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Article

Simple Process for Sidewall Modification of Multi-Walled Carbon Nanotubes with Polymer Side Chain Radicals Generated by Ultraviolet-Induced C–Cl Bond Dissociation of Polystyrene Derivatives

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Abstract: In this work, we investigated a simple one-step process for the formation of chemical bonds between multi-walled carbon nanotubes (MWCNTs) and benzyl-type side chain radicals generated by UV photolysis of polystyrene derivatives containing the chloromethyl (–CH_2Cl) group. Poly(4-chloromethyl)styrene, or styrene/4-(chloromethyl)styrene random copolymer, was mixed with MWCNTs in 1-methyl-2-pyrrolidone and irradiated with ultraviolet (UV) light. Films of polymer/MWCNT mixtures before and after UV irradiation were fabricated, and then examined by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. According to the XPS analysis, the amount of Cl atoms in the mixture was found to decrease upon UV irradiation, indicating that the Cl atoms generated by photolysis of chloromethyl groups escaped from the reaction system in the form of gaseous Cl_2. The structural change of CNTs after UV irradiation was also observed by comparing the G/D ratios (the intensity ratio of the G to D bands) of the Raman spectra obtained before and after UV irradiation. Similar phenomena were also confirmed in the case of the polymer/MWCNT mixture containing hydroxylammonium chloride as a dispersant of MWCNTs. These results confirmed the UV-induced covalent bond formation between polymer side chains and MWCNTs.

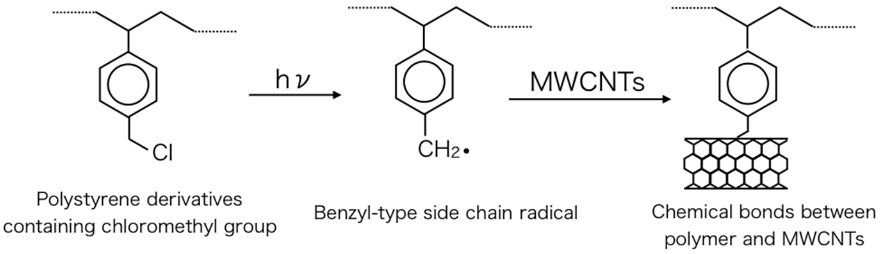
Keywords: carbon nanotubes; chemical modification; photolysis; benzyl radical

1. Introduction

The fabrication of polymer materials combined with carbon nanotubes (CNTs) has received considerable attention from a technological viewpoint. CNTs are allotropes of carbon and have a cylindrical structure comprising many hexagonal units [1]. They possess attractive electric and thermal characteristics, exhibiting electric conductivity based on their conjugated electronic structure; besides, they can be used as raw materials for fabricating organic electronic devices [2–9]. In addition, as CNTs can produce heat upon the supply of electric current, they are utilized as "molecular heaters" [10–15].

Consequently, many researchers have attempted to develop new methods of fabrication of organic conductive materials by combining polymers and CNTs. Grafting of polymers onto CNTs has been widely studied for the fabrication of polymer-CNT hybrid materials [16–22]. Grafting through chemical bond formation is a useful technique for the preparation of durable hybrid materials; however, to obtain hybrid materials via simple low-cost covalent modification processes, novel chemical treatments need to be devised. The use of photochemical reactions appears promising for this purpose because the reaction protocol entails mild operating conditions (e.g., reduced number of chemical reagents or room-temperature treatment).

In this work, we examined the formation of a chemical bond between multi-walled CNTs (MWCNTs) and side chains of polystyrene. The chemical bonds were formed through the addition of benzyl-type radicals generated by the photo-induced dissociation of the C–Cl bond of the poly(p-chloromethyl)styrene side chain. Photo-induced formation of benzyl-type radicals from corresponding benzyl halides has already been reported [23]. Notably, various free radicals smoothly attack and bind to CNT surfaces [24–27]. The reaction process is shown in Scheme 1.



Scheme 1. Reaction process of C–Cl dissociation of polymer side chains followed by chemical bond formation between polymer and multi-walled carbon nanotubes.

