REVIEWS

# Preparation and Properties of Polymer-grafted Carbon Nanotubes and Nanofibers

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ABSTRACT:    Recent advances in surface grafting of polymers onto carbon nanotubes (CNT) and nanofibers, such as vapor grown carbon fiber (VGCF), are reviewed. The grafting of polymers onto these surfaces was achieved by (1) the "grafting onto" method, (2) "polymer reaction" method, (3) "grafting from" method, and (4) "stepwise growth" method by dendrimer synthesis methodology. For the grafting of polymers, surface functional groups, such as carboxyl and phenolic hydroxyl groups, previously introduced onto the surface by oxidation with nitric acid, were used as grafting sites. These functional groups were converted into various initiating groups and surface initiated graft polymerization was achieved. The graphene sheet (polycondensed aromatic rings) of CNT and VGCF were used as grafting sites by using ligand-exchange reaction with polymers containing ferrocene moieties. The radical trapping nature of CNT and VGCF surface was used for the grafting of polymers. Dispersibility in solvents for good solvents of grafted polymer was remarkably improved by the surface grafting of polymers onto CNT and VGCF surfaces. The response of electric resistance of the composite prepared from polymer-grafted CNT and VGCF to solvent vapor and temperature is discussed.   [DOI 10.1295/polymj.37.637]
    KEY WORDS    Carbon Nanotube / Vapor Grown Carbon Fiber / Graphene Sheet / Surface Grafting of Polymer / Dispersibility / Composite / Electric Property /

Carbon nanotubes (CNTs) are of considerable interest for applications to fabricating new engineering materials, because they have unique chemical, physical, and structure properties.[1–4] Among many different applications, a composite of CNT with polymer has been extensively investigated.[4–8] The important problem for preparation of composites with polymers is the dispersion, compatibilization, and stabilization of CNT in the polymer matrices. Especially, single-walled CNT (SW-CNT) is a strikingly inert material and usually in the form of bundles. To solve the problem, surface modification of CNT has been widely investigated. The covalent attachment of polymers, grafting of polymers, onto CNT is very effective because grafted polymers on the surface prevent the aggregation of CNT. Therefore, modification of CNT surface by grafting of polymers has been widely investigated by many researchers.

Vapor grown carbon fiber (VGCF) is a new class of carbon nanofiber different from carbon nano-tube in its method of production and lower cost. It is also different from the conventional pitch-based and poly-(acrylonitrile)-based carbon fiber in nano-sized diameter.[9] VGCF is generaly by the form of annular carbon layers arranged like a tree ring structure. The carbon rods have a high aspect ratio and nano-sized diameter ranging from 50 to 200 nm, which is between those of conventional carbon fibers (5–10 μm) and of carbon nanotubes (1–50 nm).[10] Due to unique physical properties, such as excellent thermal and electrical conductivity, and good mechanical behavior, VGCF is of considerable interest.[11,12]

VGCF is usually used as reinforcement, adsorbent, and conductive filler. Recently, it is used in batteries for electrode and separator.[13,14] In most cases, it is used in the form of composite where the polymer is needed as matrices. However, the fibers intertwine, because of the very low surface free energy, nano-size, and low bulk density.

Therefore, it is difficult to disperse CNT and VGCF in polymer matrix uniformly. It is desirable that the polymers are covalently bonded to CNT and VGCF surfaces in preparation of composites with CNT and VGCF. The surface grafting of polymers provides the best possible adhesion and allows for optimal transfer of stress from the matrix to the fibers.

In the present review, our recent research topics on the surface grafting of polymers onto CNT and VGCF surfaces by several methods, as schematically shown in Figure 1, the recent advances for the surface grafting of CNT, and the dispersibility and the electric properties of polymer-grafted CNT and VGCF are described.

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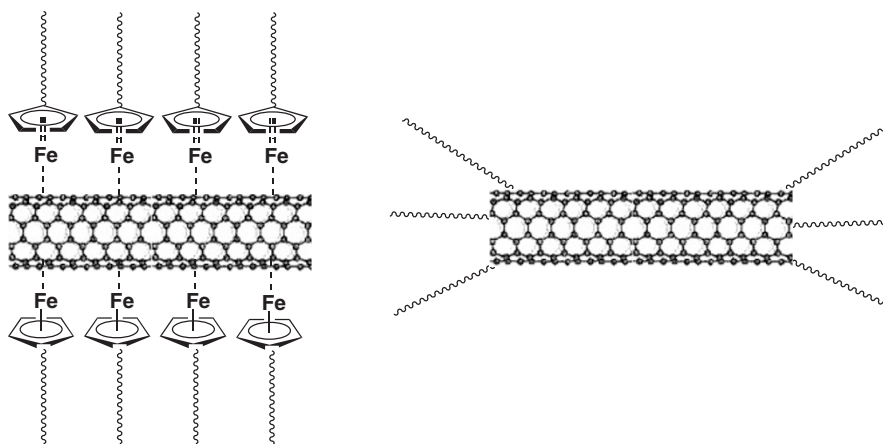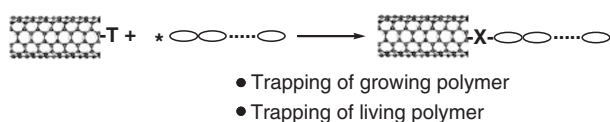
**Figure 1.** Grafting of polymers onto the surface of carbon nanotube and nanofiber.

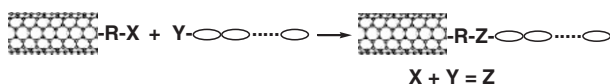## METHODOLOGY OF SURFACE GRAFTING OF POLYMERS ONTO CARBON NANOTUBE AND NANOFIBER

Several methodologies have been developed for the preparation of conventional graft and block copolymers and we have applied these methodologies to the grafting of polymers onto carbon black surface.[15,16] In general, one of the following principles, shown in Scheme 1, may be also applied to prepare polymer-grafted carbon nanotubes and nanofibers.

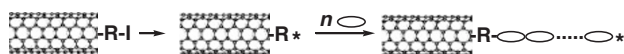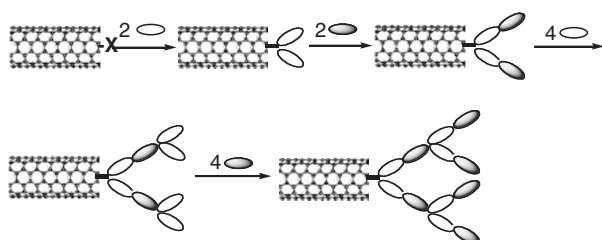(1) "Grafting onto" method: the grafting is achieved by the termination of growing polymer radical, cation, and anion, formed during the polymerization of various monomers initiated by conventional initiators in the presence of CNT and VGCF or by the deactivation of living polymer chain ends with functional groups on these surfaces.

(2) "Polymer reaction" method: polymers are grafted by reactions of surface functional groups on CNT and VGCF with polymers having functional groups, such as hydroxyl, carboxyl, and amino groups. This method can be included for "grafting onto" method.

(3) "Grafting from" method: the initiation of graft polymerization of various monomers from radical and ionic initiating groups previously introduced onto the CNT and VGCF surfaces.

(4) "Stepwise growth" method: grafted polymer chains are grown from the surface functional groups on CNT and VGCF by repeated reaction of low molecular compounds by dendrimer synthesis methodology.

By method (1), although polymer-grafted CNT and VGCF can be readily obtained without pretreatment of the surface, polymer grafting onto the surface (percentage of grafted polymer on CNT and VGCF) is less than 10%, because of the preferential formation of ungrafted polymers. By termination of living polymers on carbon nanofiber, polymers with well-defined molecular weight and narrow molecular weight distribution can be grafted onto CNT and VGCF.

An important characteristic of method (2) is that not only molecular weight and number of grafted chains on CNT and VGCF surfaces are easily controlled, but also commercially available polymers and copolymers having a well-defined structure can be grafted.

Method (3) is best for preparation of polymer-grafted CNT and VGCF with a high percentage of grafting. By initiation of living polymerization from the surface, polymers with well-defined molecular weight and narrow molecular weight distribution can be

(1) "Grafting onto" method



- Trapping of growing polymer
- Trapping of living polymer

(2) "Polymer reaction" method



X + Y = Z

(3) "Grafting from" method



(4) "Stepwise growth" method



**Scheme 1.**

grafted onto these surfaces. Grafting density on the surface is considerably high.

By method (4), hyperbranched polymers having a large number of terminal functional groups can be grafted onto the surface, although polymers with theoretical dendron structure can hardly be grafted.

## GRAFTING SITES ON CARABON NANOTUBE AND NANOFIBER

We reported the grafting of various polymers such as vinyl polymer[17,18] polyester,[19,20] polyether,[21,22] poly(organophosphazene),[23] and poly(dimethysiloxane)[24] onto carbon black surface using carboxyl and phenolic hydroxyl groups, bonded at the edges and corners of the polycondensed aromatic ring of graphene sheet or to carbon atoms in defect positions of the graphen sheet, as a grafting site as shown in Figure 2.

