

Article

The Ultraviolet-Induced Functionalization of Multi-Walled Carbon Nanotubes with Polymer Radicals Generated from Polyvinyl Benzoate Derivatives

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Abstract: In order to develop a novel technique for the fabrication of hybrid materials containing polymers and nanocarbons, we examined the surface modification of pristine multi-walled carbon nanotubes (MWCNTs) with benzyl-type polymer side chain radicals generated through photolysis of 4-(chloromethyl)benzoate moieties. The polymer with a 4-(chloromethyl)benzoate side chain was prepared by the esterification of polyvinyl alcohol (PVA) with corresponding acid chloride. The synthesized polymer and MWCNTs were mixed in *N*-methylpyrrolidone and irradiated with ultraviolet (UV) light. Structural changes of the polymer and MWCNTs were observed by means of X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The XPS results revealed that scission of the C–Cl bonds of the chloromethyl groups and benzyl-type radical formation occurred. The incremental surface defects of the MWCNTs caused by UV irradiation were confirmed by means of Raman spectroscopy. These results support the covalent bond formation between the polymer side chain and MWCNT sidewalls by radical addition reaction. The photothermal conversion characteristics of the prepared materials were also evaluated.

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

1. Introduction

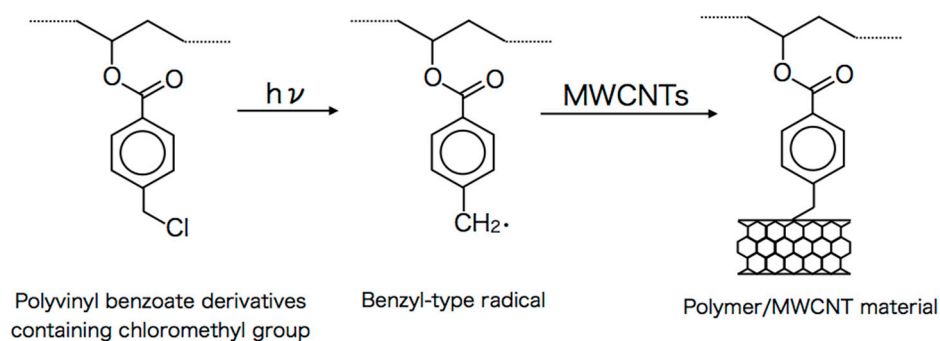
The fabrication of polymer/carbon nanotube (CNT) hybrid materials has been paid much attention from a technological point of view, especially in the field of composite materials engineering. CNTs are carbon allotropes constructed with many hexagonal units arranged in a cylindrical structure [1]. They show characteristic electric conductivity based on the conjugated pi-electron system. Accordingly, they are used in organic electronic devices [2–13].

Many studies have been reported about the development of novel techniques of preparing polymer/CNT hybrid materials. To date, various polymers have been used to prepare polymer/nanomaterial composites: for example, poly(L-lactide) [10,13], poly(trimethylene terephthalate) [11], polycarbonate/ethylene-propylene copolymer [12], polydimethylsiloxane [14], polyvinylpyrrolidone [15], etc. Many hybrid materials have been fabricated by means of physical dispersion of nanoparticles into polymers. In parallel, chemical bond formation of polymers with CNTs has been employed as a method to prepare polymer/CNT hybrids [16–22], and expected to yield mechanically durable materials in the future. Typical methods of obtaining hybrid materials have drawbacks such as harsh reagents and reaction conditions. Recently, the demand for facile and environmentally friendly methods has surged, and photoinduced reactions could be appropriate as these reactions can proceed under mild conditions (e.g., use of fewer chemical reagents and/or treatment at ambient temperature).

Recently, we reported the photoinduced chemical bond formation between CNTs and poly(*p*-chloromethyl)styrene [23]. We found that the C–Cl bonds of the chloromethyl side chains (–CH₂Cl) of the polymer dissociated with ultraviolet (UV) irradiation to form benzyl-type side chain radicals. The radicals then attacked and bound to the CNT surfaces. This reaction could be a candidate of a new grafting technique.

