

# Synthesis and Characterization of Fullerene Functionalized Poly(vinyl chloride) (PVC) and Dehydrochlorinated PVC Using Atom Transfer Radical Addition and AIBN Based Fullerenation

Narumon Seeponkai,<sup>1</sup> Jatuphorn Wootthikanokkhan,<sup>1,2</sup> Chanchana Thanachayanont<sup>3</sup>

<sup>1</sup>Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology (KMUTT), Thonburi, Bangkok 10140, Thailand

<sup>2</sup>Nanotec-KMUTT Center of Excellence on Hybrid Nanomaterials for Alternative Energy, King Mongkut's University of Technology (KMUTT), Thonburi, Bangkok 10140, Thailand

<sup>3</sup>National Metal and Materials Technology Center (MTEC), Pathumthani 12120, Thailand

Correspondence to: J. Wootthikanokkhan (E-mail: jatuphorn.woo@kmutt.ac.th)

**ABSTRACT:** The research presented details chemical modifications of poly(vinyl chloride) (PVC) and its derivative, dehydrochlorinated PVC (DH-PVC) through the use of two grafting techniques, namely a normal fullerenation, using AIBN (2,2'-Azobisobutyronitrile), and the atom transfer radical addition (ATRA). The products were characterized and the presence of new FTIR peaks at 528 and 577  $\text{cm}^{-1}$  along with new  $^1\text{H-NMR}$  signal at 3.9 ppm, suggested that fullerenes has been grafted to the polymer molecules. Percentage of  $\text{C}_{60}$  in the fullerene grafted products determined by UV/Visible spectroscopy initially increased with the amount of fullerene used to a maximum value ( $\sim 5.66\%$  wt) before decreasing again. It was also determined that the  $\text{C}_{60}$  content of the fullerene grafted PVC product prepared by using ATRA, was notably greater than that obtained using the normal fullerenation approach, regardless of the amount of  $\text{C}_{60}$  used. When the dehydrochlorinated PVC was used as the starting polymer for fullerenation, the fullerene grafted DH-PVC using ATRA, was markedly insoluble in many common solvents (THF and dichlorobenzene). This was not the cases for the fullerene grafted DHPVC prepared via an AIBN based fullerenation. Furthermore, the electrical conductivity values of the modified PVC products determined by using a four-point probe method were found to increase linearly with the amount of  $\text{C}_{60}$  present. Overall our data suggest that the suitable and efficient techniques for grafting  $\text{C}_{60}$  onto PVC and DHPVC chains are ATRA and AIBN-based fullerenation, respectively. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2410–2421, 2013

**KEYWORDS:** poly(vinyl chloride); grafting; conducting polymers; thermal properties

Received 6 August 2012; accepted 20 April 2013; Published online 25 May 2013

**DOI:** 10.1002/app.39443

## INTRODUCTION

Fullerene ( $\text{C}_{60}$ ) first discovered in 1985,<sup>1</sup> are a unique class of molecules composed entirely of carbon and by taking the form of hollow spheres, ellipsoid, or tubes, exhibit a wide variety of remarkable magnetic<sup>2</sup> and electronic properties that have the potential to be exploited.<sup>3–5</sup> Consequently,  $\text{C}_{60}$  are widely used in many applications including among many, organic solar cells.<sup>6</sup> In this case, however, aggregation of the material has been observed particularly when the amount of  $\text{C}_{60}$  used to fabricate the solar cells was in excess of a certain limit.<sup>7,8</sup> In this regard, a modification of the chemical structure of  $\text{C}_{60}$  may facilitate solubility and enhance its use in solar cells. For example, by using a derivative form of  $\text{C}_{60}$ , phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM), the solubility of the material and power conversion efficiency (PCE) of the related cells can be greatly

improved at the expense of the material cost. This improvement is likely attributed to a steric effect provided by the presence of alkyl side groups on the  $\text{C}_{60}$ . Nonetheless, preparation of  $\text{C}_{60}$  containing polymers is an important step for use in solar cells and this is largely due to the fact that many polymeric materials are soluble in many common solvents (e.g., THF and toluene), making it an easy process for fabricating thin films of  $\text{C}_{60}$  containing polymers. Collectively, the aforementioned properties of  $\text{C}_{60}$  combined with processability of polymer (via the synthesis of fullerenated polymers) can be readily exploited to make potentially advanced polymeric materials with enabling physical–chemical properties. Furthermore, the possibility exists to further improve on this process by altering some features of the product by properly controlling the chemical structure and composition of the materials.

In this study, the attachment of  $C_{60}$  onto poly(vinyl chloride) (PVC) molecules is of particular interest. This is due to the fact that PVC is thermoplastic and highly amenable of being fabricated into a thin film via solution casting and/or spin coating. Furthermore, the resin cost is also less expensive compared to that of the  $C_{60}$  and its derivative. More importantly, PVC can be chemically modified by several methods including dehydrochlorination, nucleophilic substitution, alkylation, and grafting.<sup>9</sup> For dehydrochlorination, the tertiary chlorine atoms in PVC are considered to be potential reactive sites, which can be carried out via either ionic<sup>10,11</sup> or free radical techniques.<sup>12–14</sup> In this regard, attachment of  $C_{60}$  onto PVC molecules is now routinely carried out by the free radical approach, and by using chemical initiators. In this context, Tang et al.<sup>15</sup> and Martinez et al.<sup>16</sup> synthesized  $C_{60}$  functionalized PVC through a direct chemical reaction between PVC and  $C_{60}$ , using AIBN (2,2'-azoisobutyronitrile) as the initiator. In the latter case, some useful and enhanced properties of the modified PVC were observed. These included electron acceptor properties and thermal stability, as evidenced by cyclic voltammetry and thermal gravimetric analysis (TGA) techniques, respectively.

Alternatively, the grafting of  $C_{60}$  onto PVC molecules using controlled radical reactions deserves consideration. With this technique, greater  $C_{60}$  content in the product can be expected, due to the fact that the reaction is essentially catalyzed by a transition metal complex. This reaction is also referred to as an atom transfer radical addition (ATRA). While the preparation of  $C_{60}$  functionalized PVC using ATRA has not been reported, the grafting of different polymeric chains onto PVC molecules via atom transfer radical polymerization (ATRP) techniques have been demonstrated. For example, Black et al.<sup>17</sup> prepared poly(butyl acrylate) and poly(ethyl hexylacrylate) grafted PVC's by using ATRP. After carrying out the polymerization for 7.5 h, the reported grafting yields were 162 and 52%, respectively. Lui et al.<sup>18</sup> investigated the kinetics of ATRP used for preparing surface grafted PVC particles with hydroxyl acrylate monomers and found that the rate of graft copolymerization was of first order with respect to the reaction time. A grafting yield of 190% was also claimed after a 10 h reaction time. The grafting of styrene and acrylamide onto PVC chains via ATRP have also been demonstrated by Park et al.<sup>19</sup> and Lui et al.,<sup>20</sup> respectively. In the latter case, a first order rate of reaction was also reported.

Further enhancement of the electron conductivity of the  $C_{60}$  grafted PVC can be obtained by conjugating polyene segments along the PVC molecules prior to fullereneation. This can be achieved by carrying out dehydrochlorination to obtain partial dehydrochlorinated PVC (DH-PVC). Maruthamuthu et al.<sup>21</sup> reported that the electrical conductivity of a PVC derivative, modified via dehydrochlorination is notably greater than that of normal PVC. Ghaemy et al.<sup>13</sup> prepared DH-PVC using sodium butoxide and/or piperidine as catalysts. The degree of dehydrochlorination obtained was 50 and 20%, respectively. After, styrene was grafted onto the DH-PVC chains using benzoyl peroxide and/or AIBN initiators. The grafting of poly(butyl methacrylate) onto DH-PVC molecules using ATRP has also been reported by Mehmet et al.<sup>22</sup>

From the above reports, it can be determined that PVC can be chemically modified via dehydrochlorination and ATRP, resulting

in the formations of DH-PVC and PVC grafted copolymers, respectively. In this regard, there is excellent potential of the above chemically modified PVC as semiconducting polymers for application in energy related devices. For example fullerene grafted PVC and/or the fullerene grafted DH-PVC may have use as a promising electron acceptor material for fabricating polymer solar cells. However, the grafting of  $C_{60}$  onto PVC and DH-PVC by the ATRA technique has not been previously explored or reported. Thus, the aim of this study is to investigate the effect of  $C_{60}$  content on chemical structure, thermal properties, and electrical conductivity of the chemically modified PVC and its derivative (DH-PVC). Comparison between the products obtained by using AIBN and the ATRA techniques were also considered and discussed.

