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SYNTHESIS OF A C_{60}-PARA-XYLYLENE COPOLYMER

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ABSTRACT

The preparation and purification of macroscopic quantities of buckminsterfullerenes [1] or buckyballs has ignited an explosion of research into their physical and chemical properties, and a variety of strategies for preparing new fullerene-based materials. Free radical synthesis is an appealing approach for forming polymeric fullerene materials. We report a polymeric fullerene material prepared by reacting pure C_{60} with xylylene from the thermolysis of paracyclophane. Addition of xylylene to a purple solution of C_{60} in toluene solution at -78 °C resulted in an olive-green solution from which an insoluble brown powder precipitated upon warming to room temperature. Analyses of the powder by solid state ^{13}C MAS NMR, IR, and thermal gravimetric analysis are consistent with a C_{60}-xylylene copolymer.

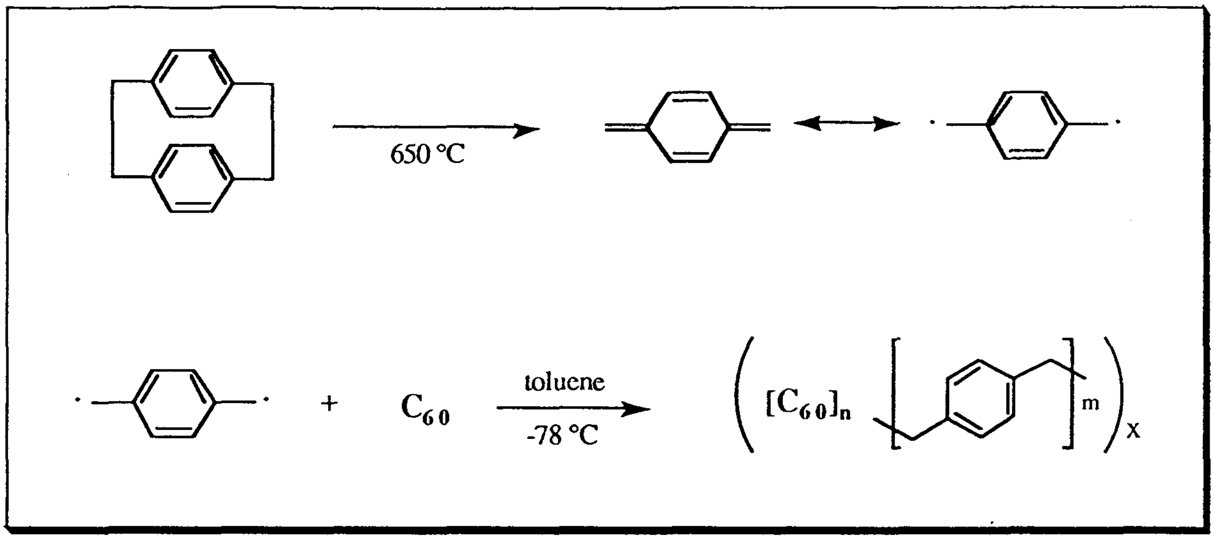
INTRODUCTION

Since the discovery of techniques allowing the isolation of large quantities of fullerenes, there has been an explosion of reports describing the preparation and properties of new fullerene derivatives. A few examples include superconducting fullerites [2], osmium-C_{60} [3] and platinum-C_{60} [4] complexes, charge-transfer adducts of C_{60} and organic electron donors [5], and fluorinated [6] and hydrogenated [1c] C_{60} fullerenes. There has been to date only one report of a fullerene derived material prepared by acid catalyzed fullerenation of polystyrene [7]. These polystyrene materials were prepared through modification of an existing polymer; no fullerene materials have been prepared through a polymerization reaction. One approach for preparing fullerene polymeric materials is to take advantage of fullerene's reactivity towards radical addition. Krusic [8] discovered that C_{60} readily reacted with benzyl radicals to afford poly-benzylated fullerene. By substituting xylylene monomers for the benzyl radicals, we prepared a C_{60}-para-xylylene copolymer, the first fullerene-derived copolymer (Scheme 1).

