Polymer Bulletin 35, 705–710 (1995)

Polymer Bulletin

A novel and versatile method for the synthesis of soluble fullerenated polymers

Yu Chen, Rui-Fang Cai, Zu-En Huang*, Sheng-Qian Kong

Department of Chemistry, Fudan University, Shanghai 200433,
People's Republic of China

Received: 19 April 1995/Revised version: 2 August 1995/Accepted: 14 August 1995

Summary

A new route for the preparation of soluble fullerenated polymer through the reaction of carbanion intermediates of polymers with fullerenes, particularly C_{60}, is demonstrated. Confirmation of the covalent attachment of C_{60} to the polystyrene backbone is by a variety of techniques such as UV-Vis, FT-IR, TGA, SEM and ^{13}C NMR etc. The product, which has a visibly brownish yellow cast when compared with the unreacted polymer, is soluble in some common organic solvents. The thermal stability of pure polystyrene is enhanced by C_{60}-chemical modification, and no bonds within the carbon sphere are broken.

Introduction

Since the discovery of the macroscopic-scale fullerene synthesis by Krätschmer, Huffman and coworkers in 1990(1) , study of the chemical reactivity of fullerenes, particularly C_{60} has grown rapidly, buckminsterfullerene and its derivatives exhibit a variety of outstanding electronic(2) ,conducting(3) and magnetic(4) properties. Addition of C_{60} moieties into polymers by chemical reaction may modify considerably the physical and chemical properties of polymers(5~9). However, some cross-linking was observed from reaction of more than one polymer chain with a given fullerene molecule, resulting in cross-linked intractable and insoluble materials readily occurs(10,11) . Noticing the fact that carbanions are important intermediates in organic synthesis, so any temporary modification of an organic substrate which increases its susceptibility to proton abstraction is of synthetic interest (12,13), We describe herein the synthesis and characterization of soluble fullerenated polystyrene.

Experimental

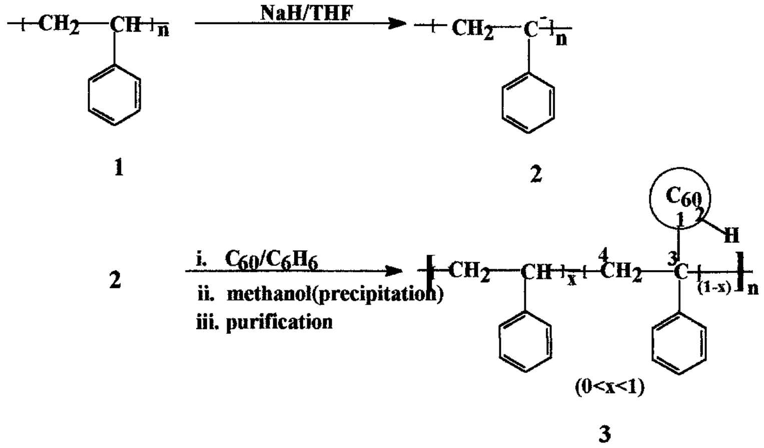
The fullerenated polystyrene was prepared according to Scheme I . The polystyrene (PS) used was a commercially produced polymer obtained from Beijing Yansan petrochemical plant of China , having a number average molecular weight Mn = 97000 . This sample is further purified before use . C_{60} was synthesized and

---

* Corresponding author

purified according to literature(1,14). HPLC analysis showed C_{60} in a purity of 99.5%. To a solution of polystyrene (1g , 1.25×10^{-2} mmol) in dry , degassed tetrahydrofuran (30 ml) was added NaH (0.231 g , 9.625 mmol) at 20 ^{0}C under a purified nitrogen atmosphere . After stirring for 48h , a dilute solution of C_{60} (0.1g , 0.139 mmol) in 80 ml dry, degassed benzene was added to the above solution dropwise with two hours, followed by stirring for one week , the polymer was precipitated with methanol , redissolved in THF , filtered to remove any unreacted C_{60} , and reprecipitated with methanol to give a brownish yellow product 2, which was soluble in some organic solvents such as C_6H_6 , $CHCl_3$,THF and so on .