## EXPERIMENTAL

### Chemicals

PVC resin ( $k$ -value = 66,  $DP_n$  = 1025) was from Thai Plastic and Chemicals Co. Sodium hydroxide (99%) and methanol (GC grade) were from Merck Co. (Darmstadt, Germany). Tetrahydrofuran (THF; AR grade) was from Fisher Scientific (Loughborough, UK). Dichlorobenzene (AR grade) was from Carlo Erba (Rodano, Italy). Fullerene (99.5%), CuBr, 2,2'-azo-bisobutyronitrile (AIBN, 0.2M in toluene) and N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) 99% were from Sigma-Aldrich Co. (Steinheim, Germany). Cu (98.0%) was from Fluka Co. (Steinheim, Germany). Nitrogen gas (99.99%) was from Praxair Co. (Thailand). THF and dichlorobenzene were purified prior to use by distillation and kept under dry conditions, using a molecular sieve. Unless specifically indicated, all of the above chemicals were used as received.

### Dehydrochlorination of PVC

The dehydrochlorination of the PVC was carried out in solution under nitrogen gas atmosphere, using sodium hydroxide as the catalyst (Figure 1). Experimentally, 10 g of PVC resin was dissolved in 100 mL of THF in a two-necked round bottom flask while stirring with a magnetic bar. Next, 50 mL of sodium hydroxide aqueous solution (3 mol/L) was added to the reaction flask. The above formulation generated a mixture of PVC/sodium hydroxide, with molar ratio of  $6.67 \times 10^{-4}$ . The reaction was allowed to proceed at 70°C. Noteworthy, the content in the reaction flask changed color from colorless to yellow, and eventually to orange as the reaction proceeded. After carrying out the dehydrochlorination for 15 h, the reaction was terminated by the addition of 100 mL of methanol to the mixture, followed by precipitation in excess (~500 mL) methanol. The precipitated polymer was then filtered, re-dissolved in THF and precipitated in methanol again. Finally, the filtered product was oven-dried at 60°C for 12 h, until a constant weight was obtained.

### Synthesis of Fullerene Grafted PVC

$C_{60}$  grafted PVC with a variety of fullerene content was prepared by ATRA, under different  $C_{60}$ /PVC feed ratios (Table I). Normal fullereneation of PVC was also prepared via direct reaction between  $C_{60}$  and PVC, using AIBN as an initiator, and used consequently for comparison purposes.

**Atom Transfer Radical Addition (ATRA).** To a three-necked flask, 50 mg of  $C_{60}$  was mixed with PMDETA (27  $\mu$ L), in

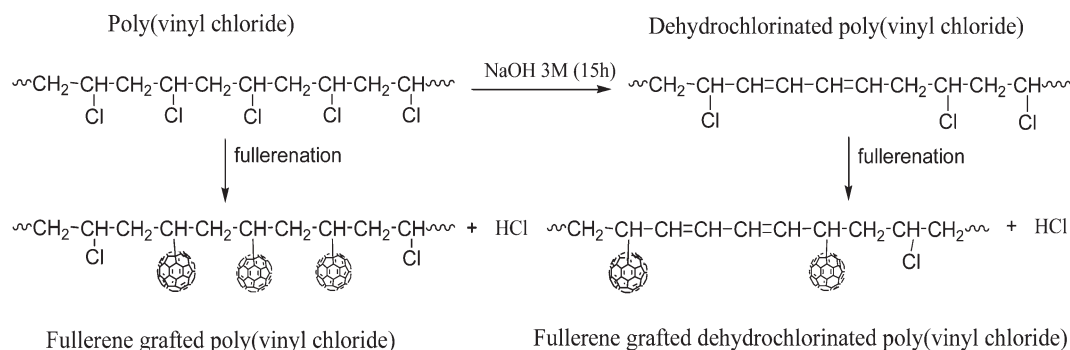


Figure 1. A schematic draw illustrating the fullereneation of PVC and DH-PVC.

dichlorobenzene (14 mL) and after 0.6 g of PVC and/or DH-PVC in THF (8 mL) was added to the mix. The solution was purged with nitrogen gas for 15 min and then sealed with paraffin film and kept until used for ATRA reaction. To a 250 mL three-necked round bottom flask, Cu (68 mg) and CuBr (42 mg) were added. The flask was closed with a rubber septum and sealed before undergoing nitrogen and vacuum purges for five cycles. Then, the above prepared polymer solution was introduced into the reaction flask containing Cu and CuBr by injection with a syringe through the rubber septum. The mixture was then refluxed at 80°C in an oil bath for 24 h. Next, after cooling to room temperature, the reaction was filtrated and precipitated in excess methanol. The crude precipitated product was re-dissolved in THF, and then precipitated in methanol again. Hexane, which is a non-solvent for the polymer, was used to remove any residual C<sub>60</sub> from the product. UV/visible spectroscopy were used to examine the presence of a characteristic absorption peak of the free C<sub>60</sub> in the leached solvent (wavelength 330 nm). The washing process was carried out until the above UV/Visible peak disappeared. Finally, the purified product was dried in a vacuum oven at 60°C until reaching a constant weight (16 h).

**Normal Fullereneation.** A typical reaction was conducted as follows; 0.6 g of polymer (PVC and/or DH-PVC) was dissolved in 8 mL of THF in a conical flask at room temperature. Once the PVC was completely dissolved, 27  $\mu$ L of AIBN and 50 mg of C<sub>60</sub> in dichlorobenzene (14 mL) were added. Oxygen was removed by purging with nitrogen gas. The solution was then injected into a three-necked round bottom flask (closed with a rubber septum) using a syringe. The reaction flask was also connected with a condenser and a nitrogen line. After that, the flask was immersed in an oil bath at 80°C, and the reaction was allowed to proceed for 24 h. After, the content of the reaction flask was precipitated in excess methanol and purified by repeatedly (two times) dissolving in THF and precipitating in methanol. The precipitated product was then filtered and dried in a vacuum oven at 60°C until reaching a constant weight (16 h).

### Characterizations

**Spectroscopic Analysis.** Changes in the chemical structure of the PVC after chemical modifications were examined by using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR), and UV/Visible

spectroscopy techniques. The FTIR experiments were carried out in transmission mode, using a Perkin Elmer instrument (Spectrum One). The samples were prepared by the KBr method and then scanned over wavenumbers ranging between 400 and 4000 cm<sup>-1</sup>. The samples for the <sup>1</sup>H-NMR experiments were prepared by dissolving 3 mg of the polymer in 5 mL of deuterated chloroform CDCl<sub>3</sub> solvent. The NMR experiments were performed using a Bruker instrument (ADVANCE 300 model) at 20°C and using tetramethylsilane (TMS) as a reference.

UV/Visible absorption spectra of various samples were recorded on a Shimadzu UV-3100 spectrophotometer over wavelengths ranging between 190 and 800 nm. The samples were prepared by dissolving in THF and the experiments carried out at room temperature. In order to determine conjugation length and concentration of polyene in the DHPVC molecules, the following equations were used. In addition, conjugation length and concentration of polyenes in the DH-PVC molecules were calculated using eq. ((1)) and ((2)), respectively<sup>23,24</sup>;

$$\varepsilon_{i,\text{THF}} = 10000 + 27700 \times (i - 1) \text{ (dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \quad (1)$$

where,  $\varepsilon$  = absorbance coefficients,  $i$  = length of polyene

$$P_i = \frac{A_i \times M}{\varepsilon_i \times c \times d} \quad (2)$$

Where,  $P_i$  = polyenes concentration,  $A_i$  = absorbance,  $M$  = formula weight of vinyl chloride monomer (63.5),  $c$  = polymer concentration (g/dm<sup>3</sup>),  $d$  = optical path length (cm).

