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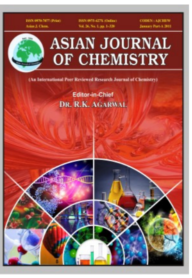

Fabrication of [60] Fullerene Grafted Polymer: Self-Assembly Behavior in Polar Solvents

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In this report, we prepared a new type of [60] fullerene grafted poly(2-bromomethyl)acrylic acid. First step was the free-radical polymerization of 2-(bromomethyl)acrylic acid by using 2,2'-azobisisobutyronitrile. Then a nucleophilic substitution reaction was performed to substitute the bromine atoms present in the polymer with azide groups. Finally, the C_{60} grafted polymer was prepared by the reaction of azido functionalized polymer with C_{60}. Results of Fourier transform infrared spectroscopy and ultraviolet-visible spectroscopy indicated that the C_{60} was chemically bonded to the polymer. The aggregation behavior of the resulting polymer in polar solvents was studied by transmission electron microscopy. The resultant polymer retained both electronic property of the C_{60} moiety and processability property of the polymer.

Keywords: Fullerene, Surface-grafting, 2-(Bromomethyl) acrylic acid, Self-assembly, Free-radical polymerization.

INTRODUCTION

Kroto *et al.*[1] discovered that buckminster fullerene C_{60} has a soccer-ball like structure, which is symmetrical and consists of 12 pentagons and 20 hexagons. This discovery led to an entirely new branch of chemistry. C_{60} has received extensive attention due to its unique chemical and physical properties[2]. The hydrophobic nature of C_{60} and its unique shape render this molecule very interesting for its potential use in superconductors, ferromagnets, lubricants, photoconductors, catalysts, medical materials, *etc.* Despite the discovery of potential applications of fullerenes in biological systems, the insolubility of fullerenes in water and organic solvents has hindered the progress in this field of research. The solubility of fullerenes can be enhanced by functionalizing the fullerenes with hydrophilic compounds, such as alcohols[3], carboxylic acids[4], amines[5], or long-chain hydrophilic polymers[6,7]. These amphiphilic fullerene derivatives self-assemble into nanoscale structures in water, which have a variety of potential applications[8]. Because of the wide range of interesting features of the C_{60} molecule, many C_{60} polymeric derivatives have been prepared in recent years[9-11]. Methodologies used range from free-radical[12], anionic[13] or step-growth[14] polymerization. In addition, functionalized C_{60} can be copolymerized with other monomers[15] or grafted onto polymers[16]. C_{60} has been incorporated into a number of polymers, for example, polystyrene[17] poly(alkyl methacrylate)s[18] poly(N-vinylcarbazole)[19] and poly(ethylene oxide)[20].

To date, monosubstituted fullerenes with well-defined polymers have been synthesized and their solution behaviour examined since these polymers retain the unique fullerene properties and may have potential biological applications. For example, core-shell-like micelles from PMMA-*b*-C_{60} and P*n*BMA-*b*-C_{60} systems in THF[21] and large spherical aggregates from single and two-arm fullerene-containing poly(ethylene oxide)s in THF and aqueous solution[22,23] have been reported. Recently, Zhou *et al.*[24] employed ATRP to synthesize well-defined fullerene-containing polystyrene and poly(methyl methacrylate). Water-soluble C_{60}-containing poly(acrylic acid)(PAA-*b*-C_{60}) synthesized by Yang *et al.*[25] formed core-shell micelles in aqueous solution, which enhanced the photoconductivity of the film. Tam *et al.* synthesized a series of well-defined C_{60}-containing water-soluble polymeric systemsusing ATRP, such as poly(methacrylic acid)-*b*-C_{60} (PMAA-*b*-C_{60}) and poly(2-(dimethylamino)ethyl methacrylate)-*b*-C_{60} (PDMAEMA-*b*-C_{60}), and their self-assembly behaviour in aqueous solution was studied as a function of pH and temperature[26,27]. However, to our best of knowledge there has been no attempt to graft C_{60} onto poly(2-bromomethyl) acrylic acid. In this paper, we report the preparation and self-assembly behaviour of C_{60} grafted poly(2-bromomethyl) acrylic acid.The C_{60} grafted polymer is confirmed by FT-IR and UV-visible. The self-assembly behaviour of C_{60} grafted polymer in polar solvents is studied by TEM.