EXPERIMENTAL PROCEDURE

C_{60} fullerene was purified from toluene-soluble soot by chromatography on alumina as described in the literature [9]. Toluene-soluble soot was obtained from Texas Fullerenes Corporation. The copolymerization was conducted using a flash thermolysis apparatus similar to that described by Szwarc for preparing poly-p-xylylene [10]. The xylylene monomer was prepared by thermolyzing paracyclophane (used as received from Aldrich Chemical Co.) at 650 °C under vacuum (1 mbar). Xylylene monomer was swept into a vigorously stirred solution of C_{60} fullerene in toluene cooled to -78 °C. The solution was allowed to warm to room temperature and the copolymer was collected by filtration, washed with toluene and diethyl ether before drying under vacuum. Solid state ^{13}C MAS NMR were performed on a Chemagnetics console interfaced to a Nicolet 1280 data station at 50.17 MHz. Samples were spun between 4-6 kHz. Direct pulse MAS experiments were carried with 16 second delays between scans and cross polarized MAS experiments utilized a 1.5 millisecond cross polarization time with 4 second delays over 4096 averages. Thermal gravimetric analysis was carried out under nitrogen at 10 °C/minute with a TA Instruments 1090 Thermal Analyzer. Infrared spectra were obtained with a Perkin-Elmer 1504 spectrometer.

DISCLAIMER



Scheme 1. Formation of xylylene and co-polymerization with C_{60}.

RESULTS AND DISCUSSION

Thermolysis of paracyclophane at 650 °C and passage of the resulting xylylene monomer into the solution of C_{60} was accompanied by a rapid color change of the solution from deep purple to olive-green. After the thermolysis of paracyclophane was complete and the solution was allowed to warm to room temperature, a brown precipitate formed. The material was insoluble in both toluene and diethyl ether and was distinctly different in appearance from the poly-p-xylylene prepared with the same apparatus. Solid state ^{13}C Magic Angle Spinning (MAS) NMR spectroscopy was used to characterize the material (Figure 1). The reference ^{13}C MAS NMR spectrum of pure C_{60} (a) reveals the single resonance at 143.7 ppm [11]. The spectrum of poly-p-xylylene (b) exhibits a methylene resonance at 37.85 ppm, and the expected two aromatic carbon resonances at 128.92 and 137.9 ppm [12]. ^{13}C CP MAS NMR spectroscopy of the C_{60}-p-xylylene copolymer (c) revealed a collection of overlapping resonances between 129 and 150 ppm rather than the single C_{60} peak. The peaks at 129.1 and 139.7 ppm are assigned to the aromatic carbons in the xylylene monomer. The remaining resonances in the aromatic region are attributed to the benzylated C_{60} monomer unit within the copolymer. No residual pure C_{60} peak at 143.7 ppm is detectable in the spectrum. The strong resonance at 58.7 ppm was initially attributed to the benzylic methylene carbons in the copolymer. However, interrupted decoupling experiments [13] failed to significantly attenuate the peak as would be expected with a methylene resonance, suggesting that the resonance may in fact be due to the new sp^3 center on the C_{60} formed by the reaction with the xylylene monomer. Reaction of excess pure C_{60} with α,α'-^{13}C-labeled xylylene [14] afforded an insoluble material whose ^{13}C CP MAS NMR spectrum confirmed that the benzylic methylene peaks lie at 38 ppm and that the peak at 58.7 ppm is likely due to the quaternary center on the C_{60} molecule. Benzylic methyls acting as polymer endgroups are found at 23 ppm.