Scheme I



FT – IR spectra of fullerenated polystyrene were recorded on the Nicolet – FT–IR – 5DX spectrometer, UV – Visible absorption spectra were measured on a UV –240 spectrophotometer using THF as reference standard . Thermal properties were measured using a Dupont 1090 thermogravimetric analyzer(TGA) . High resolution proton decoupled nuclear magnetic resonance spectra were measured in C_6D_6 using ^{13}C as probe with a Bruker MSL-300 NMR spectrometer. The surface topographical structures of the samples C_{60} , polystyrene and fullerenated polystyrene were studied by Hitachi Ho–IIB scanning electron microscope (SEM).

Result and Discussion

C_{60} is an excellent electrophile reacting with a variety of neutral and charged nucleophilic reagents(15). Carbanions could add across the carbon-carbon double bonds of C_{60} to give alkylated reaction products(16,17). Addition of polymeric lithiated polystyrene oligomers to C_{60}(6) and grafting of C_{60} moieties onto a pregenerated lithiated polyethylene surface(18) have been reported. These observations prompted us to investigate the possibility that the living polystyrene carbanions(2), which are prepared by α-position proton abstraction with NaH, might similarly add to C_{60}. Though monosubstituted and polysubstituted adducts are precedented(15,16) , steric hindrance effects of the living polystyrene carbanions(2) should preclude polysubstitution. As a result, the fullerenated polystyrene is a non-cross-linked material and is highly soluble in some organic solvents.

The fullerenated polystyrene had a visibly brownish yellow cast when compared with the unreacted polymer and the reason for this is apparent in the UV –VIS absorption spectrum of product 3 in a THF solution . Polystyrene is essentially transparent at wavelengths longer than 280 nm , while the fullerenated polymer has a new structure in the absorption spectrum in which the main bands occurred at 285 and 330 nm are characteristic absorptions for monofunctionalized organofullerenes(16). There new absorption may be attributed to the covalent attachment of C_{60} to the polystyrene backbone as compared with the UV-Vis absorbances at 213(s), 254(m), 257(s), 329(s), 404(w), 500(vw), 540(vw), 570(vw), 600(vw), 625(vw) nm of C_{60} itself in n-hexane(1, 19) (UV –Vis spectrum of C_{60} in THF cannot be observed due to its insolubility in tetrahydrofuran).

The infrared spectra of the fullerenated polystyrene and the parent polymer were basically similar, and they differed only in the presence of new peaks, which was interpreted as being associated with the two of four characteristic vibration modes of C_{60}, at 528.12 and 572.26 cm^{-1} in fullerenated polymer. TG analysis showed that the thermal stability of polystyrene was enhanced dramatically by the covalent attachment of C_{60} to the polymer backbone (433.1°C for C_{60}-PS as against 416.9°C for PS). In fact, the weight percent of C_{60} incorporated into the polymer could be roughly estimated by TGA since the polystyrene backbone decomposes at 350~420°C to leave C_{60} which undergoes only minor weight loss up to 600°C(7,20) . Comparison with starting materials and physical mixtures confirmed the TGA results.

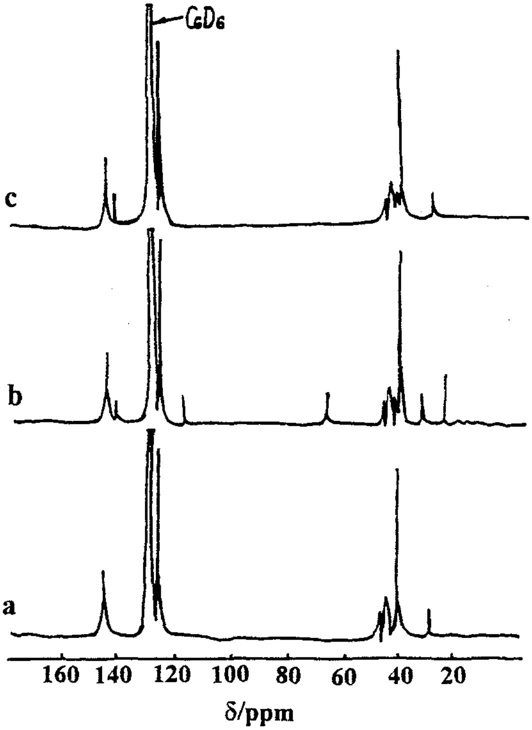


Figure 1 ^{13}C NMR spectra for (a) polystyrene, (b) fullerenated polystyrene containing 8.53% of C_{60}, and (c) the mixtures of C_{60} and polystyrene.