**Molecular Weight Analysis.** The averaged molecular weight values and polydispersity indexes (PDI) of the products were

Table I. Averaged Molecular Weight ( $M_n$ ) and Glass Transition Temperature ( $T_g$ ) Values of PVC and DH-PVC Samples Both Before and After Fullereneation

Polymers	$M_n$ (g/mol)	PDI	$T_g$ onset (°C)
PVC	67,824	1.90	78
DH-PVC	58,526	1.94	72
PVC-N12	59,051	1.85	82
PVC-A12	82,776	2.38	86
DH-PVC-N12	78,242	6.40	78

determined by Gel Permeation Chromatography (GPC) technique, using a Waters instrument (Model 2414) equipped with Styragel HR5E  $7.8 \times 300 \text{ mm}^2$  column (molecular weight resolving range = 2000–4,000,000) and a refractive index (RI) detector. Polystyrene standards were used for constructing narrow molecular weight calibration curves. The GPC experiments were performed by using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min at 40°C.

**Thermal Analysis.** The weight composition and thermal stability of the modified PVC were determined by thermal gravimetric analysis (TGA). The TGA experiments were carried out with a Mettler Toledo instrument (TGA/DSC1HT/1600/673/13558 model). Approximately 5 mg of each sample was used and the TGA experiment was scanned over temperatures ranging between 25 and 800°C under nitrogen gas and a heating rate of 10°C/min.

In addition, thermal behaviors of the polymers were investigated by using a differential scanning calorimetry (DSC) technique. The DSC experiment was carried out with a Mettler Toledo DSC 1 instrument under a nitrogen atmosphere at a heating rate of 10°C/min over temperatures ranging between 25 and 200°C.

**Electrical Conductivity Test.** Electrical conductivity of the modified polymers was measured at ambient conditions by a four-point probe method using a DC power supply and Keithley 2410 digital multimeter. The polymer solution (2% w/v in THF) was prepared and filtered through PTFE 0.45  $\mu\text{m}$  filter before casting onto a clean microscopic glass slide ( $2.5 \times 2.5 \text{ cm}^2$ ) and covered with a glass dish to prevent rapid evaporation of the solvent. Then obtained polymer films, with an average thickness of 15  $\mu\text{m}$ , were then oxidized (doping) by exposure to

iodine vapors for 4 h prior to testing. Electrical conductivity ( $\sigma$ ) was then calculated by using the following equation<sup>25</sup>:

$$\sigma = \frac{1}{4.53 \times R \times l} \quad (3)$$

where  $\sigma$  = conductivity ( $\text{S cm}^{-1}$ ),  $R$  = resistance ( $\Omega$ ), and  $l$  = film thickness (cm).

## RESULTS AND DISCUSSION

Figure 2 shows overlaid FTIR spectra of polymeric PVC and DH-PVC material. Several characteristic peaks representing PVC molecules can be observed. These include peaks at  $1428 \text{ cm}^{-1}$  (assigned to  $\delta \text{ CH}_2$  of PVC),  $1258 \text{ cm}^{-1}$  (assigned to  $\delta \text{ CH}$  of PVC), and  $965 \text{ cm}^{-1}$  (assigned to  $\nu \text{ CH}_2$  of PVC). The absorption peaks at 614 and  $695 \text{ cm}^{-1}$  also represent the  $\nu \text{ C-Cl}$  bonds of syndiotactic and isotactic structures of PVC, respectively. After dehydrochlorination, some additional absorption peaks can be noted. These include peaks at 1660, 1638, and  $803 \text{ cm}^{-1}$ , corresponding to the vibration of the conjugated  $\text{C}=\text{C}$ ,  $\text{C}=\text{C}$ – and  $\text{CH}$  bonds, respectively. This indicates the formation of polyene segments on the modified PVC molecules. The presence of a polyene chromophore is aligned with our observation noting the change in color of PVC from colorless to orange, after dehydrochlorination (to obtain DH-PVC). Notably, a broad peak at  $3400 \text{ cm}^{-1}$ , representing the OH bond can also be observed. It is believed that this may be attributed to the substitution of OH group from NaOH base catalyst onto PVC molecules. Similar results have been observed by Yoshioka et al.<sup>26</sup>

Figure 3 shows a  $^1\text{H-NMR}$  spectrum of PVC that had undergone dehydrochlorination (DH-PVC). Characteristic peaks representing protons of the pristine PVC molecules can be seen.

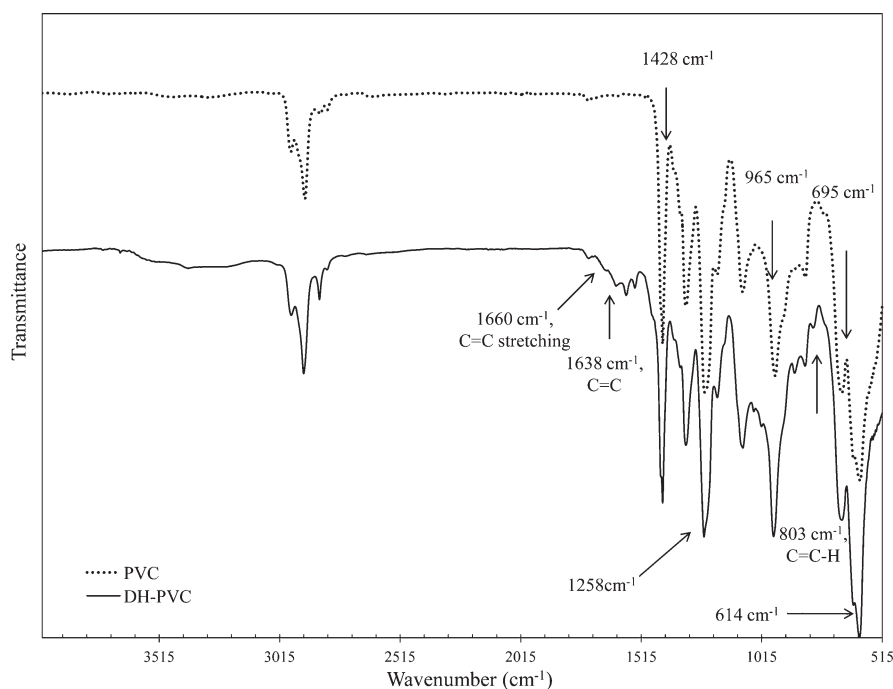


Figure 2. Overlaid FTIR spectra of PVC and DH-PVC.

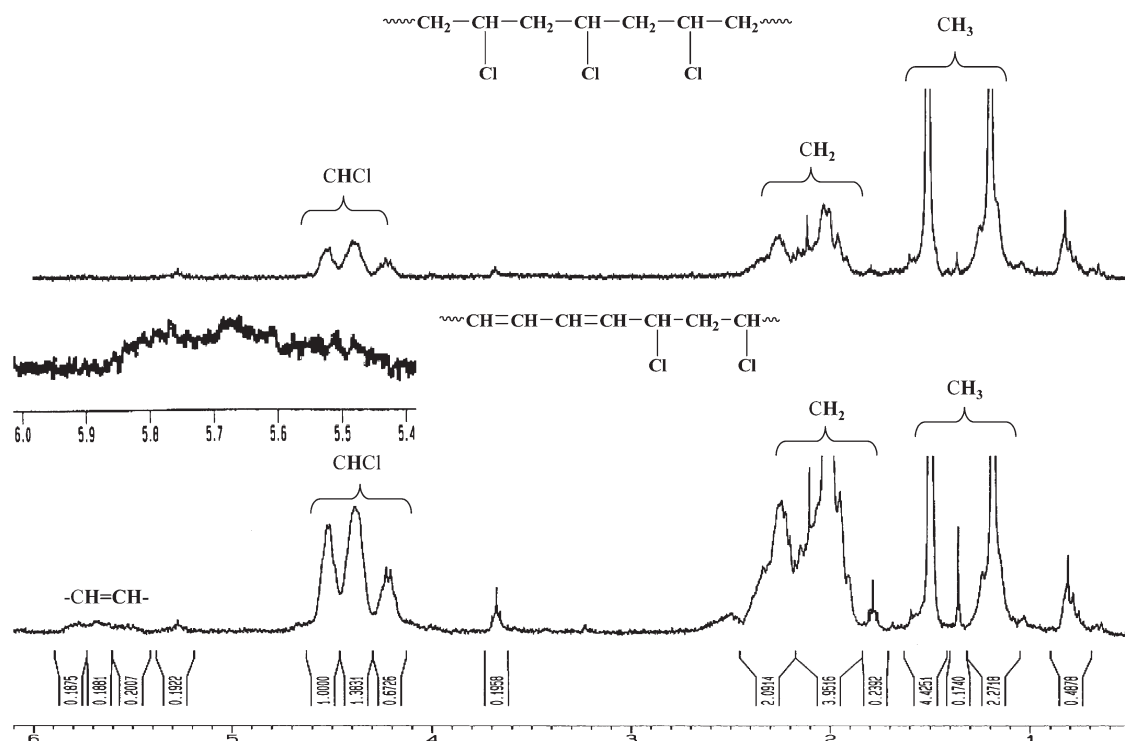


Figure 3. <sup>1</sup>H-NMR spectra of PVC (above) and DH-PVC (bottom).