Thermal gravimetric analysis of the C_{60}-xylylene copolymer (Figure 2) under nitrogen confirms that the material is crosslinked. Whereas, pure C_{60} sublimes/decomposes between 650-700 °C (a) [15] and poly-p-xylylene depolymerizes at 475 °C (b)[16], the C_{60}-xylylene copolymer begins to slowly lose mass at 380 °C and continues to lose mass until 1000 °C when 66% of the original mass remains as a black powder (c) [17].

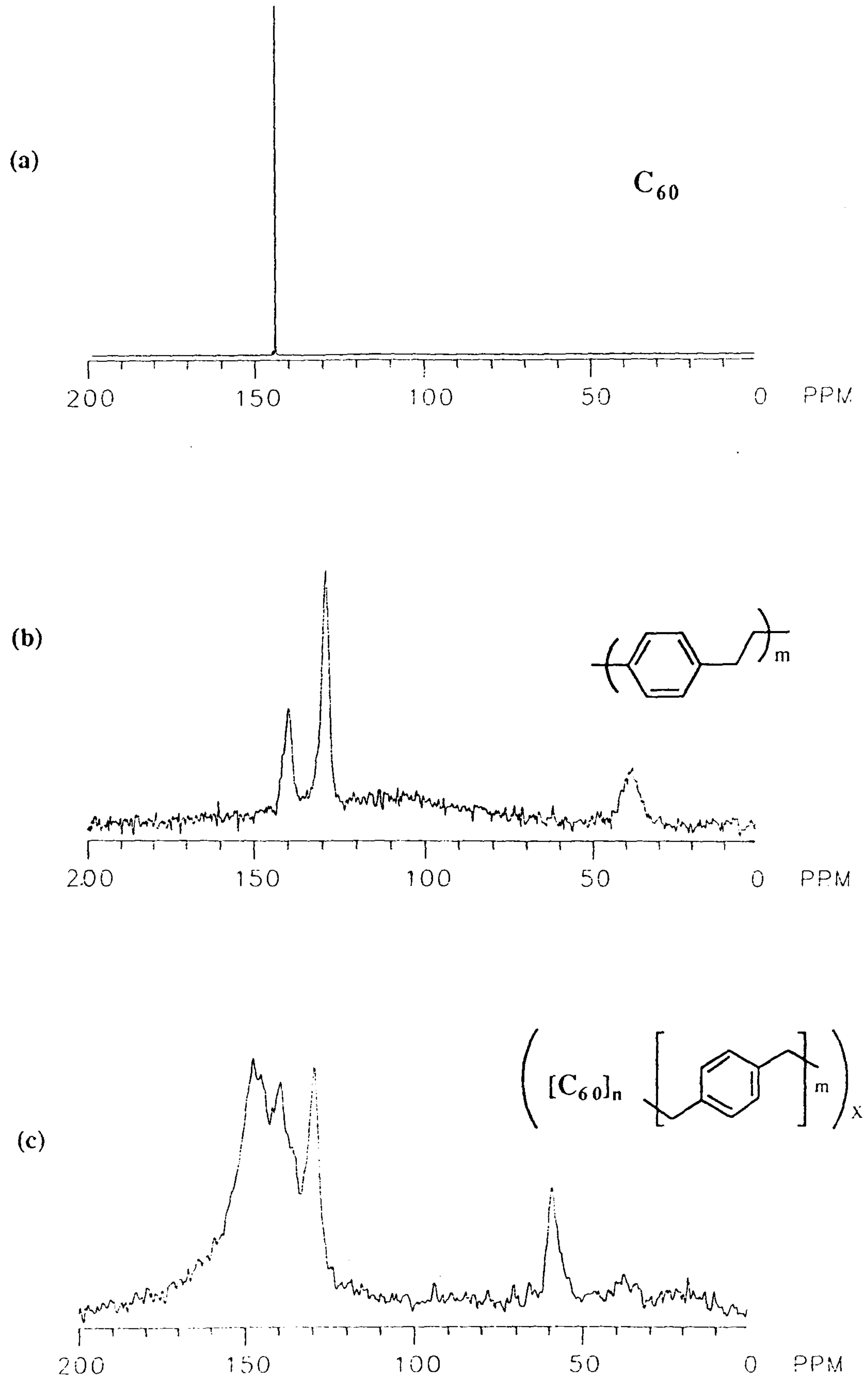


Figure 1. Solid state ^{13}C MAS NMR spectra of pure C_{60} (a), poly-p-xylylene (b), and ^{13}C CP MAS NMR spectrum of the C_{60}-p-xylylene (c).

