasingly longer wavelengths as the linear carbon chain length is increased.[18]

The UV absorption spectra of polyyne solutions prepared by laser ablation of a graphite target in *c*-hexane and *n*-hexane are shown in Figures 2. From these solutions, we observed absorption spectra of polyynes in the wavelength range of 200-300 nm. For polyynes prepared in the laser
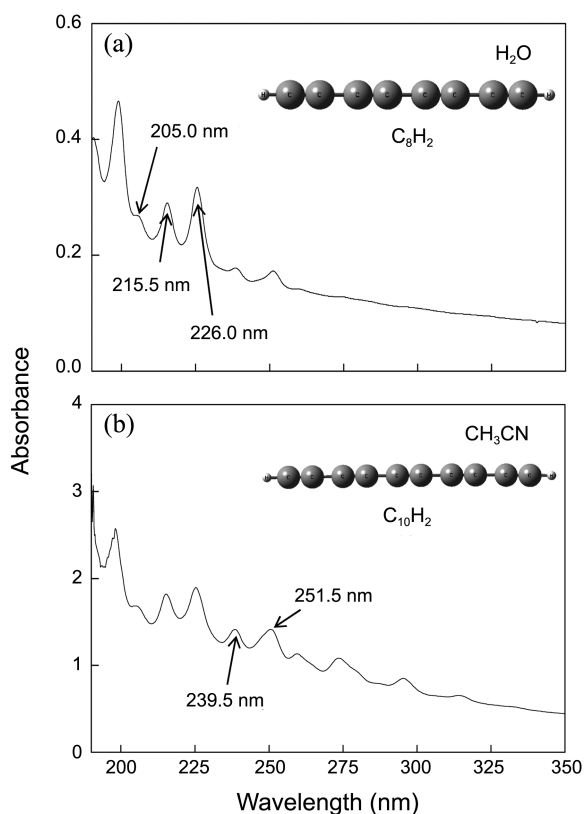

Figure 1. Typical UV absorption spectrum of a polyyne solution formed by liquid laser ablation of a graphite target in deionized water (top) and acetonitrile (bottom) at 1064 nm (40 mJ/pulse).
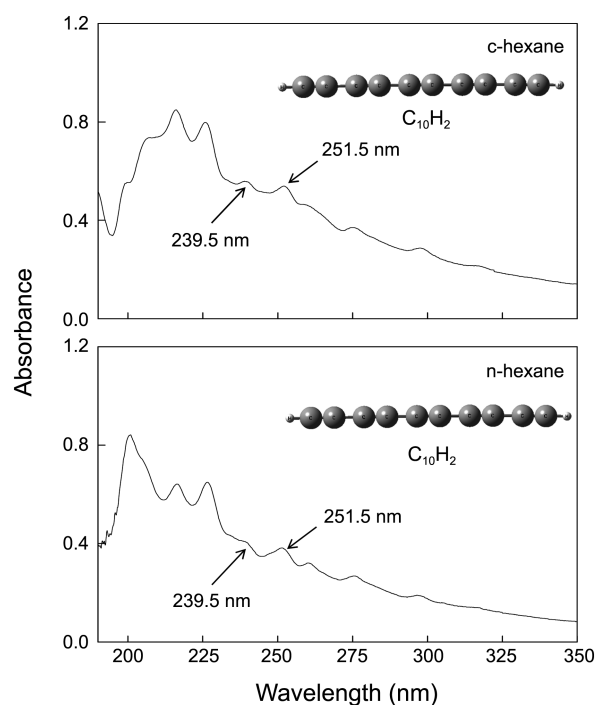

Figure 2. Typical UV absorption spectrum of a polyyne solution formed by liquid laser ablation of a graphite target in *c*-hexane (top) and *n*-hexane (bottom) at 1064 nm (40 mJ/pulse).

ablation of organic solvents, the carbon source for the formation of polyynes may be the graphite target, the solvents, or both.[15] While the main component of these samples appears to be polyynes of length 6C, Figure 2 also shows that polyynes prepared in hexanes are longer than those produced in water. This indicates that the solvent molecules may play a central role in the formation of polyynes. The carbon-carbon bonds of hexane likely fragment and then reform into longer polyynes due to their interaction with the graphitic plasma.[11]