There are numerous common polymers other than polystyrene. One of these is polyvinyl ester, which contains an ester bond (–CO–O–) in its side chain. Various derivatives can be synthesized by means of condensation between acid chlorides and polyvinyl alcohol (PVA) [24]. Similar to poly(*p*-chloromethyl)styrene, the derivatives are also expected to be used to prepare polymer/CNT hybrid materials. For this purpose, the introduction of photodissociative side chains is needed to generate radicals through photolysis. In the case of polyvinyl ester derivatives, it is necessary to check whether the bond dissociation to form benzyl-type side chain radicals occurs in the same way as that observed for poly(*p*-chloromethyl)styrene. Additionally, the undesirable photodegradation of the polymer skeleton involving carbonyl groups, such as carbon oxide (CO and CO₂) elimination, should be avoided.

In this work, we studied the chemical bond formation between pristine multi-walled CNTs (MWCNTs) and the side chains of a polyvinyl benzoate derivative, polyvinyl 4-(chloromethyl)benzoate. Chemical bonds were formed through the addition of benzyl-type radicals formed by the photoinduced dissociation of the C–Cl bonds of the polymer side chains. The photoinduced selective formation of benzyl-type radicals from corresponding halide precursors has already been observed [25]. Generally, various free radicals smoothly attack to bind with CNTs [26–29]. The bond formation process is depicted in Scheme 1.



Scheme 1. Chemical bond formation between polyvinyl 4-(chloromethyl)benzoate side chains and multi-walled carbon nanotubes (MWCNTs).

This bond can be formed under mild conditions. Although the photoinduced functionalization of CNTs and photochemical graft formation on CNT surfaces has been studied [30–40], the linkage between polymer side chains and CNTs triggered by light illumination has not been extensively studied until now. Using this process, CNTs can be modified with many common polymers possessing photodissociative side chains through one-pot irradiation. Additionally, this process can be applied to the modification of other materials that are capable of forming covalent bonds through radical addition such as graphene-related materials [41]. In this study, CNTs were used as raw materials for constructing transparent conductive networks in polymers for use in future studies.

We prepared polyvinyl 4-(chloromethyl)benzoate as a substrate of the polymer/CNT hybrid material. The structure of the polymer is shown in Figure 1. Note that, in this work, the polymer was prepared by the esterification of PVA, such that unreacted –OH groups remain after the esterification. The degree of esterification can be estimated on the basis of spectroscopic results, as described in the Materials and Methods section.

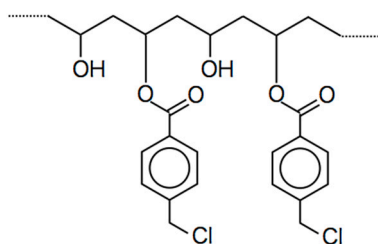


Figure 1. Structure of polyvinyl 4-(chloromethyl)benzoate.

The bond formation between the MWCNTs and polymer side chains was examined by means of X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Measurements of C, Cl, and O contents in the polymer/MWCNT samples before and after light irradiation were carried out by XPS. Raman spectroscopy was employed to observe the structural changes of the MWCNTs before and after the irradiation. In this work, hydroxylammonium chloride was used as an MWCNT dispersant. It dissolves CNTs in organic solvents and can be used to prepare polymer/CNT nanocomposites [42]. Finally, photothermal conversion of the prepared materials was also observed.