These include peaks at around 4.3–4.7 ppm (ClC–H) and 2.35 ppm (–CH<sub>2</sub>–). Furthermore, additional peaks at 5.7 and 5.8 ppm were also noted. These peaks represent the olefinic protons from the polyene segment of the DH-PVC.<sup>27</sup> The above FTIR and <sup>1</sup>H-NMR results are sufficient to confirm that DH-PVC has been efficiently prepared.

#### Grafting of C<sub>60</sub> Fullerene onto PVC and DH-PVC

Figure 4 shows FTIR spectra of PVC and DH-PVC before and after reacting with C<sub>60</sub>. After fullerenation, new absorption peaks at 528 and 577 cm<sup>-1</sup> were noted to have emerged and these can be ascribed to the characteristic bands of C<sub>60</sub>.<sup>28</sup> Additionally, the above spectra reveal the presence of peaks at 1730 and 3400 cm<sup>-1</sup>. Of interest, similar peaks were also observed by Rusen et al.<sup>29</sup> in a FTIR spectra derived from PVC that had been chemically modified with C<sub>60</sub> and the authors concluded that these may be ascribed to an interaction between C<sub>60</sub> and the azido-substituted PVC. In this study, however, the above interaction was not thought to occur largely due to the fact that different reaction mechanisms and chemical reagents were used for fullerenation. Instead, the signals at 1730 and 3400 cm<sup>-1</sup>, are very likely due to vibrations of C=O (stretching) bond and absorbed moisture on the sample surface and/or the OH groups in the molecules, respectively. This implies a reaction between PVC and oxygen during fullerenation. In this context, it is possible that some residual oxygenated species contained within the chemicals (solvent, initiator) can be capable of reacting with the dehydrochlorinated PVC during the fullerenation, which incidentally was carried out at a relatively high temperature (80°C) compared to a lower value (70°C) used by Martinez et al. (60°C).<sup>16</sup>

Figure 5 shows overlaid <sup>1</sup>H-NMR spectra of the fullerene grafted PVC (PVC-N12, PVC-A12). An additional small signal at around 3.9 ppm can be observed in all cases. This can be ascribed to the fulleryl protons.<sup>16</sup> Similar peak was noted from the NMR spectrum of DH-PVC (DH-PVC-N12). In this latter case, the relative integrated area of the peak from olefinic proton (5.7–5.8 ppm), when compared to those of the signals from CH<sub>2</sub> and CH<sub>3</sub> protons, is decreased after grafting. A similar spectral change was observed for the CH–Cl proton (4.3–4.7 ppm). The above results suggest that grafting reaction between polymer chains and C<sub>60</sub> atoms has been occurred.

Table I shows the molecular weights of the PVC products determined by using the GPC technique. After dehydrochlorination, the averaged molecular weight (*M<sub>n</sub>*) value of the modified PVC was largely found to decrease. A possible cause of this may be due to the hydrodynamic volume of the dehydrochlorinated PVC in THF (during the GPC experiment) is smaller than that of the normal PVC due to the differences in chemical structure and polarity. Consequently, the random coil of DH-PVC exits the GPC column at a relatively longer retention time, leading to a lower *M<sub>n</sub>* value.

When PVC was grafted with C<sub>60</sub> fullerene by ATRA (referred as PVC-A12 in Table I), the *M<sub>n</sub>* value was noted to increase. This was not the case, however, for PVC that had undergone AIBN based fullerenation (PVC-N12) where the *M<sub>n</sub>* values were noted to be lower. In this regard, this discrepancy might be attributed to the different percentage of C<sub>60</sub> grafted onto the PVC. Results from Table II reveal that the percentage weight of C<sub>60</sub> in PVC-A12 and PVC-N12, are 5.66 and 2.77%, respectively. In the

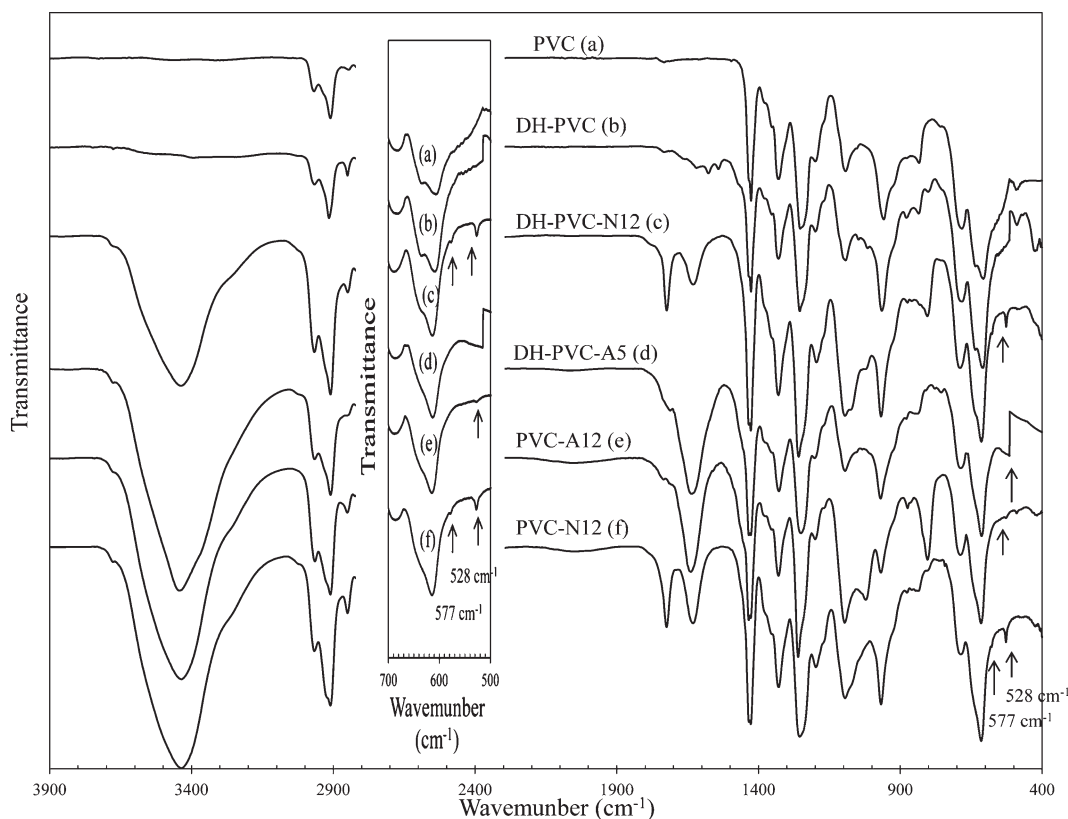


Figure 4. Overlaid FTIR spectra of PVC and DH-PVC before and after reacting with  $C_{60}$ .