However, in comparison with carbon black, the surface grafting of polymers onto graphite powder and carbon fiber surface was rarely achieved, because graphite and carbon fiber have few functional groups as grafting sites. In general, surface grafting onto graphite and carbon fiber must be achieved after the introduction of functional groups using conventional organic reactions, such as oxidation and electrophilic substitution to polycondensed aromatic rings of the surface. The introduction of nitro, hydroxymethyl, and acyl and alkyl groups onto carbon black has been achieved.[25,26]

CNTs have no functional groups and VGCF has few functional groups at the edge (open end) of the fiber. The introduction of functional groups onto CNT[27–32] and VGCF[33] surface was reported and these functional groups can be used as grafting sites of polymers.

Polycondensed aromatic rings (graphene sheet) of carbon materials, such as carbon black, carbon fiber, and graphite, act as strong radical scavengers.[34,35]
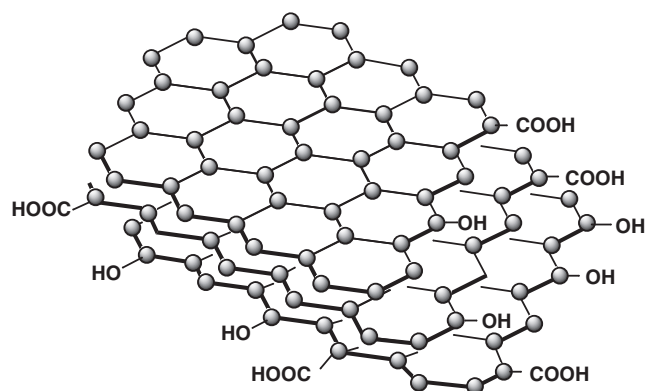
Therefore, the surface grafting of polymers onto carbon black and graphite can be achieved by the radical trapping nature of these surfaces.

CNTs and VGCF have a strong ability to trap radicals and the grafting of polymers onto the surface can be achieved through polymer radical trapping by these surfaces. Recently, we have found a novel grafting method, which uses the polycondensed aromatic rings (graphene sheet) of carbon black, carbon fiber,[36] CNT,[37] and VGCF[38] as grafting sites.

## GRAFTING OF POLYMERS ONTO CARBON NANOTUBE AND NANOFIBER SURFACES BY LIGAND-EXCHANGE REACTION

Nesmeyanov *et al.* reported that the $\eta^6$-benzene $\eta^5$-cyclopentadienyl-iron(I) cation could be readily prepared by ligand-exchange reaction of ferrocene with benzene in the presence of AlCl$_3$ and aluminum powder[39,40] and demonstrated that ligand-exchange reaction proceeds with not only benzene but also with other arenes.[41–44] Miyake *et al.* reported that ligand-exchange reaction of ferrocene can be applied to the introduction of functional groups to graphene sheet of various carbon materials, such as active carbon fiber and carbon black.[45]

*Grafting of Poly(Vf-co-MMA) onto CNT and VGCF*
The grafting of poly(vinyl ferrocene-*co*-methyl methacrylate) (poly(Vf-*co*-MMA)) onto VGCF surface by ligand-exchange reaction between ferrocene moieties of the copolymer and aromatic rings of graphene sheet of multi-walled carbon nanotube (MW-CNT) and VGCF was investigated by our group as shown in Scheme 2.[37,38]

Table I shows the results of grafting reaction of poly(Vf-*co*-MMA) ($M_n = 1.3 \times 10^4$, Vf content = 24 mol%) with VGCF surface under several conditions. As shown in Table I, even if VGCF is heated with poly(Vf-*co*-MMA) in 1,4-dioxane in the absence



**Figure 2.** Functional groups of on the edges of graphene sheets of carbon materials.
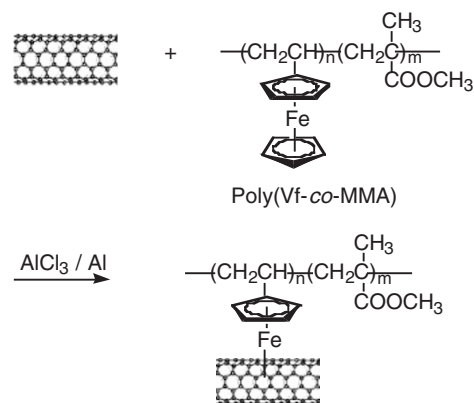


**Scheme 2.**

**Table I.** Ligand-exchange reaction of poly(Vf-*co*-MMA) with VGCF under various conditions

| Run No. | $AlCl_3$ (mmol) | Al (mmol) | Grafting (%) |
|---|---|---|---|
| 1 | — | — | trace |
| 2 | — | 0.25 | 4.3 |
| 3 | 1.0 | — | 16.5 |
| 4 | 1.0 | 0.25 | 57.5 |

VGCF, 0.20 g; poly(Vf-*co*-MMA) ($M_n = 1.3 \times 10^4$), 0.20 g; 1,4-dioxane, 20.0 mL; 80 °C; 24 h.

of $AlCl_3$ and Al powder, grafting of the copolymer onto the surface hardly occurs (Run 1). The grafting of the copolymer onto VGCF surface is scarcely observed in the presence of Al powder alone (Run 2).

The grafting of a copolymer onto VGCF considerably proceeds in the presence of $AlCl_3$ (Run 3). In the presence of $AlCl_3$ and Al powder, poly(Vf-*co*-MMA) is grafted onto side-wall of VGCF. The percentage of grafting onto VGCF reaches 57.5% after 24 h at 80 °C. The density of grafted polymer chain on VGCF surface is calculated to be $0.8/nm^2$.
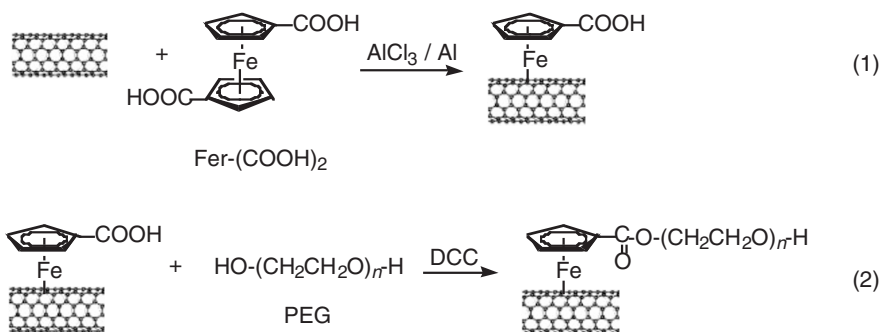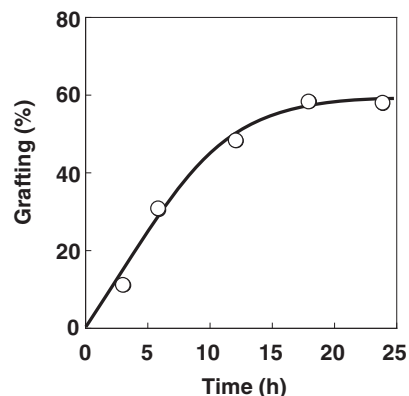
Figure 3 shows the relationship between reaction time and the percentage of grafting during ligand-exchange reaction of VGCF with poly(Vf-*co*-MMA) at 80 °C. The grafting increased with reaction time, but not after 24 h.

Table II shows the effects of Vf content of poly(Vf-*co*-MMA) on the ligand-exchange reaction with MW-CNT and VGCF. The percentage of grafting and number of grafted chains ($G_n$) onto MW-CNT and VGCF increased with Vf content of poly(Vf-*co*-MMA).

*Introduction of Carboxyl Groups onto CNT and VGCF by Ligand-exchange Reaction and Grafting of PEG onto the Surface*

The introduction of carboxyl groups onto MW-CNT and VGCF surface by ligand-exchange reaction of 1,1′-dicarboxyferrocene (Fer-(COOH)$_2$) with graphene sheet of these surfaces was investigated as shown in Scheme 3(1).[37,38]

Even in the absence of $AlCl_3$, carboxyl groups are



**Figure 3.** Relationship between reaction time and percentage of grafting in the ligand-exchange reaction of poly(Vf-*co*-MMA) with VGCF surface at 80 °C. VGCF, 0.20 g; poly(Vf-*co*-MMA) ($M_n = 1.3 \times 10^3$), 0.20 g; 1,4-dioxane, 20.0 mL; $AlCl_3$, 1.0 mmol; Al powder, 0.25 mmol.