2. Results and Discussion

2.1. Photoinduced Bond Dissociation of Polymer Side Chains Observed by X-ray Photoelectron Spectroscopy (XPS)

Figure 2 shows the X-ray photoelectron spectra (C 1s, O 1s, and Cl 2p) of the polymer/MWCNT mixture before and after UV irradiation for 24 h. The spectrum of Cl 2p observed before the UV irradiation revealed that the mixture contained a remarkable amount of Cl. The degree of esterification of the polymer prepared in this work was estimated to be 46%, indicated that almost half of the –OH groups in the PVA were replaced with a benzoyl group containing Cl. The Cl content significantly decreased during the UV irradiation. This result indicated that Cl atoms were eliminated from the polymer side chains by photolysis and escaped from the polymer/MWCNT mixture. If the eliminated Cl atoms were mainly trapped in the polymer/MWCNT mixture, the intensities of the Cl 2p spectra before and after the UV irradiation would be the same. In this case, the Cl atoms were probably released as Cl₂ molecules formed by recombination. On the other hand, the C content of the sample—the total amount of C from the polymer and the MWCNTs—remained almost constant before and after the UV irradiation. This indicated that severe photoinduced decomposition of the polymer and/or MWCNTs to form volatile compounds did not occur during the UV irradiation. Additionally, the O content of the sample remained almost constant; the photofragmentation of the polymer skeleton involving ester bonds (such as CO and CO₂ elimination) was minor. These results support the durability of the polymer skeleton against the UV irradiation and the selective scission of the C–Cl bonds of the polymer side chain.

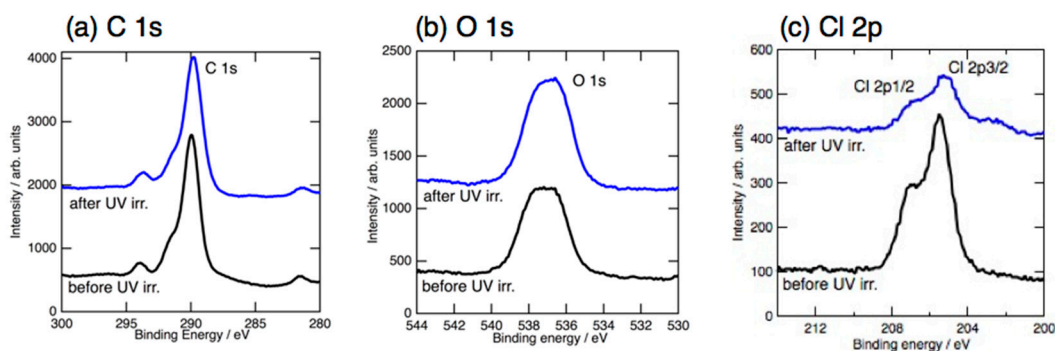


Figure 2. X-ray photoelectron spectra observed for polyvinyl 4-(chloromethyl)benzoate/MWCNT before and after ultraviolet irradiation: (a) C 1s, (b) O 1s, and (c) Cl 2p.

2.2. Structural Change of MWCNTs Observed by Raman Spectroscopy

Figure 3 shows the Raman spectra of the polymer/MWCNT mixture before and after irradiation for 24 h. Two characteristic bands associated with the MWCNTs, i.e., the G- and D-bands, were found. The G-band observed around 1570 cm^{-1} was assigned to the in-plane vibration of the MWCNTs; the D-band observed around 1340 cm^{-1} was assigned to the vibration of defect sites of the MWCNTs generated by the deformation of the sp^2 -based C–C bond network. The intensity ratio of the G- to D-bands, the G/D ratio, is a measure of the degree of structural deformation of the MWCNTs caused by the chemical reaction [43]. We compared the G/D ratios of the sample before and after the irradiation to observe the structural change of the MWCNTs as a result of the addition of polymer side chain radicals.

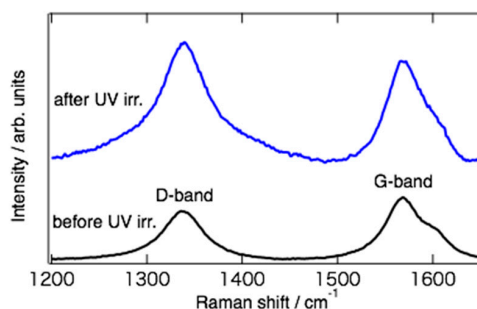


Figure 3. Raman spectra observed for polyvinyl 4-(chloromethyl)benzoate/MWCNT before and after ultraviolet irradiation.

Comparing the spectra shown in Figure 3, the G/D ratio decreased upon irradiation (from 1.2 to 0.9); the MWCNT surface defects increased with the addition of polymer side chain radicals generated through C–Cl bond scission to form covalent bonding between the MWCNTs and side chains. As described above, severe fragmentation of polymer main chain into volatile molecules does not occur during the C–Cl scission followed by the bond formation. A schematic illustration of the bond formation between polyvinyl 4-(chloromethyl)benzoate and the MWCNT surface is shown in Figure 4.

