

## Fullerene grafted hydrocarbon polymers

Abhimanyu O. Patil\* and Stanley J. Brois

Corporate Research Laboratory, Exxon Research & Engineering Company, Route 22 East, Clinton Township, Annandale, NJ 08801, USA

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We have free radically grafted fullerene onto saturated hydrocarbon polymers such as ethylene-propylene copolymer. The product is soluble in solvents such as hexane or tetrahydrofuran, in which the fullerene is essentially insoluble. The reaction of the fullerene and polymer was followed by i.r. spectroscopy and gel permeation chromatography. In these graft copolymers, fullerene may provide sites for further derivatization, including derivatization by methods which would fail for the original polymer. © 1997 Elsevier Science Ltd.

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### Introduction

Fullerenes are known to undergo various kinds of addition reactions<sup>1</sup>. Fullerenes have proved to be a highly reactive form of carbon, undergoing addition reactions similar to those of electron-poor olefins. The number of available reactions allows a substantial degree of flexibility in the construction of fullerene derivatives. There have been several reports in the last few years dealing with macromolecular fullerene chemistry<sup>2</sup>. Loy and Assink prepared the first insoluble product by a copolymerization of C<sub>60</sub> with *p*-xylylene<sup>3</sup>. Recently, the soluble copolymer of fullerene with styrene has been reported<sup>4</sup>. Polyolefins are high volume hydrocarbon polymers which are used for many applications. However, the polyolefins are unreactive and derivatization of these polymers with polar or reactive functional groups has been highly desirable. Functional polymers are technologically important for a variety of applications such as lube oil additives, emulsifiers, compatibilizers, adhesives, and coatings. Incorporation of reactive functional groups, such as fullerene, would provide sites for derivatization that are absent in the original polymer.

At the current time, fullerenes are specialty-type research chemicals rather than a commercial material. Fullerenes are produced by high temperature reactions of elemental carbon or of carbon-containing molecules<sup>5</sup>. All fullerene producing processes typically lead to mixtures of various all-carbon molecules. The portion of the product that is soluble in organic solvents such as toluene is commonly referred to as fullerenes (fullerite) or crude fullerenes. This product typically contains mostly C<sub>60</sub>, lesser amounts of C<sub>70</sub> and much smaller amounts of many different fullerenes of high carbon number. Use of a small amount of fullerene to graft and modify the properties of polymers would aid in bridging the gaps between specialty and commercial applications.

### Experimental

The present paper describes a very simple method for

the direct incorporation of C<sub>60</sub> into hydrocarbon polymers by free-radical grafting under routine conditions. In a grafting reaction, 6.185 g ethylene butylene (EB) liquid copolymer ( $M_n = 4269$ , % butylene = 70) and 40 mg of C<sub>60</sub> dissolved in 2 ml of xylene were placed in a 100 ml three-neck flask equipped with condenser, nitrogen bubbler and dropping funnel. The mixture was heated in an oil bath to 150°C and *t*-butyl peroxide (0.5 g) was then added dropwise slowly. The solution was allowed to stir at that temperature for 45 min. After the reaction, the product was diluted with 100 ml of heptane, filtered and the solvent was removed on rotary evaporator. The fullerene grafting reaction is schematically shown in *Figure 1*.

### Results and discussion

The graft copolymer was soluble in organic solvents such as hexane, tetrahydrofuran (THF) as compared to C<sub>60</sub>, which is not substantially soluble in these solvents. The reaction of EB copolymer with fullerene was followed with FTi.r. (*Figure 2*). Nearly complete reaction of the fullerene and polymer was evident from the infrared (i.r.) spectrum of the product. The characteristic i.r. bands of C<sub>60</sub> at 527 and 578 cm<sup>-1</sup> disappear in the reaction product. An independent confirmation of the reaction between the fullerene and polymer is provided by gel permeation chromatography (g.p.c.) (*Figure 3*). G.p.c. of the product showed that the molecular weight ( $M_w$ ) of the product was 55 300 as compared to the starting polymer that had the  $M_w$  of 8940. G.p.c. with u.v. detector had absorption due to grafted C<sub>60</sub> only in product because of C<sub>60</sub>, while there is no absorption in the original polymer. This suggests that there is a molecular weight increase after the reaction and one can speculate that there could be an average of six polymer chains attached to a fullerene molecule. The product polymer could be highly branched but did not reach the crosslinking gel point yet since the product is completely soluble in organic solvents.

