Synthesis of Graft Copolymers Based on Polyphenylene Xylylene and Fullerene Grafted Polystyrene

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ABSTRACT: Graft copolymers containing poly(phenylene xylyene) (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. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 433–440, 2010

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

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 con-verted 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 (0.98M) 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 (0.4M). 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
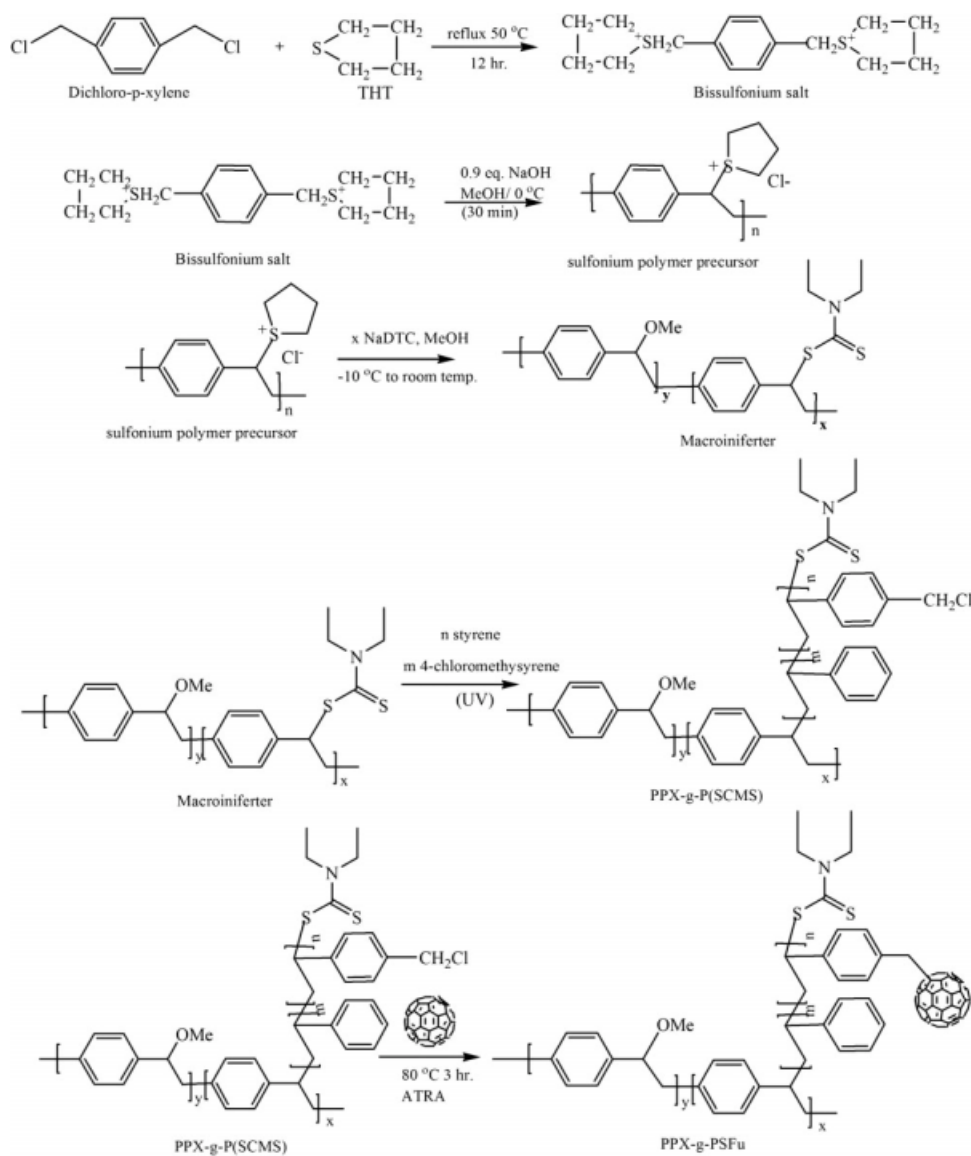
Figure 1 The proposed synthetic route for preparing the PPX-*g*-PSFu graft copolymer.