EXPERIMENTAL

2-(Bromomethyl)acrylic acid (Aldrich), fullerene (C_{60}, TCI), dichloro benzene (Aldrich), N,N'-dimethylformamide (DMF, Aldrich), sodium azide (NaN_3, Merck), tetraethyl-ammonium iodide (TCI) were purchased and used as received. 2,2'-Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized in methanol before use. All other reagents were of analytical grade and used as received.

Synthesis of precursor polymer: In a typical polymerization, a mixture of monomer, 2-(bromomethyl)acrylic acid (1 g) and AIBN (1 wt. % to monomer) in DMF was heated at 60 °C under nitrogen atmosphere. After the reaction was carried out for 8 h, the product was suspended in diethyl ether. The resulting precipitate was isolated and dried under vacuum at 50 °C for 24 h. Then the obtained pure polymer was dissolved in DMF (5 % w/v), and the bromine atoms were allowed to react with 2 equiv amounts of NaN_3 in the presence of a small amount of phase-transfer agent, tetraethyl ammonium iodide. The reaction was carried out at 75 °C for 24 h under nitrogen. The resulting polymer solution was precipitated in diethyl ether. The crude product was washed with water to remove unreacted NaN_3 and other salts. Then it was dried in a vacuum for 24 h.

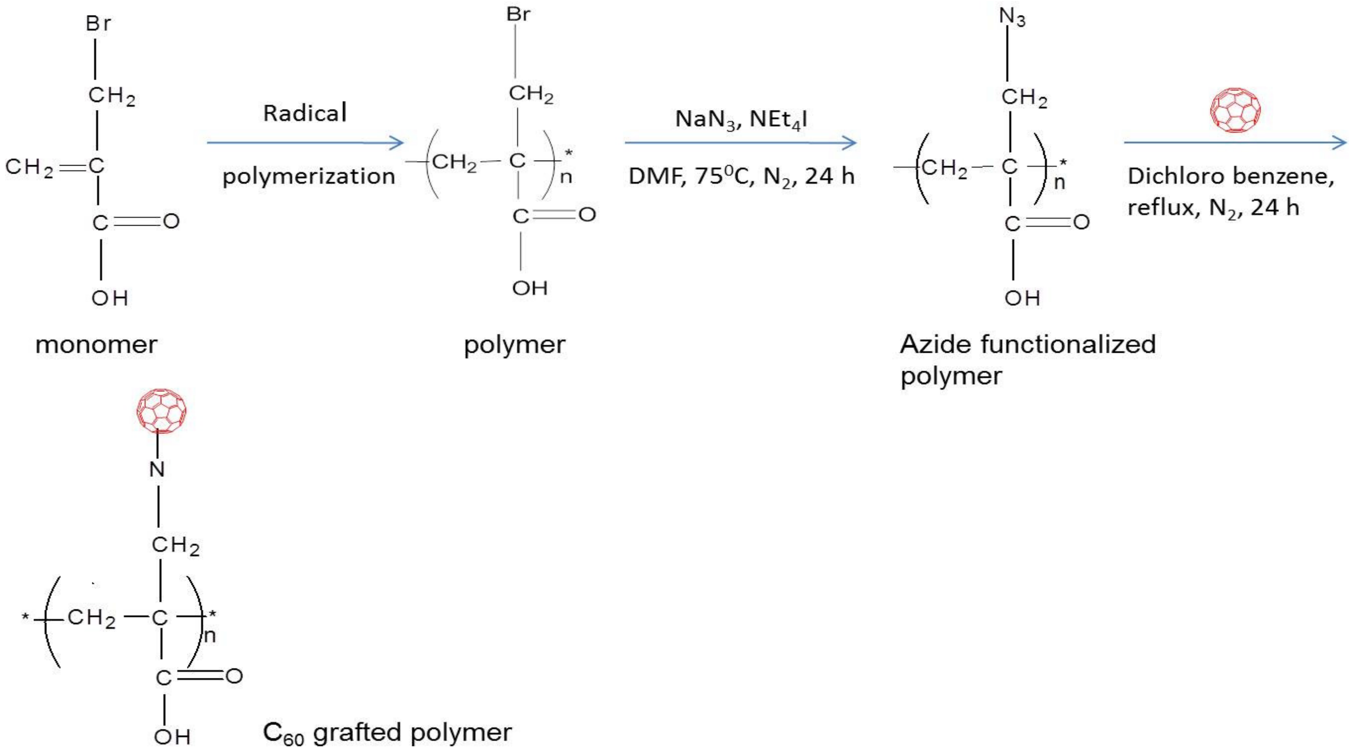
Preparation of fullerene (C_{60}) containing polymer: The precursor polymer was dissolved in DMF and added drop wise to a hot refluxing solution of C_{60} in dichlorobenzene under nitrogen. The reaction was allowed to proceed for another 24 h before most of the solvent was removed under a reduced pressure. The crude product was then isolated by precipitation in diethyl ether and dried in a vacuum for 24 h.

