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รายการ	รายละเอียด
ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ	J. Wootthikanokkhan, C. Thanachayanont, and N. Seeponkai, Synthesis of graft copolymers based on polyphenylene xylylene and fullerene grafted polystyrene. *Journal of Applied Polymer Science* 116 (2010) 433-440.
	N. Seeponkai, N. Keaitsirisart, C. Thanachayanont, J. Wootthikanokkhan, Synthesis of fullerene functionalized polystyrene (PSFu) and morphology of fullerene based materials blended with P3HT. *Thin Solid Films*, (submitted on March, 2011)
การเสนอผลงานในที่ประชุม	N. Seeponkai and J.Wootthikanokkhan, Synthesis of Donor-Acceptor Graft Copolymer Based on PPV and Fullerene Grafted Polystyrene for Solar Cell Applications. SDSE Conference, 7-9 April 2009, Millenium Hilton Bangkok Hotel, Thailand.
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Synthesis of Graft Copolymers Based on Polyphenylene Xylylene and Fullerene Grafted Polystyrene

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Received 15 June 2009; accepted 17 September 2009
DOI 10.1002/app.31468
Published online 1 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft copolymers containing poly(phenylene xylylene) (PPX) backbone and polystyrene fullerene (PSFu) grafting chains (PPX-*g*-PSFu) were prepared by using a purposed synthetic route comprising a combination of reaction mechanisms namely the modified Wessling route, an iniferter polymerization, and an atom transfer radical addition (ATRA). The monomer was first prepared by reacting dichloroxylene with tetrahydrothiophene. After that the monomer was polymerized in a sodium hydroxide solution to provide a polymer precursor. Subsequently, the polymer precursor was modified by reacting it with a dithiocarbamate (DTC) compound. The macroiniferter was obtained and then copolymerized with styrene and chloromethylstyrene via an iniferter polymerization. Finally, the graft copolymer was reacted with fullerene through an ATRA technique to attach the C60 groups onto the graft copolymer molecule. The products obtained from each of the steps were characterized by using various techniques including Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, gel permeation chromatography, differential scanning calorimetry, UV–visible spectroscopy, and thermal gravimetric analysis. The aforementioned results suggest that the graft copolymers were prepared. The grafting yield and grafting efficiency were found to increase with the monomers concentration and the amount of DTC used. Some homopolymer contaminants also occurred but those could be minimized and subsequently removed by extraction with selective solvents. These graft copolymer products might be used for the development of a bulk heterojunction polymer solar cell.
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Key words: fullerenes; polystyrene; living polymerizations; graft copolymer

INTRODUCTION

There has been a considerable interest in the development of a plastic solar cell based on semiconducting polymers. This is attributed to some advantages of the polymer solar cell including the flexibility of the material, its relatively low cost and an easy fabrication process, and the possibility of producing a larger size solar cell by using an existing fabrication process such as screen printing.

However, power conversion efficiency (PCE) of the plastic solar cells has yet to be enhanced. Until now, the highest PCE of a plastic solar cell based on a P3HT and PCBM system reported by Heeger and coworkers is 5%.[1] This is still considerably low when compared with that of conventional inorganic solar cells. In this regard, the poor PCE of plastic solar cell could be attributed to many factors including photon loss,[2] excitons loss,[3–5] and carrier loss.[6] More details concerning the attempts and strategies to cope with the photon loss and carrier loss can be found elsewhere.[7–9] In this study, enhancing the PCE of plastic solar cell by coping with the excitons loss is of interest and is focused on.

To minimize the exciton loss, it is recommended that the electron donor material and the electron acceptor material should be blended together to form a bulk heterojunction (BHJ) polymer solar cell. As a result, there will be more interfacial area for the excitons to split into free electrons and holes. Furthermore, it would have been better if the donor and the acceptor materials are combined in a form of block or graft copolymer so that gross phase separation between the donor and the acceptor will be restricted. In this regard, the BHJ with a nanophase separated, bicontinuous morphology might be expected.

To achieve the aforementioned challenging morphology, the capability to synthesize donor and acceptor materials with controlled molecular weight

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Contract grant sponsors: Thailand Research Fund (TRF), Commission of Higher Education, Ministry of Education, Royal Thai Government; contract grant number: RMU5180049.

and molecular architectures by using some suitable chemical reaction mechanisms is extremely important. A study of the literature reveals that a donor polymer such as poly(phenylene vinylene) (PPV) and its derivative can be prepared by several mechanisms including an organic xanthate route,[10] and the Wessling route.[11–13] In addition, synthesis of donor–acceptor block copolymer containing PPV and fullerene derivatives via controlled radical polymerizations have been reported.[14,15]

In this study, we attempt to propose an alternative synthetic route for preparing a graft copolymer based on PPX (which can be further converted into PPV by thermal treatment), and the fullerene grafted polystyrene (PSFu) by using a combination of reaction mechanisms including the modified Wessling route,[16] an iniferter polymerization technique,[3,17,18] and the atom transfer radical addition (ATRA).[3,19] The aim of this research work is to explore the feasibility of preparing the PPX-*g*-PSFu graft copolymer via the aforementioned synthetic route (Fig. 1). The effects of reaction parameters on the structure of the synthesized polymer are also of interest.

EXPERIMENTAL

Materials

α,α′-Dichloro-*p*-xylene (90%, GC grade), tetrahydrothiophene (THT; 97%, GC grade), tetraethyl tiuram disulfide (TD; 98%, Assay), cupper, cupper bromide, and bipyridine were supplied from Fluka (Steinheim, Germany). Sodium hydroxide (97%) and cyclohexane (assay) were supplied from Carlo Erba (Rodano, Italy). Fullerene (98%) was supplied from Sigma-Aldrich (Steinheim, Germany). Methanol and toluene (analytical grade) were obtained from Fisher Chemicals (Loughborough, UK). Dichlorobenzene and acetone were supplied from Merck (Darmstadt, Germany). Nitrogen gas (99.99%) was obtained from Praxair (Thailand). All of the aforementioned chemicals were used as received.

Styrene (99%, GC grade from Fluka, Steinheim, Germany) was free from inhibitors by passing it through an alumina column. Chloromethylstyrene (CMS) (90%, GC grade from Fluka, Steinheim, Germany) was purified by extracting with sodium hydroxide solution, followed by washing with deionized water and then dried with sodium sulfate anhydrous.