**Table II.** Effects of Vf content on the ligand-exchange reaction of poly(Vf-*co*-MMA) with MW-CNT and VGCF

| Nanofiber | Vf content in the copolymer (mol %) | $M_n \times 10^{-4}$ | Grafting (%) |
|---|---|---|---|
| MW-CNT | 9 | 1.5 | 19.6 |
| MW-CNT | 24 | 1.3 | 60.9 |
| VGCF | 1 | 1.9 | 6.4 |
| VGCF | 9 | 1.5 | 24.9 |
| VGCF | 24 | 1.3 | 57.5 |
| VGCF | 47 | 0.6 | 69.3 |

Carbon nanofiber, 0.20 g; poly(Vf-*co*-MMA), 0.20 g; 1,4-dioxane, 20.0 mL; $AlCl_3$, 1.0 mmol; Al powder, 0.25 mmol; 80 °C; 24 h.

detected on the VGCF surface by titration. This suggests that Fer-(COOH)$_2$ is strongly adsorbed onto VGCF and/or intercalated between graphene sheets of VGCF. Carboxyl group content of VGCF increased when treated with Fer-(COOH)$_2$ with VGCF in the presence of $AlCl_3$ and Al powder. The content of carboxyl group reached to 2.63 mmol/g, but not after 24 h. This indicates that carboxyl group density on VGCF wall-surface is $100/nm^2$. The amount of



**Scheme 3.**

**Table III.** Grafting reaction of MW-CNT-COOK and VGCF-COOH with PEG in the presence of DCC

| Nanofiber | $M_n \times 10^{-3}$ | Grafting (%) | $G_n \times 10^{-18}$ (No./g) |
|---|---|---|---|
| MW-CNT-COOH | 4.6 | 57.5 | 36.7 |
| MW-CNT-COOH | 3.4 | 24.6 | 43.3 |
| MW-CNT-COOH | 2.0 | 19.0 | 57.2 |
| VGCF-COOH | 10.0 | 14.7 | 9.9 |
| VGCF-COOH | 8.0 | 12.4 | 9.3 |
| VGCF-COOH | 4.6 | 8.9 | 11.6 |
| VGCF-COOH | 3.4 | 11.0 | 19.5 |
| VGCF-COOH | 2.0 | 9.6 | 28.9 |
| VGCF-COOH | 1.5 | 8.8 | 35.3 |

Carbon nanofiber-COOH, 0.10 g; PEG, 0.53 mmol; THF, 20.0 mL; DCC, 0.26 mmol; 60 °C; 48 h.

**Table IV.** Grafting reaction of VGCF-COOH with several polymers in the presence of DCC

| Polymer | $M_n \times 10^{-3}$ | Solvent | Grafting (%) | $G_n \times 10^{-18}$ (No./g) |
|---|---|---|---|---|
| PE-*block*-PEO | 1.8 | THF | 12.2 | 40.8 |
| PE-*block*-PEO | 1.4 | THF | 31.8 | 136.0 |
| PCL | 2.0 | THF | 13.7 | 41.2 |
| PEI | 10.0 | DMSO | 9.3 | 5.6 |
| PEI | 1.8 | DMSO | 11.6 | 38.8 |
| PBA | 1.0 | THF | 12.0 | 72.2 |

VGCF-COOH (COOH groups = 2.63 mmol/g), 0.10 g; Polymer, 0.53 mmol; Solvent, 20 mL; DCC, 0.26 mmol; 60 °C; 48 h.

carboxyl group introduced onto VGCF surface was extremely large in comparison with that introduced by the oxidation of open ends of VGCF with nitric acid.[46,47] Carboxyl groups were introduced onto MW-CNT surface by ligand-exchange reaction with Fer-(COOH)$_2$. The amount of carboxyl groups was determined to be 4.30 mmol/g, indicating 3/nm$^2$ density of carboxyl groups.

It is expected that the grafting of PEG onto MW-CNT-COOH and VGCF-COOH by direct condensation of carboxyl groups on the surfaces with terminal hydroxyl groups of poly(ethylene glycol) (PEG) proceeds in the presence of a condensing agent as shown in Scheme 3(2).[37,38]

By reaction of MW-CNT-COOH and VGCF-COOH with PEG ($M_n = 3.4 \times 10^3$) in the presence of $N,N'$-dicyclohexylcarbodiimide (DCC), PEG was grafted onto MW-CNT and VGCF surface. The percentage of grafting onto MW-CNT and VGCF reached 24.6% and 11.0%, respectively, for 48 h at 60 °C, but not after 48 h. This indicates that only 1–1.7% of carboxyl groups are used for the grafting site.

PEG is thus grafted onto MW-CNT and VGCF surface with ester bonds by reaction of carboxyl groups on side-wall of MW-CNT and VGCF with terminal hydroxyl groups of PEG in the presence of DCC.

Table III shows the effect of molecular weight of PEG on the grafting onto MW-CNT-COOH and VGCF-COOH. The percentage of grafting tends to decrease with decreasing molecular weight of PEG, but the number of grafted PEG chains ($G_n$) on the surface increased with decreasing molecular weight of PEG. This suggests that steric hindrance decreased with decreasing molecular weight of PEG. The same was reported in the grafting reaction of functional groups on nano-sized particle surface with polymers having terminal functional groups.[48,49]

Grafting of polymers having hydroxyl and amino (imino) groups, such as polyethylene-*block*-poly(ethy-lene oxide) (PE-*b*-PEO), poly($\varepsilon$-caprolactone) (PCL), poly(ethyleneimine) (PEI), and poly(butyleneadipate) (PBA), onto VGCF-COOH was investigated. The results are shown in Table IV. These polymers, such as PE-*b*-PEG, PCL, PEI and PBA, were grafted onto VGCF surface by the direct condensation of terminal functional groups of polymers with carboxyl groups on VGCF in the presence of DCC.[37,38]

## GRAFTING OF POLYMERS ONTO CARBON NANOTUBE AND NANOFIBER BY RADICAL TRAPPING

Carbon black is a strong radical scavenger.[34,35] Therefore, the radical polymerization in the presence of carbon black was inhibited and/or retarded, because of the trapping of growing polymer radicals and primary radicals by carbon black surface. During polymerization, a part of the polymer was grafted onto the surface, but the percentage of grafting was less than a few percent, because of preferential trapping of low molecular primary radicals formed by the decomposition of initiator.[50,51]

Our group has reported that polymer radicals formed by the thermal decomposition of macro-initiators, polymers having azo group[52] and peroxy groups,[53] are trapped by polycondensed aromatic rings of the surface to give the corresponding polymer-grafted carbon black and graphite.

*Grafting onto CNT by Trapping of Polymer Radicals Formed by the Thermal Decomposition Macro-azo Initiator*

To confirm the radical trapping nature of MW-CNT and cup-stacked CNT (CS-CNT), the effects of these CNTs on the radical polymerization of styrene initiated by benzoyl peroxide (BPO) was investigated. The results are shown in Figure 4. As shown in Figure 4, in the presence of MW-CNT and CS-CNT, radical polymerization of styrene was retarded. During radical polymerization, a part of polystyrene formed was
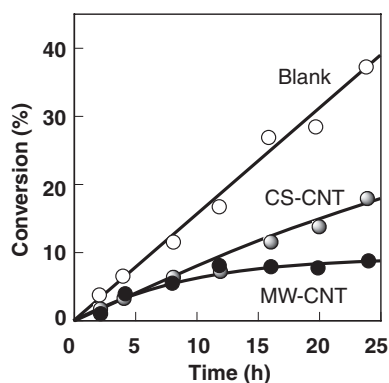
**Figure 4.** Radical polymerization of styrene in the presence of MW-CNT and CS-CNT initiated by BPO. CNT, 0.10 g; styrene, 10.0 mL; BPO, 0.10 g; 60 °C.
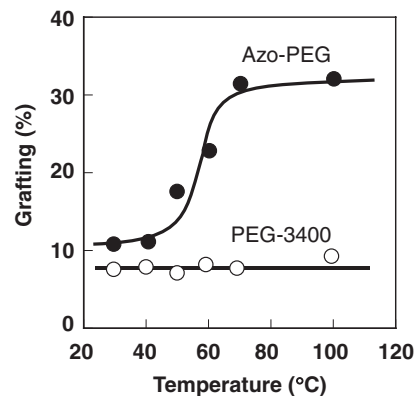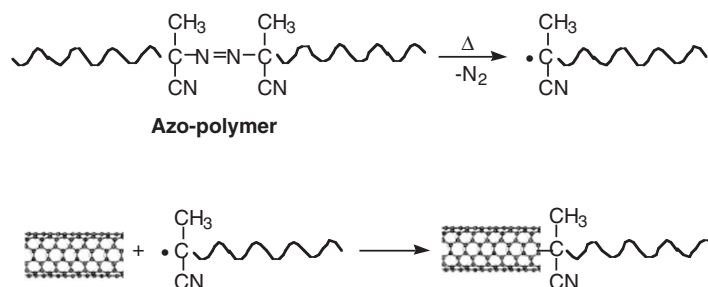


**Figure 5.** Effects of temperature on the reaction of Azo-PEG with MW-CNT and CS-CNT. CNT, 0.07 g; Azo-PEG (PEG), 2.5 g; toluene, 20.0 mL; 24 h.



**Scheme 4.**

grafted onto the surface of MW-CNT and CS-CNT, but the percentage of grafting was less than a few percent. This indicates that primary radicals, benzoyloxy radicals, may be preferentially trapped by MW-CNT and CS-CNT surfaces.

Polymer radicals formed by the decomposition of macro-initiators, such as azo-polymer, should thus be trapped by MW-CNT and CS-CNT surfaces. MW-CNT was reacted with PEG-azo initiator, Azo-PEG, in toluene and the results are shown in Figure 5. Even when PEG having no azo groups was heated with MW-CNT, no grafting of PEG onto the MW-CNT surface was observed. When Azo-PEG was reacted with MW-CNT below 40 °C, at which Azo-PEG scarcely decomposed, no grafting was observed. Grafting proceeded when MW-CNT was reacted above 60 °C, at which the thermal decomposition of Azo-PEG proceeds. The percentage of grafting onto MW-CNT reached to 31.0% at 70 °C after 24 h. The grafting of PEG onto CS-CNT also proceeded by re-action with Azo-PEG. The percentage of PEG grafting was determined to be 11.8% at the same conditions.