Characterization: Fourier transform infrared spectroscopy (FT-IR) was performed using a BOMEM Hartman and Braun spectrometer. Microscopic images were obtained using a JEOL JEM-2010 transmission electron microscope. Gel permeation chromatography (GPC) was carried out using a HP1100 apparatus with THF as the eluent and polystyrene as standards. Ultraviolet-visible (UV-visible) spectra in the 200-800 nm range were obtained using a Perkin Elmer instrument. Thermogravimetric analysis (TGA) was performed on a Setaram thermal analyzer (TGA-DSC EVO, France) from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

The schematic representation of the synthesis of C_{60} grafted polymer is shown in **Scheme-I**. First, poly(2-bromomethyl)acrylic acid was synthesized by free-radical polymerization. From GPC traces, the number average molecular weight was found to be 22,800 g/mol (Fig. 1). The polymer was then treated with excessive sodium azide in DMF at 75 °C to prepare the azide terminated precursor polymer, poly(2-azidomethyl)acrylic acid. Because of the high concentration of bromine atoms, a high mole ratio of NaN_3/polymer (2/1) was supplied to expedite the reaction and to ensure the complete substitution of bromine atoms with azide group. It is difficult to identify the precursor polymer by ^1H NMR spectrum. Therefore characterization of the product precursor by infrared spectroscopy at ambient temperature is shown in Fig. 2a. The small peak at around 3400 cm^{-1} was due to the stretching vibration of -OH group. The peak at 2936 cm^{-1} was attributed to the stretching vibration of $-CH_2$ group in the polymer, 1710 cm^{-1} indicated the stretching vibration of C=O, 1381 cm^{-1} was attributed to the COO- group and the peak at 2110 cm^{-1} was assigned to the stretching vibration of azide (N=N=N) group. Such spectroscopic evidence coupled with the absence of bromine in the polymer suggested that all the bromine atoms were converted into azide groups[25].

C_{60} grafted polymer has been successfully prepared by refluxing the precursor polymer (azide functionalized polymer) with C_{60}. The C_{60} grafted polymer is a brown powder and is



Scheme 1: Schematic representation of the synthesis of C_{60} grafted polymer

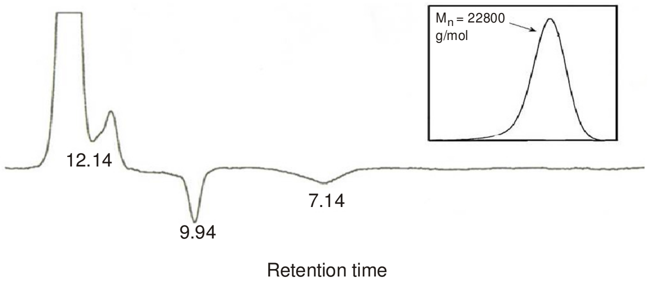


Fig. 1. GPC traces of poly(2-bromomethyl)acrylic acid

insoluble in common organic solvents. But C_{60} can dissolve in hexane. It is sure that the unreacted C_{60} can be separated by the process of precipitation. Characterization of the C_{60} grafted polymer product by infrared spectroscopy clearly showed that the disappearance of peak at 2110 cm^{-1} confirmed that all the azide groups have completely reacted (Fig. 2b).