Synthesis of the graft copolymer

Figure 1 shows the outline of the synthetic route that was used for the synthesis of the PPX-*g*-PSFu graft copolymer. In this study, we started with the system related to the PPX (which can simply be converted to the PPV donor material by heat treatment). In this regard, the bis-sulfonium salt monomer must be first prepared from a reaction between dichloroxylene and THT. It is noteworthy that an extension of this synthetic route to the system containing MEHPPV donor material is also an aspect of our future work. In this latter case, the first step can be eliminated since the monomer for the synthesis of the MEHPPV backbone is commercially available even though the price of the chemical is considerable. Once the monomer was obtained, it was polymerized into a polymer precursor via the Wessling route. Subsequently, the precursor was further modified by reacting it with dithiocarbamate (DTC) compound to obtain a macroiniferiter. Next, styrene and CMS were graft copolymerized onto the macroiniferter chains by using an iniferter polymerization technique. Finally, fullerene was attached onto the poly(styrene-*r*-chloromethylstyrene) [P(SCMS)] grafting chains via an ATRA technique. More details concerning experimental procedures for each step are described as follows:

Synthesis of bis-sulfonium salt monomer

Ten grams of α,α′-dichloro-*p*-xylene in methanol solution (6% w/v) was reacted with THT (15 mL) in a reaction flask at 50°C for 12 h. After that, the product was precipitated into acetone. The precipitated product was then dried and characterized by using a Fourier transform infrared (FTIR) spectroscopy technique.

Polymerization of the monomer into a polymer precursor

Three grams of the product obtained from the aforementioned step was further reacted with a dried-methanolic NaOH solution (0.98*M*) in an ice-cold water bath, under N_2 purged atmosphere. The polymerization was allowed to proceed at 0°C for about 30 min. After that, the content in the reaction flask was neutralized with hydrochloric acid (0.4*M*). The neutralized solution was then purified by dialysis using Spectra/Por® cellulose tubing (molecular weight cut off: 12,000–14,000 Da) for 3 days. At this stage, the product was considered to be a sulfonium polymer precursor.

Modification of the polymer precursor into a macroiniferter

A given amount of sodium diethyldithiocarbamate (NaDTC) (ranging between 0.1 and 1.3 g) was added into the reaction flask containing the aforementioned polymer precursor. The solution in the flask was kept stirring at −10°C for 1 h. After that, the

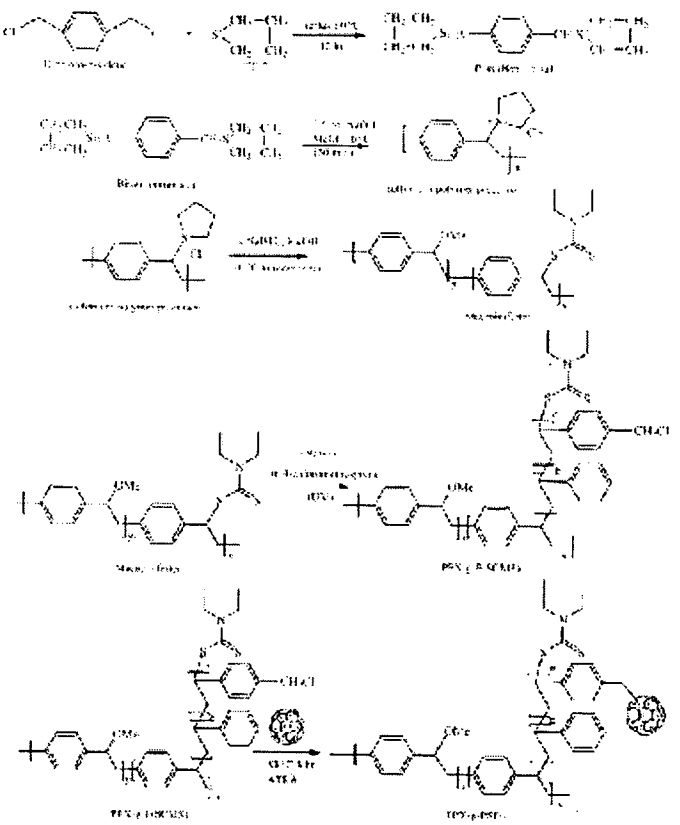

Figure 1 The proposed synthetic route for preparing the PPX-g-PSFu graft copolymer.

solution was gradually warmed to 5°C and the temperature maintained for 1 h. Next, the solution was allowed to warm to room temperature slowly. Of note, the product obtained by treating the polymer precursor with NaDTC is phase separated from the top layer of the MeOH solution. On the other hand, if the polymerization was carried out without the use of NaDTC, the product tended to be more homogeneous and take a longer period of time to phase separate into two layers.

Next, the product was washed with methanol by stirring for 30 min and then redissolved in CH_2Cl_2 before precipitating again in methanol. This process was repeated four times to remove some low-molecular weight impurities. Finally, the product was dried in a vacuum oven at 65°C for 1 h, followed by further drying at room temperature for 12 h.

Graft copolymerization

To a 250 mL reaction flask, 0.027 g of the macroiniferter was mixed with a solution of purified styrene (0.045 mol) and chloromethyl styrene (0.0113 mol) in THF (7 mL). The solution was purged with nitrogen for about 10 min and then vacuum-sealed after freeze-pumping. The reaction flask was exposed to UV radiation for 4 h. After that, the content in the reaction flask was precipitated into a large amount of methanol and then dried in a vacuum oven at 60°C until reaching a constant weight.

The product was further purified by extracting it with some selective solvents to isolate graft copolymer from some homopolymer contaminants. In this regard, methanol and a cosolvents containing a

mixture of xylene and isopropanol (1/1, v/v) were used. The former was found to be a good solvent for PPX but cannot dissolve P(SCMS), whereas the latter was vice versa. After the extraction, the product was dried in a vacuum oven at 60°C until reaching a constant weight.

The grafting yield and grafting efficiency were determined by using the following equations:

$$\text{Grafting yield}(\%) = [(W_1 - W_2)/W_3] \times 100\% \quad (1)$$

$$\text{Grafting efficiency}(\%) = [W_1/(W_1 + W_4)] \times 100\% \quad (2)$$

where W_1, W_2, W_3, and W_4 are the weights of graft copolymer, macroiniferter, monomer, and homopolymer, respectively.

Attachment of fullerene onto the graft copolymer chains

A total of 0.1 g of the graft copolymer obtained from the aforementioned step was mixed with fullerene (0.013 g), bipyridine (0.03 g), and toluene (15 mL) in a reaction flask. The solution was purged with nitrogen for 10 min, sealed with paraffin film, and kept for a further ATRA reaction. To a 250 mL three-necked round bottom flask, Cu (0.013 g) and CuBr (0.0086 g) were added. The flask was closed with a rubber septum and sealed before undergoing nitrogen purging and vacuum pumping for five cycles. Then, the polymer solution prepared earlier was introduced into the reaction flask by injection through the rubber septum, using a syringe. The mixture was then refluxed at 100°C in an oil bath for 24 h. After cooling to room temperature, the reaction was filtrated and precipitated into a large amount of methanol. The crude precipitated product was redissolved in THF, and then precipitated in methanol again. Hexane, which is a selective solvent for C60/PSFu system, was used to remove some residual fullerene (C60) from the product. UV–visible spectroscopy was used to examine the presence of an absorption peak of the free fullerene in the leached solvent. The washing process was carried out until the aforementioned UV–visible peak disappeared. Finally, the product was dried in a vacuum oven at 60°C for 16 h.