Production of polyynes can be confirmed most easily by UV-vis absorption spectroscopy through the assignment of the characteristic absorption peaks which reflect the lengths of polyynes. As well as UV-vis method, we also employed Raman spectroscopy to verify the molecular structures of
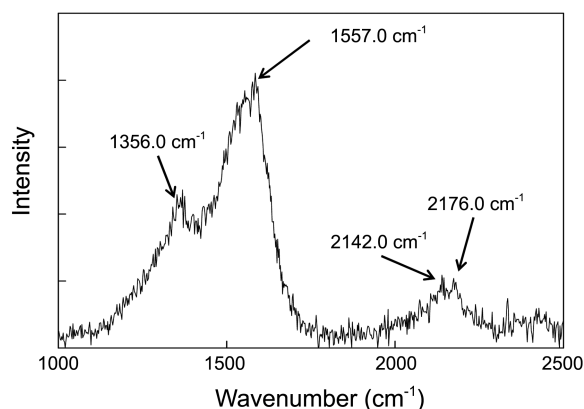

Figure 3. Raman spectra of polyynes prepared by laser ablation of graphite target in water at 1064 nm.
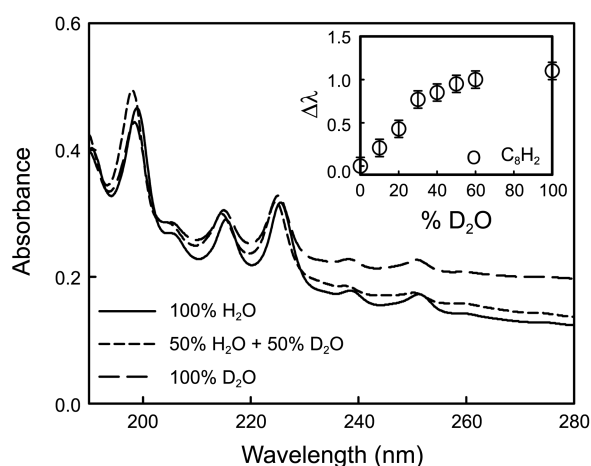
Figure 4. UV absorption spectra of polyynes prepared by laser ablation of a graphite target at different volume fractions (H₂O: D₂O). The inset shows the difference of polyynes peak position at different volume fractions.

Figure 5. Effects of holding time on the UV absorption peak intensities of a polyyne solution at 215.5 nm (C_8H_2 (○)) and 251.5 nm ($C_{10}H_2$ (□)) after base-line subtraction at different temperatures (273 (a), 283 (b), 303 (c), and 313 K (d)). The solid line in each panel represents a profiles fitted using $y = R_0 + R_1 e^{-kt}$.

polyynes. Raman spectra of hydrogen-capped linear carbon chains are characterized by the presence of Raman bands located around 2100 cm⁻¹, which are related to the carbon triple bonds.[12,17] Figure 3 shows the Raman spectrum of hydrogen-capped linear carbon chain in water. The peaks centered at 2156 cm⁻¹ result from the C≡C stretching vibrations of polyynes of various length. The first peak can be attributed to C_8H_2,[17] while the second one at 2176 cm⁻¹ is assign to the carbyne asymmetric stretching mode.[19] This agrees well with the Raman shifts previously reported for the symmetric stretching vibrational mode of polyynes.[11,12,17]

Not only H-capped polyynes but D-terminated polyynes were also produced as we irradiate a graphite target in D₂O. Figure 4 shows the absorption spectra of polyynes obtained by laser ablation of a graphite target at different volume fractions (H₂O:D₂O). The formation rate of D-terminated polyynes inferred from the peak intensities was nearly the same as that of H-terminated ones. With increase in the fraction of the D₂O volume, the absorption peaks of the polyynes show an apparent blue shift. This indicates that D-termination induces slight changes in the electronic structures of polyynes; unfortunately, however, no theoretical works on the electronic structures of D-terminated polyynes have been reported as yet.