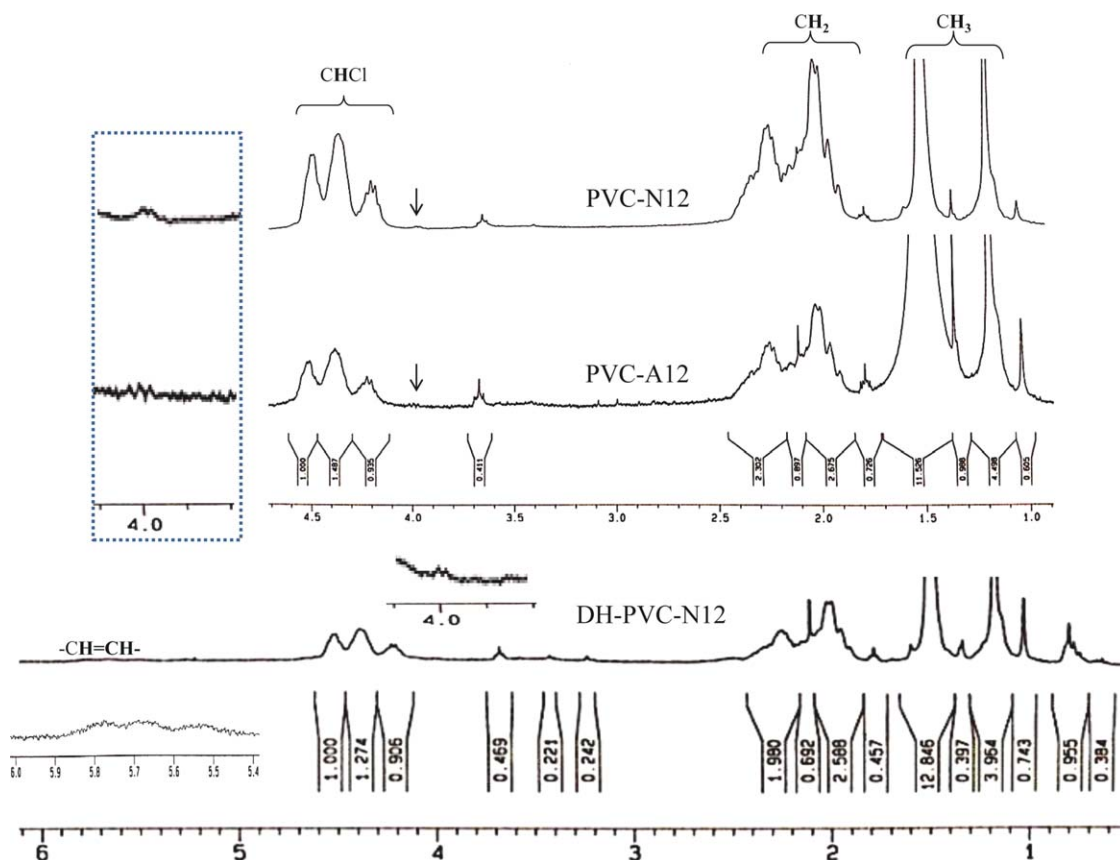
former case, it is likely possible that the amount of  $C_{60}$  in the fullerene grafted PVC molecules is sufficiently high so that an interaction occurring between the polymer and THF changed the hydrodynamic volume of the polymer in the chromatography column and made the random coil of the polymer exit the GPC column at a relatively shorter time. This contributed to the higher  $M_n$  value of PVC-A12. Similar results were observed for DH-PVC products chemically modified via AIBN based fullerenation (DHPVC-N12). The results can be likely explained in a similar fashion, taking into account that the percentage fullerene in DHPVC-N12 (4.65%) and PVC-A12 (5.66%) are comparable. Noteworthy, the above changes in the  $M_n$  values of both PVC and DHPVC after fullerenation, is now considered to be indirect evidence of grafting of  $C_{60}$  having occurred onto the polymer molecules.

#### Thermal Properties

Figure 6 shows DSC thermograms of PVC and DH-PVC both before and after fullerenation and the glass transition temperature ( $T_g$ ) values of the various samples are summarized in Table I. After dehydrochlorination, the  $T_g$  values of PVC are seen to decrease from 78°C to 72°C. This suggests that PVC chains became more flexible after dehydrochlorination. This effect can be attributed to a decrease in polar interaction between the polymer chains, due to lower chlorine atoms in DH-PVC. After fullerenation,  $T_g$  values of PVC increased to above 80°C.  $T_g$  value of the fullerene grafted PVC, prepared via ATRA (sample PVC-A12; 86°C) is marginally higher than that of corresponding products undergone AIBN based fullerenation (sample

PVC-N12; 82°C). This discrepancy could be ascribed to the fact that  $C_{60}$  content of the former is greater (Table III). In this regard, a higher content of  $C_{60}$  groups in the polymer may lead to increased rigidity of the PVC chains, due to a steric effect. This contributed to a greater  $T_g$  value of the material. Similarly,  $T_g$  value of DH-PVC increased after fullerenation and the result can be explained in a similar fashion.

Figure 7 shows overlaid TGA thermograms of PVC and DH-PVC. Two transitions can be readily observed from the thermogram of normal PVC. The first transition is seen at the onset temperature of 240°C and accounting for 65% of the weight loss of the PVC sample. This can be essentially ascribed to dehydrochlorination process of PVC, which leads to the formation of polyene intermediates. Next, the second transition occurs at the onset temperature of about 400°C. This involves several chemical reaction processes including cracking, cyclization and cross-linking of the polyene intermediates. Major by-products generated from the above decompositions include low molecular weight aromatic hydrocarbons such as benzene, toluene, and styrene.<sup>30</sup> Above 530°C, solid residual (char), weighing approximately 8% weight of the initial PVC was obtained and this can be attributed to some cross-linked polymeric molecules. The TGA thermogram of DH-PVC shows differences. The first transition, accounting for 15% of the weight loss, starts at the onset temperature of 135°C. This can be ascribed to an evaporation of some absorbed moisture on the sample surface. This implies that DH-PVC is more polar than normal PVC. Next, further dehydrochlorination of the DH-PVC occurs over temperatures



**Figure 5.** Overlaid  $^1\text{H-NMR}$  spectra of PVC and DH-PVC after fullerene grafting. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.**  $\text{C}_{60}$  Contents and Solubility of Various  $\text{C}_{60}$  Grafted PVC and DH-PVC Prepared via ATRA and Normal Fullerene Grafting Techniques

Sample codes	Reaction systems	Fullerene/PVC feed ratio (w/w)	Solubility in THF	Fullerene content <sup>b</sup> (wt %)
PVC-N5	AIBN <sup>a</sup>	0.083	√	0.26
PVC-N8	AIBN <sup>a</sup>	0.13	√	5.21
PVC-N12	AIBN <sup>a</sup>	0.20	√	2.77
PVC-N15	AIBN <sup>a</sup>	0.25	√	0.40
PVC-A5	ATRA	0.083	√	1.72
PVC-A8	ATRA	0.13	√	5.32
PVC-A12	ATRA	0.20	√	5.66
PVC-A15	ATRA	0.25	√	4.81
DH-PVC-N1	AIBN <sup>a</sup>	0.017	√	0.33
DH-PVC-N5	AIBN <sup>a</sup>	0.083	√	1.18
DH-PVC-N8	AIBN <sup>a</sup>	0.13	√	3.60
DH-PVC-N12	AIBN <sup>a</sup>	0.20	√	4.65
DH-PVC-N15	AIBN <sup>a</sup>	0.25	√	1.65
DH-PVC-A1	ATRA	0.017	Insoluble	n/a
DH-PVC-A5	ATRA	0.083	Insoluble	n/a

<sup>a</sup> Refers to AIBN based fullerene grafting.

<sup>b</sup> Determined by UV/Visible spectroscopy.