Characterizations

FTIR spectroscopy was used to monitor some changes in the chemical structure of various products after reactions. The FTIR spectrum was recorded, using a Bruker FTIR (Equinox 55). The sample was prepared in the form of a KBr pellet, and the spectrum was scanned over the wavenumber ranging between 600 cm^{-1} and 4000 cm^{-1}. In addition, the chemical structures of some products were characterized using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. Typically, a graft copolymer sample was dissolved in deuterated benzene (C_6D_6) and then the spectrum recorded in a Bruker instrument (Advance DPX400), using TMS as a reference.

The molecular weight of polymer was determined by use of a gel permeation chromatography (GPC) technique (Waters 600 instrument). Three connected columns (Water Styragel) containing crosslinked styrene-divinyl benzenecopolymer particles with a molecular weight resolving range of 100–500,000 were used. The eluent rate of tetrahydrofuran (THF) was 1.0 mL/min and polystyrene standards were used to establish a universal calibration curve.

The thermal stability of the product was examined by use of a thermogravimetric analyzer (TGA, NETZSCH STA 409 C/CD). About 20 mg of the sample was used and the TGA experiment was scanned over temperatures ranging between 25°C and 600°C under oxygen (air) atmosphere, at a heating rate of 10°C/min. In addition, the thermal behaviors of the polymers were investigated by using a differential scanning calorimetry (DSC) technique. The DSC experiment was carried out with a Netzsch (Bavaria, Germany) DSC 240F1 instrument under a nitrogen atmosphere at a heating rate of 10°C/min over temperatures ranging between 25 and 200°C.

Finally, UV–visible absorption spectra of various samples were recorded on a Shimadzu UV-3100 spectrophotometer, over wavelength ranging between 190 and 700 nm.

RESULTS AND DISCUSSION

Synthesis of the monomer and the PPX precursor

Figure 2 shows an overlaid FTIR spectrum of dichloro-*p*-xylene and that of the product obtained from the reaction between dichloro-*p*-xylene and THT. A new peak at the wavenumber of 645 cm^{-1} corresponding to the vibration of C—S (ν) bonds was observed in the spectra of the product. In addition, the absorption peak at 756 cm^{-1}, representing the vibration of C—Cl bonds disappeared. Other relevant peaks such as those at 1619 cm^{-1} [C=C, (ν)] of an aromatic ring, and 870 cm^{-1} (out of plane bending of C—H ring) were also noted. Similar FTIR results for the same compound were reported by Damlin[20] and Bradley.[11]

After carrying out a polymerization of the aforementioned product by reacting it with sodium hydroxide solution, a viscous solution in the reaction flask was obtained. This solution contains a polymer precursor which was dialyzed prior to reacting with NaDTC to obtain a macroinifeter.

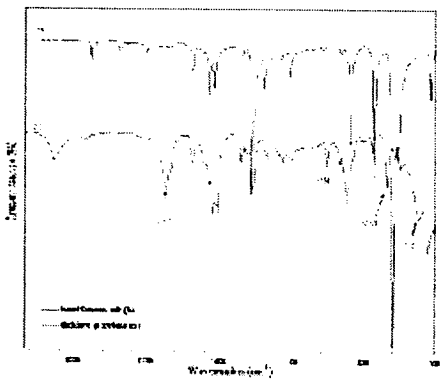

Figure 2 Overlaid FTIR spectra of dichloro-p-xylene and bis-sulfonium salt monomer.

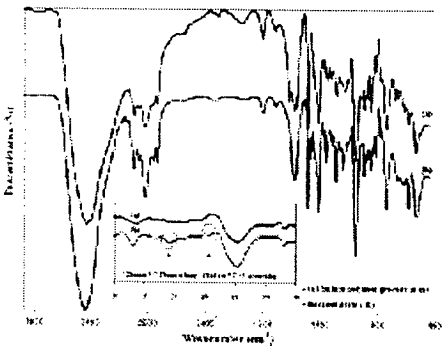

Figure 3 Overlaid FTIR spectra of the sulfonium polymer precursor before and after modification with NaDTC.

Modification of the polymer precursor into macroinferter

Figure 3 shows overlaid FTIR spectra of the sulfonium polymer precursor before and after modification with 0.2 g of NaDTC. An FTIR spectrum of the modified polymer shows two new peaks at 1206 $cm^{-1}$and 1140 cm^{-1}. These could be ascribed to the vibration of the C—N (ν) and that of the C=S (ν), respectively. Notably, the absorption peaks at 1635 cm^{-1} and 1676 cm^{-1} were also present. This might be ascribed to vibration of the C=C bonds that could be attributed to some side reactions such as the elimination of the sulfonium groups, partly occurring during the polymerization. This is consistent with our observation noting that color of the product is green which could be attributed to a very short conjugated sequence arising from an unavoidably limited amount of elimination.[21] However, from our research experience, we found that this side reaction can be minimized by maintaining a constant reaction temperature and gradually adding of the NaOH solution during the polymerization. Of note, we have carried out a heat treatment for this polymer at 200°C in a vacuum oven for 2 h and observed that color of the material changed from green to yellow. This suggests that more of the unsaturated PPV repeating units have been formed in the molecules.[22]

Figure 4 shows a ^{1}H-NMR spectrum of the modified polymer. The strong peak at 7.0 ppm represents a signal from the proton in an aromatic ring of the PPX backbone. Another strong peak at 4.15 ppm could be ascribed to the methine proton adjacent to the methoxy groups (—HC—OCH_3), whereas the peak at 3.19 ppm can be related to a signal from the protons in methoxy groups (OCH_3). The NMR peak at 3.7 ppm could be attributed to a proton adjacent

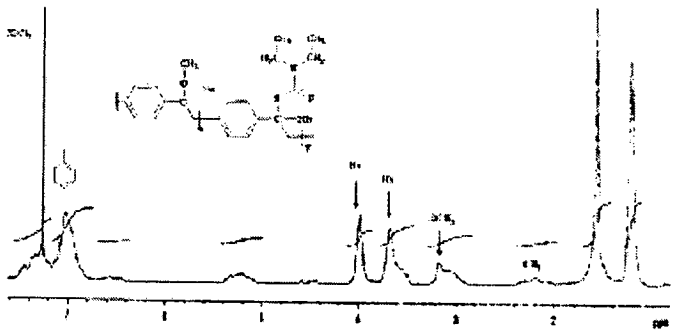

Figure 4 ^{1}H-NMR spectrum of the sulfonium polymer precursor modified with NaDTC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
The Grafting Yields and Grafting Efficiency of the Products Obtained from Various Graft Copolymerization Conditions

PPX-DTC ratio (by weight)	Monomers (mL)		Grafting yield (%)	Grafting efficiency (%)
	Styrene	CMS		
1 : 0.1	2.61	0.83	4.90	44.18
1 : 0.2	10.40	3.20	5.61	63.45
1 : 0.3	10.40	3.20	20.65	85.09
1 : 0.5	10.40	3.20	21.11	94.45
1 : 0.7	2.61	0.83	10.16	73.55
1 : 0.7	10.40	3.20	38.58	94.77

to the (DTC) group [—CH—S(C=S)]. In addition, there is a small peak at 5.35 ppm which could be due to the presence of some olefinic proton (—CH=C) in the molecule. The aforementioned results from FTIR and NMR spectroscopy suggested that the macroiniferter was prepared. In addition, results from GPC technique reveal that number average molecular weight (M_n) and polydispersity index of the aforementioned macroiniferter are ~ 280,000 g/mol and 1.5, respectively.