This bond formation can be achieved without using highly hazardous chemicals or external heating. Moreover, although photo-induced graft polymerization initiating from CNT surfaces has been reported [28], photo-induced linkage of polymer side chains with CNTs has not been extensively investigated yet. By using this technique, CNTs and many common polymers functionalized with photochemically reactive groups can be hybridized through one-pot light irradiation. Therefore, the approach proposed in this work is expected to be a promising candidate to develop an eco-friendly process for the fabrication of organic electronic materials.

We prepared two polystyrene derivatives, poly(p-chloromethyl)styrene (poly-CMSt) and styrene/p-(chloromethyl)styrene random copolymer (poly-St-co-CMSt); the structures of these polymers are shown in Figure 1. Bond formation between poly-CMSt and CNTs has been attempted also by Chen et al. [29]; they conducted the esterification between poly-CMSt and carboxylated CNTs by utilizing a phase-transfer catalyst. However, their method required the oxidation of CNTs with nitric acid prior to the bond formation. Conversely, our approach does not require this type of strong oxidation treatment.

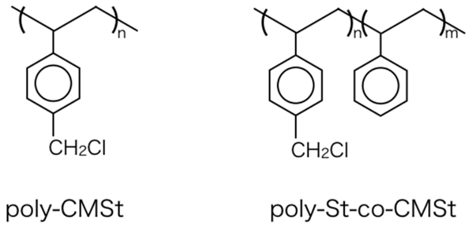


Figure 1. Structures of poly (p-chloromethyl)styrene and styrene/p-(chloromethyl)styrene random copolymer. The subscripts n and m represent the number of corresponding monomer units.

We used the homopolymer and copolymer to observe the effect of dissociative site density on the reaction yield. Bond formation between MWCNTs and polymer side chains was examined by using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Measurements of Cl content in the polymer-CNT samples before and after light irradiation were obtained by XPS. Raman spectroscopy was used to analyze the structural changes of the MWCNTs before and after light irradiation. In addition, the influence of hydroxylammonium chloride, added as a MWCNT dispersant, on the reaction efficiency was examined. Hydroxylammonium chloride dissolves CNTs in organic solvents, and it can be used to make polymer-CNT nanocomposites in solution [30]. By using this dispersant, the development of a novel fabrication method of transparent or translucent polymer/CNT hybrid materials was expected. XPS and Raman spectroscopies were also used to analyze the samples containing the dispersant; the spectra were compared with those obtained for the dispersant-free samples to check if the adsorption of the dispersant interfered with the addition of polymer radicals on the MWCNT surface.

2. Results and Discussion

2.1. Photoinduced C–Cl Bond Dissociation of Chloromethyl Group Observed by XPS

Figure 2 shows the X-ray photoelectron spectra (C 1s and Cl 2p) of the poly-CMSt/MWCNT mixture before and after ultraviolet (UV) irradiation for 24 h. The spectra recorded for neat poly-CMSt are also shown. Transverse shifts of the spectra, probably induced by charge-up of the samples, were observed. However, as the transverse shifts did not quantifiably affect C and Cl, no manipulation (numerical correction) of the shifts was conducted here. The Cl content was found to significantly decrease during the irradiation, indicating that the C–Cl bonds of the polymer side chains were dissociated by photolysis. The separated Cl atoms escaped from the poly-CMSt/MWCNT mixture; if Cl trapping in the polymer and Cl adsorption on the MWCNT surface had been dominant, the intensities of the Cl 2p spectra would have been similar. In the present case, the Cl atoms were probably released in the form of gaseous Cl_2 generated through the recombination of Cl atoms. Conversely, the C content of the sample remained almost constant during the irradiation. The C content comprised the amounts of C from both the polymer and the MWCNTs in the sample. The polymer/MWCNT weight ratio of the sample was 25 mg/1.3 mg; therefore, the signal assigned to C in the polymer appeared as dominant in the spectra. These results indicated that the polymer did not decompose to form volatile compounds, and was durable against UV irradiation. These findings supported the selective dissociation of photo-induced C–Cl bonds of the polymer side chain.

