http://dx.doi.org/10.5012/bkcs.2012.33.7.2439

The Solvent Effects on the Formation of Polyynes by Laser Ablation

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Received January 2, 2012, Accepted April 20, 2012

Key Words : Polyyne, Laser ablation, Graphite

Polyynes have a unique molecular structure: a linear carbon chain with alternating carbon-carbon single and triple bonds.[1] They are typically terminated by hydrogen atoms to be described as H-(C≡C)$_n$-H but they are also often terminated by bulky groups. Recently, polyynes are of extensive research target molecules not only in astrophysics area but also in nano-electronics and optical devices.[2] Polyynes are important precursor molecular components in the production of carbon nanotubes[3,4] and they have been employed as nano-conductors because of their intriguing electrical properties.[2] Besides, their one-dimensional systems have attracted utmost research interest due to strong non-linear optical properties as well.[5]

In general, the formation of polyynes in a liquid phase can be achieved by two different methods: one is the electric arc[6] and the other is the laser ablation.[7] Cataldo *et al.*[6] carried out formation of polyynes by the electric arc between graphite electrodes submerged in organic solvents such as aceto-nitrile, *n*-hexane, and methanol. A widely employed synthesis technique uses the interaction of nanosecond laser pulses with suspended carbon particles in organic solvents to produce polyynes.[8,9] On the other hand, Tsuji *et al.* have reported that hydrogen-terminated polyynes were also produced directly by laser ablation of graphite particles in organic solvents like as benzene, toluene, or hexane solution.[10]

In particular, the laser ablation in liquid has been proved to be highly effective to produce polyynes and, even better, it is a simple technique, where high-vacuum apparatus is not required and ablation surroundings such as solvents can be easily changed. Furthermore, the recovery of the product is higher than in laser ablation in the gas phase.

Here, in order to examine the effects of the chemical and physical properties of various solvents such as *n*-hexane, *c*-hexane, *n*-heptane, and *n*-octane on the production of polyynes, we examined the branching ratios in the formation of polyynes with different chain lengths by laser ablation in several different solvents.

Experiment

The apparatus employed in this study was described in the earlier studies.[3,7] Briefly, polyynes were produced by laser ablation of a graphite target (99.99%) in a stainless steel vessel filled with 30 mL of various organic solvents such as *n*-hexane (≥ 98.5%), *c*-hexane (≥ 99.9%), *n*-heptane (≥ 99.0%), *n*-octane (≥ 99.0%). 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 laser was maintained at 20 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 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 polyynes solutions were studied at room temperature in various solvents by a UV-vis absorption spectrophotometer (Shimadzu UV1800) and normal Raman spectra were recorded by a spectrophotometer (HORIBA T64000).

Results and Discussion

The molecular structures of polyynes can be verified by Raman spectroscopy most conveniently. The Raman spectrum of polyynes prepared by laser ablation of a graphite target in *n*-hexane is displayed in Figure 1. The broadened band in the 1300-1700 cm^{-1} region can be attributed to amorphous graphite-like particles,[11-14] which can be further decomposed to the D band at around 1400 cm^{-1} and the G band at 1600 cm^{-1} region. The D and G band indicate

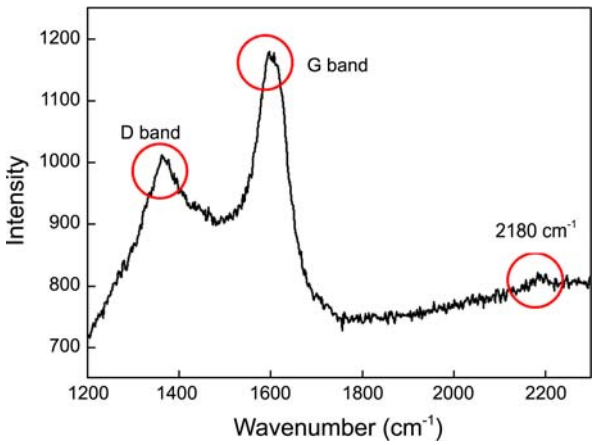

Figure 1. Raman spectrum of polyyne solution prepared by laser ablation of graphite target in *n*-hexane at 1064 nm.