These results indicate that at above 60 °C, PEG radicals formed by the thermal decomposition of Azo-PEG are trapped by the surface of MW-CNT and CS-CNT to give PEG-grafted CNTs as shown in Scheme 4.[37]

It is interesting to note that the percentage of grafting onto MW-CNT was higher than that onto CS-CNT, although CS-CNT has more open ends (edges) as radical trapping sites than MW-CNT. This may be due to the fact that the open ends of CS-CNT were readily shielded by grafted PEG chains.

*Grafting onto CNT by Trapping of Living Polymer Radical*

Lou and his coworkers reported the grafting of polymers onto MW-CNT by the trapping of living polymer radicals formed by the thermal dissociation of alkoxyamine, 2,2,6,6-tertamethylpiperidinyl-1-oxyl (TEMPO), end-capped polymers, such as polystyrene (PS) and poly(ε-caprolactone) (PCL), and their block copolymers (PCL-*b*-PS), as shown in Scheme 5.[54]

As shown in Table V, by the grafting methods, polymers with controlled molecular weight and narrow molecular weight distribution were grafted onto MW-CNT. It is also reported that the grafting density (mol/mg) decreases with increasing molecular weight of TEMPO-terminated polystyrene.[54]

Poly(2-vinylpyridine) was grafted onto MW-CNT by trapping of polymer radicals formed by the decomposition of the corresponding TEMPO end-capped polymers.[55] The polymer-grafted MW-CNT gave a stable dispersion in acidic water, but precipitated in
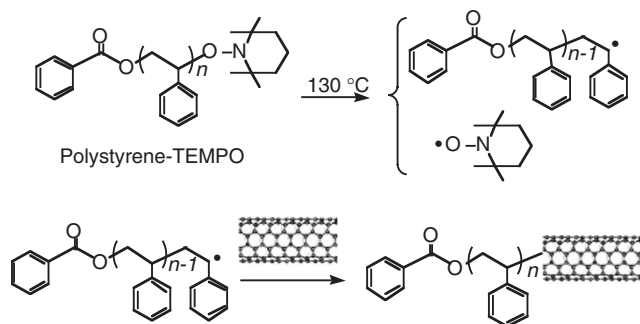
**Scheme 5.**



**Scheme 6.**

**Table V.** Grafting of TEMPO-terminated polymers onto MW-CNT

| Polymer | $M_n \times 10^3$ | $M_w/M_n$ | Time (h) | Grafting (%) |
|---|---|---|---|---|
| PS-TEMPO | 3.0 | 1.20 | 24 | 12 |
| PS-TEMPO | 3.0 | 1.20 | 43 | 12.5 |
| PS-TEMPO | 17.5 | 1.25 | 24 | 20 |
| PS-TEMPO | 19.5 | 1.20 | 24 | 17 |
| PS-TEMPO | 28.5 | 1.25 | 24 | 24 |
| PCL-TEMPO | 7.0 | 1.20 | 24 | 25 |
| PCL-TEMPO | 14.5 | 1.15 | 24 | 28 |
| (PCL-co-PS)-TEMPO | 15.5 | 1.20 | 24 | 30 |

MW-CNT, 0.02 g; polymer, 2.0 g; toluene, 6 mL; 130 °C.



**Figure 6.** Relationship between percentage of PE-b-PEO grafting and irradiation dose of the radiation grafting of PE-b-PEO onto VGCF at various temperatures. The amount of adsorbed PE-b-PEO on VGCF before irradiation was 74% (weight percent of PE-b-PEO on VGCF).
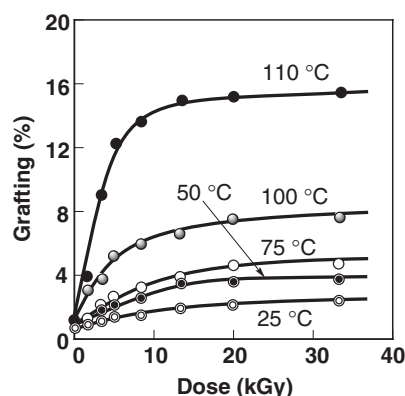
alkaline water. Datsyuk *et al.* reported the preparation of composite from double-walled CNT and polymer *via in-situ* niroxide mediated polymerization of amphiphilic block copolymers, although the grafting of the block copolymer was not been clarified. They used 2-methyl-2-*N*-tert-butyl-*N*-[diethoxyphoshoryl-2,2-dimethypropylaminoxy] propionic acid as niroxide.[56]

*Grafting onto VGCF by Trapping of Polymer Radicals Formed by γ-Ray Irradiation*

The γ-ray radiation grafting of polymers by trapping of polymer radicals formed by the γ-ray irradiation has been reported by our group. The grafting of PE-b-PEO onto VGCF surface was carried out in a solvent-free system. That is, the PE-b-PEO was pre-adsorbed onto VGCF surface from PE-b-PEO solution of THF; then, the PE-b-PEO-adsorbed VGCF was irradiated at the definite dose and temperature (Scheme 6).[57]

Figure 6 shows the relationship between the percentage of grafting and irradiation dose at 25, 50, 75, 100, and 110 °C. The irradiation dose rate was fixed to 10 kGy/h. The points at the 0 (dose axial) indicate that the samples are only heated at the corresponding temperatures for 6 h. As shown in Figure 6, grafting reaction is remarkably affected by irradiation temperature. At lower irradiation temperatures of 25, 50, and 75 °C, the grafting was less than 5.0%. At 100 °C, the grafting at 60 kGy dose reached 7.3%,

and at 110 °C, near the melting point (109 °C) of PE-b-PEO, the grafting suddenly increased to 15.0%.

Grafting increased with irradiation dose at every irradiation temperature. Without irradiation, the grafting of PE-b-PEO on the VGCF was less than 1.0%. At lower irradiation temperatures, such as 25 °C, even if the radiation dose increased to 100 kGy, the percentage of PE-b-PEO grafting was less than 2.3%. This may be due to the fact that PE-b-PEO radicals hardly reacted with the VGCF surface because of the crystalline structure of PE-b-PEO.

The grafting of PE-b-PEO onto VGCF surface is considered to proceed through the trapping of PE-b-PEO radical by the graphene sheet of the VGCF.[57] Compared with the rate of PE-b-PEO radical generation in the above irradiation dose rate, the rate of radical trapping by VGCF was relatively slow. Therefore, at higher irradiation dose rate, some PE-b-PEO radical is quenched before the grafting reaction, resulting in no increase of PE-b-PEO grafting.

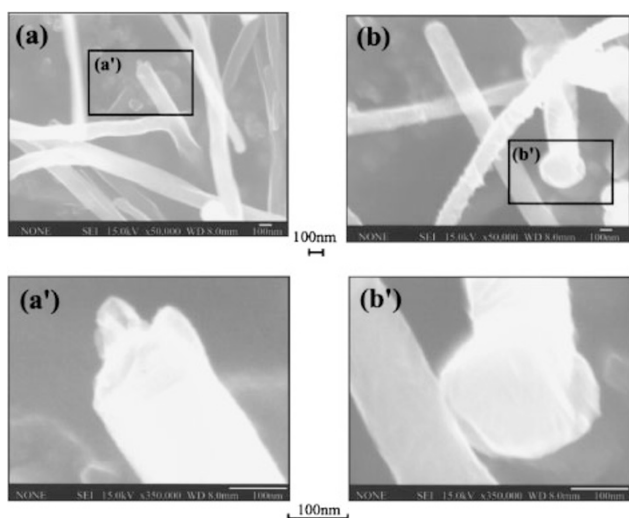Crosslinked PE-b-PEO formed by irradiation is unable to be removed by Soxhlet extraction with

**Figure 7.** FE-SEM aspects of (a, a′) untreated VGCF and (b, b′) PE-*b*-PEO-grafted VGCF.



**Figure 8.** Effects of temperature on the introduction of peroxyester groups onto MW-CNT and CS-CNT by the reaction with BDOC. CNT, 0.02 g; BDOC, 10.0 mL; hexane, 10.0 mL.

THF. However, for the γ-ray irradiated PE-*b*-PEO in the absence of VGCF, crosslinking of PE-*b*-PEO was less than 7.3% even if irradiated under 60 kGy. FE-SEM observation indicated that all of polymer covered the VGCF surface. Therefore, the grafting of PE-*b*-PEO onto the VGCF surface through the trapping of PE-*b*-PEO radical is considered as the main reaction under the above condition.

Field-emission scanning electron microscope (FE-SEM) was used to monitor changes in surface structure induced by the grafting of PE-*b*-PEO on VGCF. FE-SEM imagines of original VGCF are shown in Figure 7a and a′, and those of PE-*b*-PEO-grafted VGCF, grafting = 15.0% in Figure 7b and b′. As shown in Figure 7a and a′, the diameter of the original VGCF was about 100 nm, and the surface was very clean and smooth. However, the end of the VGCF was not smooth and annular carbon layers could be seen.

