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Fullerene functionalized polymers

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Summary

The recent synthesis and macroscopic isolation of C_{60} (buckminsterfullerene) has stimulated interest in its properties and chemical reactivity. Fullerenes are known to be attacked by nucleophiles and it has been reported that they react with small amines. There is, however, no report on the reaction of fullerenes with polymeric amines. Fullerenes were found to add to amine containing flexible hydrocarbon polymers such as ethylene propylene terpolymer (EPDM-amine) to obtain novel C_{60} functionalized polymers. These materials are soluble in commom solvents. The reaction of the fullerene and polymer was followed by infra-red spectroscopy and viscosity measurements.

Introduction

With the availability of macroscopic quantities of fullerenes (1), chemical modification of buckyballs has become an active area of research (2). Among many reactions, fullerenes are also known to be attacked by amines (3). Fullerenes are interesting materials with unique structures, which may modify the properties of polymers. Although copolymers of fullerenes with other species have been reported (4), no report of the reaction of fullerenes with polymers has yet appeared. We have found that fullerenes add to amine-containing polymers to give novel functionalized grafted polymers. In this communication, we report the fullerene functionalization of ethylene propylene terpolymer (EPDM-amine).

Experimental

Detailed procedures for the preparation and characterization of the amine functionalized ethylene propylene terpolymer (EPDM-amine) have been published elsewhere (5). In the grafting experiment the EPDM-amine was dissolved in toluene and mixed with an equivalent amount of fullerene, based on the nitrogen content of the polymer (6). After stirring for one week at room temperature, the polymer was precipitated with acetone, redissolved in THF or heptane, filtered, and reprecipitated with acetone to give a reddish product. In contrast, EPDM-amine is a colorless polymer, highly soluble in THF or heptane, and C_{60} is insoluble in heptane. Films can be prepared from grafted material. The schematic reaction for EPDM-amine with C_{60} is shown on next page. (The presence of hydrogen directly attached to the fullerene is assumed. It has not been conclusively proven.)

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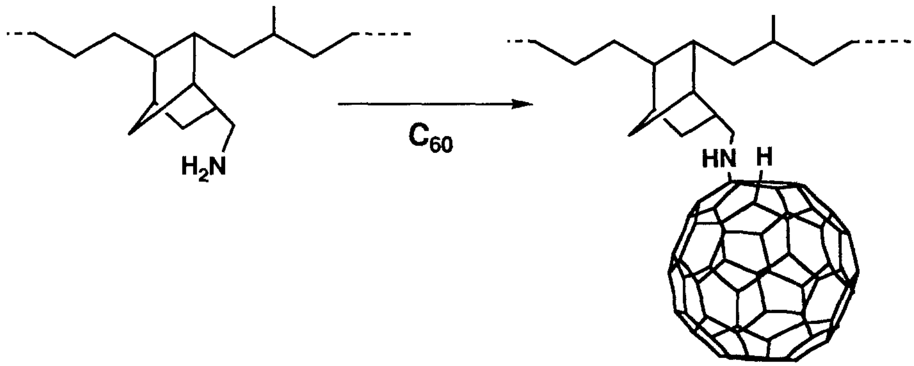

Results and Discussion

Nearly complete reaction of the fullerene and polymer was evident from the infra-red spectrum of the product. The characteristic IR bands (7) of C_{60} at 527 and 578 cm^{-1} disappear in the reaction product. Likewise, a broader peak at 615 cm^{-1} due to the unfunctionalized polymer disappears upon reaction. These features are present in mixtures of C_{60} and EPDM-amine. (Figure 1)

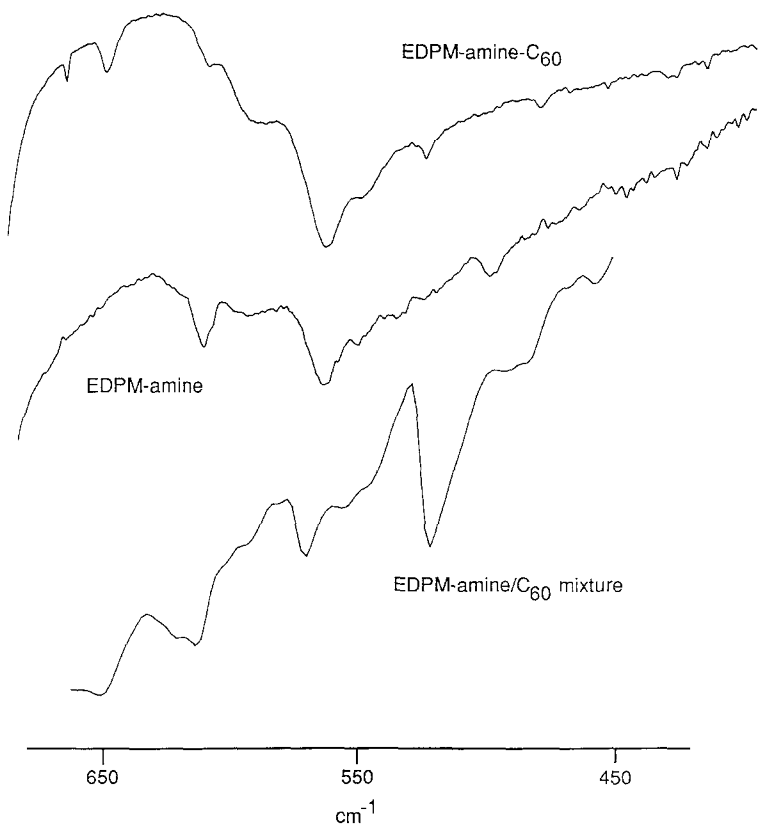

Figure 1. Infra-red spectra of polymer samples (in the mixture of EPDM-amine and C_{60}, proportions are the same as in the product).