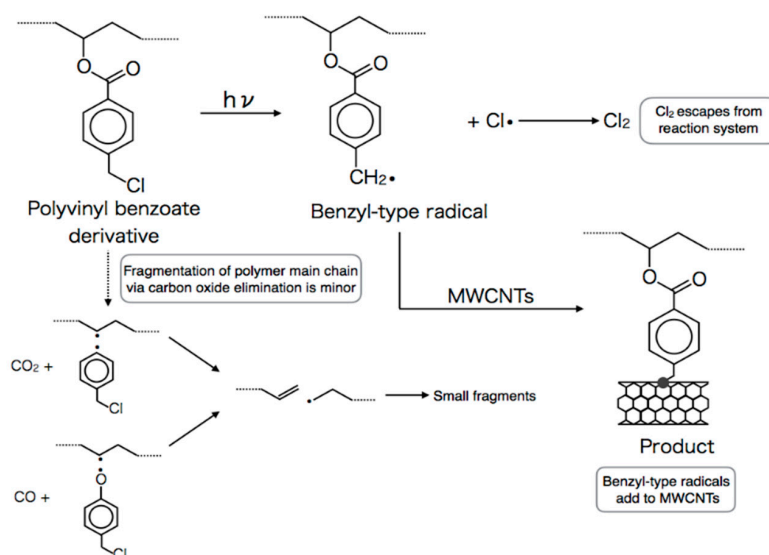


Figure 4. Schematic illustration of the chemical modification of MWCNT with radicals generated from polyvinyl 4-(chloromethyl)benzoate side chain.

Judging from the observed G/D ratio, deformation of the MWCNTs caused by the radical addition is not so significant, and the morphology of the MWCNTs remains similar before and after the reaction.

If severe morphological change had occurred during the reaction, the G/D ratio after irradiation would differ from that before irradiation; the intensity of the D-band would have markedly increased through defect formation caused by the radical addition. On the other hand, the present result also implies a low yield of the bond formation. Relation between the functionalization yield and the morphological change remains an issue and should be investigated in subsequent studies.

2.3. Photothermal Conversion Characteristics of the Prepared Materials

It is known that CNTs can increase their temperature upon infrared irradiation [44]. In this work, the photothermal conversion characteristics of the prepared materials were also evaluated. Samples containing different concentrations of MWCNTs were prepared and their time–temperature profiles during infrared irradiation were observed. Figure 5 shows the temperature change observed for three samples containing 0.0043–0.43 mg of MWCNTs per 1 mg of the polymer.

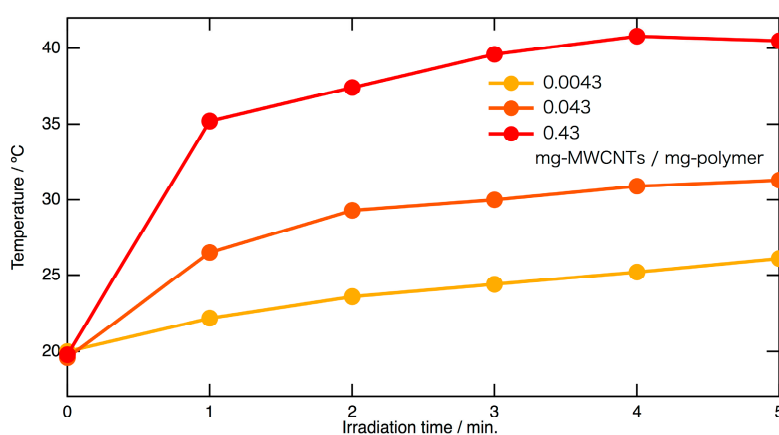


Figure 5. Temperature change observed for polyvinyl 4-(chloromethyl)benzoate/MWCNT with different MWCNT amounts.