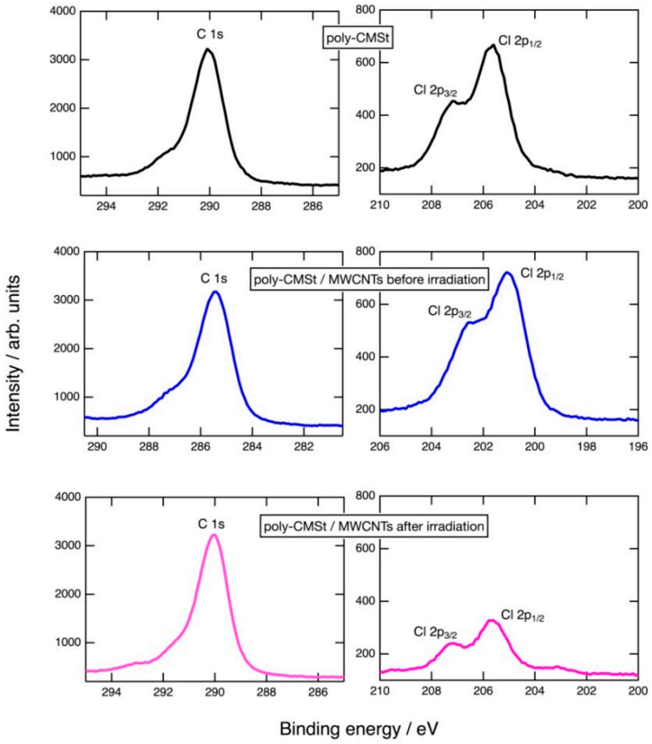


Figure 2. C 1s and Cl 2p X-ray photoelectron spectra observed for intact poly(p-chloromethyl)styrene (poly-CMSt) and for poly-CMSt/multi-walled carbon nanotube mixture before and after ultraviolet irradiation.

Figure 3 shows the X-ray photoelectron spectra (C 1s and Cl 2p) of the poly-St-co-CMSt/MWCNT mixture before and after UV irradiation for 24 h. The spectra recorded for neat poly-St-co-CMSt are also shown. The spectra were similar to those observed for the poly-CMSt/MWCNT sample. Namely, the Cl content decreased upon irradiation, while the C content remained constant. The Cl 2p signal was considerably weaker than that observed for the poly-CMSt/MWCNT mixture, implying that quite a small amount of chloromethylated moiety was introduced to the polymer during polymerization. This was also supported by the nuclear magnetic resonance (NMR) results shown later. Therefore, radical recombination between C and Cl was expected to occur; when the chloromethyl group density is low, the radical recombination between C and Cl generated through C–Cl dissociation often dominantly occurs instead of the generation of Cl_2 molecules, owing to the so-called "cage effect" in liquid media [31]. Radicals formed through bond scission in a condensed phase tend to recombine, as radicals surrounded by a medium cannot easily diffuse and separate from each other. However, in this case, the radical recombination was not significant. This means that the radical formation through C–Cl dissociation effectively proceeded even in the copolymer with a low density of chloromethyl groups; thus, the present method for polymer-MWCNT bond formation can be also applied to chemical hybridization of copolymers and MWCNTs.