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 (v) 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, (v)] 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.
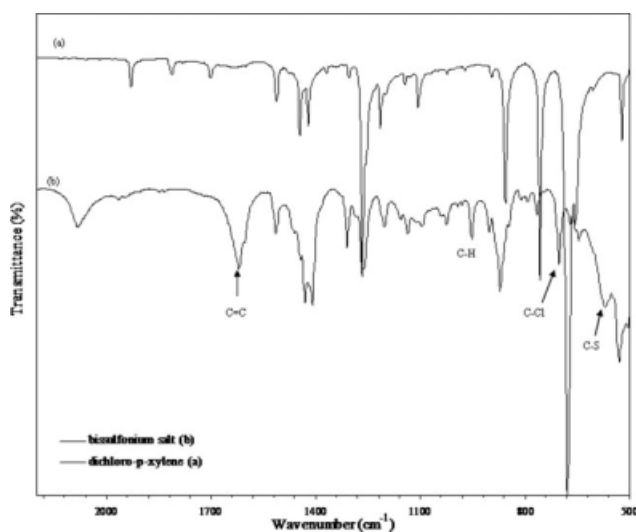
Figure 2 Overlaid FTIR spectra of dichloro-*p*-xylene and bis-sulfonium salt monomer.

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

Modification of the polymer precursor into macroiniferter

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 (v) and that of the C=S (v), 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 unavoid-
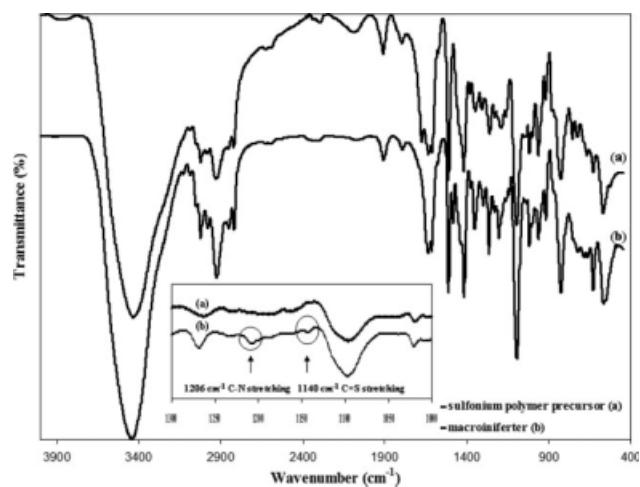
ably limited amount of elimination.[21] However, from our research experience, we found that this side reaction can be minimized by maintaining a constant reaction temperature and gradually adding of the NaOH solution during the polymerization. Of note, we have carried out a heat treatment for this polymer 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—OCH₃), whereas the peak at 3.19 ppm can be related to a signal from the protons in methoxy groups (OCH₃). The NMR peak at 3.7 ppm could be attributed to a proton adjacent
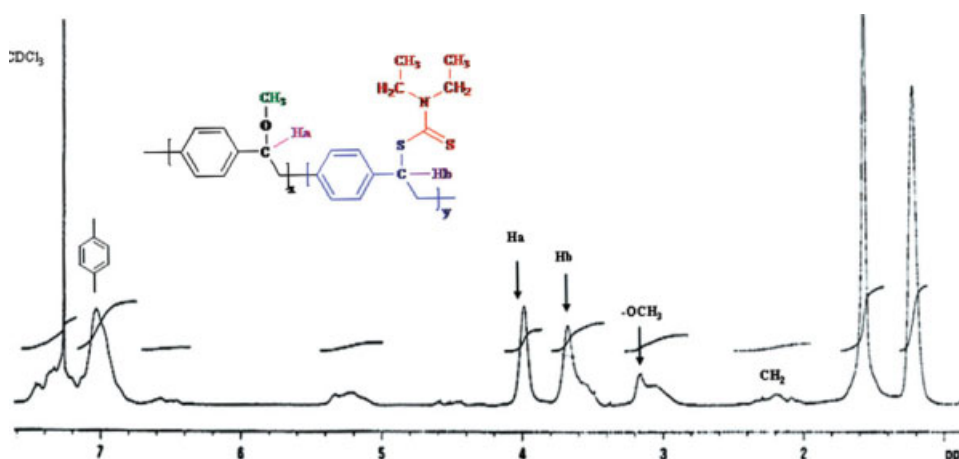