All the samples showed increased temperature upon irradiation. The maximum temperature reached during irradiation corresponded to the MWCNT content. These results indicate that the photothermal conversion capacity of MWCNTs remains, even after trapping in the polymer and surface modification with polymer radicals. Based on this characteristic, this material is expected to be used for sheet heaters and thermotherapy devices in the future.

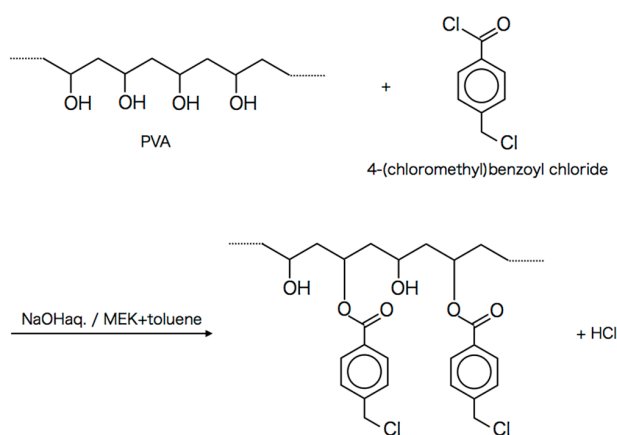
3. Materials and Methods

3.1. Materials

MWCNTs (10–30 nm in diameter, 1–10 μ m in length) were purchased from Wako, Osaka, Japan. The MWCNTs were purified by removal of carbon impurities through firing with a muffle furnace, followed by dissolution of metal residues by immersing into hydrochloric acid. After the purification, the MWCNTs were dried in air. Thus, pristine MWCNTs were obtained. PVA (average polymerization degree: 500, saponification degree: 86–90 mol %), 4-(chloromethyl)benzoyl chloride, and sodium hydroxide, used for the polymer preparation, were purchased from Wako, Osaka, Japan. Ethyl 4-(chloromethyl)benzoate, used as a standard compound for the absorption measurement, was purchased from Tokyo Chemical Industry, Tokyo, Japan. The solvents used for esterification, UV-irradiation, and absorption spectroscopy, i.e., methyl ethyl ketone (MEK), toluene, methanol, dichloromethane, and *N*-methylpyrrolidone (NMP), were purchased from Wako, Osaka, Japan (MEK, toluene, methanol, and NMP) or Junsei Chemicals, Tokyo, Japan (dichloromethane). They were used without further purification. Hydroxylammonium chloride ($\text{NH}_2\text{OH HCl}$), used as a dispersant, was purchased from Wako, Osaka, Japan and used without further purification.

3.2. Preparation of Polyvinyl 4-(Chloromethyl)Benzoate

Polyvinyl 4-(chloromethyl)benzoate was prepared according to the method reported by Giménez et al. [18]. This method is based on the Shotten–Baumann reaction. Briefly, PVA was dissolved in water and then aqueous sodium hydroxide was added to the solution. The acid chloride for esterification, 4-(chloromethyl)benzoyl chloride, was dissolved in an MEK/toluene solvent mixture. These two solutions were mixed and stirred at 0 °C. The aqueous and organic layers were then separated, and the polymer was isolated from the organic layer by adding the solution dropwise to methanol. The polymer precipitate was filtered and successively dissolved in MEK. The solution was added dropwise to methanol, and polymer was precipitated and filtered again. This precipitation–filtration cycle was repeated twice. The product obtained was dried under reduced pressure. The esterification reaction is illustrated in Scheme 2.



Scheme 2. Esterification of polyvinyl alcohol (PVA) with 4-(chloromethyl)benzoyl chloride.

The formation of ester side groups was confirmed by means of proton nuclear magnetic resonance (^1H NMR) spectroscopy (JEOL JNM-ECP400). The conversion of hydroxyl groups to 4-(chloromethyl)benzoyl groups was observed, indicating that the PVA was successfully esterified. The ^1H NMR spectrum of the product is shown in Figure 6.