The surface of PE-*b*-PEO-grafted VGCF shown in Figure 7b and b′ was rough in comparison with the original one. This may be due to the fact that a layer of grafted PE-*b*-PEO covered on VGCF uniformly. The end of the VGCF has more grafted by PE-*b*-PEO.
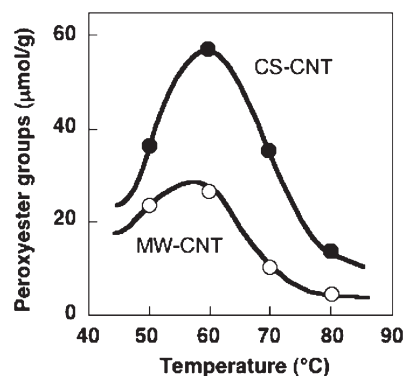
Therefore, it could be concluded that the PE-*b*-PEO is grafted onto the VGCF surface, and the grafting of polymer to end of VGCF readily proceeds. There was no distinct difference in the diameter before and after PE-*b*-PEO grafting. Because the grafted layer on the VGCF surface was too thin. The thickness of PE-*b*-PEO grafted layer from the weight of grafted PE-*b*-PEO is only about 10 nm.

*Introduction of Peroxyester Groups onto CNT by Radical Trapping*

1,1-Bis(*t*-butyldioxy)cyclohexane (BDOC) thermally decomposes near 70 °C to give radicals having peroxyester groups and *t*-butoxy radical [Scheme 7(1)].[58] We introduced peroxyester groups onto carbon black surface by the trapping of the radicals having peroxyester moiety and the radical graft polymerization of vinyl monomers initiated by the peroxyester groups on the surface.[59] Therefore, the introduction of peroxyester groups onto MW-CNT and CS-CNT by the treatment with BDOC was examined in hexane as shown in Scheme 7(1).[37]

The results are shown in Figure 8. Peroxyester groups are readily introduced onto MW-CNT and CS-CNT surfaces. Peroxyester groups on the surface increased with reaction temperature, but decreased
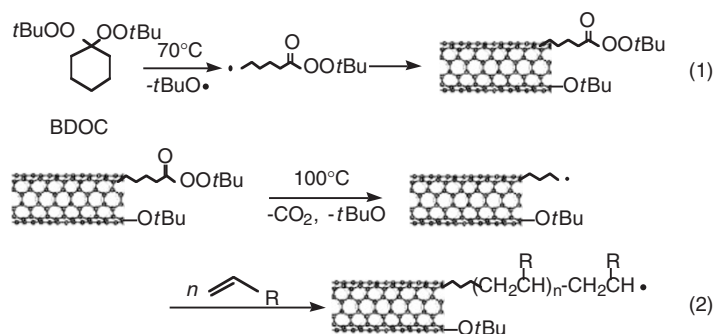


**Scheme 7.**

**Table VI.** Introduction of peroxyester groups onto MW-CNT by the reaction with BDOC in hexane and solvent RTIL

| Solvent | Time (h) | Peroxyester groups ($\mu$mol/g) |
|---------|----------|----------------------------------|
| RTIL | 8 | 30.1 |
| RTIL | 10 | 34.9 |
| RTIL | 12 | 38.3 |
| Hexane | 10 | 9.5 |

MW-CNT, 0.02 g; BDOC, 10.0 mL; solvent, 10 mL; 70 °C.

above 60 °C. This indicates that the thermal decomposition of peroxyester groups on the surface proceeds with increasing reaction temperature. The amount of peroxyester groups introduced onto CS-CNT was larger than that onto MW-CNT. This may be due to the fact that the edge of CS-CNT traps low molecular weight radicals more than MW-CNT, different from polymer radicals with large molecular weight.

The effect of 1-butyl-3-methylimidazolium hexafluorophosphate (RTIL) as reaction solvent on the trapping of radicals by CNTs was investigated. The results are shown in Table VI. The amount of peroxyester groups introduced onto MW-CNT by the reaction with BDOC in RTIL was much larger than that in hexane, because of the stabilization of free radicals in RTIL.[60]

## RADICAL GRAFTING OF POLYMERS FROM CARBON NANOTUBE AND NANOFIBER SURFACES

### The Radical Graft Polymerization from Peroxyester Groups on CNT

The radical graft polymerization of vinyl monomers initiated by MW-CNT and CS-CNT having peroxyester groups was carried out as shown in Scheme 7(2).[37,60] Radical graft polymerizations of vinyl monomers were initiated by peroxyester groups introduced onto the MW-CNT and CS-CNT surfaces at 100 °C to give the corresponding vinyl polymer grafted MW-CNT and CS-CNT. The percentage of grafting of poly(methyl methacrylate) (poly(MMA)) onto MW-CNT in hexane and RTIL reached to 6.6 and 60.2%, respectively. Polymer-grafted CNT with considerably higher grafting can be obtained in RTIL, because of stabilization of free radicals in RTIL.[60]

### Radical Grafting of Polymers from CNT Surface by Atom Transfer Radical Polymerization

Kong *et al.* reported the grafting of polyMMA from MW-CNT *via* atom transfer radical polymerization (ATRP) by three steps as shown in Scheme 8;[61] (1) introduction of acyl chloride groups onto MW-CNT by the reaction of carboxyl groups with thonyl chloride, (2) introduction of initiating sites for ATRP,
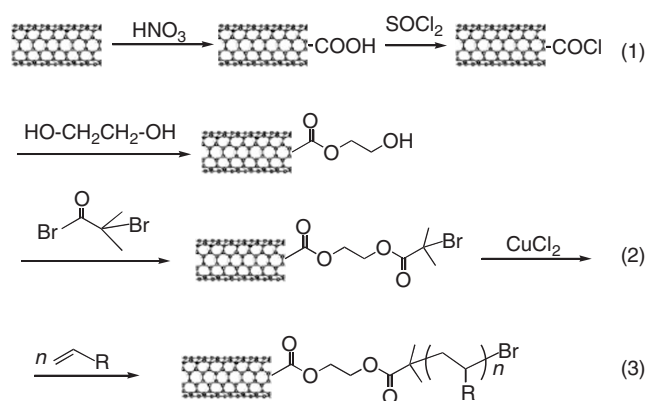


**Scheme 8.**

2-bromo-2-methylpropionate groups, onto MW-CNT by the reaction of acyl chloride groups with ethylene glycol followed by the treatment with 2-methyl-2-bromopropionyl bromide, and (3) graft polymerization of MMA from the bromopropionate groups in the presence of CuBr/$N,N,N',N',N'$-pentamethyldiethylenediamine by *in-situ* ATRP. The thickness of the polymer layer in the graft polymerization can be well controlled by the feed ratio of MMA to MW-CNT having 2-bromo-2-methylpropionate groups.

Quin *et al.* reported the grafting of *n*-butyl methacrylate (*n*BMA) and polystyrene onto SW-CNT by ATRP system consisting of 2-bromopropionate groups on SW-CNT and CuBr/bipyridyl.[62,63] The initiators of ATRP were covalently attached to SW-CNT by esterification of 2-hydroxymethyl-2′-bromopropionate with acyl chloride groups on the surface. Methyl 2-bromopropionate (MBP) was added as free initiator during the graft polymerization from SW-CNT surface to control growth of grafted chains and monitor the polymerization kinetics.

Figure 9 shows the relationship between conversion and $M_n$ (number average molecular weight) and $M_w/M_n$ (molecular weight distribution) of polystyrene in the grafting of polystyrene onto SW-CNT by the ATRP.[63] The molecular weight linearly increased with monomer conversion and the molecular weight distribution of free polymer was relatively low. Thus the number of grafting sites on SW-CNT is almost constant during the course of polymerization; *i.e.*, the growth of polystyrene from SW-CNT is controlled.

### Radical Grafting of Polymers from VGCF Initiated by the System Consisting of Trichloroacethyl Groups and Mo(CO)₆

Bamford *et al.* reported a system consisting of haloalkyl compounds and transition metal carbonyl derivatives, such as $Mo(CO)_6$ and $Mn_2(CO)_{10}$, to initiate radical polymerization of vinyl monomers.[64–67] The radical graft polymerization of vinyl monomers
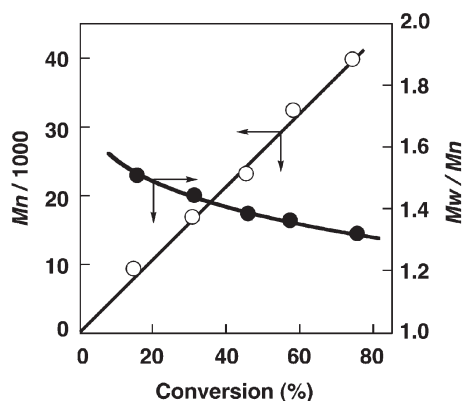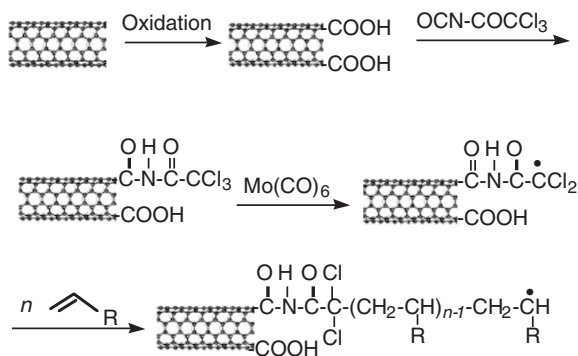
**Figure 9.** Relationship between conversion and $M_n$ ($M_w/M_n$) of polystyrene in the grafting of polystyrene onto SW-CNT by the ATRP. [St]:[initiator]:[CuBr]:[Bipy] = 500:1:1:2 in dichlorobenzene at 110 °C. Initiator = SW-CNT-initiator + MBP with [SW-CNT-initiator]/[MBP] = 1/20.