**Table III.** Conjugation Length and Concentration of Polyene in DH-PVC and the Various C<sub>60</sub> Grafted DH-PVC

Polymers	Length of polyene (i)	Polyene concentration ( $\times 10^{-3}$ )
DH-PVC	3-8	1.06-0.17
DH-PVC-N1	3-6	1.06-0.41
DH-PVC-N5	3-6	1.06-0.41
DH-PVC-N8	3-6	1.06-0.41
DH-PVC-N12	3-6	1.06-0.41
DH-PVC-N15	3-5	1.06-0.82

ranging between 230 and 330°C. This corresponds to approximately 45% of weight loss of the initial DH-PVC. The extent of dehydrochlorination during the TGA experiment of DH-PVC was lower than that of the normal PVC (65% weight), owing to the fact that DH-PVC has been partially dehydrochlorinated. Finally, the remaining weight of about 6% can be attributed to solid residual (char). This value is lower than that observed from the TGA thermogram of the normal PVC. This is due to the fact that the chemical structures, the actual percentage chlorine atoms, and formula weight of PVC are not the same as those of DH-PVC.

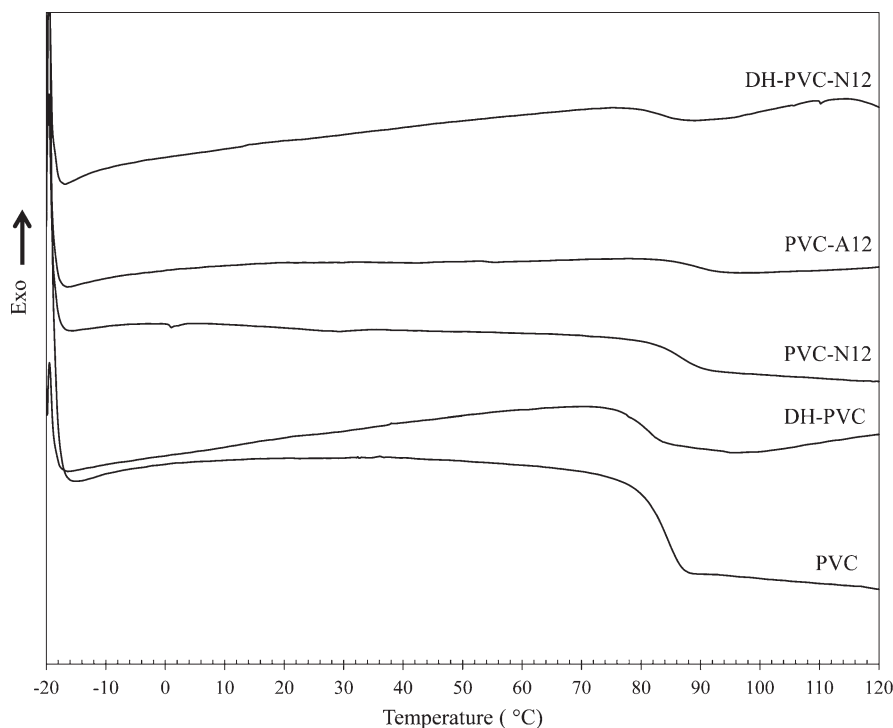
From the TGA thermogram of fullerene grafted PVC, the percentage weight observed over temperatures of 530°C, is greater than that of the normal PVC. This difference reflects the presence of the C<sub>60</sub> groups that have been chemically bonded to the grafting chain.<sup>31</sup> Noteworthy, the onset of temperature involving dehydrochlorination shifted lower (from 280 to 220°C) after fullerenation via ATRA (sample PVC-A5). This indicates that

the thermal stability of PVC molecules bearing C<sub>60</sub> groups has decreased. This was not the case for the AIBN based fullerene grafted PVC (PVC-N5) where the thermal stability was improved as compared to that of the neat PVC sample. The similar effect was reported by Martinez et al.<sup>16</sup> In our opinion, the discrepancy between thermal stability of ATRA based- and AIBN based fullerene grafted PVC might be attributed to the different content and distribution of fullerene on the polymer chains. This is an aspect deserving further investigation and clarification.

#### UV-Visible Spectra

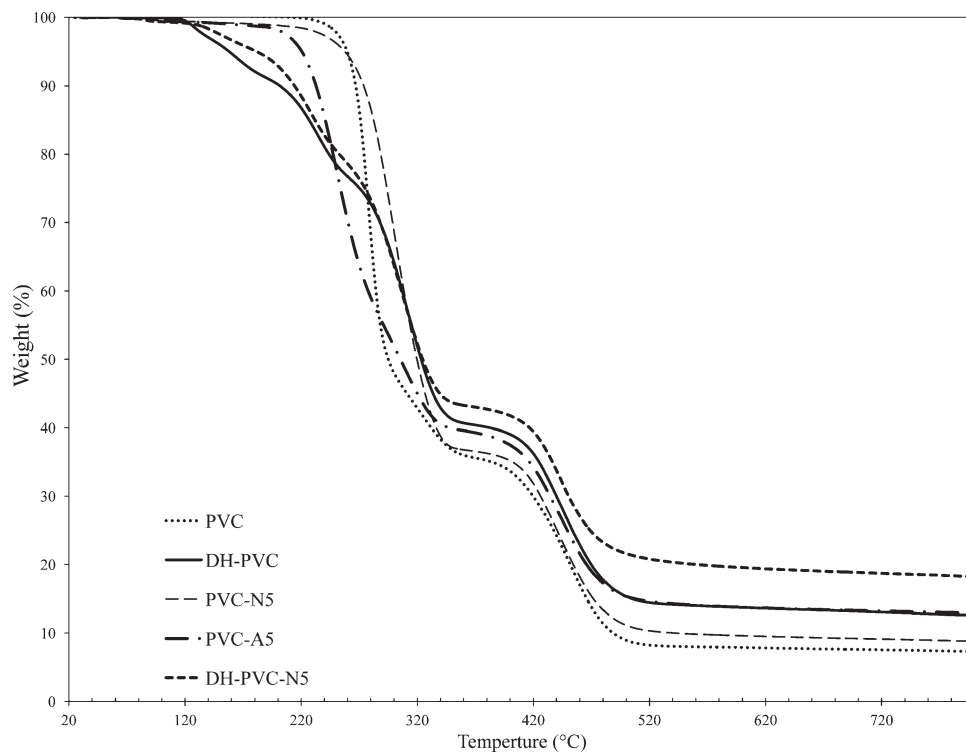
Additional experimental evidence supporting the presence of C<sub>60</sub> in the chemically modified PVC molecules can be seen from UV/Visible spectra (Figure 8). C<sub>60</sub> spectra exhibits well defined and characteristic absorption peaks at 280 and 330 nm. Notably, pristine PVCs are essentially transparent at wavelengths above 320 nm but with the presence of C<sub>60</sub> in the polymer an additional absorption band at 330 nm appears as a result of a characteristic absorption pattern of monofunctionalized organo-fullerene<sup>32</sup> (as seen for PVC-A12, PVC-N12, and DH-PVC-N12, respectively). However, it is worth pointing out that residual free C<sub>60</sub> atoms were removed from the chemically modified polymeric products by washing with hexane before the characterization studies and in this regard, the above additional peak at 330 nm is highly likely attributed to the C<sub>60</sub> covalently bonded to the PVC and DH-PVC chains.<sup>16</sup>

Collective data from these aforementioned characterization experiments are summarized in Table II. It can be noted that the C<sub>60</sub> content of fullerene grafted PVC initially increased with the amount of C<sub>60</sub> feed to a maximum value before decreasing again with further increases of C<sub>60</sub> feed. This implies that the fullerenation of PVC was limited and no enhancement was