Graft copolymerization

After carrying out graft copolymerization of the macroiniferter with a varied amount of styrene and CMS, the product was extracted with selective solvents and the product yield was determined via gravimetry. Noteworthy, some control experiments in which styrene and CMS solution was exposed to the UV irradiation in an absence of any initiator or iniferter were also carried out. Using this method, some product yields were obtained after a precipitation of the content in the reaction flask. This could be attributed to the self-polymerized styrene and CMS. However, these product yields are much less than those of the solution containing the macroiniferter. Furthermore, the self-polymerized product was completely soluble and removed after extraction with selective solvents. This was not the case for the products polymerized with the use of a macroiniferter. The aforementioned results suggest that the product obtained was a graft copolymer and not a mixture of the related homopolymers.

Table I shows the grafting yields and grafting efficiency obtained from various graft copolymerization conditions. It can be seen that by increasing the amount of monomers (at a fixed macroiniferter weight), the grafting yield and grafting efficiency increased. In addition, by increasing the weight ratio between the DTC and the polymer precursor during the modification step, both parameters (yield and efficiency) increased. This is due to the fact that the greater the ratio, the more the capping agents on the macroiniferter molecules. Consequently, the monomers had more chances to experience the graft copolymerization. In this study, it seems that the optimum condition leading to the maximum grafting efficiency and yield is that obtain by using 1/0.7 by weight of the precursor to the DTC and a high monomer feed volume (10.4 and 3.2 mL of styrene and CMS, respectively).

Figure 5 shows the ^{1}H-NMR spectrum of the product obtained from a graft copolymerization of styrene and CMS using the monomers mole ratio of 75/25 (%). It can be seen that, after the reaction, the NMR peaks corresponding to those of the DTC group disappeared. This is due to the fact that the polymer chains have been grafted with the

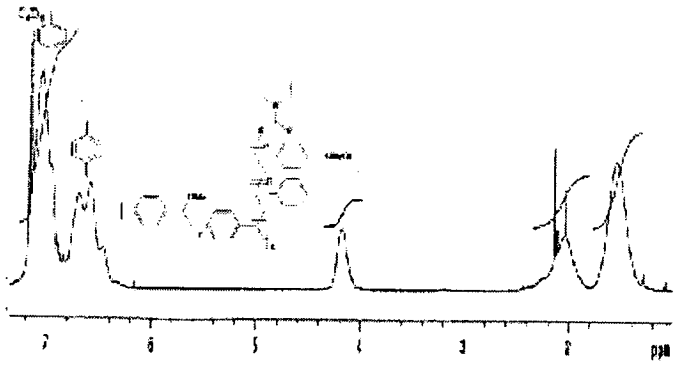

Figure 5 ^{1}H-NMR spectrum of the product obtained from graft copolymerization of styrene and chloromethylstyrene (CMS) with PPX macroiniferter. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

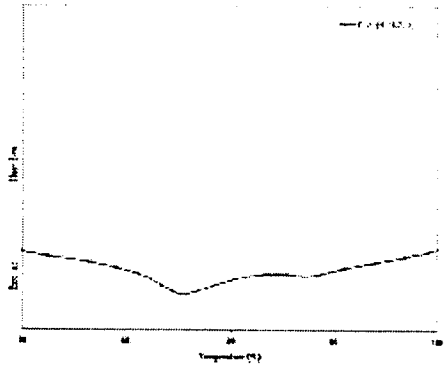

Figure 6 DSC thermogram of the product obtained from graft copolymerization of styrene and chloromethylstyrene (CMS) with PPX macroiniferter.

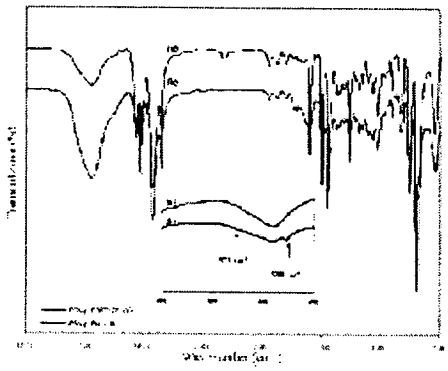

Figure 7 FTIR spectra of the PPX-g-P(SCMS) graft copolymer before and after reacting with the fullerene via an ATRA.

aforementioned monomers through a decomposition of this group, which is considered to be a capping agent. In addition, the spectrum shows a peak at 4.2 ppm which could be attributed to a signal of the methine proton adjacent to the methoxy groups [—HC—OCH_3] being overlapped with that of the methylene proton from the benzyl chloride group (—CH_2—Cl). There are also some new peaks occurring at about 7.2 ppm and 6.6 ppm. The former is ascribable to the protons in aromatic rings of polystyrene overlaps with that associated with the PPX backbone, whereas the latter peak represents the signal from protons in the aromatic ring of PCMS repeating units. No further attempts were made to determine the copolymer composition in the P(SCMS) grafting chains, since the broad peak at about 7.1–7.2 ppm are overlapping.

Other indirect evidence supporting the formation of graft copolymer can be seen from a DSC thermogram of the product (Fig. 6). There are two endothermic transitions occurring at the onset temperatures of 52°C and 81°C. These can be ascribed to the glass transition temperatures of the polyphenylene xylylene (PPX) backbone and the P(SCMS), grafting chains, respectively. The aforementioned results suggest the product is not a random copolymer. In addition, it is worth remembering that this product has already been purified by using selective solvents and thus it is unlikely that the product is a mixture or blend of PPX and P(SCMS) polymers.

Atom transfer radical addition with fullerene

Finally, attempts were made to attach fullerene to the graft copolymer molecules via the chlorine atoms of the PCMS repeating units, using an ATRA technique. Figure 7 shows FTIR spectra of the graft copolymer before and after reacting it with the fullerene. The spectrum shows two new weak transmission bands at 528 cm^{-1} and 577 cm^{-1}, which represent the characteristic of the fullerene-bonded polymers.[18] In addition, UV–vis absorption spectra of the product from ATRA (Fig. 8) shows a strong absorption peak at 340 nm which is attributed to the fullerene covalently bonded to the P(SCMS) grafting chain.

