Synthesis of a C₆₀–p-Xylylene Copolymer

Douglas A. Loy* and Roger A. Assink

Fuel Science Department and Physical Chemistry and Mechanical Properties of Polymers Department Sandia National Laboratories Albuquerque, New Mexico 87185

Received December 27, 1991

Procedures allowing the preparation and purification of macroscopic quantities of buckminsterfullerenes,[1] or buckyballs, have ignited an explosion of research into their physical and chemical properties. Recently, it was discovered that C₆₀ reacted with benzyl radicals to form polybenzylated fullerenes.[2] Substitution of a diradical species for the benzyl radicals would allow C₆₀ molecules to be linked together, resulting in a polymeric material. Xylylene, a diradical analogue of a benzylic radical, is easily prepared by the flash thermolysis of paracyclophane and is known to readily react with itself to form poly(p-xylylene).[3] We report the first C₆₀ copolymer prepared by reacting pure C₆₀ with xylylene (Scheme I).[4]

The polymerizations were carried out using a slightly modified version of the apparatus used by Errede[3a] in generating poly(p-xylylene) from p-xylene or paracyclophane. In this experiment, paracyclophane was sublimed at 200 °C (under a 1-mbar vacuum) into a tube furnace set at 650 °C where the xylylene comonomer was formed. The xylylene was then swept into a reaction vessel containing a vigorously stirred solution of pure C₆₀ in toluene cooled with a dry ice/acetone bath to –78 °C. Addition of the xylylene to the C₆₀ was heralded by an immediate change in the color of the solution from purple to olive-green. When the solution was allowed to warm to room temperature, a brown precipitate formed. The insoluble precipitate was washed with toluene and
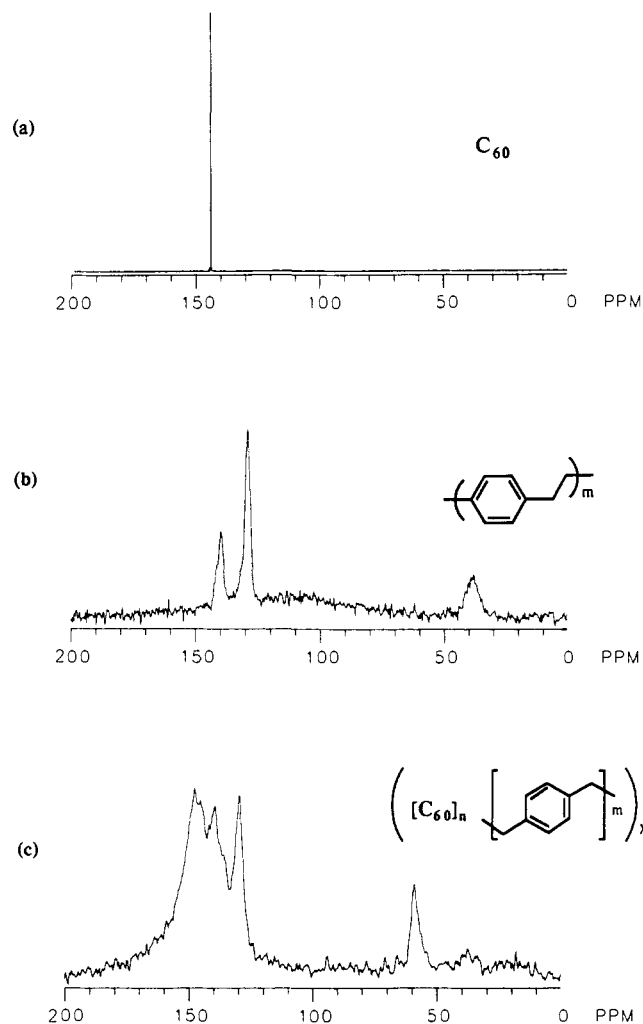
Figure 1. ¹³C MAS NMR spectra of (a) C₆₀ and (b) poly(p-xylylene). (c) ¹³C CP MAS NMR spectrum of C₆₀–p-xylylene copolymer. Spectra were obtained at 50.17 MHz with a Chemagnetics console interfaced to a Nicolet 1280 data station. Samples were spun between 4 and 5 kHz in rotors. Direct pulse MAS experiments were carried with 16-s delays between 64 scans. Cross-polarized MAS experiments utilized a 1.5-ms cross polarization time with 4-s delays over 4096 averages.