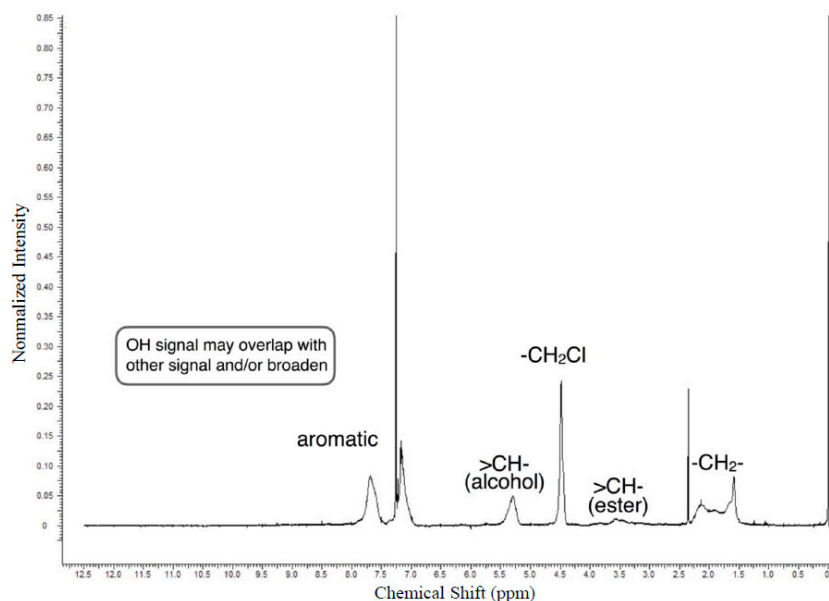


Figure 6. ^1H NMR spectrum observed for the prepared polymer. Chloroform containing tetramethylsilane was used as a solvent.

3.3. Determination of Degree of Esterification

The degree of esterification of the polymer was determined by means of absorption spectroscopy. Ethyl 4-(chloromethyl)benzoate was used as a standard compound. The molecular structure of this compound is quite similar to that of the polyvinyl 4-(chloromethyl)benzoate side chain, as shown in Figure 7.

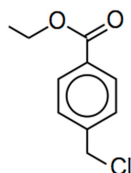


Figure 7. Structure of ethyl 4-(chloromethyl)benzoate.

A brief description of the method for determining the degree of esterification is as follows. Ethyl 4-(chloromethyl)benzoate was dissolved in dichloromethane to produce a stock solution. Standard solutions of several concentrations were prepared by diluting the stock solution with dichloromethane. The UV absorbances of the standard solutions at 270 nm (maximum absorption wavelength of ethyl 4-(chloromethyl)benzoate) were measured using a spectrophotometer (V-630, JASCO, Tokyo, Japan) and a linear function representing the relationship between the concentration and absorbance was derived on the basis of the measured absorbances. A solution of a certain amount of prepared polymer was also made in a same manner and its absorbance was measured. Based on the derived linear function, the content of 4-(chloromethyl)benzoyl group in the polymer (i.e., the degree of esterification) can be estimated. The degree of esterification is defined as the yield of benzoyl ester group derived from the –OH group contained in the original PVA.

3.4. Irradiation of Polymer/MWCNT Mixtures with UV Light

MWCNTs were mixed with $\text{NH}_2\text{OH HCl}$ aqueous solution to make them solvophilic and then filtered prior to the UV irradiation. The polymer (0.1 g) was dissolved in 10 cm^3 of NMP, and the treated MWCNTs (0.06 g) were then added. MWCNTs were thoroughly dispersed in the NMP/polymer mixture.

The mixture was subsequently irradiated with UV light using a xenon light source (MAX-303, Asahi Spectra, Tokyo, Japan) for 24 h at room temperature. The wavelength of the irradiated UV light was in the range of 250–385 nm. As mentioned above, the maximum absorption wavelength of the 4-(chloromethyl)benzoyl derivatives is located around 270 nm. In the wavelength region around this maximum, the absorbance of the polymer was larger than that of pure NMP.

3.5. Spectroscopic Analysis of the Samples

The polymer/MWCNT mixtures in NMP before and after the irradiation were put on separate glass slides (approximately 1 cm^2) by using Pasteur pipettes (Fisher Scientific, Hampton, NH, USA). The samples were then dried at 60 $^\circ\text{C}$ in air to completely vaporize the NMP. The prepared samples were black, indicating that MWCNTs trapped in the polymer were aggregated even though they were dispersed well in the NMP/polymer solution.