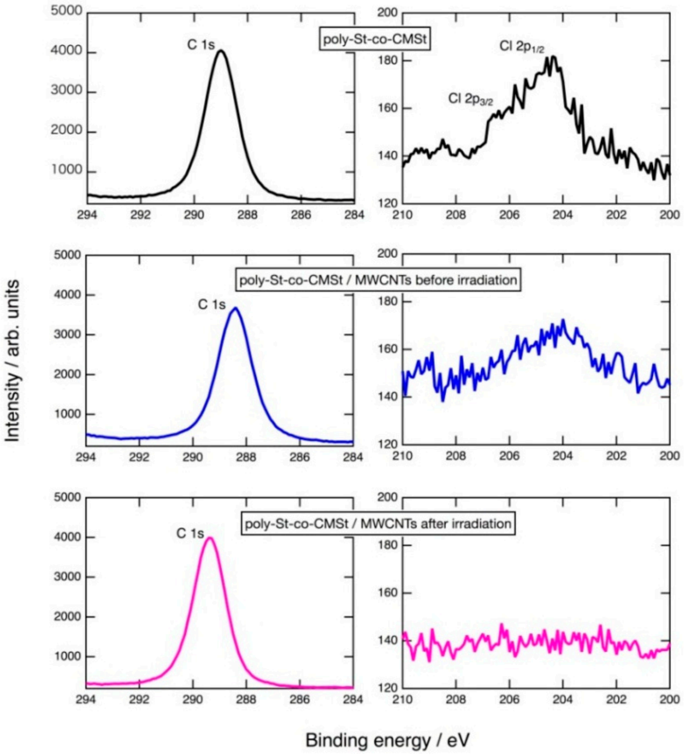


Figure 3. C 1s and Cl 2p X-ray photoelectron spectra observed for intact styrene/p-(chloromethyl)styrene random copolymer (poly-St-co-CMSt) and for poly-St-co-CMSt/multi-walled carbon nanotube mixture before and after ultraviolet irradiation.

2.2. Structural Change of MWCNTs Observed by Raman Spectroscopy

Figure 4 shows the Raman spectra of poly-CMSt/MWCNT and poly-St-co-CMSt/MWCNT mixtures before and after irradiation for 24 h. The intensities of the recorded signals were adjusted to equalize the intensities of the G bands observed before and after irradiation. In both cases, for poly-CMSt/MWCNT and poly-St-co-CMSt/MWCNT mixtures, two characteristic bands belonging to MWCNTs, i.e., the G and D bands, were visible. The G band observed at ~1570–1590 cm^{-1} was assigned to the in-plane vibration of the MWCNT aromatic rings; the D band observed at ~1310–1340 cm^{-1} originated from MWCNT defects generated by the deformation of the original sp^2-based structure.

The intensity ratio of the G to D bands, the G/D ratio, is an index of the degree of surface structural deformation induced by the chemical reaction [32]. We compared the G/D ratios of the samples before and after irradiation to observe the structural change in MWCNTs caused by the attack of the polymer side chain radicals.

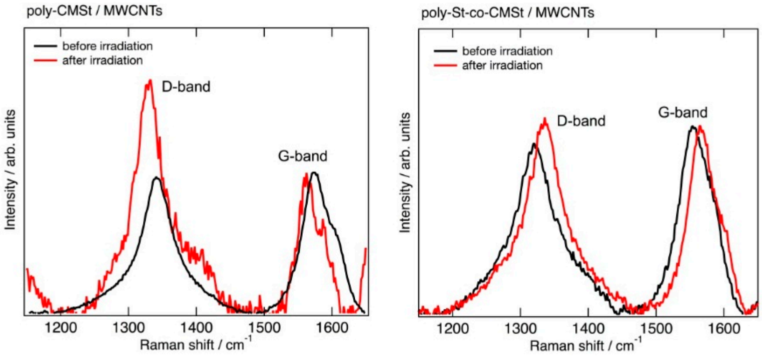


Figure 4. Raman spectra observed for poly(p-chloromethyl)styrene/multi-walled carbon nanotube (MWCNT) and styrene/p-(chloromethyl)styrene random copolymer/MWCNT mixtures before and after ultraviolet irradiation.

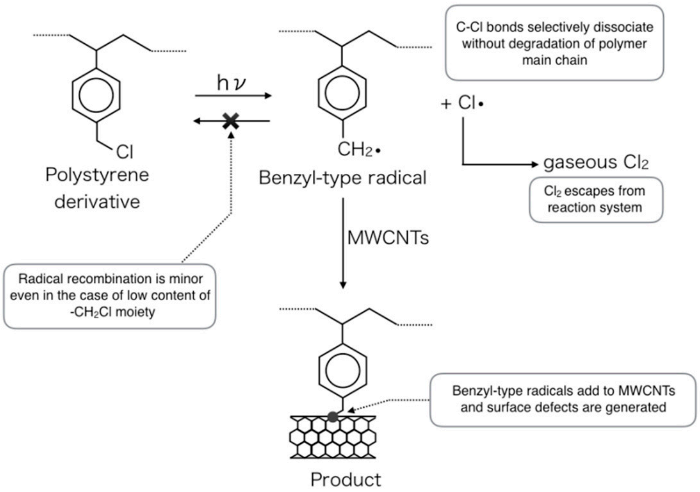


Figure 5. Schematic illustration of the chemical modification of multi-walled carbon nanotubes with polymer side chain radicals.

