Water-soluble Carbon Nanotube Chain-transfer Agents (CNT-CTAs)

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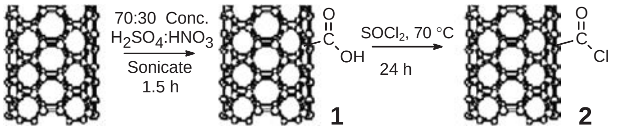
Acyl chloride groups on carbon nanotubes are reacted with a magnesium chloride dithiopropanoate salt to create novel carbon nanotube chain-transfer agents (CNT-CTAs) for potential use in reversible addition–fragmentation chain-transfer (RAFT) polymerizations.

Carbon nanotube (CNT)/polymer nanocomposites are of enormous importance because of their unique electrical, mechanical, optical, and thermal properties. Direct functionalization of CNTs has greatly improved their usefulness and relies mainly on pre-treatments such as sonication/wet oxidation in concentrated and diluted H_2SO_4/HNO_3 to produce surface OH, COOH, and C=O moeities[1] that are readily derivatized allowing direct covalent attachment of a polymer matrix.[2]

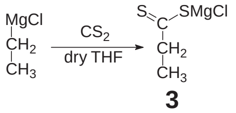
An increasingly important free radical polymerization technique is RAFT polymerization.[3] These reactions require chain-transfer agents (CTAs), typically dithioesters of the generic formula (Z–(C=S)–SR),[4,5] which are introduced with the monomer and initiator at the beginning of the reaction. The CTAs produce polymers with predicable molecular weights, narrow molecular weight distributions and more importantly control over superstructure architectures. They can be used on an extensive range of monomers[6] and at temperatures from ambient to 150 °C.[4] You et al.[7] have recently functionalized multiwalled carbon nanotubes with single dithioester groups by reaction of bromoisobutyrate moieties to acyl chloride groups then substitution with dithiobenzoic magnesium bromide. Li and Benicewicz[8] have derivatized silica nanoparticles with RAFT–silane coupling agents for the controlled polymerization of styrene (St), *n*-butyl acrylate (*n*BuA), and PSt-*block*-PBuA copolymers. Most recently, we have shown that CNT-CTAs can be produced by the treatment of nanotubes with phosphorus pentasulphide.[9] However, this process has many side reactions and produces agents that are soluble in only nonpolar based systems.

Here, we report another unique approach in the advancement toward the direct functionalization of CNTs with acyl chloride groups by reaction with a magnesium chloride dithiopropanoate salt. These CNT-CTAs are soluble in polar solvents/monomers and, therefore, offer an alternative to the previous method.

Full details are supplied in the Supporting Information.[12] Briefly, acid treated nanotubes **1** were heated in thionyl chloride to produce acyl chloride groups **2** (Scheme 1).[10] A magnesium chloride dithiopropanoate salt **3** was produced by the addition of CS_2 to ethyl magnesium chloride (Grignard reagent) in which CS_2 is inserted into the Mg–C bond.[10] The Grignard solution changed from a dark purple to an orange/red color as the magnesium chloride dithiopropanoate salt **3** forms (Scheme 2).



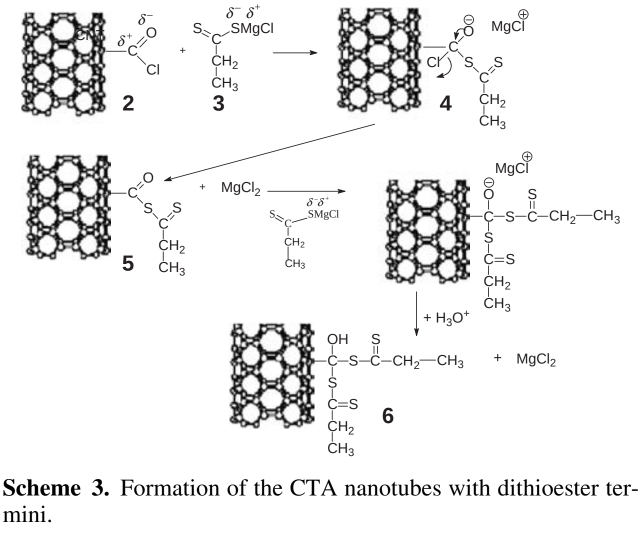
Scheme 1. Acid treatment then acyl chloride functionalization of nanotubes.



Scheme 2. Formation of the magnesium chloride dithiopropanoate salt.

Excess addition of the newly formed magnesium chloride dithiopropanoate salt to acyl chlorides leads to alcohol products[10] (Scheme 3).

This reaction occurs by sequential addition–elimination–addition reactions. The organometallic reagent **3** is a source of a nucleophilic thiol group, which bonds to the electrophilic carbon of the carbonyl group of the thionyl chloride-treated nanotubes **2**. The chloride is eliminated from the tetrahedral intermediate as its anion **4**. The ketone product **5** of this elimination then adds a second equivalent of the organometallic reagent **3**, terminating with the hydrolysis of the resulting alkoxide salt to produce the dithioester functionalized nanotubes or CNT-CTAs **6**. High-resolution transmission electron micrographs (HRTEM) show the pristine nanotube surface to be clean of amorphous material (Figure 1a). After functionalization the CNT-CTAs



Scheme 3. Formation of the CTA nanotubes with dithioester termini.

