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Two-Step Alkylation of Single-Walled Carbon Nanotubes: Substituent Effect on Sidewall Functionalization

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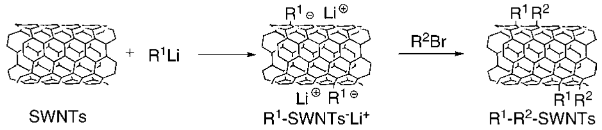
ABSTRACT



A two-step alkylation of single-walled carbon nanotubes was investigated. The functionalized SWNTs were characterized with vis-NIR and Raman spectrometers, scanning electron microscope, and thermogravimetric analysis. This one-pot alkylation of SWNTs with alkyllithium followed by alkyl halide is useful for the sidewall functionalization of SWNTs. This reaction shows significant substituent effects on the degree of functionalization of SWNTs. The degree of functionalization on SWNTs sidewall upon SWNTs may influence their characteristic properties on SWNTs sidewall by the substituent effects.

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have given rise to many potential applications.[1−3] The functionalization of SWNTs, which controls their solubility and electrochemical properties, is a current subject of intense research.[4−9] Hirsch et al. reported the sidewall functionalization of SWNTs by an addition reaction. After treatment of SWNTs with *tert*-butyllithium, the resulting *tert*-butylated-SWNTs anion intermediate (t-Bu-SWNTs$^-$Li$^+$) was then oxidized by oxygen.[10,11] They repeated the addition−oxidation or addition−protonation cycle three times because the efficiency

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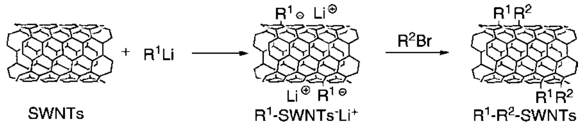
of the functionalization in one cycle is not high. Billups et al. reported that reductive alkylation of SWNTs using lithium and organic halides in liquid ammonia yields highly functionalized SWNTs by corresponding alkyl or aryl groups via an electron-transfer pathway.[12,13] Prato et al. reported a new strategy for a synthesis of multifunctionalized SWNTs.[14] They prepared SWNTs having two different functional groups through two chemical reaction processes. The functionalization introducing more than one group would be useful for practical applications. In this paper, we describe a novel one-pot synthesis of SWNTs having two different functional groups using alkyllithium and alkyl halide. One-pot dialkylation of SWNTs shows a strong substituent effect on the degree of functionalization of SWNTs. Because the influence of the degree of functionalization on SWNTs sidewall upon SWNTs characteristic properties is high, it is noteworthy to control the degree of functionalzation on SWNTs sidewall by the substituent effects.

Scheme 1



Functionalization of SWNTs (R^1-R^2-SWNTs) was achieved by the addition of alkyllithium (R^1Li) and alkyl bromide (R^2Br) under argon (Scheme 1). The degree of functionalization of SWNTs was confirmed by means of absorption and Raman spectra. Haddon et al. reported that the characteristic absorption of SWNTs decreases with an increase of the degree of sidewall functionalization of SWNTs.[15,16] Three absorption regions are identified in the absorption spectra of SWNTs: the first interband transitions for metals (M_{11}) from 400 to 600 nm, and the first and second ones for semiconductors (S_{11} and S_{22}) from 900 to 1600 nm and from 600 to 900 nm, respectively[17,18] (Figure 1). The decrease of the absorption intensities of the R^1-R^2-SWNTs in the region of the M11, S22, and S11 transitions is observed. Because the decrease of S11 bands is significant, the degree of sidewall functionalization of SWNTs was estimated from the attrition rate of the S11 band from 928 to 1600 nm (A_{abs}: 100 − (R^1-R^2-SWNTs/SWNTs × 100)), as shown in Table 1. The relative degree of functionalization of SWNTs estimated from absorption spectra (A_{abs}) is the following: *t*-Bu-H-SWNTs < *t*-Bu-*t*-Bu-SWNTs < *t*-Bu-Dmp-SWNTs (Dmp: 2,2-dimethylpropyl) < *t*-Bu-*i*-Bu-SWNTs < *t*-Bu-*i*-Pr-SWNTs < *t*-Bu-*n*-Bu-SWNTs (Dmp: 2,2-dimethylpropyl; *i*-Bu: isobutyl; *i*-Pr: isopropyl; *n*-Bu: *n*-butyl).