Figure 9 shows overlaid TGA thermograms of the PPX-g-P(SCMS) graft copolymer both before and after carrying out an ATRA with the fullerene. From a thermogram of the polymer before reaction, three transitions can be observed. The first transition

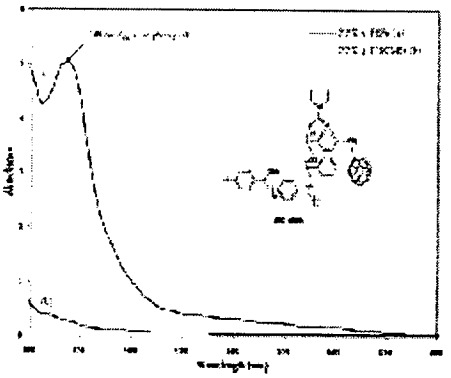

Figure 8 UV–visible absorption spectra of the PPX-g-P(SCMS) graft copolymer before and after reacting with fullerene via an ATRA.

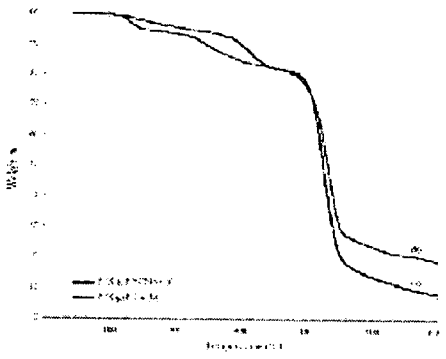

Figure 9 Overlaid TGA thermograms of the PPX-*g*-PSCMS) graft copolymer before and after reacting with fullerene via an ATRA.

occurred at 120°C involving the loss of about 8% by weight of the sample. This could be related to a decomposition of the DTC fragment present at the end of the grafting chains.[16] Next, there was a second weight loss (12%) at 300°C which can be attributed to a decomposition of the PPX chain.[17,18] Third, there was ~ 70% weight loss occurred at 420°C which might be due to a decomposition of the PS and PCMS repeating units. Beyond this temperature, the sample weight tends to reach a plateau and the remaining weight could be ascribed to the residual solid.

Similarly, TGA thermogram of the PPX-*g*-PSFu, which is a product obtained from the ATRA, shows three weight loss transitions. However, it is noteworthy that the residual weight of the product was 10% greater than that of the starting graft copolymer before ATRA. The difference is attributed to the presence of the fullerene groups, chemically bonded to the grafting chain.[3,19,23] The aforementioned result implies that the C60 content in the donor–acceptor graft copolymer is ~ 10% by weight.

CONCLUSION

In this study, it can be concluded on the basis of the results from FTIR, ^{1}H-NMR, DSC, and TGA that the preparation of PPX-*g*-PSFu graft copolymer using the suggested synthetic route is possible. This route comprise three main reaction mechanisms namely the modified Wessling route, an iniferter polymerization and the ATRA, which are practical and do not involve any severe or stringent reaction conditions. It was also found that, in the graft copolymerization step, yield and grafting efficiency of the product increased with the monomers concentration and the amount of DTC used.

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Elsevier Editorial System(tm) for Thin Solid Films
Manuscript Draft

Manuscript Number:

Title: Synthesis of fullerene functionalized polystyrene (PSFu) and morphology of fullerene based materials blended with P3HT.

Article Type: Full Length

Section/Category: A. Synthesis and Characterization

Keywords: Conjugating Polymer; Fullerene; Polystyrene; Spin Coating.

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Abstract: Fullerene functionalized polystyrene (PSFu) with a variety of fullerene content was prepared via an atom transfer radical addition (ATRA) mechanism, using various types of synthesized poly(styrene-chloromethylstyrene) random copolymer, [PS-r-PCMS] as a precursor. The chemical structure, molecular weight, thermal properties and HOMO-LUMO energy levels of the above prepared polymers were characterized using various techniques including: 1H-NMR, FTIR, UV/Vis, GPC, TGA, and Cyclic voltammetry (CV), respectively. The best PSFu was selected on the basis of its solubility and band gap energy for further blending with regio-regular polyhexylthiophene (rr-P3HT). Morphology of the blends with a variety of mixing ratios was investigated by optical microscopy and atomic force microscopy. Micrograph of the above various blends were also compared with those of the blends containing P3HT and fullerene. It was found that the use of PSFu as a replacement of fullerene lead to the blend with a finer dispersed particle morphology. However, when a regio-random grade P3HT (rd-P3HT) was used as a replacement of rr-P3HT, the opposite effect was observed. The above changes and discrepancies were discussed in the light of solvent effects and some changes in morphology of various blend with type and content of fullerene based materials.

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To whom it may concern,

Please find the attached files containing my recent manuscript entitle "Synthesis of fullerene functionalized polystyrene (PSFu) and morphology of fullerene based materials blended with P3HT" to be submitted to the Thin Solid Films Journal. I hope that the above manuscript would be suitable for publication in your Journal. However, if there is any enquiry regarding the publication of this paper, please do not hesitate to contact me. Thank you in advance for your support and I will look forward to hearing from you soon.

Best Regards,
Dr. Jatuphorn Wootthikanokkhan

Synthesis of fullerene functionalized polystyrene (PSFu) and morphology of fullerene based materials blended with P3HT.

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ABSTRACT

Fullerene functionalized polystyrene (PSFu) with a variety of fullerene content was prepared via an atom transfer radical addition (ATRA) mechanism, using various types of synthesized poly(styrene-chloromethylstyrene) random copolymer, [PS-r-PCMS] as a precursor. The chemical structure, molecular weight, thermal properties and HOMO-LUMO energy levels of the above prepared polymers were characterized using various techniques including: ^{1}H-NMR, FTIR, UV/Vis, GPC, TGA, and Cyclic voltammetry (CV), respectively. The best PSFu was selected on the basis of its solubility and band gap energy for further blending with regio-regular polyhexylthiophene (rr-P3HT). Morphology of the blends with a variety of mixing ratios was investigated by optical microscopy and atomic force microscopy. Micrograph of the above various blends were also compared with those of the blends containing P3HT and fullerene. It was found that the use of PSFu as a replacement of fullerene lead to the blend with a finer dispersed particle morphology. However, when a regio-random grade P3HT (*rd*-P3HT) was used as a replacement of *rr*-P3HT, the opposite effect was observed. The above changes and discrepancies were discussed in the light of solvent effects and some changes in morphology of various blend with type and content of fullerene based materials.

Key words: Blending; Conjugated Polymer; Fullerene; Polystyrene; Spin Coating

1 Introduction

Photovoltaic [PV] devices based on semiconducting polymers have gained immense interest over the past few years, partly stimulated by the fact that the production process of the polymer-based PV cell is relatively simple, inexpensive and less polluting. In addition, by tailor-making some chemical structures of the polymeric materials, the flexibility and photo-electric properties of the material can be tuned. Furthermore, it is also possible to enlarge the scale of production by adapting some existing industrial processes such as ink-jet or doctor blade screen printing.