**Scheme 9.**

initiated by the system consisting of carbon black and nano-sized silica having trichloroacetyl groups and Mo(CO)$_6$ was reported by our group.[68,69]

Therefore, the polymerization of styrene initiated by the system consisting of VGCF-R-COCCl$_3$ and Mo(CO)$_6$ was investigated as shown in Scheme 9.[47] The introduction of trichloroacetyl groups onto the surface was achieved by reaction of surface carboxyl and phenolic hydroxyl groups with trichloroacetyl isocyanate.

Figure 10 shows the time-percentage of grafting curves for MMA and styrene initiated by the system consisting of VGCF-R-COCCl$_3$ and Mo(CO)$_6$ at 100 °C. The percentage of grafting increased with polymerization and percentage of polyMMA and polystyrene grafting exceeded 40% and 25%, respectively, after 6 h. The system consisting of untreated VGCF and Mo(CO)$_6$ was unable to initiate the polymerization. The graft polymerization of vinyl monomers, such as vinyl acetate and glycidyl methacrylate, onto VGCF was initiated by a system consisting of VGCF-R-COCCl$_3$ and Mo(CO)$_6$ to give the corresponding polymer-grafted VGCF.[47]



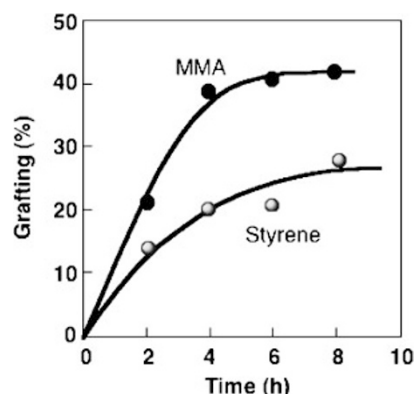**Figure 10.** Graft polymerization of MMA and styrene initiated by the system consisting of VGCF-R-COCCl$_3$ and Mo(CO)$_6$ at 100 °C. VGCF-R-COCCl$_3$, 0.10 g; Mo(CO)$_6$, 0.02 g; monomer, 10.0 mL.

These results indicate that the radical polymerization is initiated by surface radicals formed by the reaction of trichloroacetyl groups on VGCF surface with Mo(CO)$_6$ and grafted polymer chains are propagated form the surface as shown in Scheme 9.

*Grafting of Polymer onto CNT in-situ Radical Polymerization in the Presence of Radical Initiator*

Park *et al.* reported the grafting of polyMMA onto MW-CNT by *in-situ* radical polymerization by use of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The molecular weight of polyMMA increased with MW-CNT content. During the polymerization, MW-CNT was shown to be consumed AIBN by opening $\pi$-bonds on MW-CNT surfaces to make radicals and the radical initiate the radical graft polymerization from the surface.[70] FT-IR spectra for the supporting the generation of new $\pi$-bonds between MW-CNT and polyMMA were shown.

## GRAFTING OF POLYMERS FROM CARBON NANOTUBE AND NANOFIBER BY ANIONIC AND COORDINATION POLYMERIZATION

*Grafting of Polymers onto CNT by the Reaction with Polymeric Carbanions*

Wu *et al.* reported the grafting of poly(*N*-vinyl-carbazole) (polyNVC) and poly(butadiene) onto SW-CNT by nuclerophilic reaction of polymeric carbanions generated from organometallic reagents such as sodium hydride or butyllithium.[71] This method is effective for functionalization of C$_{60}$ fullerenes. The photoinduced electron transfer was observed in the polyNVC-grafted SW-CNT systems to give large optical limiting effects.[71]

Viswanathan *et al.* reported the one-step *in-situ* synthesis of polystyrene-grafted SW-CNT composite.[72] Carbanions are introduced onto the SW-CNT
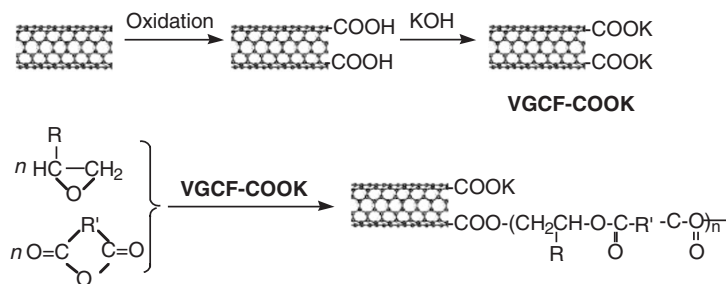
**Scheme 10.**

**Table VII.** Anionic ring-opening alternating copolymerization of SO with PAn initiated by COOK groups on VGCF

| VGCF | SO (mol) | PAn (mol) | Conversion (%) | Grafting (%) |
|---|---|---|---|---|
| Untreated | 0.01 | 0.01 | 0 | — |
| VGCF-COOH | 0.01 | 0.01 | 0 | 0 |
| VGCF-COOK | 0.01 | — | 0 | 0 |
| VGCF-COOK | — | 0.01 | 0 | 0 |
| VGCF-COOK | 0.01 | 0.01 | 9.2 | 4.8 |

VGCF, 0.10 g; 18-crown-6, 0.02 g; 120 °C; 8 h.

**Figure 11.** Grafting of polyesters onto VGCF by anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by COOK groups on the surface. VGCF, 0.10 g; epoxide = cyclic acid anhydride = 0.01 mol; 18-crown-6, 0.02 g; 120 °C.

surface by treatment of anionic initiator that serves to exfoliate bundles and provide initiating sites for the anionic polymerization of styrene.

*Grafting of Polyesters onto VGCF by Surface Initiated Anionic Ring-opening Alternating Copolymerization of Epoxides and Cyclic Acid Anhydrides*

We reported the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides is initiated by COOK groups on carbon black surface to give the corresponding polyester-grafted carbon black.[73–75] Therefore, the ability of VGCF having COOK groups to initiate the anionic ring-opening alternating copolymerization of styrene oxide (SO) with phthalic anhydride (PAn) was investigated as shown in Scheme 10.[46]

The introduction of COOK groups onto VGCF surface was readily achieved by the neutralization of carboxyl groups on VGCF. The results are shown in Table VII. The polymerization was carried out in the presence of crown ether to accelerate the polymerization.[75] As shown in Table VII, no polymerization of SO with PAn was initiated in the presence of untreated VGCF and VGCF-COOH. VGCF-COOK didn't initiate the polymerization of SO and PAn alone. The anionic ring-opening alternating copolymerization of SO with PAn was initiated by VGCF-COOK to give the corresponding polyester-grafted VGCF.

The anionic ring-opening alternating copolymerization of several epoxides with cyclic acid anhydrides
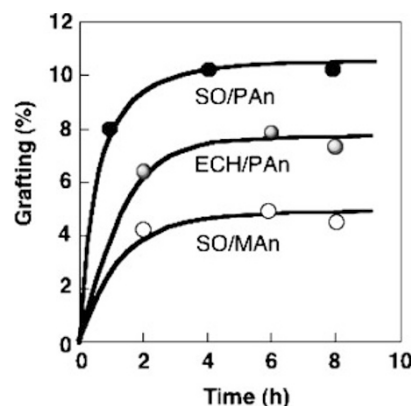
was investigated. Epoxides used were SO and epichlorohydrin (ECH), and cyclic acid anhydrides were PAn and maleic anhydride (MAn). The results are shown in Figure 11. VGCF having COOK groups initiated the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polyester-grafted VGCF.[46]

*Grafting of Poly(p-dioxanone) onto CNT by Surface Initiated Ring-opening Polymerization*

Ring-opening polymerization of *p*-dioxanone is usually initiated by a metal-alkoxide species, derived from alkoxide-ligand exchange reaction. In the case of tin(II) 2-ethylhexanoate (Sn(Oct)$_2$), polymerization is initiated by a Sn(OR) species.[76] Yoon *et al.* reported the grafting of biodegradable poly(*p*-dioxanone) onto shortened SW-CNT by surface initiated ring-opening polymerization of *p*-dioxanone in three steps [Scheme 11(1), (2), and (3)];[77] (1) chemical preparation of shorted SW-CNT, (2) covalent attachment of a polymerization initiator to the SW-CNT, and (3) surface initiated ring-opening polymerization.

They point out that the intrinsic properties of poly-

**Scheme 11.**



a) R=     b) R=     c) R=

d) R=     e) R=

f) R=     g) R=

h) R=     i) R=

j) R=     k) R=

l) R=

m) R=     n) R=

**Scheme 12.**

(*p*-dioxanone) can be changed by interaction between polymers and CNTs, and interaction was strengthened more by the surface initiated grafting of the polymer than the simple mixing.