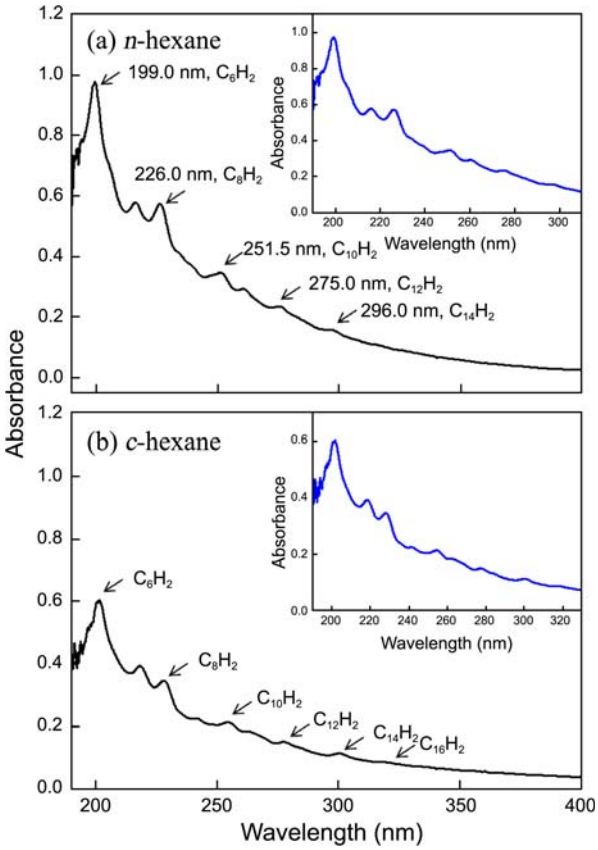

Figure 2. Typical UV absorption spectrum of a polyyne solution produced by laser ablation of a graphite target in *n*-hexane (a) and *c*-hexane (b) at 1064 nm (20 mJ/pulse).

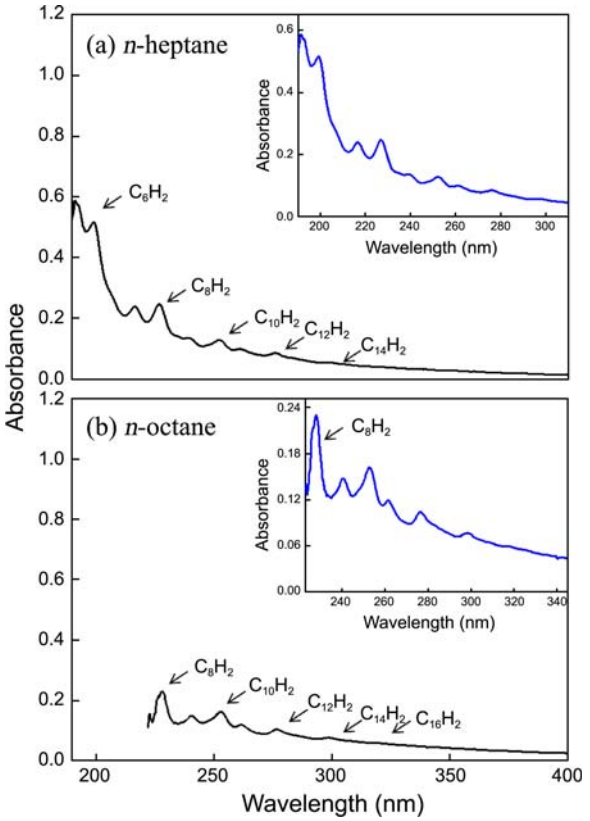

Figure 3. Typical UV absorption spectrum of a polyyne solution produced by laser ablation of a graphite target in *n*-heptane (a) and *n*-octane (b) at 1064 nm (20 mJ/pulse).

characteristic features of highly distorted bond length and angle.[15] The disordered component (G band) was slightly higher than that of the D band. Hydrogen-capped linear carbon chain are characterized in their Raman spectrum by the presence of the band located around 2200 cm^{-1}, which can be attributed to the vibrational stretching of the carbon triple bonds.[10-14]

The UV-vis spectra of polyynes solution prepared by liquid laser ablation in *n*-hexane and *c*-hexane are displayed in Figures 2(a) and 2(b). In addition, Figures 3(a) and 3(b) show the UV-vis spectra of polyynes in *n*-heptane and *n*-octane, respectively. Characteristic absorption peaks of polyynes in the wavelength region of 190-350 nm were observed in all the UV-vis spectra,[6,10] which indicate that polyynes in *n*-hexane and *n*-heptane were produced up to C14 linear carbon chains. Under the same experimental conditions, while the intensities of polyynes were smaller, polyynes prepared in *c*-hexane and *n*-octane were generated up to C16 long-chain polyynes. Based on these UV-vis spectra of polyynes prepared in different solvents, it is apparent that the length and the amount of polyynes depend on the solvents.