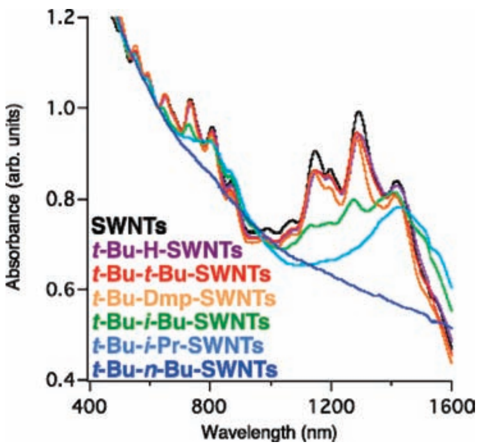


Figure 1. Vis-NIR spectra of SWNTs and functionalized SWNTs (*t*-Bu-R^2-SWNTs) dispersed in THF containing 1 M octylamine.

Table 1. A_{abs} and Raman (D/G) ratio of SWNTs and Functionalized SWNTs (*t*-Bu-R^2-SWNTs)

product	$A_{abs}{}^{a}$	$[D/G]_{514.5}{}^{a,b}$	$[D/G]_{633}{}^{a,c}$
t-Bu-H-SWNTs	1.4	1.2	1.0
t-Bu-*t*-Bu-SWNTs	2.2	1.3	1.2
t-Bu-Dmp-SWNTs	4.6	1.1	1.1
t-Bu-*i*-Bu-SWNTs	5.0	2.5	4.9
t-Bu-*i*-Pr-SWNTs	9.2	3.0	7.8
t-Bu-*n*-Bu-SWNTs	20	5.7	13

[a] Relative ratios to the pristine SWNTs. [b] D/G values determined from the Raman spectra measured under 514.5 nm excitation. [c] D/G values determined from the Raman spectra measured under 633 nm excitation.

Raman spectroscopy is one of the most powerful methods for determination of the covalent sidewall functionalization.[15,16,19] The intensity of the D-band becomes stronger with the expense of the radial breathing mode (RBM) and the intensity of the G-band goes up stronger with an increase of the degree of sidewall functionalization. The degree of functionalization was estimated on the basis of the intensity ratio of the D-band to the G-band (D/G ratio) (Figure 2). Table 1 shows the D/G ratio for the functionalized SWNTs relating to the D/G ratio of the pristine SWNTs determined from the Raman spectral measurement under the two different wavelength excitations. The relative degree of functionalization of SWNTs estimated from the D/G ratio

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is the following: *t*-Bu-H-SWNTs, *t*-Bu-Dmp-SWNTs < *t*-Bu-*t*-Bu-SWNTs < *t*-Bu-*i*-Bu-SWNTs < *t*-Bu-*i*-Pr-SWNTs < *t*-Bu-*n*-Bu-SWNTs. The presence of functional groups on the SWNTs was further confirmed with use of a TGA by heating under nitrogen to 800 °C at a rate of 10 deg/min.

The observed weight loss of SWNTs, *t*-Bu-*t*-Bu-SWNTs, *t*-Bu-*i*-Pr-SWNTs, and *t*-Bu-*n*-Bu-SWNTs is 7.5%, 16.3%, 18.6%, and 29.0%, respectively. This corresponds to the presence of one functional group for about 69, 47, and 24 carbon atoms, respectively. These values were adjusted from the content of the catalytic metal of starting SWNTs (24 wt %). Finally, we observed a qualitative and consistent trend from absorption and Raman spectroscopic data and TGA results.

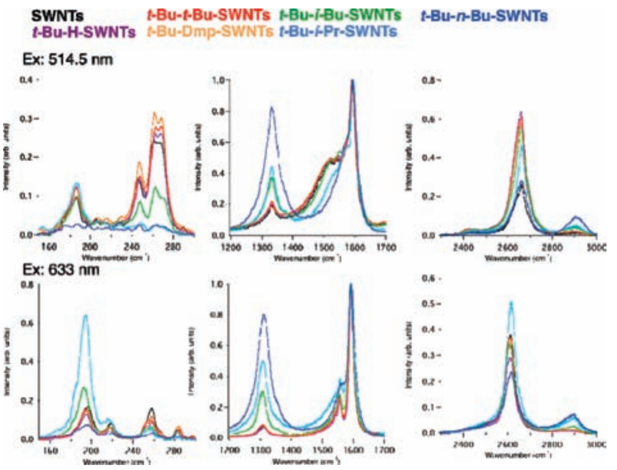

Figure 2. Raman spectra of SWNTs and functionalized SWNTs (t-Bu-R^2-SWNTs).