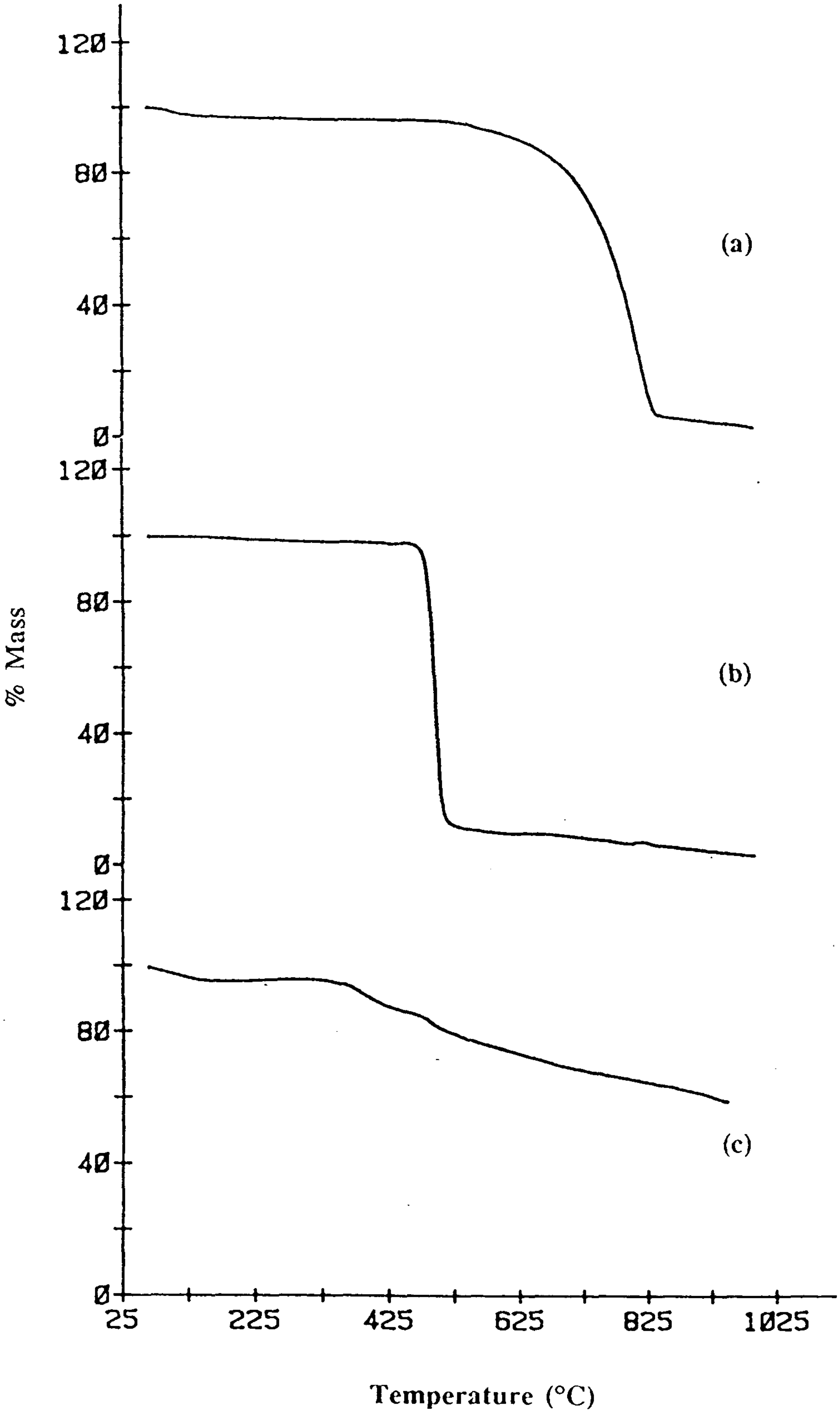


Figure 2. Thermal gravimetric analyses of C_{60} (a), poly-p-xylylene (b), and the C_{60}-p-xylylene copolymer (c). Samples were heated at 10 °C/min. under 60 cc/min. nitrogen.

At 475 °C, there is a minor mass loss (3%) attributed to depolymerizing poly-p-xylylene existing either as a contaminant or as blocks of oligomeric poly-p-xylylene incorporated into the copolymer. Elemental analysis [18] was used to calculate the composition of the copolymer. Based on the carbon:hydrogen ratio, the ratio of xylylene to C_{60} in the copolymer was determined to be 3.4:1 [19].

The infrared spectrum of the C_{60}-xylylene copolymer [20a] resembles neither that of the poly-p-xylylene [20b] nor pure C_{60} [1b]. Both aromatic and aliphatic stretching C-H, aromatic C-C stretching bands confirm the NMR data that xylylene units are incorporated within the material. A slight band at 1780 cm^{-1} indicates that some oxidation to ketone has occurred in the copolymer. After standing under air for four weeks, the infrared spectrum revealed a much stronger and broader carbonyl absorption and a strong new C-O stretching band at 1098 cm^{-1} indicating that the material is not air stable.

CONCLUSION

We have demonstrated that C_{60} fullerene can be copolymerized through a free radical process to form crosslinked materials. Flash thermolysis of paracyclophane or xylene was used to generate the xylylene monomer which was then reacted with C_{60} in solution to form the C_{60}-p-xylylene copolymer with approximately 3.4 xylylene monomer units per C_{60} molecule. By varying the ratio of the xylylene to C_{60} it may be possible to prepare soluble C_{60}-p-xylylene copolymers. The potential for crosslinking and branching during the polymerization process is significant due to the number of reactive sites on each C_{60} molecule.