Figure 4 ^{1}H-NMR spectrum of the sulfonium polymer precursor modified with NaDTC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 precipita-

tion 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
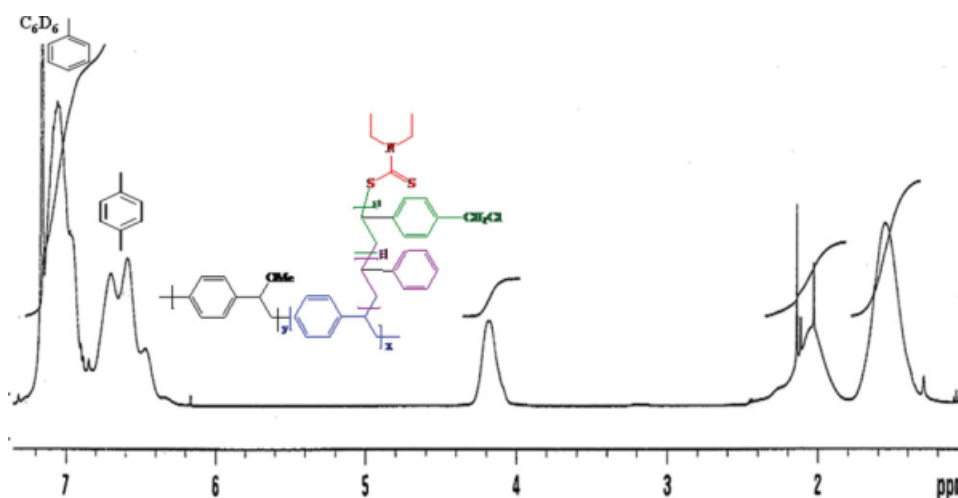

Figure 5 ^{1}H-NMR spectrum of the product obtained from graft copolymerization of styrene and chloromethylstyrene (CMS) with PPX macroiniferter. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
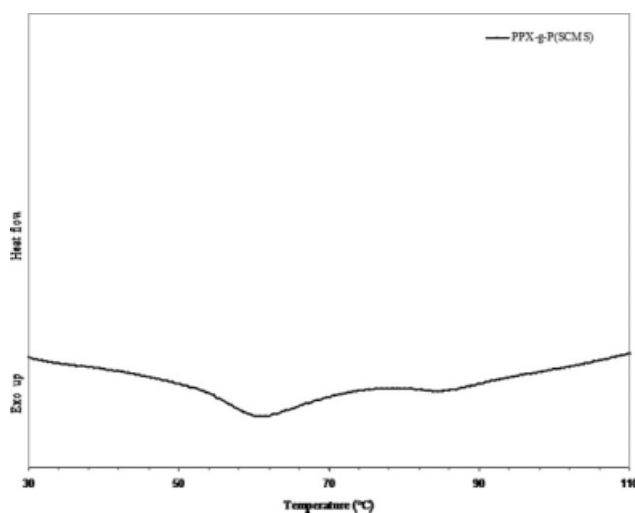
Figure 6 DSC thermogram of the product obtained from graft copolymerization of styrene and chloromethylstyrene (CMS) with PPX macroiniferter.

