Supplementary information

Experimental Section

Materials

A commercially available methacrylate terminated poly(dimethylsiloxane methacryalte) (PDMS-ma, M_n~10,000, Aldrich), C_{60} (origin MTR Ltd., Cleveland, OH), high purity carbon dioxide (SFC grade, BOC Gases) were used as received. Styrene (Aldrich) was distilled under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN, Fisher Chemicals) was purified via recrystallisation from THF. C_{60} was dissolved in styrene to give a characteristic purple solution (70 mg C_{60} in 20 ml styrene), which was filtered prior to use.

Typical Procedure for the Preparation of polystyrene-C_{60} composite microparticles

The whole procedure was performed in a 60 ml stainless steel autoclave equipped with a magnetically coupled overhead stirrer. The autoclave was charged with PDMS-ma (0.5g) stabilizer, then pressurised to ca. 3000 psi with high grade N_2. This procedure was designed to leak test the equipment and to degas the reaction system. After venting, the autoclave was then filled with CO_2 to ca. 800 psi, then stirred and heated to the desired reaction temperature (65 ^{o}C). Once the reaction temperature was reached, the desired pressure (3500 psi) was attained with the addition of CO_2. Whilst stirring at 300 rpm, the solution of AIBN (0.1 g) and C_{60} (35 mg) in styrene (10 ml) was injected into the autoclave at a flow rate (2 mL min^{-1}). After injection, the stirring rate was kept at 300 rpm throughout the reaction, and the reaction was allowed to proceed for 48 hours. At the end of the reaction, the reaction system was allowed to cool down to room temperature. The pressure was then slowly released and once at atmospheric pressure the polymeric product was recovered from the autoclave as a fine brown powder, which was then characterized.

Characterisation

The monomer conversion was measured gravimetrically. Molecular weight data were obtained by gel permeation chromatography (PL-ELS 1000) with two PLgel 5 μm Mixed-D columns (Polymer Laboratories) and an evaporative light scattering detector (Polymer Laboratories) using chloroform as the solvent at 30 ºC. Calibration was accomplished with PSt narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 ml min^{-1}. Scanning Electron Microscopy (SEM) data were collected using a JEOL 6400. Samples were mounted on an aluminum stub using an adhesive carbon tab and were coated with gold. At least hundred particles were measured. Transmission Electron Micrograph (TEM) images were collected using a JEOL JEM-2000FX II electron microscope operating at 100 keV. The samples were ground up in preparation for TEM analysis and a suspension of the solid matrices were sonicated in methanol for a short time before 2–3 drops of the suspension were transferred onto a 3 mm diameter holey carbon coated copper grid. The solvent was allowed to evaporate at room temperature before loading the sample in the microscope. Conventional bright field imaging was used to observe the particle morphology with diffraction patterns. Raman spectra were collected with an Almega (Thermo Nicolet) spectrometer, which has a 180º geometry (also known as "back-scattered" geometry). A NIR laser (532 nm) was used at Ca. 300 mW output power and a slit 100 μm provided sufficient resolution. UV/VIS diffuse reflectance spectra were collected on a Perkin Elmer Lambda 35 UV/VIS spectrometer. Powder X-ray diffraction (XRD) analysis was performed using a Philips 1710 powder diffractometer with Cu Kα radiation (40 kV, 40 mA). Tg data were collected on a TA Instruments MDSC 2920 under nitrogen at a heating and cooling rate of 10 ºC/min. TGA data were collected on a TA Instruments TGA 2950 under nitrogen, at heating rate of 50 ºC/min.

Figure 1. Polystyrene-C_{60} composite microparticles: brown powder; and neat polystyrene microparticles: white powder.

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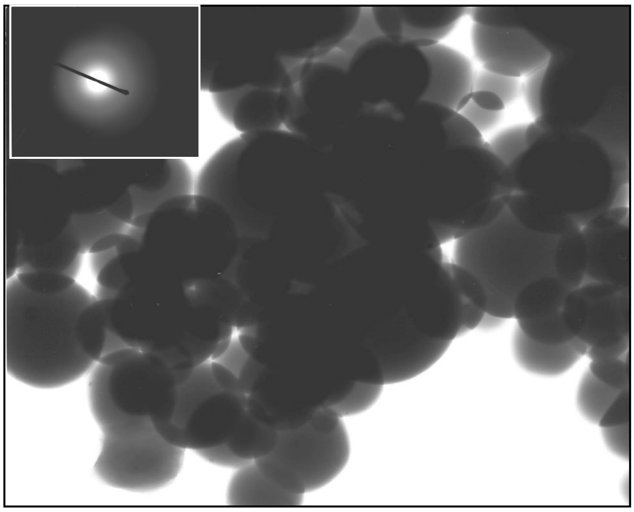

Figure 2. TEM of Polystyrene-C_{60} composite microparticles

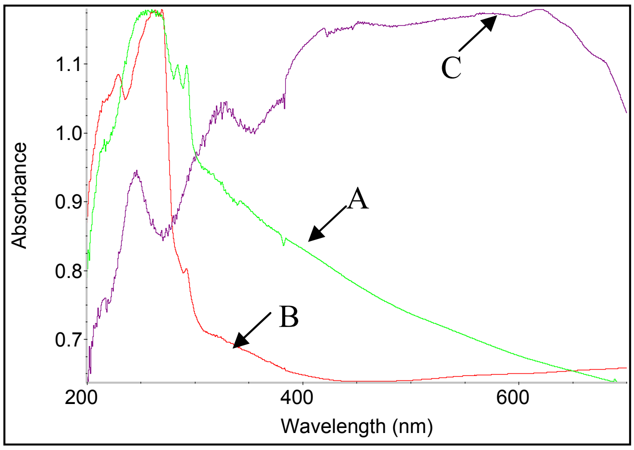

Figure 3. UV/VIS diffuse reflectance spectra.
A) Polystyrene-C_{60} composite ; B) Neat polystyrene ; C) C_{60}

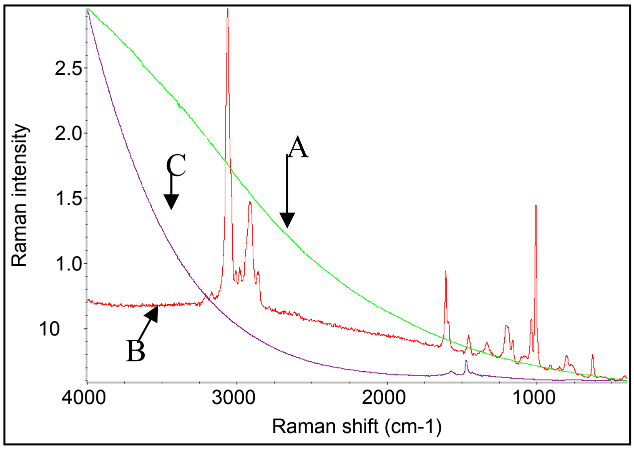

Figure 4. Raman spectra. A) Polystyrene-C_{60} composite ; B) Neat polystyrene ; C) C_{60}