In a previous study,[20] the effects of holding time of the polyynes solution at room temperature were analyzed. In polyynes solutions prepared by laser ablation of graphite and stored at room temperature, the UV polyynes absorption peaks were found to decrease as the holding time increased. We can also estimate the effects of the holding time of the polyyne solution and Figure 5 illustrates the relative concentrations of polyynes C_8H_2 (○) and $C_{10}H_2$ (□) in deionized water at various temperatures. The peak intensities at 215.5 and 251.5 nm, corresponding to C_8H_2 (○) and $C_{10}H_2$ (□), respectively, are shown in Figure 5 after subtracting the baseline. At low holding temperatures (273 and 283 K), the absorption peak intensity of the polyynes samples remained
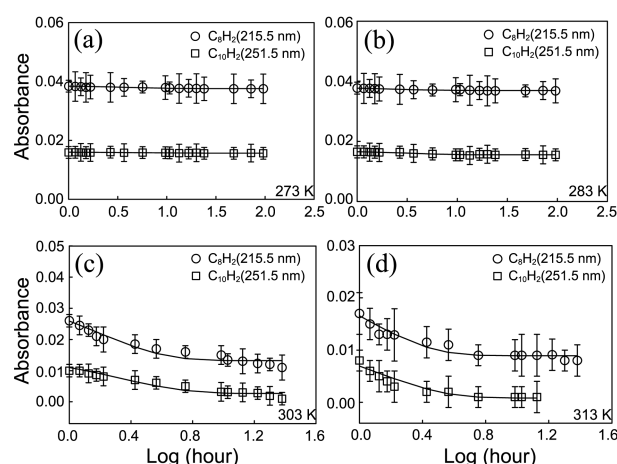
Table 1. Fitting parameters for the exponential plus a rate constant of the UV absorption peak intensities of a polyyne solution at 215.5 nm (C_8H_2 (○)) and 251.5 nm ($C_{10}H_2$ (□)) after base-line subtraction at different temperatures

	C_8H_2		$C_{10}H_2$	
	R_0	k	R_0	k
313 K	0.0091	0.0091	0.0008	0.7579
303 K	0.0132	0.6403	0.0027	0.4674
283 K	0.0369	0.3949	0.0155	0.2968
273 K	0.0376	0.2157	0.0157	0.1582

nearly the same even after several weeks. However, as the holding temperatures increased (303 and 313 K) the polyynes absorption peaks decreased significantly in a short period of time. The rate constant was computed from the data in Figure 5 using a relation equation by an exponential decay plus a constant: $y = R_0 + R_1 e^{-kt}$. We could obtain the rate constant from the reduction of the peak intensities of the polynnes at several different temperatures (see Table 1). This indicates that the polyynes in a warm aqueous environment are more unstable than those held at lower holding temperatures. Casari *et al.*[21] investigated to the thermal stability of polyynes, characterizing the C peak (at 2100 cm⁻¹) in Raman spectra of thermally annealed films at various temperatures. They reported the intensity of C peak as a function of time at several temperatures and obtained the values of two decay constants; one is fast, the other is slow.[21] This implies the presence of two activated processes with energy barriers.

Summary

Polyynes were prepared by liquid-phase laser ablation and identified by UV absorption spectra. Gratifyingly, we were able to demonstrate the formation of polyynes as large as $C_{2n}H_2$ (n = 3-8) at 1064 nm. From normal Raman spectra, we also identified the polyynes prepared by laser ablation at

1064 nm, and found Raman bands related to carbon triple bonds that were located around 2150 cm^{-1}.

With an increase in the holding temperature the UV absorption peak intensities of a polyyne solution decreased as a function of holding time. The absorption spectra of polyynes obtained by laser ablation of a graphite target at different volume fractions (H$_2$O:D$_2$O) indicate that a termination of polyynes with D gives a blue shift in UV absorption. For further insight into the formation of polyynes by liquid-phase laser ablation of a graphite target, it would be beneficial to observe polyynes spectra as a function of the ablation laser wavelength.

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