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
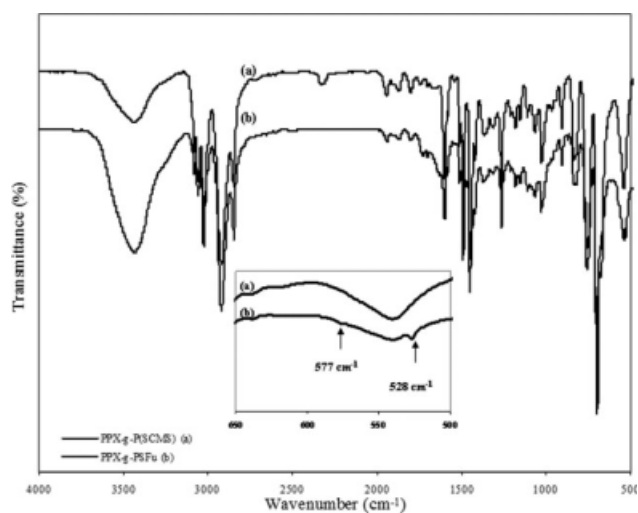
technique. Figure 7 shows FTIR spectra of the graft copolymer before and after reacting it with the fullerene. The spectrum shows two new weak transmission bands at 528 cm^{-1} and 577 cm^{-1}, which represent the characteristic of the fullerene-bonded polymers.[18] In addition, UV–vis absorption spectra 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
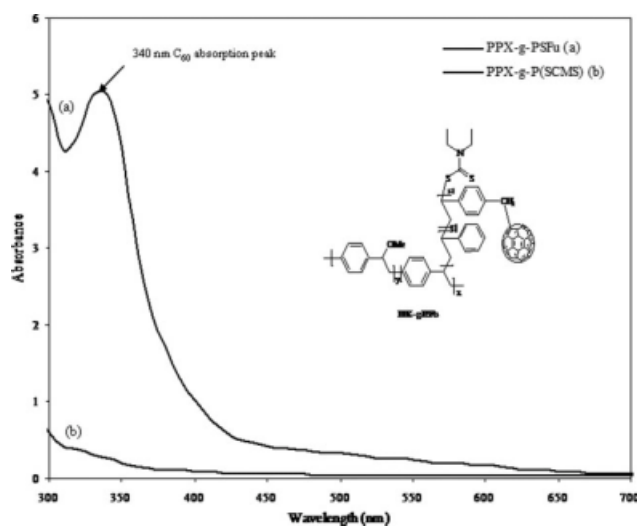

Figure 8 UV–visible absorption spectra of the PPX-*g*-P(SCMS) graft copolymer before and after reacting with fullerene via an ATRA.
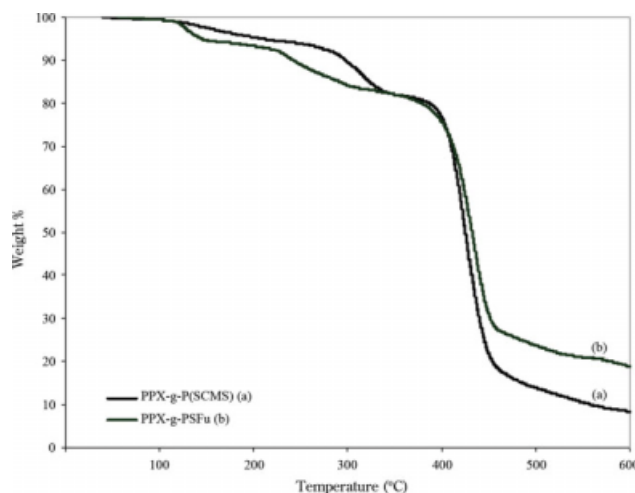
Figure 9 Overlaid TGA thermograms of the PPX-*g*-P(SCMS) graft copolymer before and after reacting with fullerene via an ATRA.

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.[18] 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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