As shown in Figure 4, the G/D ratio calculated for the poly-CMSt/MWCNT mixture considerably decreased upon irradiation (from 1.07 to 0.61), indicating that the MWCNT surface defects increased with the addition of radicals generated through the C–Cl bond dissociation of the polymer side chains; the chemical bonding between MWCNTs and side chains was successfully achieved after irradiation. The variation of the G/D ratio observed for the poly-St-co-CMSt/MWCNT mixture was not significant, compared with that of the poly-CMSt/MWCNT mixture. This divergence in the G/D ratio change was due to the different densities of chloromethyl groups of poly-CMSt and poly-St-co-CMSt; as the amount of radicals generated from poly-St-co-CMSt was lower than that originating from poly-CMSt, the degree of surface modification of MWCNTs with poly-St-co-CMSt was lower than that with poly-CMSt. However, a decrement of the G/D ratio was observed after irradiation also in the case of the poly-St-co-CMSt/MWCNT mixture (from 1.10 to 0.96), indicating that the addition of radicals to the MWCNT surface occurred even if the chloromethyl group content in the polymer was low. This is consistent with the XPS results obtained for the poly-St-co-CMSt/MWCNT mixture; the side chain radicals of poly-St-co-CMSt smoothly formed through C–Cl bond dissociation without recombination of C and Cl, which should have been caused by the cage effect. A schematic illustration of the chemical modification of MWCNTs with polymer radicals is shown in Figure 5. For comparison, we recorded the Raman spectra of pristine MWCNTs before and after irradiation for 24 h (see Supplementary Information). The G/D ratios before and after irradiation were almost equal (from 1.30 to 1.24); the G/D ratio change calculated for the poly-CMSt/MWCNT and poly-St-co-CMSt/MWCNT mixtures was caused solely by the addition of radicals to the MWCNT surface.

2.3. Influence of Hydroxylammonium Chloride Added as Dispersant on the Reaction Efficiency

In this work, the influence of hydroxylammonium chloride ($NH_2OH\cdots HCl$) as dispersant on the efficiency of the radical addition reaction was also examined. The hydroxylammonium cation (NH_3OH^+), generated from $NH_2OH\cdots HCl$, is typically adsorbed on the MWCNT surface, and improves the dispersibility in solvents [30]. If NH_3OH^+ and Cl^- adhere on the surface, the radical addition reaction may possibly be hindered by the adsorption of the dispersant.

To check the influence of $NH_2OH\cdots HCl$ on the reaction, the XPS and Raman spectra of poly-CMSt/MWCNT mixtures containing $NH_2OH\cdots HCl$ were compared with those obtained for the mixtures without $NH_2OH\cdots HCl$; they are shown in Figures 6 and 7, respectively. The spectral features of the sample containing $NH_2OH\cdots HCl$ were quite similar to those of the samples without $NH_2OH\cdots HCl$; the decrease in Cl content and the MWCNT structural deformation occurring after UV irradiation were confirmed (the G/D ratio went from 1.04 to 0.73). These results revealed the addition of polymer side chain radicals, generated through photo-induced C–Cl bond cleavage, to the MWCNT surface. Therefore, the adsorption of $NH_2OH\cdots HCl$ did not interfere with the radical addition to the MWCNT surface.