Hirsch et al. reported that the protonation of SWNTs$^-$Na$^+$, produced from the reaction of SWNTs with sodium metal, with ethanol results in a lower degree of functionalization than the reaction of SWNTs$^-$Na$^+$ with primary aliphatic halides.[19] The degree of functionalization producing *t*-Bu-H-SWNTs is lower than that of *t*-Bu-R-SWNTs, which is consistent with their reported results.[20] Substituents in aliphatic halides affected the degree of functionalization. Fukuzumi et al. reported that t-Bu-C$_{60}{}^-$ reacts with benzyl bromide (BnBr), but not with *t*-BuBr because of steric hindrance.[21] Hirsch et al. reported that the rotation barrier of the *t*-Bu group in t-BuC$_{60}{}^-$ is high with $\Delta G^\ddagger = 9.3$ kcal/mol.[10,11] The rotational barrier of the *t*-Bu group in *t*-Bu-SWNTs is expected to be higher than that of t-BuC$_{60}{}^-$, because the carbon atoms of SWNTs are less pyramidalized than those of C$_{60}$.[10,11] The substituent effect on the degree of functionalization in t-Bu-R^2-SWNTs might be due to the steric repulsion between the *t*-Bu group on t-Bu-SWNTs$^-$Li$^+$ and R^{2}Br.

Table 2. A_{abs} and Raman (D/G) Ratio of SWNTs and Functionalized SWNTs (t-Bu-R^2-SWNTs)

product	$A_{\text{abs}}{}^a$	$[\text{D/G}]_{514.5}{}^{a,b}$	$[\text{D/G}]_{633}{}^{a,c}$
n-Bu-H-SWNTs	4.4	1.1	0.9
n-Bu-*t*-Bu-SWNTs	18	3.6	10
n-Bu-Dmp-SWNTs	5.1	1.7	2.0
n-Bu-*i*-Bu-SWNTs	8.0	3.3	7.8
n-Bu-*i*-Pr-SWNTs	9.2	3.3	6.8
n-Bu-*n*-Bu-SWNTs	12	3.5	8.1

[a] Relative ratios to the pristine SWNTs. [b] D/G values determined from the Raman spectra measured under 514.5 nm excitation. [c] D/G values determined from the Raman spectra measured under 633 nm excitation.

To clarify the reaction mechanism and the substituent effect, the reaction of n-Bu-SWNTs$^-$Li$^+$, prepared from the reaction of SWNTs with *n*-BuLi, with an alkyl halide was carried out. The functionalization degree of SWNTs is estimated from the absorption spectra (A_{abs}) and Raman spectra (D/G ratio). The order of the functionalization degree of SWNTs is the following: *n*-Bu-H-SWNTs < *n*-Bu-Dmp-SWNTs; *n*-Bu-*i*-Bu-SWNTs < *n*-Bu-*i*-Pr-SWNTs < *n*-Bu-*n*-Bu-SWNTs < *n*-Bu-*t*-Bu-SWNTs, as shown in Table 2. Interestingly, n-Bu-SWNTs$^-$Li$^+$ shows a higher degree of functionalization than t-Bu-SWNTs$^-$Li$^+$. This indicates that less steric hindrance of n-Bu-SWNTs$^-$Li$^+$ controls the degree of functionalization. Fukuzumi et al. reported that the reaction of $C_{60}{}^{2-}$ with alkyl halides proceeding via a one-electron transfer process though that of t-BuC$_{60}$ with alkyl halides is the S$_\text{N}$2-type reaction.[21] The higher degree of functionalization of *t*-Bu-*n*-Bu-SWNTs and *n*-Bu-*t*-Bu-SWNTs seems to exclude a nucleophilic substitution mechanism. The reaction of R^1-SWNTs$^-$Li$^+$ with alkyl halides might involve a one-electron transfer process as is the case with the reaction of SWNTs$^-$Li$^+$ with alkyl halides reported by Billups et al.[12,13] When R^1-SWNTs$^-$Li$^+$ was treated with BnBr (Bn: benzyl), 1,2-diphenylethane was detected in the reaction mixture. The formation of 1,2-diphenylethane as a byproduct strongly suggests that R^1-SWNTs$^-$Li$^+$ reacts with alkyl halides via a one-electron transfer process. The reactivity of BnBr toward R^1-SWNTs$^-$Li$^+$ may not be high due to a high stability of the benzyl radical compared with aliphatic radicals (*t*-Bu-Bn-SWNTs: $A_{\text{abs}} = 2.6$, D/G$_{514.5\text{ nm}} = 1.3$, D/G$_{633\text{ nm}} = 2.4$; *n*- Bu-Bn-SWNTs: $A_{\text{abs}} = 6.8$, D/G$_{514.5\text{ nm}} = 3.0$, D/G$_{633\text{ nm}} = 6.4$). The benzyl radical might prefer to recombine with the benzyl radical to afford 1,2-diphenylethane rather than with a R^1-SWNTs radical. In the reaction of n-Bu-SWNTs$^-$Li$^+$ with *t*-BuBr, a higher degree of functionalization was observed, as shown in Table 2. The higher degree of functionalization of *n*-Bu-*t*-Bu-SWNTs might be due to steric hindrance of the *t*-Bu radical. The bulky *t*-Bu radical prefers to recombine with the *n*-Bu-SWNTs radical rather than with the *t*-Bu radical. A plausible reaction mechanism is shown in Scheme 2.