Among various types of semiconducting polymers, poly(3-hexylthiophene) [P3HT] has been widely studied and developed because of its good solubility, chemical stability and excellent electronic properties. Of note, the above polymer is normally available in two different types, depending on its regio-regularity structure. The first is a regio-random poly(hexyl thiophene) [*rd*-P3HT] which contains a relatively low content of head-to-tail linkages. The second type is a regio-regular poly(hexylthiophene) [*rr*-P3HT] which contains more than 99% head-to-tail linkages. The latter type is also referred to as an electronic grade polymer and is widely used in solar cell applications due to its lower band gap energy.

Upon exposure of the semiconducting polymer to sunlight, the polymer will be photo-doped and some tightly-bound electron-hole pairs (also known as *excitons*) will be created. The excitons may recombine again unless they can diffuse into an interfacial area between the polymer and the electrodes, where some differences in work function exist. To minimize exciton recombination and to enhance the power conversion efficiency [PCE] of the polymer solar cell, it is common to blend the semiconducting polymer with some electron acceptor materials such as fullerene (C_{60}) and its derivatives. As a result, an interface between the donor material (the polymer) and the acceptor material will be created. Across this donor-acceptor interface, a large HOMO-LUMO energy level offset will produce a large enough internal electric field gradient, capable of splitting the excitons into free electrons and holes. This kind of PV cells containing a blend of donor-acceptor materials is also known as a bulk hetero-junction [BHJ] solar cell.

It should be noted that one of the main problems inhibiting the development of this type of BHJ cell toward a higher PCE includes the limited solubility of the fullerene. Some aggregation of the material has been observed in many cases [1-2] when the amount of C_{60} used in the BHJ cell is in excess of a certain limit. By using a derivative form of the fullerene such as PCBM, the solubility of the material and PCE of the related cell improves at the expense of the material cost. This improvement is ascribed in relation to a steric effect provided by the presence of an alkyl side group on the fullerene. In this study, attempts were made to attach the fullerene onto a polymeric

molecule, namely polystyrene. In this regard, it was assumed that the fullerene groups would be distributed along the polymer chain and thus some aggregation of the acceptor material be reduced and/or delayed.

In this regard, it is necessary to synthesize the fullerene grafted polystyrene (PSFu) with a variety of molecular architecture. This may be achieved by carrying out a co-polymerization of styrene and chloromethylstyrene. The obtained copolymer which contain C-Cl bonds in the poly(chloro methylstyrene) repeating units can be further functionalized by reacting it with the fullerene via an Atom Transfer Radical Addition [ATRA] mechanism.

A survey of the literature reveals that synthesis of the above PSFu has not been directly reported, however, some work on the preparation of donor-acceptor copolymers containing the PSFu has been found. For example, Chen *et al.*,[3] prepared P3HT-*graft*-PSFu copolymer using a multiple reaction mechanism, including a nitroxide mediated radical polymerization [NMRP] and atom transfer radical addition [ATRA] technique. It was found that the presence of grafting chains did not affect the electronic state of the conjugated polymer in solution. The morphology of the graft copolymer precursor [P3HT-*graft*-P(SCSM)] significantly changed from a bi-continuous morphology to a dispersed particle morphology after reacting it with C_{60}. It was also suggested that relationships between the graft copolymer structure (graft length, graft density, morphology) and opto-electrical properties of the semiconducting copolymer should be explored. Similarly, van der Veen et al. [4] synthesized DEH-PPV-*block*-PSFu copolymers using NMRP and ATRA techniques. In that study, the method used to introduce C_{60} into the polymer chains was improved by circumventing the formation of radicals through the utilization of azide intermediates.

In our present study, PSFu with a variety of fullerene contents were synthesized by using iniferter polymerization and ATRA (Fig. 1).The best PSFu was selected on the basis of its band gap energy for further blending with *rr*-P3HT and/or *rd*-P3HT. The aim of this work is to examine morphology of the P3HT/PSFu blends and compare to that of P3HT/C_{60} blends. In addition, effect of P3HT with different regio-regularity on morphology of the related blends is also of our interested.

2 Experimental

2.1 Materials

Copper, copper bromide, and bipyridine were supplied from Fluka Co. Ltd. (Steinheim, Germany). Fullerene (98%) was supplied from Sigma-Aldrich Co. Ltd. (Steinheim, Germany). Methanol and toluene (analytical grade) were obtained from Fisher Chemicals Co. Ltd. (Loughborough, UK). Nitrogen gas (99.99% was obtained from Praxair

Co. Ltd. (Thailand). All of the above chemicals were used as received. Tetraethylthiuram disulfide (TD) was supplied from Fluka (Steinheim, Germany) and was purified by re-crystallization prior to use.

Styrene (99%, GC grade from Fluka Co. Ltd. Steinheim, Germany) was freed from inhibitors by passing through an alumina column. Chloromethylstyrene (CMS) (90%, GC grade from Fluka Co. Ltd., Steinheim, Germany) was purified by extracting with sodium hydroxide solution, followed by washing with de-ionized water and then dried with sodium sulfate anhydrous.

Poly(hexyl thiophene) [P3HT] (both regio-random grade and regio-regular electronic grade) were purchased from Sigma-Aldrich Co. Ltd. Fullerene (C_{60}) (purum grade) was supplied from Fluka Co. Ltd. A platinum rod (Pt), used as a counter electrode, $Ag/AgNO_3$ used as a reference electrode and glassy carbon electrode (BSTR10A) used as a working, were obtained from Auto Lab. Ammonium tetrafluoroborate [Bu_4NBF_4] used as an electrolyte was supplied from Aldrich Co. Ltd.

2.2 Synthesis of PSFu.

In this experimental part, poly(styrene-chloromethyl styrene) random copolymer (PS-r-PCMS) was firstly synthesized via a controlled free radical polymerization technique using tetraethylthiuram disulfide (TD) as an iniferter. More details concerning the mechanism of the iniferter polymerization can be found elsewhere [5]. Experimentally, 0.016 g of TD (0.75 mmol) was added into a solution of purified styrene (0.045 mol dissolved in 30 ml of toluene) and chloromethylstyrene (0.0113 mol). The monomer solution was purged with nitrogen and sealed. After that, the reaction flask was exposed to UV radiation for 4 h. After a given time, the content in the reaction flask was precipitated into a large amount of methanol and then dried in a vacuum oven at 60 °C until reaching a constant weight.

2.3 Preparation of fullerene functionalized graft copolymers

Next, the PS-r-PCMS was reacted with fullerene via an atom transfer radical addition (ARTA) reaction in order to obtain PSFu. This was commenced by mixing fullerene (0.013g), bipyridine (0.03g), toluene (15 ml), and 0.1g of PS-r-PCMS in a flask. The solution was purged with nitrogen for 10 min and then sealed with paraffin film and kept for a further ATRA reaction. After that, Cu (0.013g) and CuBr (0.0086g) were added To a 250 ml three-necked round bottom flask. The flask was closed with a rubber septum and sealed before undergoing nitrogen purging and vacuum pumping for 5 cycles. Then, the above prepared polymer solution was introduced into the reaction flask by injection through the rubber septum, using a syringe. The mixture was then refluxed at 80 °C in an oil bath for 3 h.