Attempts to incorporate polar functional groups into non polar polyolefins include both direct incorporation of polar functional groups during the polymerization as well as post polymerization functionalization<sup>6</sup>. The

\* To whom correspondence should be addressed

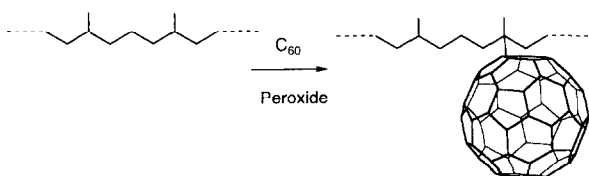


Figure 1 The reaction scheme showing fullerene grafting reaction

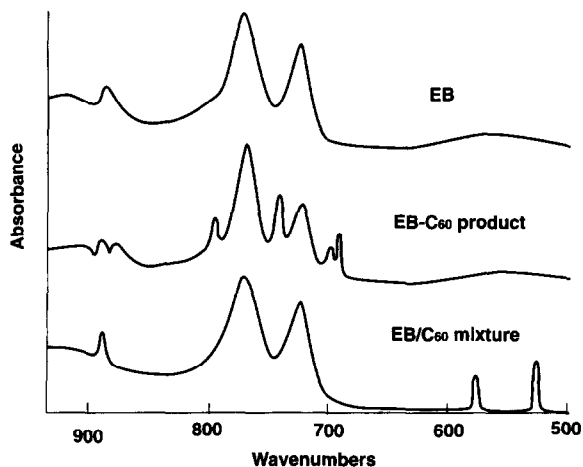


Figure 2 FTIR spectra of EB copolymer (top), EB copolymer + C<sub>60</sub> mixture (bottom) and C<sub>60</sub> grafted EB copolymer (middle)

direct polymerization with Zeigler–Natta catalysts is synthetic challenge since most organic polar functional groups react with the catalyst and terminate polymerization. The post-functionalization route is an indirect route through a bridging group. For example, maleic anhydride can be grafted onto hydrocarbon polymers using free-radical chemistry and utilize the reactivity of anhydride of graft polymer to attach a polar functionality such as polyamine. Similar to maleic anhydride, one can envision using fullerene, as a novel bridging group to incorporate polar functionality which could not be accomplished with saturated hydrocarbon polymers.

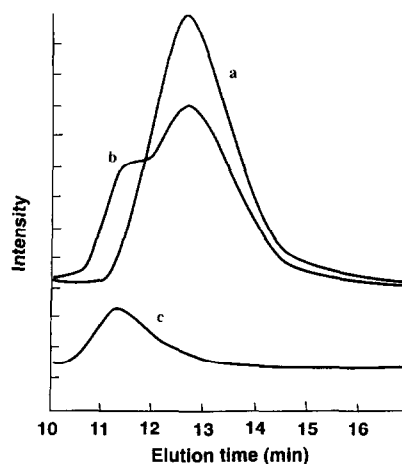


Figure 3 G.p.c. traces of (a) EB copolymer, (b) C<sub>60</sub> grafted EB copolymer (RI detector) and (c) C<sub>60</sub> grafted EB copolymer (u.v. detector)

Thus fullerenes can be free radically grafted onto saturated hydrocarbon polymers such as EB copolymers. This is a general reaction and can be applicable to other polymers.

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