

Grafting of C₆₀ onto Polyethylene Surfaces

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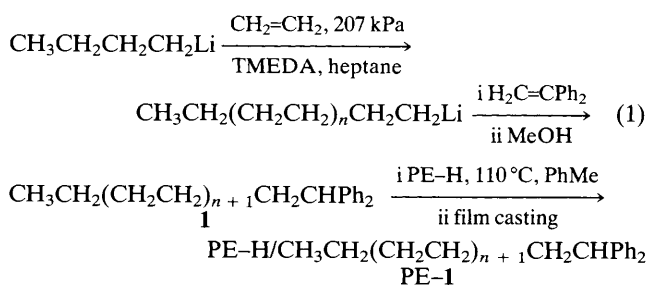
Polyethylene films functionalized with diphenylmethyl groups are deprotonated to form a nucleophilic lithiated surface which is in turn used to covalently bind C₆₀ to polyethylene.

Previous work has shown that C₆₀¹⁻³ is an excellent electrophile reacting with a variety of neutral and charged nucleophilic reagents.⁴ More recently, Hirsch *et al.*⁵ and Fagan *et al.*⁶ have described the monoaddition of *tert*-butyllithium to C₆₀ to form Bu^tC₆₀H and Bu^tC₆₀ - Li⁺, respectively. Addition of polymeric lithiated polystyrene oligomers to C₆₀ has also been reported.⁷ We here report our work which takes advantage of this C₆₀ reactivity by grafting electrophilic C₆₀ moieties on to a pregenerated lithiated polyethylene surface.

Previously, our group reported a procedure for the surface functionalization of polyethylene (PE) powders and films in which terminally functionalized ethylene oligomers were entrapped from solutions of the oligomer and high molecular weight virgin polyethylene.⁸ This technique called entrapment functionalization produces surface-functionalized polyethylene films and powders. Here, we have used an oligomer with a terminal diphenylmethyl group that contained a weakly acidic proton. The polyethylene films formed with these diphenylmethyl groups at the film-solution interface could be deprotonated by BuLi-(*N,N,N',N'*-tetramethylethylenediamine (TMEDA) to yield an anionic polyethylene surface.⁹

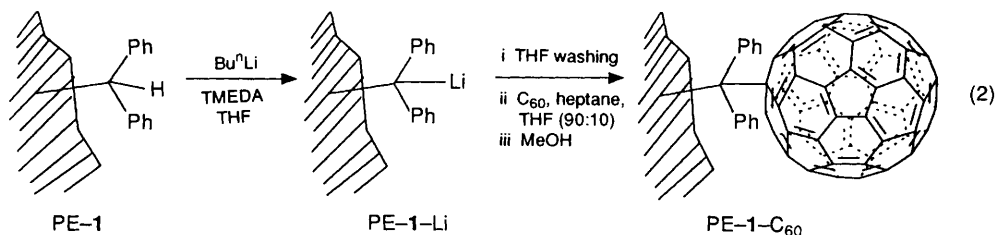
The diphenylmethyl terminated oligomer was prepared from a living oligomer (H₂C=CH₂, BuⁿLi·TMEDA, 207 kPa) by reaction with 1,1-diphenylethylene followed by protonation [eqn. (1)]. Films containing **1** were then prepared by

codissolving oligomer **1** with virgin high density polyethylene and then casting films from a hot dichlorobenzene solution. The resulting films contained 3% by weight of oligomer **1**.



The entrapped film was dried *in vacuo* and cut into strips. A 1 cm² piece of the film was then treated with BuⁿLi·TMEDA (0.08 mol dm⁻³) in dry tetrahydrofuran (THF) under argon to produce PE-1-Li. This lithiated film was washed twice with THF to remove any residual BuⁿLi and was then treated with 20 ml of a 4.6 × 10⁻⁴ mol dm⁻³ solution of C₆₀ in heptane-THF (90:10) for 16 h with stirring to form PE-1-C₆₀ [eqn. (2)].