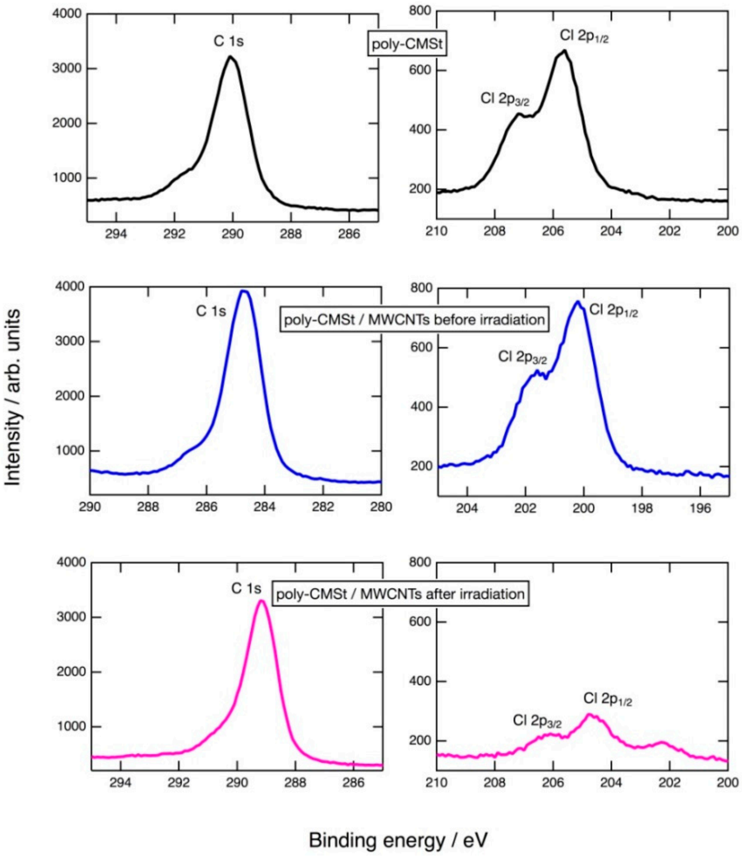


Figure 6. C 1s and Cl 2p X-ray photoelectron spectra observed for intact poly(p-chloromethyl)styrene (poly-CMSt) and for poly-CMSt/multi-walled carbon nanotube mixture containing $NH_2OH\cdots HCl$, before and after ultraviolet irradiation.

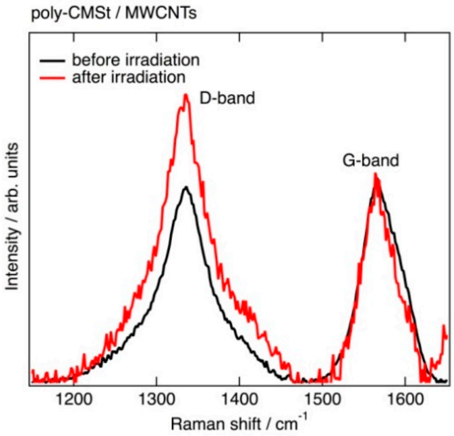


Figure 7. Raman spectra observed for poly(p-chloromethyl)styrene/multi-walled carbon nanotube mixture containing $NH_2OH \cdots HCl$, before and after ultraviolet irradiation.

The obtained poly-CMSt/MWCNT films were not transparent, and contained visible MWCNT particles. This indicated that $NH_2OH \cdots HCl$ could not sufficiently disperse the MWCNTs in the polymer used in this work, although it can disperse MWCNTs in organic solvents. The fabrication of transparent polymer/MWCNT materials will be the subject of future studies.

3. Materials and Methods

3.1. Materials

MWCNTs (10–30 nm in diameter, 1–10 μm in length) were purchased from Wako (Osaka, Japan). The MWCNTs were purified by removal of amorphous carbon through heating with a muffle furnace, followed by dissolution of metal impurities by using hydrochloric acid. After the purification, the MWCNTs were dried in air at 70 °C. Styrene (St) and 4-(chloromethyl)styrene (CMSt) were purchased from Junsei Chemicals (Tokyo, Japan) and Tokyo Kasei (Tokyo, Japan), respectively. The monomers were purified by passage through a silica-gel-activated alumina column. The initiating agent, azobisisobutylonitrile (AIBN), was purchased from Wako, Japan, and used without further purification. The solvents used for polymerization and UV-irradiation, i.e., tetrahydrofuran (THF) and N-methylpyrrolidone (NMP), were purchased from Wako, Japan. THF was dehydrated by using molecular sieves. NMP was used without further purification. Hydroxylammonium chloride ($NH_2OH \cdots HCl$) was purchased from Wako, Japan, and used without further purification.

3.2. Preparation of Poly(4-shloromethyl)styrene and Styrene/(4-chloromethyl)styrene Copolymer

Poly(4-chloromethyl)styrene (poly-CMSt) was prepared by conventional radical polymerization of CMSt. CMSt and AIBN were mixed in THF and stirred for 24 h at 65 °C. The mixture was subsequently poured into methanol to precipitate the resultant polymer, which was then vacuum-dried at room temperature.