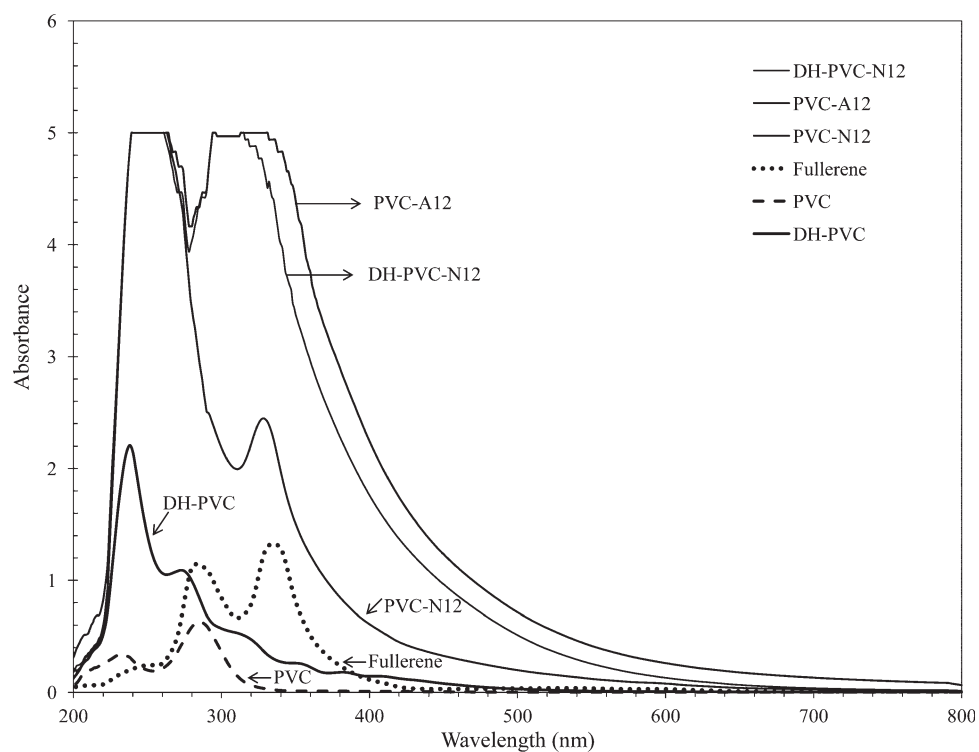


**Figure 6.** DSC thermograms of PVC and DH-PVC both before and after fullerenation.





**Figure 7.** Overlaid TGA thermograms of PVC, DH-PVC and the  $C_{60}$  grafted polymers prepared via the ATRA and/or the normal fullerenation techniques.



**Figure 8.** Overlaid UV/Visible spectra of PVC, DH-PVC, and the  $C_{60}$  grafted polymers.

gained with increased amount of  $C_{60}$ , and this may be likely due to aggregation of the fullerene. The unreacted fullerene's are almost all removed from the product prior to the characterization studies. Interestingly, with the same amounts of  $C_{60}$  feed it was also noted that the  $C_{60}$  content of PVC modified via the ATRA technique was much greater than the corresponding product modified by AIBN. This is likely attributed to the ATRA system catalyzed by the transition metal complex (CuBr/Ligand), robust and extremely efficient. Consequently, the formation of polymer radicals and grafting is more effective and productive.

In addition, from the above UV/Visible spectra, attempts were made to determine the length and concentration of polyene in the DH-PVC molecules, both before and after reacting with fullerene, using equations the equations detailed above and the method as described by Szaka'cs et al.<sup>23</sup> As observed from the data (Table III), polyene concentration increases at the expense of the conjugation length after reacting DH-PVC with fullerene using the AIBN method. The likely rational for this is that fullerene groups grafted onto DH-PVC chains at the unsaturated carbon-carbon double bonds, results in the disruption of the conjugation length with a corresponding increase in polyene concentration. However, this relationship concentration and length of polyene and, the fullerene content (Table I) is non-linearly. This is likely due to the fact that fullerene can be grafted onto either saturated or unsaturated segments of the DH-PVC chains.

#### Solubility of the Fullerene Grafted Polymeric Products

From the results detailed in Table I, it is interesting to note that the solubility of  $C_{60}$  grafted DH-PVC products differ depending on the reaction techniques used. Essentially, the products obtained by fullerenation via the ATRA technique (DH-PVC-A1 and DH-PVC-A5) were insoluble in many common solvents, including THF and dichlorobenzene, which are efficient solvents for PVC and  $C_{60}$ , respectively. Additionally, control ATRA experiments for DH-PVC consisting of reactions been carried out in the absence of  $C_{60}$ , also showed similar results. This suggests that the insolubility observed is likely related to the PVC molecules and not attributed to aggregation or crosslinking of fullerene. Conversely, all the DH-PVC products obtained through normal fullerenation by the AIBN method (DH-PVC-N5 and DH-PVC-N15) were found to be soluble in these solvents, irrespective of the percentage  $C_{60}$ . Moreover, it is worth mentioning that when neat PVC was used as a starting chemical for fullerenation, the resulting products were also soluble in the common solvents, regardless of the reaction mechanisms used. Our results indicate that the insolubility of ATRA fullerene grafted DH-PVC products is likely related to the nature of the chemical reaction and structural changes at the double bonds of the DH-PVC molecules. In this regard, there are likely two competing chemical reactions occurring during the fullerenation process of DH-PVC, i.e., grafting of  $C_{60}$  onto the polymeric chains and a concurrent cross-linking of the DH-PVC molecules. The likely scenario when fullerenation occurs via the ATRA mechanism is that chlorine atoms are "transferred" from DH-PVC molecules into the transition metal catalyst complex,

**Table IV.** Conjugation Length and Concentration of Polyene in DH-PVC and the Various  $C_{60}$  Grafted DH-PVC

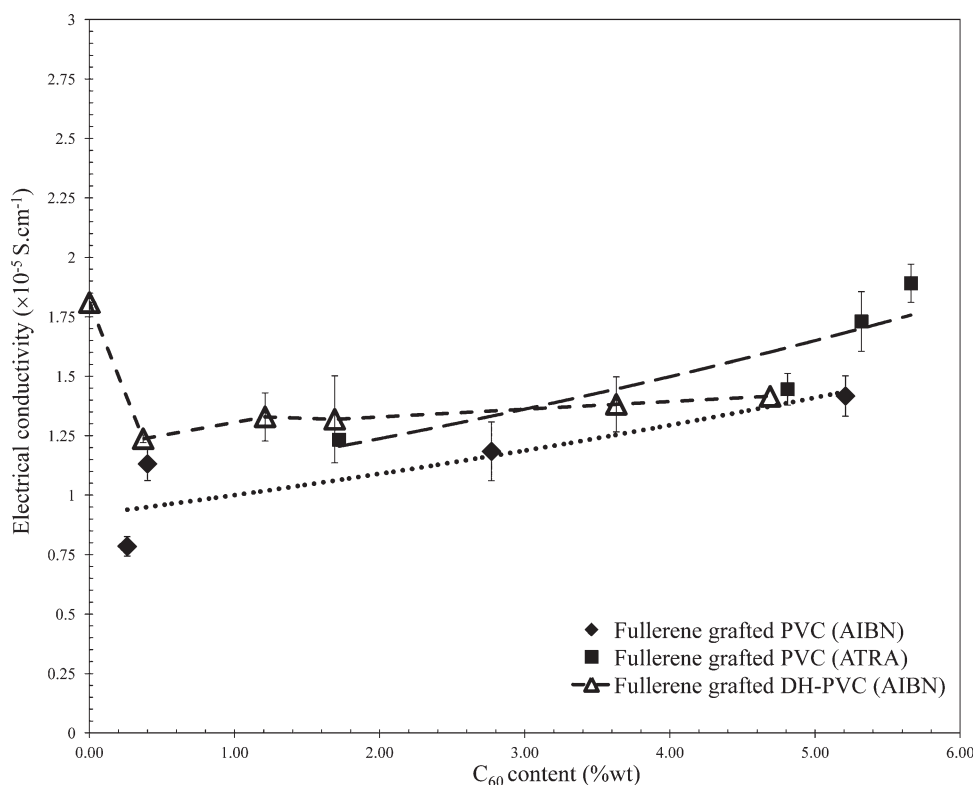
Polymers	Electrical conductivity ( $\times 10^{-5}$ S $\text{cm}^{-1}$ )	
	undoped	doped
PVC	0.0002	0.004
DH-PVC	0.37	1.81
PVC-N12	0.61	1.18
PVC-A12	0.69	1.73
DH-PVC-N12	0.32	1.38

resulting in the formation of free radical chains. In this regard,  $C_{60}$  atoms get readily grafted onto the polymer molecule by replacing the chlorine atoms of the repeating units. The remaining double bonds along the DH-PVC chains might also be dissociated into radicals facilitating the cross-linking process. The above phenomenon may not be the case for AIBN based normal fullerenation. In this case, radical species are induced by the dissociation of AIBN which then facilitate the grafting of  $C_{60}$  atoms at the double bonds of DH-PVC chains. This data is further supported by the  $^1\text{H-NMR}$  analysis of the fullerene grafted DH-PVC (Figure 5). As observed, the relative integrated area of the peak from olefinic proton (5.7–5.8 ppm), when compared to those of the signals from  $\text{CH}_2$  and  $\text{CH}_3$  protons, is decreased after grafting. A similar spectral change was observed for the  $\text{CH-Cl}$  proton (4.3–4.7 ppm). It was believed that the above-mentioned cross-linking reaction was suppressed by grafting reaction between polymer chains and  $C_{60}$  atoms.