Surprisingly, there has been no clear explanation on the nature of the solvent which has significant effects on the formation of polyynes even though there are experimental results on the wavelength dependence: Matsutani *et al.*[16] investigated the amount of linear carbon chain molecules generated by laser ablation in several different wavelength and observed that the production of polyynes were optimized at 1064 nm.

In order to examine the solvent effects on the carbon chain length, we compared the branching ratios of C_8H_2 and $C_{10}H_2$, C_8H_2 and $C_{12}H_2$ in the UV-vis spectra of polyynes prepared by laser ablation of graphite target in several solvents after baseline correction. Figure 4(**I**) shows the peak intensities of polyynes in various solvents before normalization, where (a), (b) and (c) correspond to C_8H_2, $C_{10}H_2$ and $C_{12}H_2$, respectively. After normalization, we obtained the intensity ratios of polyynes peaks, $C_8H_2/C_{10}H_2$ and $C_8H_2/C_{12}H_2$, when they were prepared in different solvents, as shown in Figure 4(**II**). Based on Figure 4(**II**), the magnitudes of the branching ratios of the polyyne peaks in various solvents can be ranked in the following order: *c*-hexane, *n*-octane, *n*-heptane, and *n*-hexane. That is, shorter carbon chain polyynes were preferentially generated in the order of *c*-hexane, *n*-octane, *n*-heptane, and *n*-hexane. Note that the peaks around 300 nm, corresponding to $C_{14}H_2$ were most prominent in *n*-octane.

Now, it would be certainly worthwhile to explore what kinds of the properties of the solvents affect the formation of polyynes prepared by liquid laser ablation of graphite target in several solvents. In case of *n*-alkane solvents, the formation of polyynes were claimed to be dependent on the boiling point of the solvent by Cataldo.[6] He also reported

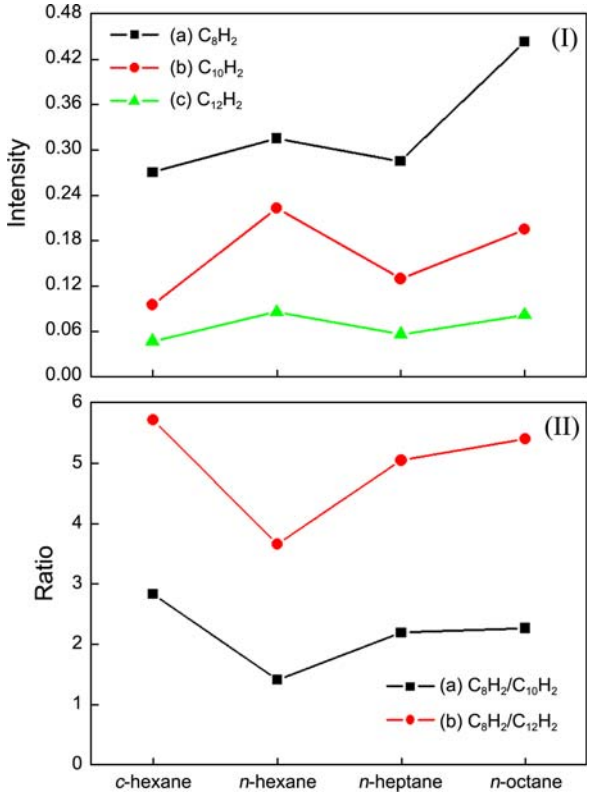

Figure 4. The ratio $C_8H_2/C_{10}H_2$ and $C_8H_2/C_{12}H_2$ in polyyne solution prepared by laser ablation of a graphite target in *n*-hexane, *c*-hexane, *n*-heptane, and *n*-octane, before (I) and after (II) normalization.

that the higher the boiling point of the solvent is, the faster the rate of formation of polyynes is. Tsuji *et al.* demonstrated that polyynes are produced through laser ablation of C_{60} particles suspended in hexane or methanol and showed that polyynes are produced more in hexane than in methanol.[8] This indicates that the donation of hydrogen atom, which is determined by the solvent, plays a key role in the formation of polyynes by laser ablation.