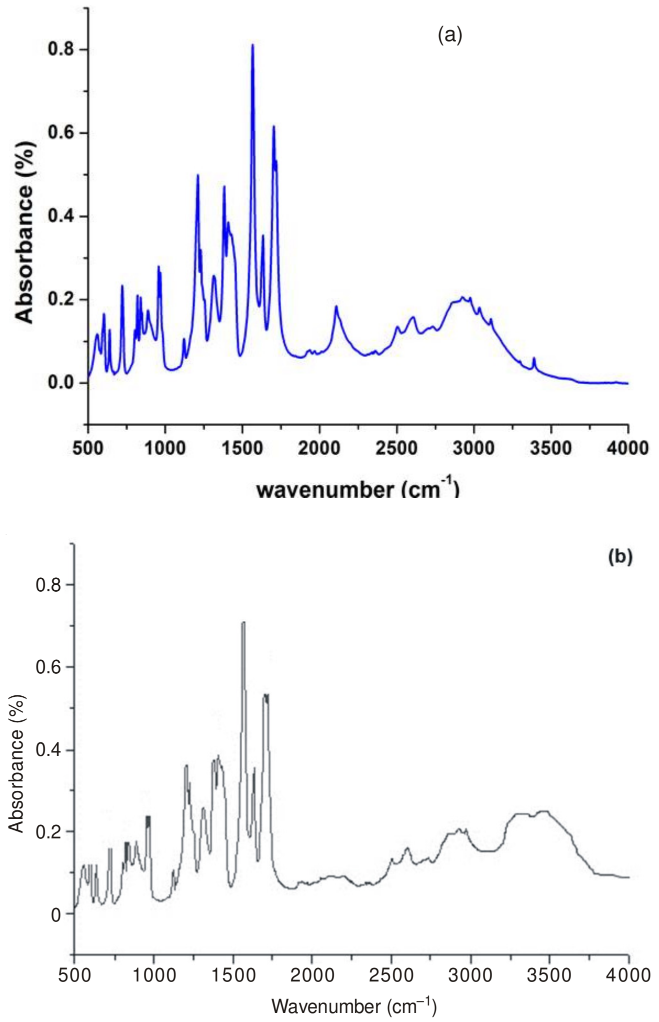


Fig. 2. FT-IR spectra of (a) azide functionalized polymer and (b) C_{60} grafted polymer

Fig. 3 shows the UV-visible spectra of pure C_{60} in cyclohexane and C_{60} grafted polymer in toluene. From the Fig. 3, it is evident that the C_{60} grafted polymer has three characteristic absorption peaks at 214, 255, and 335 nm, and these peaks were identical with the absorption peaks of C_{60}. The C_{60} absorption peak at 335 nm was known to be sensitive to the chemical reaction, and its intensity weakened upon the chemical modification of C_{60} molecules. Hence, the reduction in the absorption peak (335 nm) intensity may be attributed to the conjugation of C_{60} to the polymer[28]. This is also reinforced by the change in the color of the solution from purple (C_{60}) to yellow (C_{60} grafted polymer).