Scheme I. Formation of Xylylene and Copolymerization with C₆₀
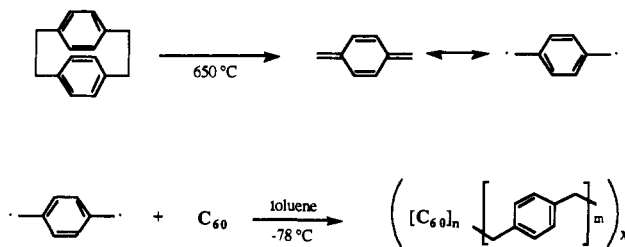
diethyl ether before drying under vacuum (2 mbar).

The C₆₀–xylylene copolymer was characterized using solid-state ¹³C MAS NMR (Figure 1c). Pure C₆₀ exhibited the expected resonance at 143.7 ppm (Figure 1a).[5] We also obtained the first reported ¹³C NMR spectrum of poly(p-xylylene) (Figure 1b).[6]

(1) (a) Kratschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. (b) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634–8636. (d) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499–7503.

(2) (a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274. (b) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.

(3) (a) Szwarc, M. *J. Polym. Sci.* **1951**, *6*, 319. (b) Errebe, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1960**, *82*, 5218.

(4) (a) We recently learned that polystyrene has been covalently modified with C₆₀ at the University of Southern California: Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.*, in press. However, there are no reports of polymers derived from C₆₀. (b) The C₆₀ fullerene was purified from toluene-soluble soot by chromatography on alumina as described by Allemand et al.: Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. The soot was obtained from Texas Fullerenes Corporation.

(5) In addition to the major resonance, a second peak was observed 0.7 ppm downfield due to molecular oxygen in the crystal lattice; complete details will be discussed in a forthcoming paper. The ¹³C NMR resonance of C₆₀ has been reported at 142.7 ppm: Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205–3206.

(6) The poly(p-xylylene) was prepared from paracyclophane using the same apparatus as for the copolymerization of C₆₀ and xylylene, save that the xylylene was allowed to condense and polymerize on the quartz tube at room temperature.

Poly(p-xylylene) exhibits three resonances at 37.85, 128.92, and 137.9 ppm. In place of the single sharp peak observed for C_{60}, an overlapping collection of resonances ranging from 129 to 150 ppm was observed for the C_{60}–p-xylylene copolymer (Figure 1c). Resonances due to the xylylene monomer unit in the copolymer lay at 38.0, 129.1, and 139.0 ppm. The remaining resonances are attributed to the functionalized C_{60} monomer unit. Identification of the peak at 57.8 ppm as arising from the benzylated C_{60} carbons was accomplished using interrupted decoupling experiments[7] and ^{13}C-labeling NMR experiments in which a copolymer prepared by reacting C_{60} with α,α'-^{13}C-labeled xylylene[8] displayed only benzylic methylene and methyl resonances at 37 and 23 ppm, respectively.

Thermal gravimetric analysis of the C_{60}–xylylene copolymer under nitrogen suggests that the material is cross-linked.[9] Whereas pure C_{60} decomposes between 650 and 700 °C[10] and poly(p-xylylene) depolymerizes at 475 °C,[11] the C_{60}–xylylene copolymer begins to slowly lose mass at 380 °C and continues to lose mass until 1000 °C where 66% of the original mass remains as a black powder.[12] At 475 °C, there is a minor mass loss (3%) attributed to depolymerization of poly(p-xylylene) existing either as a contaminant or as blocks of oligomeric poly(p-xylylene) incorporated into the copolymer. Elemental analysis[13] was used to calculate the composition of the copolymer. On the basis of the carbon:hydrogen ratio, the ratio of xylylene to C_{60} in the copolymer was determined to be 3.4:1.0.[14]

The infrared spectrum of the C_{60}–xylylene copolymer[15a] resembled that of neither the poly(p-xylylene)[15b] nor pure C_{60}.[16] Both aromatic and aliphatic C–H stretching bands and aromatic C–C stretching bands confirm the NMR data that xylylene monomer 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 exposure of the material to air for 4 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.[17]

In conclusion, we have discovered that free radical polymerization of C_{60} and p-xylylene leads to polymeric materials. The C_{60}–p-xylylene copolymer is insoluble, due to cross-linking through multiple benzylations on the C_{60} molecules. Solid-state ^{13}C CP MAS NMR revealed both xylylene and C_{60} components. Simple free radical chemistry can, therefore, be used to generate polymeric materials from fullerene compounds. The real challenge in such chemistry will be to limit the extent to which the radical additions take place so as to allow soluble polymeric derivatives of C_{60} to be prepared. A complete description of the chemical and physical

properties of the copolymers will be forthcoming.