Here, we further investigated other properties of the solvent such as bond dissociation energy, thermal conductivity, and contents of hydrogen atoms by either the mass or the number, which might have certain effects on the production of polyynes. Firstly, we have performed density functional theory calculation at the B3LYP/6-311+G level of theory to obtain dissociation energies of hydrogen atoms in solvent molecules by employing the *Gaussian 09W* program package[17] as listed in Table 1. From the results, the bond dissociation (D_0(R-H)) energies turned out to decrease in the order of *n*-octane, *n*-hexane, *n*-heptane, and *c*-hexane, which is contradictory to our experimental results and leads us to suggest that the bond dissociation energy is not a crucial factor in the formation of polyynes.

Secondly, we examined the effects of the thermal conductivity of the solvents on the formation of polyynes. In case of laser ablation in liquid, high intensity pulsed laser beam is focused to a small spot on the target surface, which brings about a sudden increase in temperature. It is of note that the boiling point of the solvent has certain effect on the formation of polyynes.[6] Accordingly, the thermal conductivity of the solvent is also expected to play a role. As listed in Table 1, the thermal conductivities of the solvents at 293 K are in the order of *n*-heptane > *n*-octane > *n*-hexane > *c*-hexane. However, the formation rates of polyynes were rather independent on the magnitude of the thermal conductivity.

As hydrogen atoms are provided from the solvent in the formation of polyynes, the content of hydrogen atoms in the solvent may have strong influence on the production of polyynes. The mass of hydrogen atoms contained in 1 mL of each solvent is list in Table 1. Since there is no tendency, it is difficult to justify that the mass of hydrogen atoms contained in 1 mL of solvents affect the generation of polyynes significantly. Finally, we investigated the effects of the number of hydrogen atoms per carbon in the solvent molecule on the formation of polyynes. The relative numbers of hydrogen atoms per carbon atom in various solvent molecules is listed in Table 1, which are in the order *n*-hexane > *n*-heptane > *n*-octane > *c*-hexane as shown in Table 1. This is in line with the previous results by Tsuji *et al.*[8] They reported that the concentration of hydrogen atoms affected on the amount of formation of polyynes by laser ablation at 355 nm in *n*-hexane and methanol and concluded that the relative amount of polyynes in hexane was greater than that in methanol. To conclude, among several physical and chemical properties of the solvents, the relative number of hydrogen or the relative concentration of hydrogen atoms in solvents turned to play a significant role in the formation of polyynes. 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

In order to explore the effects of the solvent on the

Table 1. Physical and chemical properties of the solvents: the C-H bond dissociation energy, thermal conductivity (293 K), H mass per 1 mL, and number of H atoms at room temperature

	n-hexane	*c*-hexane	*n*-heptane	*n*-octane
Bond dissociation energy[a]	82.2633 kcal/mol	79.8112 kcal/mol	82.2037 kcal/mol	108.4107 kcal/mol
Thermal conductivity (293 K)[b]	0.120 W/mK	0.118 W/mK	0.140 W/mK	0.128 W/mK
H mass per 1 mL	0.1073 g	0.1111 g	0.1094 g	0.110 g
Number of H atoms per Carbon	2.3333	2.0000	2.2857	2.2500

[a]Bond dissociation energy D_0(R-H) = H(R) + H(X) – H(R-X). The energies were calculated at the B3LYP/6-311+G level of theory. [b]Ref. 18

formation rate of polyynes, we investigated the absorption spectra of polyynes obtained by laser ablation of a graphite target in different solvents at 1064 nm. Polyynes so produced were confirmed by the Raman band around 2200 cm^{-1} which corresponds to the carbon triple bonds. The production of polyynes by laser ablation turned out to be significantly affected by the ratio of the hydrogen and carbon atoms in the solvent molecule. No clear correlations were observed in the formation of polyynes for other properties of the solvent such bond dissociation energy, thermal conductivity, and total mass of hydrogen atoms per volume of solvent.

Acknowledgments. This study was supported by a grant from the Kyung Hee University in 2010 (KHU-20100117).

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