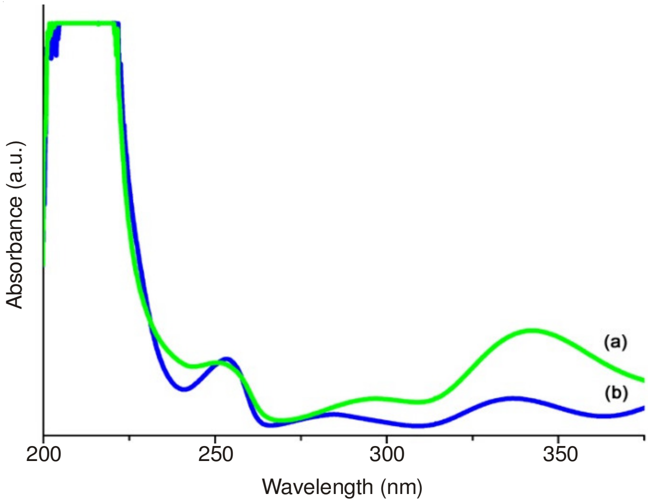


Fig. 3. UV-visible spectra of (a) C_{60} and (b) C_{60} graftedpolymer

The amount of C_{60} grafted to polymer was determined by TGA under nitrogen flow. Fig. 4 shows the TGA curves of C_{60} grafted polymer and pure C_{60}. It can be seen that the polymer showed two main stages of degradation with maximal decomposition rates at around 200-250 and 475-550 °C. The first stage of decomposition was mainly due to the formation of anhydride and release of CO_2, whereas the second stage was attributed to the degradation of anhydride ring structure with evolution of CO_2, CO, alkenes, *etc*. But the pure C_{60} was still stable until 600 °C. The residual mass left at 800 °C was found to be 40 % for the C_{60} grafted polymer.

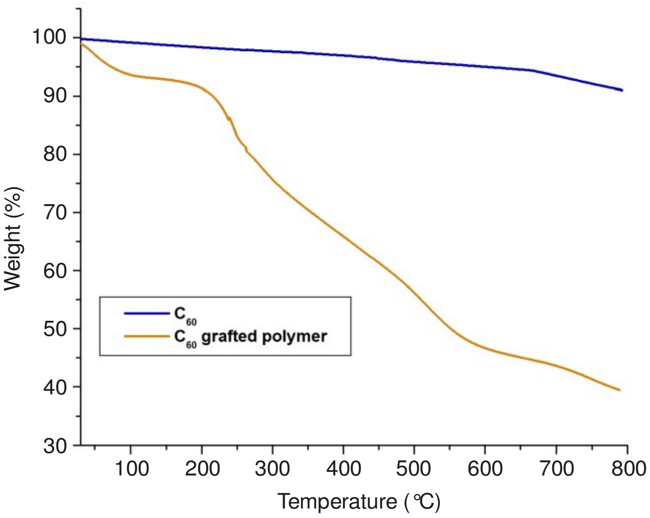


Fig. 4. TGA curves of (a) C_{60} and (b) C_{60} grafted polymer

TEM has been used as a reliable technique to determine the micelle formation of polymers in solution, and to demonstrate the aggregation behaviour of C_{60} or C_{60} derivatives. The aggregation of C_{60} derivative of polymer in DMF and THF was confirmed by TEM using dried sample obtained from dilute solutions. The TEM micrographs of C_{60} grafted polymer aggregates are shown in Fig. 5. It can be clearly observed that the samples consist of isolated spherical clusters and secondary aggregates consisting of large compound micelles. The average diameters of the micelles were found to be 80 and 90 nm, for the samples obtained from DMF and THF solution, respectively.

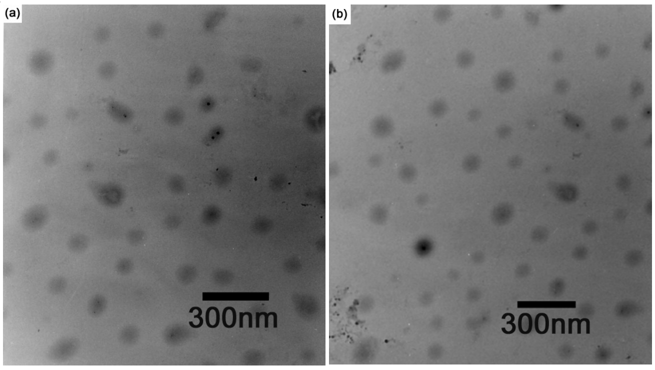


Fig. 5. TEM micrographs of C_{60} graftedpolymer aggregates in (a) DMF and (b) THF

Conclusion

We have successfully synthesized C_{60} grafted poly(2-bromomethyl)acrylic acid. FT-IR and UV-visible characterizations showed that the C_{60} was chemically grafted to the polymer. TGA analysis confirmed the amount of C_{60} grafted on the polymer. The aggregation behaviour of C_{60} grafted polymer in polar solvents was investigated by TEM. In polar solvents, spherical isolated micelles clusters and secondary aggregates consisting of large compound micelles were observed. The presence of C_{60} causes the polymer more hydrophobic and to form aggregates in polar solvents. This type of polymeric C_{60} derivatives can be used as photoconductive materials.

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