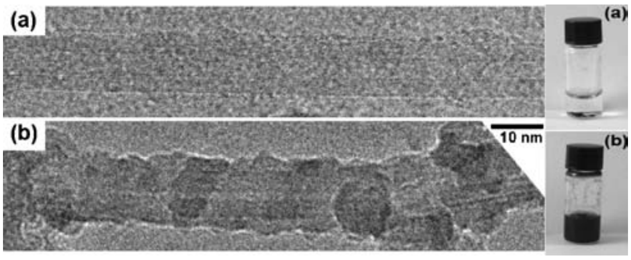


Figure 1. Left: HRTEM of (a) pristine CNTs and (b) CNT-CTA; Right: (a) pristine CNT in water and (b) CNT-CTAs in water.

show amorphous material on the surface as a direct result of the new chemical treatment (Figure 1b). Figure 1 (Right (a)) shows the prisitne CNTs are insoluble in water while the CNT-CTAs show superior solubility and dispersion (Figure 1 (Right (b))).

Treatment of the carbon nanotubes with magnesium chloride dithiopropanoate salt results in the emergence of multiple low-frequency vibrations in the Raman spectrum (see Figure 2A(c)). Observed at $\nu/\mathrm{cm}^{-1} = 445$ and 464 (overlapping S=C–S scissor and C–S–C scissor), 516 and 597 (S–C stretch + CH_3 rock), 766 ($CH_2 + CH_3$ rock), 819 and 849 (C–S stretch), and 938 (C–C stretch in ethyl).[11] The high-frequency region shows the extent of disorder in the system given by the $I_{\mathrm{D}(\approx 1350\mathrm{cm}^{-1})}/I_{\mathrm{G}(\approx 1592\mathrm{cm}^{-1})}$ ratios (Figure 2B). Initially, the nanotubes have a high degree of disordered sp^3 carbon ($I_\mathrm{D}/I_\mathrm{G} = 0.6$), this is preferentially removed during acid treatment ($I_\mathrm{D}/I_\mathrm{G} = 0.3$). Treatment with the $MgCl_2$ dithiopropanoate salt renews this sp^3 carbon ($I_\mathrm{D}/I_\mathrm{G} = 0.6$), with the formation of new carbonaceous material as CH_2CH_3 termini.

Thermogravimetric data[12] shows a single mass loss profile at approximately 600 °C for the pristine CNTs upon acid treatment and acyl chloride formation this profile becomes a double mass loss at approximately 220 and 580 °C. While the CNT-CTA shows a single mass loss at a far lower temperature, approximately 320 °C. This confirms the presence of the weakly bonding dithioester groups and not carboxylate moieties.

XPS spectra show further evidence of CNT-CTAs formation observed in the appearance of the S 2p energy peak between 161–166 eV (Figure S4(c)).[12] Peak fitting shows a $\Delta E = 1.18$ eV between S $p_{3/2}$ (163.7 eV) and S $p_{1/2}$ (164.9 eV) and fixed intensity ratio of 2:1. An additional peak appears at 162.0 eV potentially from the binding energy of residual Mg bound to the C–S–C(=S)CH_2CH_3 groups.

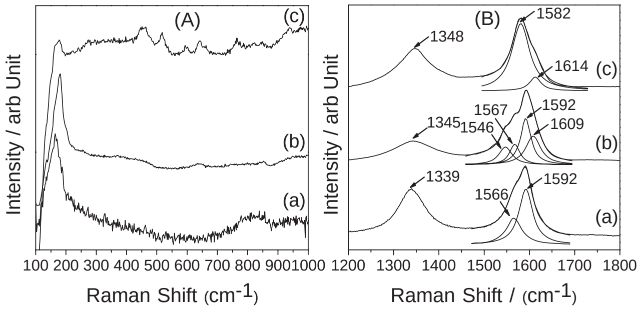


Figure 2. (A) Raman spectra taken at 514.5 nm for the low-frequency region of (a) pristine CNTs, (b) acid-treated CNTs, and (c) CNT-CTAs; (B) Normalized high-frequency region of (a) pristine CNTs, (b) acid-treated CNTs, and (c) CNT-CTAs.

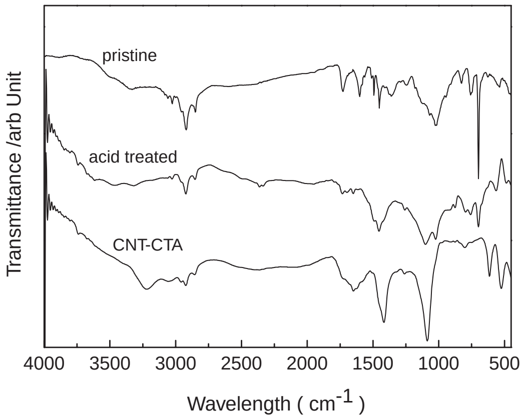


Figure 3. FT-IR spectra of carbon nanotubes (pristine), after acid treatment, and formation of CNT-CTA.

FT-IR spectra of the CNT-CTAs shows the appearance of an OH stretch at 3226 cm^{-1}, verifying double addition of the magnesium chloride dithiopropanoate moiety, a C=S stretch (1090 cm^{-1}) and two C–S peaks (615 and 526 cm^{-1}) (Figure 3).[7]

In conclusion, we have provided a powerful protocol to effectively rendered carbon nanotubes water soluble, with high dispersibility, by functionalizing them with dithioester groups. This makes them highly useful as chain-transfer agents in hydrophilic polymer-based systems.

As a next step we will investigate their use as chain-transfer agents in polar monomers for RAFT polymerisations increasing the diversity of chemical reactions in carbon nanotechnology in polymer and material science.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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