After quenching with MeOH, the product film was washed several times with hexanes and chloroform and was finally



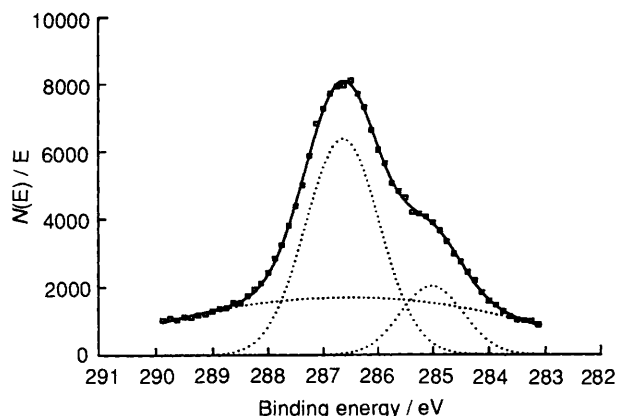


Fig. 1 The X-ray photoelectron spectrum of a C_{60} -grafted polyethylene film (PE-1- C_{60}) at a takeoff angle of 35° showing the C 1s electron peak and its curvefit components at 285.2 and 286.7 eV

extracted for 4 h with hot chloroform using a Soxhlet apparatus to remove any absorbed C_{60} .

The X-ray photoelectron spectrum (XPS) of the film (Fig. 1) provided the best evidence for incorporation of C_{60} at the polyethylene surface. The XPS spectrum contained a lower energy shoulder on the normal carbon 1s ionization of polyethylene that is not present on the nongrafted film. Curve fitting of this signal using Peakfit (Jandel Scientific) showed that the peak under the shoulder was centred at 285.2 eV and constituted 20.8% of the total area under the curve, establishing the presence of a substantial C_{60} component in the outermost 35 Å of the film surface. Lichtenberger *et al.* have reported that thin films of C_{60} prepared by the vapour deposition on gold contain a single narrow carbon 1s ionization at 285.14 eV.¹⁰ Decreasing the takeoff angle to 25° increased the area under the peak due to C_{60} to 26.7% of the total area under the curve, indicating that C_{60} is indeed at or near the surface.

Other evidence for covalent incorporation of C_{60} onto the functionalized polyethylene film was obtained using UV-VIS and fluorescence spectroscopy. After covalent grafting of C_{60} onto lithiated polyethylene, the UV-VIS spectrum contained absorption peaks at 213, 257 and 323 nm. Additional small peaks were at 404 and 640 nm in rough agreement with UV-VIS spectra of other alkylated C_{60} derivatives in solution.^{5,6} The fluorescence spectrum for C_{60} in hexane (λ_{EX} 255 nm) contained several bands in the region between 300 and 400 nm. The C_{60} grafted film had a similar fluorescence spectrum albeit with a lower intensity fluorescence. However, although the spectrum of the modified film was similar to that of C_{60} , it was not identical. The film PE-1- C_{60} did not have the

band C_{60} did at 350 nm and had an extra band near 380 nm. More significantly, the starting polymer film, PE-1, did not exhibit this same fluorescence.

While XPS, UV-VIS and fluorescence all provided evidence for C_{60} incorporation, advancing water contact angles of the C_{60} grafted film and the starting film were identical within experimental error (PE-1, 110° ; PE-1- C_{60} , 108°). This suggests that practically no change in surface hydrophilicity occurred.

We have demonstrated the ability to covalently attach buckminsterfullerene to an anionic polyethylene surface. The presence of the C_{60} graft was confirmed using XPS, UV-VIS spectroscopy and fluorescence spectroscopy. The mode and mechanism of attachment is not known. However, recent work suggests that hindered organolithium reagents can add to C_{60} . While both monosubstituted and polysubstituted adducts are preceded, both steric effects of a diphenylmethyl group and the entropic constraints of a surface should preclude polysubstitution.†

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† Note added in proof: A recent report describes attachment of C_{60} to amine-modified electrode surfaces, cf. C. W. Kaimin, W. B. Caldwell and C. A. Mirkin, *J. Am. Chem. Soc.*, 1993, **115**, 1193.