#### Electrical Conductivity

Last but not least, electrical conductivity of the various fullerene grafted polymers deserves a mention as this has a direct relevance for their use in solar cell technology. First, it is worth noting from Table IV that conductivity of DH-PVC is significantly higher ( $1.81 \times 10^{-5}$  S/cm) compared to PVC ( $0.004 \times 10^{-5}$  S/cm). This was probably due to the fact that PVC consists of saturated molecules and generally lacks conjugated double bonds. It was also found that when samples were tested without doping, the conductivity of the material is relatively low compared to that of the doped samples. For example, conductivity of the doped DHPVC ( $1.81 \times 10^{-5}$  S/cm) is significantly higher than that of the undoped DHPVC ( $0.37 \times 10^{-5}$  S/cm).

After reacting DH-PVC with fullerene with AIBN, conductivity values of the doped fullerene grafted DH-PVC initially dropped to  $1.24 \times 10^{-5}$  S/cm (Figure 9). This effect can be ascribed to disruption of conjugation length of the polymer molecules due to the substitutions of fullerene atoms on the double bonds. However, when the  $C_{60}$  content was further increased the conductivity correspondingly increased. This is likely due to the fact that fullerene, which have robust electrical conductive, became dominant and contribute to the overall conductivity of the polymer. It follows that with the above conductivity values, DH-PVC and fullerene grafted DH-PVC can be classified as potential semi-conductor material.<sup>33,34</sup>



**Figure 9.** Changes in electrical conductivity values of the various C<sub>60</sub> grafted PVC and DH-PVC with C<sub>60</sub> contents (after doping).

Similarly, conductivity values of the fullerene grafted PVC linearly increases with the C<sub>60</sub> content, regardless of the reaction mechanism used. However, conductivity values of AIBN grafted PVC were relatively lower compared to those of grafted DH-PVC, experiencing the same fullerenation mechanism. Again, this may be attributed to the fact that the PVC backbone lack conjugated double bonds in the molecule. Finally, the conductivity values of fullerene grafted PVC by ATRA, are higher than those of the polymers modified by AIBN irrespective of a similar C<sub>60</sub>. It is likely that the above discrepancy could be attributed to factors such as different distribution of fullerene groups in the grafted PVC molecules, which might affect conjugation length and planarity of the polymer molecules.

## CONCLUSION

The grafting of C<sub>60</sub> onto PVC and DH-PVC was carried out using two different techniques, i.e., AIBN based fullerenation and ATRA techniques. Results from FTIR, <sup>1</sup>H-NMR, and UV/Visible spectroscopy suggest that the fullerene grafted polymers were readily and efficiently prepared. Grafting of fullerene onto PVC via the ATRA technique was more effective than that carried out via AIBN based fullerenation with the same amount of C<sub>60</sub> provided as feed for the reactions. On the other hand, the fullerene grafted DH-PVC, prepared via ATRA mechanism, the resulting products are all essentially insoluble. After grafting with fullerene, electrical conductivity values of PVC and its derivative (DH-PVC) linearly increased with the fullerene content.

## ACKNOWLEDGMENTS

This study was supported by the Nanotechnology Center (NANO-TEC), Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network. Ms. Seeponkai would also like to thank the Thailand Graduate Institute of Science and Technology (TGIST; TG-33-20-52-010D) and the National Science and Technology Development Center (NSTDA) for a scholarship supporting her Ph.D study.

## REFERENCES

1. <http://global.britannica.com/EBchecked/topic/221916/fullerene>; April 17, 2013.
2. Buntar, V.; Weber, H. W. *Supercond. Sci. Technol.* **1996**, *9*, 599.
3. Saito, Y.; Shinohara, H. *Chem. Phys. Lett.* **1992**, *189*, 236.
4. Tokunaga, K. *Chem. Phys. Lett.* **2009**, *476*, 253.
5. Andreoni, W.; Gygi, F.; Parrinello, M. *Phys. Rev. Lett.* **1992**, *68*, 823.
6. Fan, B.; Wang, P.; Wang, L.; Shi, G. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 3547.
7. Hoppe, H.; Sariciftci, N. S. *J. Mater. Chem.* **2006**, *16*, 45.
8. Ltaief, A.; Davenas, J.; Bouazizi, A.; Chaabane, R. B.; Alcouffe, P.; Ouada, H. B. *Mater. Sci. Eng.* **2005**, *25*, 67.
9. Moulay, S. *Prog. Polym. Sci.* **2010**, *35*, 303.

10. Lechermeier, G.; Pillot, C.; Gole, J.; Revillon, A. *J. Appl. Polym. Sci.* **1975**, *19*, 1979.
11. Kenedy, J. P.; Nakao, M. *J. Macromol. Sci. Chem.* **1978**, *A12*, 197.
12. Mukherjee, A. K.; Gupta, A. *J. Appl. Polym. Sci.* **1983**, *28*, 1245.
13. Ghaemy, M.; Gharaebi, I. *Eur. Polym. J.* **2000**, *36*, 1967.
14. Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.
15. Tang, B. Z.; Yu, N. T.; Peng, H.; Leung, S. M.; Wu, X. Z. US Patent 6, **2000**, 66, 272.
16. Martinez, G.; Gomez, M.A.; Gomez, R.; Segura, J. L. *J. Polym. Sci. A1* **2007**, *45*, 5408.
17. Black, N.; Ozlem, M. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3457.
18. Lui, P.; Lui, Y.; Su, Z. *Ind. Eng. Chem. Res.* **2006**, *45*, 2255.
19. Park, H. J.; Gaynor, S. G.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1998**, *19*, 47.
20. Lui, P. *Surf. Rev. Lett.* **2006**, *13*, 785.
21. Maruthamuthu, M.; Selvaraj, M.; Anmadurai, S. *J. Mater. Sci.* **1993**, *16*, 273.
22. Mehmet, C.; Gamze, B.; Relli, D. *J. Macromol. Sci. A* **2007**, *44*, 475.
23. Szakács, T.; Iván, B. *Polym. Degrad. Stab.* **2004**, *85*, 1035.
24. Daniels, V. D., Rees, N. H., *J. Polym. Sci. Part A: Polym. Chem.* **1974**, *12*, 2115.
25. Iovu, M. C.; Zhang R.; Cooper, J. R.; Smilgies D. M.; Javier A. E.; Sheina E. E.; Kawalewski, T.; McCullough R. D. *Macromol. Rapid Commun.* **2007**, *28*, 1816.
26. Yoshioka, T.; Kameda, T.; Imai, S.; Okuwaki, A. *Polym. Degrad. Stab.* **2008**, *93*, 1138.
27. Mayeda, S.; Tanimoto, N.; Niwa, H.; Nagata, M. *J. Anal. Appl. Pyrol.* **1995**, *33*, 243.
28. Wakai, H.; Shinno, T.; Yamauchi, T.; Tsubokawa, N. *Polymer* **1972**, *48*, 2007.
29. Rusen, E.; Marculescu, B.; Butac, L.; Preda, N.; Mihut, L. *Fullerenes Nanotubes Carbon Nanostruct.* **2008**, *16*, 178.
30. Wootthikanokkhan, J.; Jaturapiree, A.; Meeyoo, V. *J. Polym. Environ.* **2003**, *11*, 1.
31. Olah, G.A. *Fullerene Sci. Technol.* **1997**, *5*, 389.
32. Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem. Int. Ed.* **1992**, *31*, 766.
33. Guo, L.; Shi, G.; Liang, Y. *Synth. Methods* **1999**, *104*, 127.
34. Ocura, K.; Kisaka, K., Furukawa, H. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1375.