## GRAFTING OF POLYMERS ONTO CARBON NANOTUBE AND NANOFIBER BY THE OTHER REACTIONS

*Grafting of Polymers by the Reaction with Azide Compounds*

Grafting of polymers onto SW-CNT *via* addition of (R-)oxycarbonyl nitrenes allows for covalent bonding of various functional groups such as alkyl chains, aromatic rings, dendrimers, crown ethers, and oligoethylene glycol as shown in Scheme 12.[78] The polymer-grafted SW-CNT gave a stable dispersion in various solvents. AFM and TEM indicated that the grafted SW-CNT forms thin bundles with typical diameter of 10 nm.

The grafting of polystyrene with controlled molecular weight and narrow molecular weight distribution was grafted onto SW-CNT by SW-CNT with polystyrene having terminal azide groups. Polystyrene

having terminal azide groups was prepared by reaction of sodium azide with bromine terminated polystyrene obtained from ATRP.[63]

*Grafting of Polymers by Direct Friedel–Crafts Reaction*

We grafted polymers onto carbon black surface by Friedel–Crafts reaction of chlorine-terminated polymers with aromatic rings of carbon black in the presence of AlCl$_3$.[79] Recently, Baek and his coworkers reported the *in-situ* polymerization of 3-phenoxybenzoic acid in the presence of VGCF in poly(phosphoric cid) (PAA)/phosphorus pentoxide medium.[80] In the polymerization *via* Friedel–Crafts acylation, poly-(oxy-1,3-phenylenecarbonyl-1,4-phenylene) was grafted onto VGCF surface. They point out that PAA is quite effective in dispersing VGCF because of its acidic and viscous character.

## GRAFTING OF POLYMERS ONTO CARBON NANOTUBE AND NANOFIBER BY ELECTRO CHEMICAL POLYMERIZATION

Baibarac and his coworkers reported the covalent functionalization of SW-CNT by aniline electrochemical polymerization (Scheme 13).[81] They investigated the electropolymerization of aniline in HCl solutions onto SW-CNT film and pointed out that the covalent functionalization of SW-CNT with polyaniline is obtained in two ways. The first is electrochemical polymerization of aniline on SW-CNT film using HCl solution which results in composites on the type of polyaniline (leuucoemeraldine base) and polyaniline (emeraldine base) functionalized SW-CNT. The second is NH$_4$OH post treatment on polyaniline functionalized SW-CNT and involves internal redox reaction between polyaniline (emeraldine base) and SW-CNT, which transforms the polymer chain from the semi-oxidized state into a reduced one.

Feng *et al.*[82] and Wu *et al.*[83] reported the preparation of polyaniline/MW-CNT composite *via in-situ* chemical oxidation polymerization of aniline.
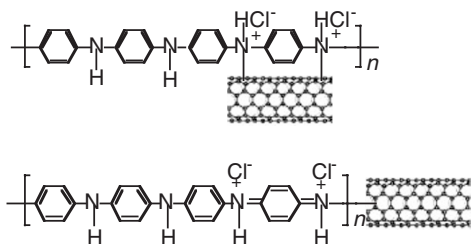


**Scheme 13.**

## GRAFTING REACTION OF CARBOXYL GROUPS ON CARBON NANOTUBE WITH FUNCTIONAL POLYMERS

*Grafting of Dendrimer and Dendron onto CNT*

Sano *et al.* reported the construction of shortened CNT "stars" with dendrimers.[84] The carboxyl groups on SW-CNT were converted to acyl chloride groups by treatment with thionyl chloride. The SW-CNT having acyl chloride groups was reacted with terminal amino groups of poly(amidoamine) (PAMAM) starburst dendrimer (tenth generation) [Scheme 14(a)]. AFM on cast film of the reaction mixture on mica indicated star-shaped objects. The average spine length is approximately 0.8 µm, which agrees well with the length of SW-CNT. This indicates that the acyl chloride groups at the open ends of shortened SW-CNT are more reactive than those at the side-wall, although carboxyl groups are present at the side-wall and open ends.

Sun and his coworkers reported the functionalization of SW-CNT and MW-CNT by lipophilic and hydrophilic dendron species under classical amidation and esterification reaction as shown in Scheme 14(b).[85,86] Lipophilic dendron-grafted CNTs are soluble in hydrocarbon and weakly polar organic solvents, while CNT grafted with oligomeric PEG moieties are soluble in both organic solvents and water.

*Grafting of Hydroxyl-terminated Polymers onto CNT*

Poly(vinyl alcohol) (PVA) was grafted onto SW-CNT by reaction of surface carboxyl groups with PVA in the presence of a condensing agent such as DCC [Scheme 14(c)]. PVA-grafted SW-CNT composite films are of high optical quality, without any observable phase separation.[87]

We grafted hydroxyl terminated polymers, such as PEG and PE-*b*-PEO, onto MW-CNT and VGCF by direct condensation reaction of carboxyl groups, previously introduced by the ligand-exchange reaction, in the presence of DCC.[37,38]

*Grafting of Amino-terminal Polymers*

The grafting of MW-CNT with amino polymers, such as poly(propenylethyleneimine-*co*-ethyleneimine) random copolymer, by reaction with acid chloride groups on the surface has been reported.[88,89] The polymer-grafted MW-CNT thus obtained was also soluble in many common organic solvents and in water.

Zhao *et al.* reported that poly(*m*-aminobenzene sulfonic acid) (PABS) was grafted onto SW-CNT by reaction with SW-CNT having acid chloride groups to give water soluble SW-CNT as shown in Scheme 14(d).[90] The PABS-grafted SW-CNT exhibits an order
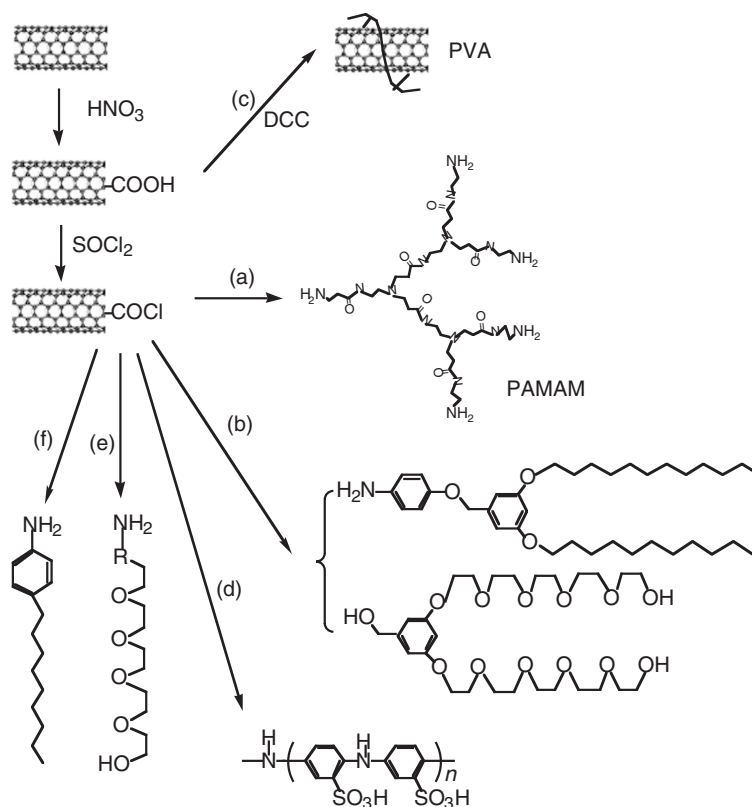
**Scheme 14.**

of magnitude increase in electrical conductivity over neat PABS.

PEO-grafted SW-CNT was synthesized by reaction of acid-cut SW-CNT with SOCl₂, followed by a reaction with monoamine-trerminated PEO.[91] The conformation of SW-CNT can be controlled by solvent quality and the self-organized structures can be manipurated as if PEO-grafted SW-CNT is an ordinary block copolymer [Scheme 14(e)].

The grafting of long alkyl chains onto short cutted SW-CNT was done by reaction of acyl chloride groups with long chain aliphatic amine, such as octadodecylamine and 4-dodecylaniline [Scheme 14(f)].[92]

*Grafting of Biological Compound, Such as Protein, Enzyme, and DNA onto CNT*

Grafting of a biological compound onto CNT to monitor a biochemical event results in promising electrochemical sensors.[93] Proteins and enzymes can effectively be grafted onto CNT.[93–96] Kerman *et al.* reported the DNA-direct attachment of MW-CNT using surface acyl chloride groups for enhanced label-free electrochemical detection of DNA hybridization.[97]

Cai *et al.* reported a novel and sensitive electrochemical DNA biosensor based on MW-CNT with a carboxyl group for covalent DNA immobilization and enhanced hybridization detection.[98] The sensing mechanism is schematically shown in Scheme 15. A

MW-CNT modified glassy carbon electrode (GCE) was fabricated and oligonucleotides with the 5′-amino group were covalently bonded to the carboxyl group of MW-CNT. The hybridization reaction on the electrode was monitored by differential pulse voltammetry (DPV) analysis using an electroactive intercalator daunomycin as an indicator.