Styrene/(4-chloromethyl)styrene copolymer (Poly-St-co-CMSt) was prepared by using the same procedure. CMSt, St, and AIBN were mixed in THF and treated following the procedure described above. The molar ratio of CMSt/St in the mixture was 0.05 mol/0.02 mol.

Polymer formation was confirmed by means of proton NMR (^1H NMR) spectroscopy (JEOL JNM-ECP400, JEOL Ltd., Tokyo, Japan). In both poly-CMSt and poly-St-co-CMSt syntheses, conversions of vinyl groups to alkyl chains were observed, indicating that the monomers were successfully polymerized. The ^1H NMR spectra of St, CMSt, poly-CMSt, and Poly-St-co-CMSt are shown in Figure 8.

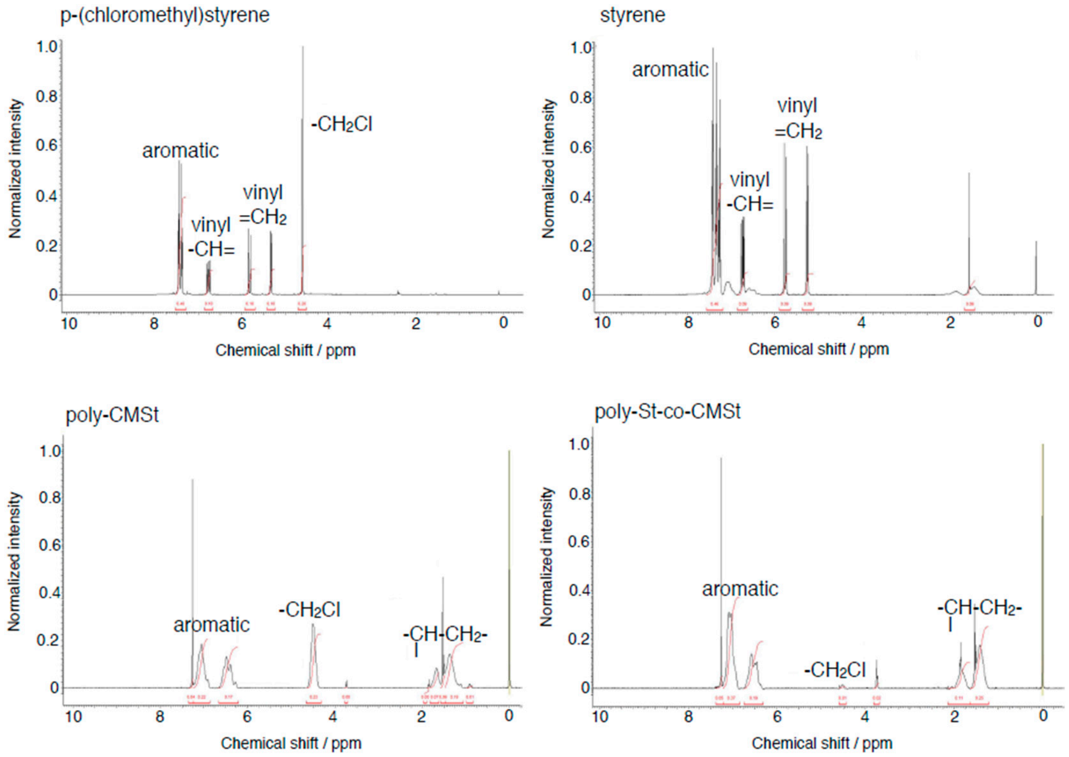


Figure 8. ^{1}H nuclear magnetic resonance spectra observed for monomers (p-(chloromethyl styrene and styrene) and polymers (poly(p-chloromethyl)styrene and styrene/p-(chloromethyl)styrene random copolymer).

3.3. Irradiation of Polymer/MWCNT Mixtures with UV Light

Poly-CMSt, or poly-St-co-CMSt, (25 mg) was dissolved in 2.5 cm^3 of NMP; then 1.3 mg of MWCNTs was added. The mixture was subsequently irradiated with UV light using a Xenon light source (Asahi Spectra MAX-303, Asahi Spectra, Co. Ltd., Tokyo, Japan) for 24 h at room temperature. The wavelength of the irradiated UV light was in the range of 250–385 nm. Ultraviolet absorption spectra of NMP and polymer/NMP solutions are shown in Figure 9. In the wavelength region of 250–300 nm, the absorbance of the polymers was substantially larger than that of pure NMP. The absorbance in the longer wavelength region (>300 nm) approached zero.