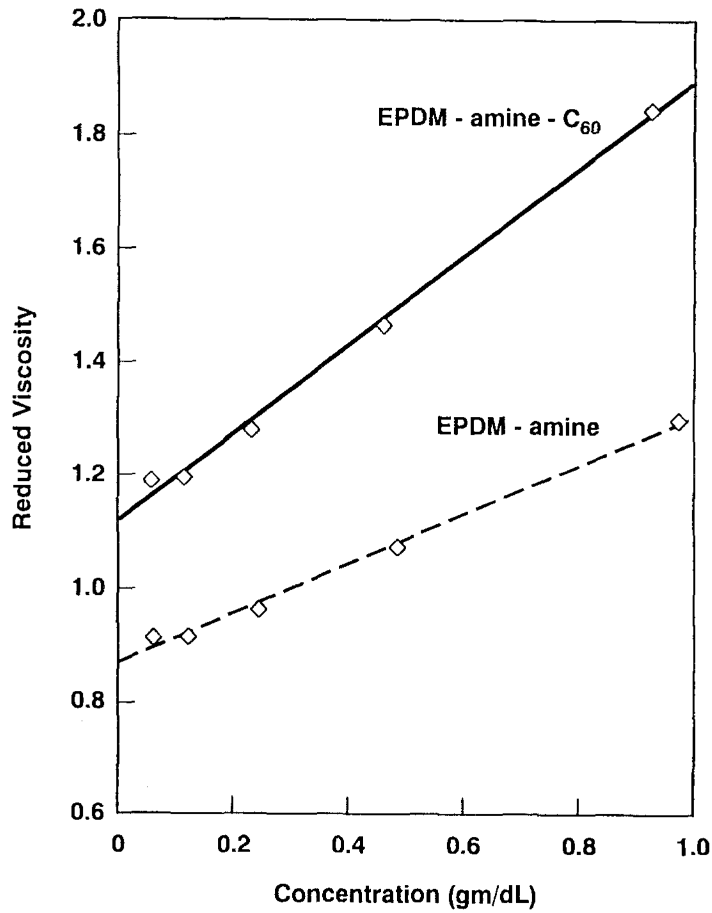

Figure 2 Plots of reduced viscosity versus concentration for the EPDM-amine-C_{60} product (solid line) and starting EPDM-amine (dashed line). Reduced Viscosity = $(\eta_s - \eta_o)/(\eta_o\ C)$, where η_s is the viscosity of the polymer solution, η_o is the viscosity of the solvent, and C is the polymer concentration measured in gm/deciliter. Viscosity measurements were conducted on the soluble portion of the polymer.

An independent confirmation of the reaction between the fullerenes and polymer is provided by viscometric studies. Figure 2 illustrates the reduced viscosity-concentration profiles of the starting EPDM-amine polymer compared with that for the fullerene reaction product as measured in xylene at 30°C (8). Reduced viscosity provides a measure of the hydrodynamic volume of these polymers, and Figure 2 clearly shows a substantial increase in the value for the adduct. The intercepts of the two lines (or intrinsic viscosities) are substantially different, showing the functionalized polymer is not a simple mixture or complex of C_{60} and EPDM-amine. The increase in reduced viscosity (or intrinsic viscosity) is a consequence of more than one EPDM-amine reacting with the same fullerene molecule. This degree of extention is, in part, controllable by the ratio of reagents employed.

Incorporation of reactive functionality, such as fullerenes, is desirable for several reasons. The fullerenes, themselves, will alter the properties of the polymers to which they are attached. A simple example is the color change of the EPDM-amine upon addition of fullerenes. They may also provide sites for further functionalization, including functionalization by methods which would fail for the original polymer. A special case of this is cross-linking or chain extension of the original polymer by reaction of more than one polymer chain with a given fullerene molecule.

Acknowledgement

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References

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2. See, for example: Hawkins JM, Meyer A, Lewis TA, Loren S, Hollander FJ, (1991) Science 252:312. Bausch JW, Surya Prakash GK, Olah GA, Tse DS, Lorents DC, Bae YK, Malhotra R, (1991) J. Am. Chem. Soc. 113:3205. Tebbe FN, Becker JY, Chase DB, Firment LE, Holler ER, Malone BS, Krusic PJ, Wasserman E (1991) J. Am. Chem. Soc. 113:9900.
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5. Datta S, Verstrate G; Kresge EN, (1992) Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem. 33:899. Datta S, Kresge EN, U.S. Patent 4,987,200 (Exxon), Patil AO, Datta S, Gardiner JB, Lundberg RD, U.S. Patent 5,030,370 (Exxon).
6. The EPDM-amine samples used for this study had Mn of 20,000 and contained 39% ethylene by weight. Elemental analysis (Microanalysis, Inc., Wilmington, DE) gave 0.05% N, or one amine per polymer chain on average.
7. Hare JP, Dennis TJ, Kroto HW, Taylor R, Allaf AW, Balm S, Walton, DRM, (1991) J. Chem. Soc., Chem. Commun. 412.
8. About 4% of the product was insoluble in xylene, presumably due to chain extension or crosslinking.

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