## DISPERSIBILITY OF POLYMER-GRAFTED CARBON NANOTUBE AND NANOFIBER

By grafting of polymers onto CNT and VGCF, dispersibility in good solvents of grafted polymer chain is remarkably improved. Figure 12 shows the dispersibility of PEG-grafted MW-CNT in methanol. Untreated MW-CNT completely precipitated in methanol within 1 h. PEG-grafted MW-CNT gave a stable dispersion in methanol. This indicates that by the grafting of PEG onto MW-CNT surface, the intertwined structure of MW-CNT is effectively destroyed and grafted polymer chains on the side-wall interfere with aggregation of the MW-CNT.[37,38]

Qin reported that the dispersibility of polystyrene-grafted SW-CNT in dichlorobenzene and THF can be controlled by chain length of the grafted polystyrene.[63]

Viswanathan *et al.* reported that carbanions are introduced onto SW-CNT by treatment with *sec*-BuLi
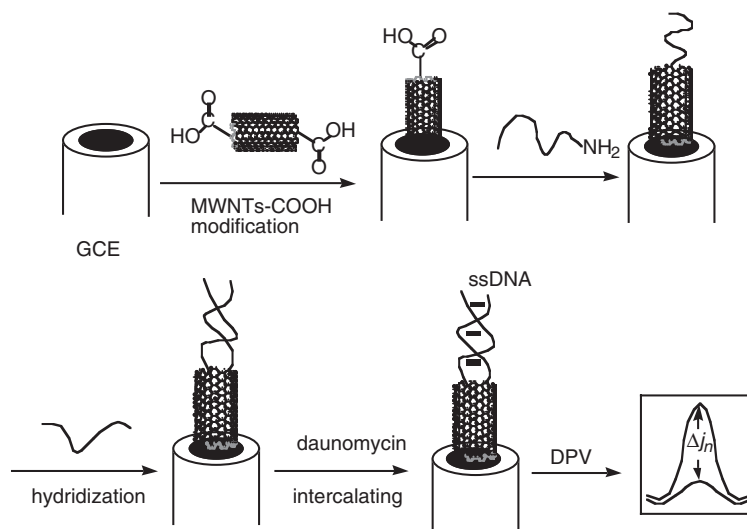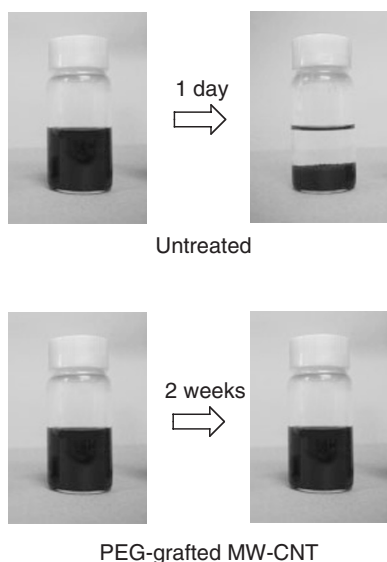
**Scheme 15.**



**Figure 12.** Dispersibility of ungrafted and PEG-grafted MW-CNT in methanol at room temperature.
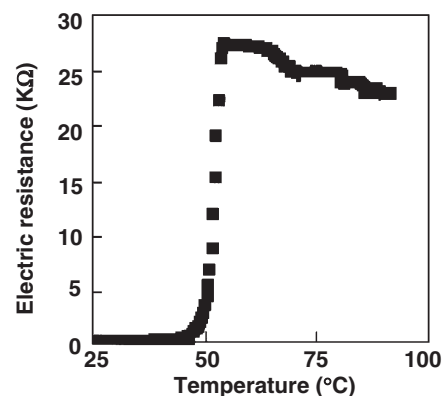


**Figure 13.** Effects of temperature on the electric resistance of the composite prepared from PEG ($M_n = 3.4 \times 10^3$)-grafted VGCF (grafting = 12.4%) and PEG ($M_n = 8.0 \times 10^3$). VGCF content = 5.0 wt %.

that exfoliates the bundle.[72] Negative charged CNTs are separated from the bundles and disperse in solution due to mutual electrostatic repulsion between individual tubes.

## ELECTRIC PROPERTIES OF POLYMER-GRAFTED CARBON NANOTUBE AND NANOFIBER

*Effects of Temperature on the Electric Resistance of Composite from Polymer-grafted VGCF*

Vinyl polymer-grafted carbon black, crosslinked with a variety of crosslinking agents, shows a positive temperature coefficient of resistance, *i.e.*, PTC, at temperatures near the glass transition temperature of the grafted polymer.[99–101] We reported the effects of temperature on the electric resistance of crystalline polymer-grafted carbon black.[102]

Figure 13 shows the effect of temperature on the electric resistance of composite prepared from PEG-grafted VGCF. Electric resistance of the composite from PEG-grafted VGCF drastically increased at melting point of PEG, 50 °C. Therefore, the composite from PEG-grafted VGCF shows positive temperature coefficient (PTC) characteristic.[37,38]

The drastic increase of electric resistance of the composite at the melting point of PEG is due to the widening of gaps between VGCFs based on the melting of matrix and grafted PEG.

*Effects of Organic Vapor on the Electric Resistance of Composite from Polymer-grafted VGCF*

We reported that composites prepared from crystalline polymer-grafted carbon black and crystalline
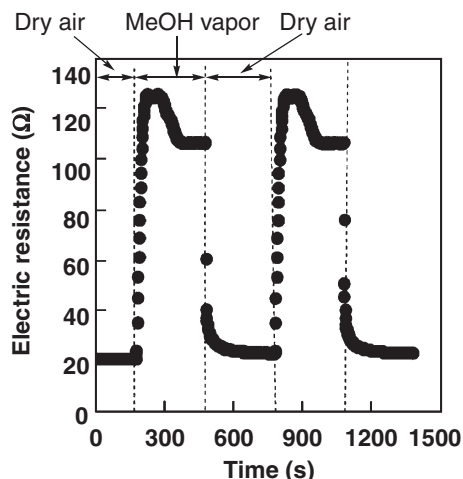
**Figure 14.** Response of the electric resistance of the composite prepared from PEG $(M_n = 3.4 \times 10^3)$-grafted VGCF (grafting = 12.4%) and PEG $(M_n = 8.0 \times 10^3)$ to methanol vapor at 25 °C. VGCF content = 5.0 wt %.
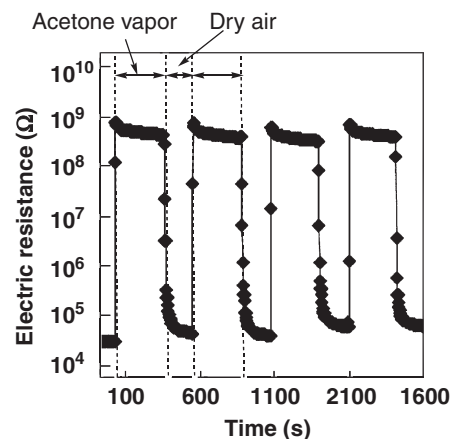


**Figure 15.** Response of electric resistance of composite prepared from poly(SO-*alt*-PAn)-grafted VGCF and PCL to acetone vapor at 25 °C. VGCF content = 5.0 wt %.

polymer can be used as novel gas sensors.[103–108] The electric resistance of conductive composites prepared from polymer-grafted CNT and VGCF also respond to various solvent vapors.

Figure 14 shows the electric resistance change of composites prepared from PEG-grafted VGCF and PEG in methanol vapor at 25 °C. The electric resistance of the composite suddenly increased in methanol vapor, and returned immediately to initial resistance when the composite was transferred to dry air. The responsiveness of electric resistance was reproducible even after 20 cycles of exposure to methanol vapor and dry air.[37,38] The electric resistance of the composite hardly responded to *n*-hexane and acetone vapor, which are poor solvents of PEG.

Figure 15 shows the electric resistance change of the composites prepared from poly(SO-*alt*-PAn)-grafted VGCF and PCL in acetone vapor at 25 °C. The electric resistance of these composites also suddenly increased in acetone, and returned immediately to initial resistance when the composites were transferred to dry air. The responsiveness of electric resistance was also reproducible even after 20 cycles of exposure to acetone vapor and dry air.[46]

This is due to a slight change of gaps between VGCFs based on the absorption of vapor of a good solvent by grafted chain and matrix polymer. Detection of a slight change of crystalline structure of polymer by the absorption of solvent as a large change of electric resistance of the composite may be possible.

## CONCLUDING REMARKS

In this review, recent studies are summarized on the functionalization of carbon nanotubes and nanofibers,

such as SW-CNT, MW-CNT, CS-CNT, and VGCF, by grafting of polymers. The method for surface grafting of polymers presented here can be applied for the grafting of polymers onto fullerenes[109] and inorganic particles,[110–112] such as silica, titanium dioxide, and ferrite, organic pigments,[113,114] and polymer powders.[115,116]

The solubilization of CNTs by use of $\pi$–$\pi$ interactions of aromatic compounds and CNT surface and by polymer wrapping of CNTs is also reviewed.[117,118]

Modification of CNT and VGCF surfaces will become more and more important for the design of high performance conductive composite materials. Surface-modified CNT and VGCF by grafting of polymers have a large potential as electrode material for fuel cells and high performance nano-composites.

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