Elemental analyses of the samples were carried out by means of XPS using a spectrometer (JPS-9200, JEOL, Tokyo, Japan) installed in the photoelectron spectroscopic analysis laboratory of Hokkaido University, Japan. Signals originating from C 1s, O 1s, and Cl 2p electrons were precisely observed by narrow scans. Mg $\text{K}\alpha$ radiation was used in the XPS analyses.

Structural changes of the MWCNTs caused by radical addition were observed using a Raman spectrometer (InVia, Renishaw, Wotton-under-Edge, UK). The excitation laser wavelength was 532 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 1200–1650 cm^{-1} were recorded.

3.6. Observation of Temperature Change of the Samples Induced by Infrared Irradiation

The samples for temperature change observation under infrared irradiation were prepared as follows. Three portions of solution of the polymer were made by dissolving the polymer (2.5 mg) in NMP (2.5 cm³). A dispersion of MWCNTs was also prepared by adding MWCNTs (1.3 mg) to NMP (2.5 cm³). The MWCNT dispersion was added to the polymer solution to make three mixtures with different MWCNT amounts (0.43, 0.043, and 0.0043 mg of MWCNTs per 1 mg of polymer). These mixtures were irradiated with UV light under similar conditions, as described in Section 3.4. After the irradiation, the mixtures were put on separate glass slides. Films of the polymer/MWCNT mixtures were fabricated by spin-coating and dried at 60 °C in air.

Infrared irradiation for temperature change observation was carried out using a xenon light source (Asahi Spectra MAX-303). The wavelength of the irradiated infrared light was in the range of 750–1050 nm. The time–temperature profiles of the samples during the irradiation were observed using a thermography camera (C2, FLIR, Wilsonville, OR, USA).

4. Conclusions

In this work, a novel method for the surface functionalization of MWCNTs with polyvinyl benzoate derivatives possessing chloromethyl side chains was investigated by means of XPS and Raman spectroscopy. The spectroscopic observations revealed C–Cl bond dissociation (benzyl-type radical formation) induced by UV irradiation and structural deformation of the MWCNTs. These results support the chemical bond formation through addition of polymer side chain radicals to the MWCNT surface. This bond formation was found to proceed without severe fragmentation of the polymer main chain. Increases in the temperature of the prepared materials induced by infrared light were also confirmed. The method reported here is expected to be applied to synthesizing functional polymer/CNT hybrid materials in the future.

To quantitatively determine the efficiency of the photoinduced functionalization, thermogravimetric analysis (TGA) is a useful tool. The mass of the polymer linked to the MWCNTs after irradiation can be determined based on the weight loss during temperature elevation and compared with overall mass of the polymer contained within the sample. Though the direct measurement of the amount of grafted side chain had not been performed previously, this measurement will be necessary to confirm the validity of the method proposed in this study. Precise measurement and quantitative determination of the reaction efficiency is a subject for upcoming studies.

The transparency of the prepared materials is also an important subject to be examined. The samples prepared in this work were opaque because of insufficient dispersion of the MWCNTs in the polymer. To judge whether the MWCNTs were highly dispersed at a microscopic level, observation by transmission electron microscopy (TEM) is an effective method. If the MWCNTs are highly dispersed in a polymer, the materials should be transparent and the MWCNTs invisible to the naked eye. The materials prepared in this study clearly were not transparent; hence, microscopic observation of the MWCNT particles trapped in the polymer was not performed. If transparent materials containing well-dispersed MWCNTs were obtained, TEM observation would provide useful data for determining the degree of dispersion. Additionally, TEM will help in understanding the mechanism of aggregation of the MWCNTs involving the pi–pi interaction of the aromatic polymer side chains. TEM observation of the materials prepared under conditions for fabrication of transparent samples is now in progress in our laboratory, and the results are forthcoming.

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Author Contributions: Tomoya Takada designed this study, analyzed the data, and wrote the paper; Yuya Nishioka and Takuma Baba prepared the materials and performed the measurements.

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

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