The diameter selectivity in the reaction of R^1-SWNTs$^-$Li$^+$ with alkyl halides was confirmed by the absorption and RBM part of the Raman spectra under excitation at 514.5 and 633 nm. The decrease in diameter selectivity confirmed by the

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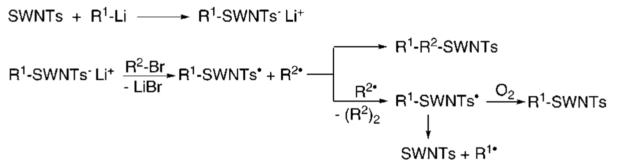
Scheme 2



absorption spectra of *t*-Bu-*i*-Bu-SWNTs, *t*-Bu-*i*-Pr-SWNTs, *t*-Bu-Dmp-SWNTs, *n*-Bu-*i*-Bu-SWNTs, *n*-Bu-*i*-Pr-SWNTs, and *n*-Bu-Dmp-SWNTs shows that SWNTs with smaller diameters are considerably more reactive than those with larger diameters.[11,20] The diameters of the SWNTs are estimated to be 1.28, 0.96, and 0.89 nm (514.5 nm) and 1.23, 1.08, 0.91, and 0.83 nm (633 nm) from the equation $\omega_{\mathrm{RBM}} = Ad_t^{-1} + B$ ($A = 223.5$ cm^{-1} and $B = 12.5$ cm^{-1}).[22−24] The Raman spectra of *t*-Bu-*i*-Bu-SWNTs, *t*-Bu-*i*-Pr-SWNTs, *n*-Bu-*i*-Bu-SWNTs, *n*-Bu-*i*-Pr-SWNTs, *n*-Bu-*t*-Bu-SWNTs, and *n*-Bu-*n*-Bu-SWNTs show that the RBM intensity of large-diameter SWNTs increased with a decrease of that of small-diameter SWNTs. This indicates the reaction is strongly diameter selective.

Recently, Fantini et al. reported that a peak is observed at ~2900 cm^{-1} in the spectra of functionaized SWNTs, and the appearance of the peak is due to a combination of two disorder-induced modes (D + D′ mode).[25,26] We compared the Raman spectra of R^1-R^2-SWNTs with that of SWNTs doped with *o*-dichlorobenzene (ODCB), as shown in Figure 3. The doping of SWNTs by exposing ODCB (SWNTs-ODCB) decreases their resistivity and changes thier spectroscopic patterns.[27,28] The peak intensity at ~2900 cm^{-1} is increased in the spectra of highly functionalized R^1-R^2-SWNTs. On the other hand, a peak at ~2900 cm^{-1} is not obviously observed in the spectra of SWNTs-ODCB. This result suggests that the D + D′ band can be used for the characterization of the functionalization of SWNTs.

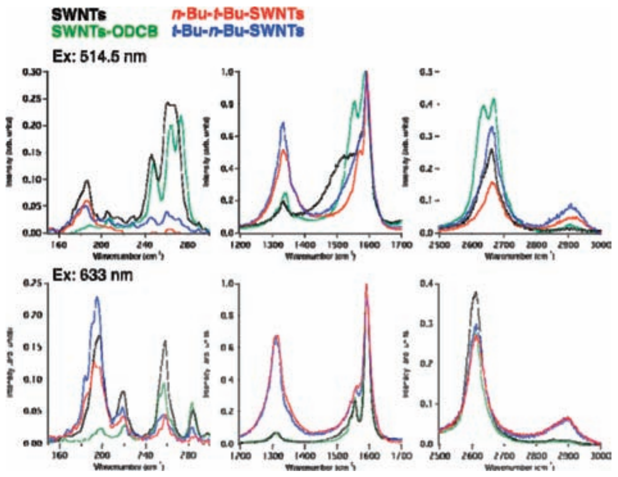


Figure 3. Raman spectra of SWNTs, functionalized SWNTs (*n*-Bu-*t*-Bu-SWNTs and *t*-Bu-*n*-Bu-SWNTs), and SWNTs-ODCB.

In conclusion, we have developed a two-step alkylation using the reaction of SWNTs with alkyllithium and alkyl halides. The degree of functionalization is sensitive for the alkyl group of the alkyllithium and alkyl halides. It is noteworthy that the alkylation leads to a high degree of functionalization on SWNTs sidewall.

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Supporting Information Available: Experimental details, AFM and SEM images, Raman and NIR spectra, and TGA data of SWNTs and functionalized SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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