The covalent attachment of C_{60} to the polystyrene backbone is also confirmed by the proton decoupled ^{13}C NMR spectra shown in Figure 1 . Comparison of Figure 1a with Figure 1b shows that three new signals are observed in the aliphatic region of the ^{13}C NMR spectrum of product 3 (Figure 1b), including the sp^3 hybridized carbons of C_{60} appearing at 66.772 ppm for C-1(21) (see Scheme I) , 33.796 ppm and 25.770ppm for C-3, C-4, respectively(22,23). The other two new signals in the

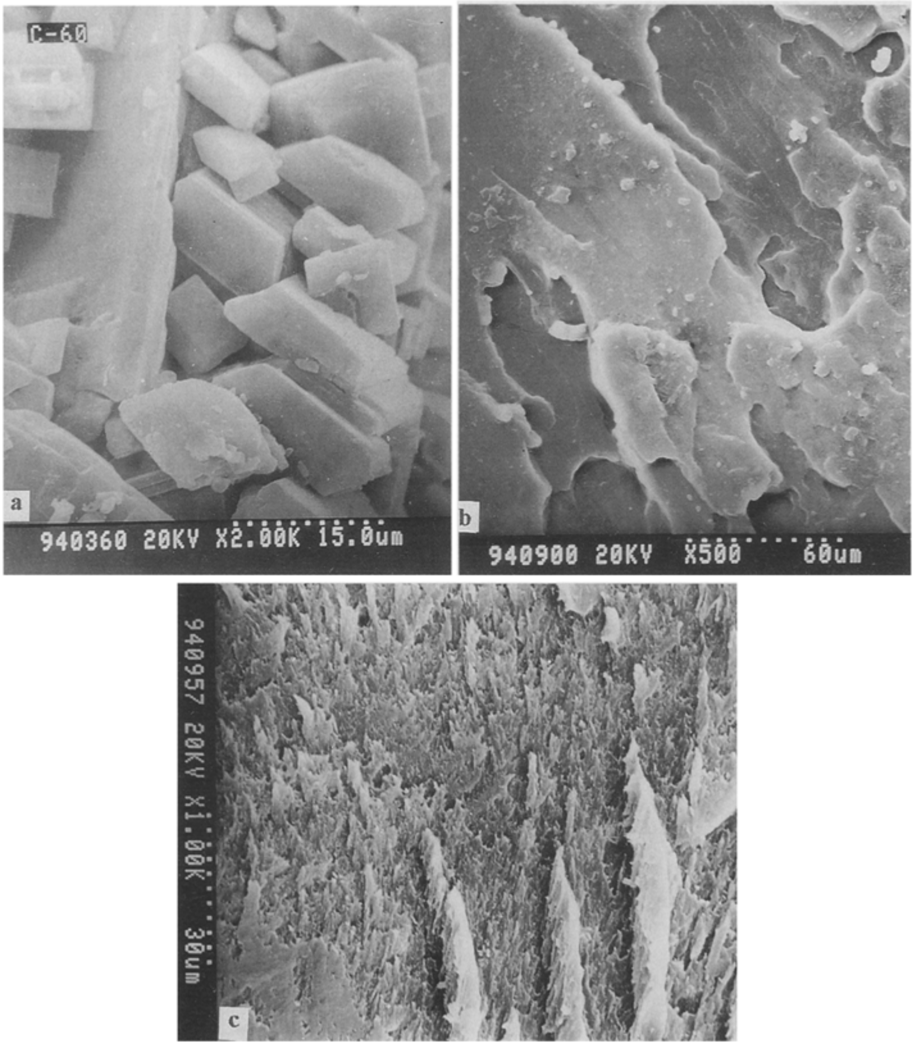


Figure 2 Scanning electron micrographs of: (a) C_{60} ; (b) PS; (c) C_{60}-PS

aromatic region at 118.820 ppm, 143.233 ppm may be ascribed to C-2 bonded to hydrogen(24), fullerene carbons(21b,25), respectively. Meanwhile, the signal at 30.154 ppm in Figure 1a disappeared after C_{60}-chemical modification. ^{13}C NMR spectrum (Figure 1c) of the mixtures of C_{60} and pure polystyrene (proportion of C_{60} in the mixtures is the same as in the product 3) shows only a new signal at 143.236 ppm with respect to pure C_{60} compared to Figure 1a. Therefore, these findings indicate the covalent attachment of C_{60} to the polystyrene backbone, and show conclusively that no bonds within the carbon sphere were broken.