After cooling to room temperature, the reaction was filtrated and precipitated into a large amount of 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 some residual fullerene (C_{60}) from the product. UV/visible spectroscopy was used to examine the presence of an absorption peak of the free fullerene in the leached solvent. 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).

2.4 Characterizations

2.4.1 Spectroscopy analysis

A Fourier Transform Infrared Spectroscopy (FTIR) technique was used to monitor changes in chemical structure of various products after chemical reaction. The FTIR spectrum was recorded using a Bruker FTIR (Equinox 55). The sample was prepared in the form of a KBr pellet, and the spectrum was scanned over wavenumbers ranging between 600 cm^{-1} and 4000 cm^{-1}. In addition, the chemical structures of some products were characterized using ^{1}H-NMR spectroscopy. Typically, a graft copolymer sample was dissolved in deuterated benzene (C_6D_6) and then the spectrum was recorded in a Bruker instrument (Advance DPX400), using TMS as a reference.

UV-Visible absorption spectra of various samples were recorded on a Shimadzu UV-3100 spectrophotometer, over wavelengths ranging between 300 and 700 nm. Sample was prepared by dissolving it in THF and the experiment was carried out at room temperature. In addition, to determine optical energy band gap of some samples, the following equation was used;

$$E\,(eV) = hc/\lambda \qquad (1)$$

Where;

h = Planck Constant, C= Speed of light, and λ – Onset of the UV/Vis absorption peak

2.4.2 Elemental analyses

Elemental analysis of PS-r-PCMS copolymers was carried out by using X-ray fluorescence (WD-XRF) spectrometer (Bruker, Madison, WI, Axis S4).

2.4.3 Molecular weight analysis

The molecular weight of the product was determined by using a gel permeation chromatography technique, using a Water E2695 instrument equipped with RI detector (Viscotek model 3580). THF was used as an eluent and 100 µL of the sample solution [2 mg/ml in THF] was prepared and filtered with a nylon 66 membrane before injection. The solution was passed through PL gel 10 µm mixed B columns, at a flow rate of 1.0 ml/min. The obtained GPC chromatogram was then translated into a molecular weight distribution [MWD] curve via the use of a polystyrene narrow molecular weight calibration curve. Finally, the average molecular weight and polydispersity indexes were determined using standard equations.

2.4.4 Thermal characterization

The thermal stability of the polymers were investigated using a thermal gravimetric analysis (TGA) technique. The TGA experiment was carried out with a Netzsch (STA 409 C/CD) instrument. About 10 mg of the sample was used and the TGA experiment was scanned over temperatures ranging between 25°C and 600 °C under nitrogen atmosphere, at a heating rate of 10 °C/min.

2.4.5 Morphological characterization.

For an optical microscope analysis, a solution of various blends (*rr*-P3HT/C_{60}, *rr*-P3HT/PSFu, *rd*-P3HT/C_{60} and *rd*-P3HT/PSFu) with a variety weight ratios of the fullerene based materials (20, 60, 80 and 100 pph) was spin-coated onto the glass slide (1,000 rpm for 60 sec), at room temperature to obtained 100 nm thick film. Of note, the solvents used for dissolving the blends containing rr-P3HT and rd-P3HT are dichlorobenzene and toluene/THF (60/40 %v/v), respectively. After that, the solvent was evaporated and removed by drying the film at 80 °C for 1 hr, followed by annealing at room temperature overnight.

The morphology of the various blends were also examined by using an Atomic Force Microscope (Digital instrument), scanning probe microscope (Nano scope III). Samples were prepared by spin coating on a glass slide. An AFM image was obtained using a phase image- tapping mode.

2.4.6 Cyclic Voltammetry.

Cyclic voltammetry was performed with a Potentiostat (Auto Lab 302N) machine, using acetonitrile solution with 0.1 M tetrabutylammonium hexafluoroborate [Bu_4NBF_4] as a supporting electrolyte. Platinum wire was used as a counter electrode, whereas glassy carbon and $Ag/AgNO_3$ were used as a working electrode and reference electrode,

respectively. The films of the polymers were coated onto the glassy carbon working electrode. The solution was de-aerated by bubbling with nitrogen prior to carrying out the experiment. The CV experiments have been repeated for three times for each sample.

From the obtained cyclic voltammogram, the onset oxidation potential and the onset reduction potential were determined. Subsequently, the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}) and band gap energy of the semiconducting materials were calculated using the following equations [6].

$$E_{HOMO}\ (eV) = -(E_{ox} + 4.39) \quad (2)$$

$$\text{Band Gap Energy (eV)} = -(E_{HOMO} - E_{LUMO}) \quad (3)$$

3. Results and discussion

3.1 Preparation of the poly(styrene-chloromethyl styrene) copolymer.

Fig. 3 shows ^{1}H-NMR spectra of product obtained from copolymerization of styrene and chloromethylstyrene (CMS) with TD iniferter. From the spectrum, a chemical shift of the benzyl chloride protons (CH_2 of CMS repeating units) occurs at 4.2 ppm. The NMR peak at 7.2 ppm can be ascribed to the *metha-* and *para*-aromatic protons of both PS and PCMS repeating units whereas the peak over the chemical shift ranged between 6.5 and 6.8 ppm is attributed to the *ortho*-protons in the aromatic rings. The PCMS composition was evaluated from the integration of benzyl chloride protons (at 4.2 ppm) and comparison with the sum of the integral for all *ortho-* aromatic protons (6.5-6.8 ppm). The above calculation has also been used by Stancik *et al.* in a related study [7].

In addition, XRF experiment was carried out to determine Cl content (representing the PCMS repeating units) in the various copolymer molecules. The results are summarized in Table 1. Similarly, percentage Cl content tends to increase with the CMS monomer feed ratio, except that for the copolymer No.4. In this case, the discrepancy could be attributed to some factors such as a relatively low molecular weight of the copolymer and the fact that the XRF is a kind of surface analysis. It might be possible that composition on the specific surface does not represent that of the whole bulk material. In addition, the present of sulfur can be used as an evidence of thiocarbamate group or capping agent at the chain end.

3.2 Preparation of the fullerene grafted polystyrene (PSFu).

Fig. 4 shows overlaid FTIR spectra of PS-r-PCMS copolymers both before and after reacting it with fullerene via an ATRA mechanism. An FTIR spectrum of the product shows two new weak transmission bands at 528 and 577 cm^{-1}, which represent the characteristic of the fullerene-bonded polymers. The similar FTIR spectral changes have been also reported by Wu *et al.* in a study on a synthesis of C_{60} end-functionalized four-armed PS [8]. In addition, Fig. 5 shows UV-Vis absorption spectra of PS-r-PCMS copolymer (No.1) and the corresponding fullerene functionalized copolymer [PSFu]. The spectrum of the PS-r-PCMS copolymer shows a small absorption peak at a wavelength of about 320 nm, which is attributed to the thiocarbamate group. In addition, the spectrum of the PSFu shows a strong absorption peak at about 335 nm, which could be ascribed to the fullerene groups covalently bonding with the copolymer molecules.