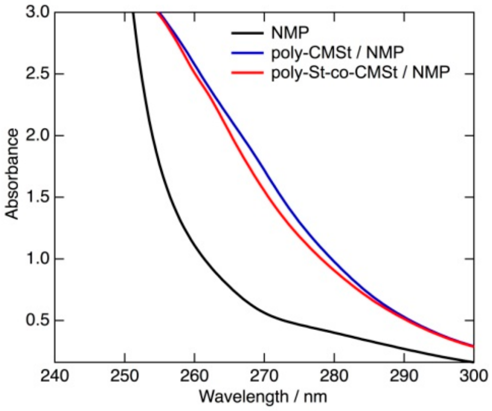


Figure 9. UV absorption spectra of solvent (NMP) and polymer/NMP solutions.

To prove the effect of $NH_2OH\cdots HCl$, added as dispersant, on the reaction efficiency, solvophilic MWCNTs were also prepared prior to the irradiation by adding $NH_2OH\cdots HCl$, and then used as reactants. First, 10 g of $NH_2OH\cdots HCl$ and 100 mg of MWCNTs were mixed in 90 mL of water. The mixture was sonicated for 20 min and stored for 24 h. The MWCNTs in the mixture were separated by filtration, and then washed with deionized water and NMP. After mixing with $NH_2OH\cdots HCl$, the MWCNTs were steadily dispersed in NMP.

3.4. Preparation of Samples for Characterization and Spectroscopic Analysis

The polymer/MWCNT mixtures in NMP before and after irradiation were dropped onto glass pieces (about 1 cm^2 square) by using Pasteur pipettes. The samples were then dried at 70 °C in air until NMP was completely evaporated.

Elemental analyses of the samples were conducted by means of XPS with a spectrometer (JEOL JPS-9200) installed in the photoelectron spectroscopic analysis laboratory of Hokkaido University (Sapporo, Japan). Signals arisen from C 1s and Cl 2p electrons were precisely observed by narrow scans. In the XPS analyses, Mg K_α radiation was used. As the electron gun for the cancellation of X-ray-induced charge up was not used in this work, transverse shifts of the spectra were observed. However, the transverse shifts were not corrected, as they did not cause severe problems in the quantitative elemental analysis of C and Cl.

The structural change of MWCNTs caused by photo-induced radical addition was observed by means of Raman spectroscopy with a Renishaw InVia spectrometer; the excitation wavelength was 523 nm. As the intensities of the D and G bands were especially important for the purpose of this work, the spectra in the range of 1150–1650 cm^{-1} were recorded. The intensities of the spectra were numerically manipulated to equalize the intensities of the G bands before and after irradiation.

4. Conclusions

In this work, a novel photochemical method for the formation of a chemical bond between chloromethylated polystyrene side chains and MWCNTs was investigated by means of XPS and Raman spectroscopy. Photoinduced C–Cl bond dissociation (benzyl-type radical formation) and deformation of MWCNT carbons were revealed by XPS and Raman measurements, confirming the chemical bond formation through the addition of polymer side chain radicals to the MWCNT surface. The influence of the dispersant ($NH_2OH\cdots HCl$) on the efficiency of the radical addition was also examined, indicating that $NH_2OH\cdots HCl$ did not interfere with the radical addition.

Currently, we have not obtained direct evidence of the chemical bond formation. To this end, ^1H and ^{13}C NMR spectroscopies may be useful, as the dissociation of $-CH_2-Cl$ bonds and the formation of $-CH_2-$MWCNT bonds can be observed by using these techniques. These experiments are currently in progress in our laboratory.

Supplementary Materials: Supplementary materials can be found at http://www.mdpi.com/2311-5629/2/3/20/s1.

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Author Contributions: Tomoya Takada supervised this study, analyzed the data, and wrote the paper; Takuma Baba prepared the materials and performed the spectroscopic measurements; Shigeaki Abe provided his expertise on carbon materials and participated in the discussion to interpret the experimental data.

Conflicts of Interest: The authors declare no conflict of interest.

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