Figure 2 compares the submicro-morphological structure of fullerenated polystyrene containing 8.53% of C_{60} with that of the pure polystyrene and C_{60}. Obviously, fullerenated polystyrene exhibits clearly resolvable tendency of diameter fibrous growth which differs greatly from that of C_{60} or pure polymer.

In conclusion, we have demonstrated a novel and versatile method for the synthesis soluble fullerenated polystyrene through the reaction of carbanion intermediates of polystyrene with fullerene(C_{60}). The confirmation of the covalent attachment of C_{60} to the polystyrene backbone is by a variety of techniques. Further characterization and study of the properties of the products, as well as other routes toward the synthesis of soluble fullerenated polymers, are currently being investigated.

Acknowledgment We thank associate Professor Tong-Run CAI, Tai-Liu WU for assistance with SEM and NMR measurements and helpful discussions. This work was supported by the National Natural Science Foundation of China and the Science Foundation of Shanghai Committee of Science and Technology.

Reference

1. Krätschmer W, Lamb LD, Fostiropoulos K, Huffman DR (1990) Nature 347:354
2. Dubois D, Moninot G, Kutner W, Jones M T, Kadish K (1992) J Phys Chem 96: 7137
3. Haddon RC (1992) ACC Chem Res 25: 127
4. Allemand P-M, Khemani KC, Koch A, Wudl F, HolczerK,Donovan S, Gruner G Thompson JD (1991) Science 253: 301
5. Hawker CJ, Wooley KL, Frechet JMJ (1994) J Chem Soc Chem Commun 925
6. Samulski ET, Desimone, JM, Hunt MO, Menceloglu YZ, Jarnagin RC, York GA, Labat KB, Wang H (1992) Chem Mater 4: 1153
7. Hawker CJ (1994) Macromolecules 27: 4836
8. Shi S, Khemani KC, Li QC, Wudl F (1992) J Am Chem Soc 114: 10656
9. Patil AO, Schriver GW, Carstensen B, Lundberg RD (1993) Polym Bull 30: 187
10. Geckeler KE, Hirsch A (1993) J Am Chem Soc 115: 3850
11. Loy DA, Assink RA (1992) J Am Chem Soc 114: 3977
12. Jaouen G, Merer A and Simonneaux G (1975) J Chem Soc Chem Commun 20: 813
13. Semmelhack MF, Hall HT, Yoshifugi M and Clark G (1975) J Am Chem Soc 97: 1247
14. Isaacs L, Wehrisg A, Diederich F (1993) Helv Chim Acta 76: 1231
15. Wudl F (1992) Acc Chem Res 25:157

16. Hirsch A, Soi a and Karfunkel HR (1992) Angew Chem Int Engl Ed 31:766
17. Fagan PJ, Krusic PJ, Evans DH, Lerke SA and Johnston E (1992) J Am Chem Soc 114: 8647
18. Bergbreiter DE and Neil Gray H (1993) J Chem Soc Chem Commun 645
19. Hare JP (1991) Chem Phys Lett 177:394
20. Gallagher PK, Zhong Z (1992) J Thermal Anal 38: 2247
21. (a) Hirsch A, Grosser T, Skiebe A, Soi A (1993) Chem Ber 126: 1061
(b) Averdung J and Mattay J (1994) Tetrahedron Letters 35: 6661
22. Paul EG and Grant DM (1963) J Am Chem Soc 85: 1701
23. Spiesecke H, Schneider WG (1961) J Chem Phys 35: 722
24. (a) Stothers JB(1972) Carbon-13 NMR Spectroscopy, Academic Press, New York, London (b) Breitmaier E and Bauer G (1977) ^{13}C-NMR-Spektroskopie eine Arbeitsanleitung mit Übungen, Geory-hieme Verlag, Stuttgart
25. Beer E, Feuerer M, Knorr A, Mirlach A and Daub J (1994) Angew Chem Im Ed Engl 33: 1087