Fig. 6 shows overlaid TGA thermograms of different types of PSFu copolymers obtained by reacting fullerene with various types of the above PS-r-PCMS copolymers. The TGA thermogram of PSFu copolymer No. 3, for example, indicates almost 20% weight loss over temperatures ranging between 240 and 400 °C. This weight loss could be due to the decomposition of the polystyrene repeating units. Next, there is a second transition (40% weight loss) occurring over temperatures ranging between 400 and 600 °C and that could be related to the decomposition of poly(chloromethylstyrene) [PCMS] repeating units. Finally, the amount of residue left at 600 °C and the above temperature represent the weight percentage of fullerene attached to the polymer chains. The residue was thought not to be un-reacted fullerene given the fact that the synthesized polymer has been purified and freed from the un-reacted fullerene by washing with hexane. Similarly TGA analyses of other types of PSFu were also carried out and the fullerene content in each PSFu polymer is summarized in Table 1.

At this stage, it is worth mentioning that different grades of the prepared PSFu exhibit different solubility. For example, the PSFu prepared using PS-r-PCMS copolymer No. 4 was not completely soluble in many common solvents. However, the PSFu copolymers prepared using PS-r-PCMS copolymers No. 1-3 were found to be well soluble in THF/Toluene mixture (60/40 %v/v), which was used as the co-solvent for fabricating the polymer solar cells in this study. The above phenomena might be related to the fact that each PSFu copolymer contains different PCMS compositions and different percentages of the fullerene group. In this regard, it could be possible that the higher the fullerene content, the greater the aggregation of the fullerene groups. In addition, it is conceivable that the pendant fullerene groups act as a cross-linker, attaching two polymer chains together. Similar behaviors were observed by Chen *et al.* [3] in a study on a synthesis of P3HT-*graft*-PSFu copolymers and by Stalmach *et al.* [9] in a study on the synthesis of PPV-PSFu diblock copolymers. According to the above literature, insolubility of some

copolymers was observed and the result was discussed in the light of crosslinking of the fullerene groups. In relation to this study, no further attempts were made to fabricate and test this insoluble polymer product (copolymer No.4).

3.3 HOMO-LUMO energy levels and band gap energy of PSFu

Table 2 summarizes the HOMO-LUMO energy levels and band gaps energy of various PSFu polymers and related materials. It can be seen that HOMO and LUMO energy levels of all the PSFu are lower than those of the P3HT. It was also found that the band gap energy of these polymers was comparable to that of the pure fullerene (C_{60}) determined by using the same technique. The above results indicate that it is possible to explore the use of these PSFu materials as an acceptor phase in a BHJ cell. Notably, the band gap energy of these PSFu polymers ranges between 2.81 and 2.95 eV, depending on the copolymer's composition and the actual C_{60} content. It seems that the band gap energy of PSFu copolymers tends to decrease with increasing C_{60} content. In this regard, PSFu copolymer No. 3, which has the lowest band gap energy, was selected for further study.

3.4 Morphology of the blends.

Fig. 7 shows optical micrographs of *rd*-P3HT blended with different types and amount of fullerene base materials. A larger size of the fullerene (dark phase) can be clearly seen when the C_{60} was used (Fig. 7(a)- 7(b)). This indicates some aggregation of the material. On the other hand, optical micrographs of the blend containing PSFu show a smaller particle size with a better distribution of the dark phase, which represents the PSFu [Fig. 7(c)-7(d)].

For a comparison purpose, optical micrographs of various *rr*-P3HT blended with different types and amount of fullerene based materials were examined (Fig. 8). The dark phase representing the fullerene is dispersed within the continuous polymer matrix phase. By increasing the content of fullerene the size and area of the fullerene phase increased, suggesting that greater fullerene aggregation had occurred (Figs. 8 (a)-8 (c)). On the other hand, Figs. 8 (d)-8 (f) indicate that PSFu are poorly miscible with the *rr*-P3HT in this case. The bright phase, representing PSFu, obviously increased with the content of PSFu.

The different morphology of the blend containing different type of P3HT might be partly attributed to a solvent effect. This is due to the fact that the solubility of *rd*-P3HT and *rr*-P3HT is different. In the former case (*rd*-P3HT system), a co-solvent comprising THF/toluene mixture (60/40 % v/v) was used. By contrast, dichlorobenzene was used to dissolve and prepare the blend containing *rr*-P3HT. In this regard, it seems that the THF/toluene mixture, which is a good co-solvent for *rd*-P3HT, also favors the solubility of PSFu. Consequently, the blends with

finer and well dispersed phase separated morphology may be obtained. On the other hand, dichlorobenzene which is a good solvent of electronic grade *rr*-P3HT also promotes a better solubility and prolongs some aggregation of the C_{60}.

Last but not least, some changes in morphology of the P3HT/PSFu blends as a function of PSFu content are worth considering. Fig. 9 shows AFM micrographs (phase image mode) of the various blends containing different type of P3HT. It can be seen that the morphology of the *rr*-P3HT/PSFu blends containing 20 pph of the PSFu are of dispersed particle morphology type. A nano-scale PSFu phase was dispersed within the P3HT continuous matrix phase (Fig.9 (a)). By increasing PSFu content, the size of the bright domains, which represent the PSFu phase, increased. At 60 pph of the PSFu content, the gross phase separated morphology was obtained (Fig. 9 (b)). By further increasing the PSFu content from 60 pph to 100 pph, the morphology of the blend changed significantly, from the disperse particle morphology into a co-continuous morphology (Fig. 9 (b)-9 (d)).

On the contrary, Fig. 10 show that PSFu phase in *rd*-P3HT/PSFu blend, (Fig. 10 (a)-(b)) was finely dispersed in the matrix. Phase size of the PSFu tends to increase with the PSFu content but that was not as large as that in the *rr*-P3HT/PSFU system (Fig. 9). Results from AFM are in a good agreement with that from optical micrograph and re-affirm our above discussion.

4 Conclusions

Attempts have been made to prepare fullerene functionalized polymer, namely PSFu. Results from spectroscopy techniques, and TGA confirmed that the above PSFu copolymers, with a variety of composition and fullerene content, were successfully synthesized. By blending the fullerene based materials with regio-random grade P3HT, It was found that aggregation of fullerene phase decreased when PSFu was used as a replacement of C_{60}. This was not the case when a regio-regular grade P3HT was used as a donor material. The differences can be ascribed in the light of solvent effects.

Acknowledgement The authors are sincerely grateful to the Thailand Research Fund (TRF) and the Commission of Higher Education, Ministry of Education for providing research grant (Grant number: RMU 5180049) to support this work. Miss Seeponkai would also like to thank Thailand Graduate Institute of Science and Technology (TGIST; TG-33-20-52-010D) and the National Science and Technology Development Center (NSTDA) for providing a scholarship to support her Ph.D. study.

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