Supplementary Material Available: Thermal gravimetric analyses, infrared spectra, interrupted decoupling experimental data, and ^{13}C-labeling experimental data (4 pages). Ordering information is given on any current masthead page.

Electrochemical Detection of C_{60}^{6-} and C_{70}^{6-}: Enhanced Stability of Fullerides in Solution

Qingshan Xie, Eduardo Pérez-Cordero, and Luis Echegoyen*

Department of Chemistry
University of Miami
Coral Gables, Florida 33124
Received February 6, 1992

Although theory predicts that the LUMO of C_{60} should be able to accept at least six electrons to form diamagnetic C_{60}^{6-},[1–3] the latter species has so far eluded direct characterization in solution.[4–9] The existence of the hexaanionic molecule in the solid state is inferred from the formation of species such as K_6C_{60}, which have been well characterized by a variety of techniques, including solid-state ^{13}C NMR spectroscopy.[10] Part of the impetus behind the present work stemmed from the desire to generate and detect C_{60}^{6-} in a relatively stable environment in order to confirm the theoretical predictions.[1–3] The development of a general method capable of generating stable C_{60}^{n-} species, where $n = 1$–6, was another important driving force behind the present work.

There have been several reports concerning the electrochemical properties of C_{60} (and C_{70}).[4–9] One recent report by Wudl et al. described the reversible, three-electron electrochemical reduction leading to C_{60}^{3-}.[4] After this communication, Dubois and Kadish reported the observation of an additional reduction wave for C_{60} and the electrochemical formation and detection of C_{70}^{4-}.[4,5] The most recent and, to our knowledge, the only report of five reversible reduction processes for C_{60}, leading to C_{60}^{5-}, was also reported recently by Kadish et al.[6] These authors also studied the electrochemical properties of C_{70}, but no voltammetric data were presented for this compound.[6] They pointed out that several new peaks appeared after the fourth reduction of C_{70}, but that none could be unambiguously assigned to C_{70}^{5-}.

A wider expansion of the available potential window down to -3.3 V vs Fc/Fc$^+$ is reported in this communication. This was accomplished by the use of a mixed solvent system and low temperature. On the basis of supporting electrolyte and fullerene solubility considerations, the optimal solvent composition was between 15 and 20% by volume of acetonitrile in toluene. These new conditions have allowed the first observation of the sixth

(7) In interrupted decoupling experiments, delays of 60–90 μs were 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.

(8) 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.

(9) It is also possible, as pointed out by one of the referees, that branching in conjugation with the buckyball's intermolecular attractive forces could yield the same thermal stability.

(10) Milliken, J.; Keller, T. M.; Baronavsky, A. P.; McElvany, S. W.; Callanhan, J. H.; Nelson, H. H. *Chem. Mater.* 1991, *3*, 386–387.

(11) Joesten, B. L. *J. Appl. Polym. Sci.* 1974, *18*, 439.

(12) Infrared analysis of the residue reveals loss of the majority of the absorption bands from the copolymer.

(13) Elemental analyses for carbon and hydrogen were carried out in duplicate on a Perkin-Elmer CHN elemental analyzer. The copolymer is relatively resistant to combustion, and care must be taken to insure that the sample is completely combusted.

(14) The xylylene:C_{60} ratio was calculated from the ratio of carbon to hydrogen (C, 96.6%; H, 3.4%) with the assumptions that all of the hydrogen in the material originated from xylylene monomers and that the comtribution from terminal xylylene monomers was negligible.

(15) (a) Infrared spectral data 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) Joesten, B. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1972, *13*, 1948.

(16) Vassallo, A. M.; Pang, L. S. K.; Cole-Clarke, P. A.; Wilson, M. A. *J. Am. Chem. Soc.* 1991, *113*, 7820.

(17) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* 1991, *350*, 600.

(1) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* 1986, *125*, 459.

(2) (a) Haymet, A. D. *Chem. Phys. Lett.* 1985, *122*, 421. (b) Disch, R. L.; Schulman, J. N. *Chem. Phys. Lett.* 1986, *125*, 465.

(3) Scuseria, G. E. *Chem. Phys. Lett.* 1991, *176*, 423.

(4) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, *113*, 1050.

(5) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* 1991, *113*, 4364.

(6) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* 1991, *113*, 7773.

(7) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* 1990, *94*, 8634.

(8) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, *113*, 2780.

(9) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* 1991, *113*, 2940.

(10) Tycko, R.; Dabbagh, G.; Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Ramirez, A. P.; Tully, J. C. *Science* 1991, *253*, 884.