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[12] Both Cross Polarization Magic Angle Spinning (CP MAS) and direct pulse MAS NMR spectroscopy were used to characterize poly-p-xylylene. Details of these studies will be published elsewhere. The poly-p-xylylene was prepared from paracyclophane using the same apparatus as with the co-polymerization of C_{60} and xylylene, save that the xylylene was allowed to polymerize on the quartz tube at room temperature.

[13] In interrupted decoupling experiments, delays of 60 and 90 μsec was inserted between cross polarization and acquisition. Because dipolar coupling depends on the inverse cube of the C-H distance, carbons with hydrogen substituents are typically more attenuated.

[14] α,α'-^{13}C-labeled xylylene was prepared by the flash thermolysis of α,α'-^{13}C-labeled p-xylene, 99 atom%, at 1000 °C.

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[17] Infrared analysis of the residue reveals loss of the majority of the absorption bands from the copolymer.

[18] Elemental analyses for carbon and hydrogen were carried out in duplicate on a Perkin-Elmer CHN Elemental Analyzer. The copolymer is relatively resistant to oxidation and care must be taken to insure that the sample is completely combusted.

[19] The xylylene:C_{60} ratio was calculated from the ratio of carbon to hydrogen with the assumption that all of the hydrogen in the material originated from xylylene monomers and that the contribution from terminal xylylene monomers was negligible.

[20] a) Infrared spectrum of the C_{60}-p-xylylene copolymer (KBr): 3018, 2921, 2854, 1780, 1607, 1512, 1438, 1418, 1186, 1021, 820.4, 765.1, 727.8, 674.8, 543.2, 525.4 cm^{-1}. b) B.L. Joesten, *Polymer Preprints* 13, 1948, (1972).