Chem. Mater. **1994,** *6,* 2023–2025

Preparation and Characterization of Poly(arylamine sulfones) and Poly(aryl ether sulfones) Carrying the C_{61} Fulleroid Pendant Group

M. Berrada,* Y. Hashimoto, and S. Miyata

Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received April 27, 1994. Revised Manuscript Received July 19, 1994®

This study described the synthesis of soluble polymers carrying fulleroid pendant groups. The starting monomer 4,4′-difluorodiphenyl fulleroid $(FPh)_2C_{61}$ was synthesized and polycondensed with aromatic diamine sulfone to give poly(4,4′-diphenyl-C_{61} amines) or with aromatic dialcohol sulfone to give poly(4,4′-diphenyl-C_{61} ethers). Polycondensation was carried out in different solvents with and without catalyst. Soluble polymers having an average molecular weight in the range $M_w = (5-20) \times 10^3$ were obtained. Molecular structural characterization of monomer and of fullerene moiety in the polymers was achieved by NMR, infrared, and UV–visible spectroscopies, mass spectrometry, and thermal analysis.

Introduction

Buckminsterfullerene, C_{60} molecule, was discovered in 1985 by Kroto, Smalley, et al.,[1–3] and the preparation of macroscopic quantities of C_{60} was reported 5 years later by Huffman, Krätschmer, et al.[4] Research on fullerenes is expanding at a rapid rate. The modifications of fullerene's surface are achieved by the addition reaction to its π-bond which is aromatic but as reactive as an electron-deficient olefin. Various types of addition reactions have been surveyed in these years, ranging from ionic (both nucleophilic and electrophilic) to concerted reaction (cycloaddition).[5,6] From the fullerenes, two types of polymer have been already reported: fullerenes are included in the backbone[7] or they are pendant groups.[8–10] The synthesis of well-defined fullerenes in polymer backbone is still very challenging. Most of these fullerene polymers are insoluble or sparingly soluble in common solvents and the soluble part of the polymer has low molecular weight. In this paper we report for the first time, a study of soluble polyarylamines and polyarylethers grafted with C_{60} using new monomer having an high reactivity, the p,p′-disubstituted diphenyl fulleroids capable to react with aromatic nucleophiles such as amines or alcohols. So far, there are no reports on polyarylamines or polyaryl ethers derived from C_{61}.

It has been already shown that the soluble polymers are useful supports and reagents for wide applications.[11,12] The present paper describes some recent investigations on the synthesis of C_{60} and modified C_{60} then the synthesis of poly(arylamine sulfones) and poly(aryl ether sulfones) carrying C_{61} fulleroid pendant group. The present work is especially focused on the synthesis of modified C_{60} as well as the difunctionality of the monomers to obtain polysulfones having the highest molecular weight.

Experimental Section

Starting Materials. 4,4′-Difluorobenzophenone was recrystallized from absolute ethanol and 4,4′-difluorodiphenyl hydrazone was prepared as previously described.[13] 4,4′-Difluorodiphenyldiazomethane was prepared from hydrazone derivative by oxidation with peracetic acid in the presence of a base and a trace of iodine according to literature.[14] 4,4′-Diaminodiphenyl sulfone and 4,4′-dihydroxydiphenyl sulfone were used as received. Potassium bicarbonate was dried under vacuum at 180 °C. Buckminsterfullerene, C_{60}, was prepared in our laboratory in good yields.[15] Pure C_{60} was obtained by column chromatography, and its purity was checked by HPLC. For further purification, C_{60} was dissolved in benzene, precipitated with hexane, filtered, and dried under vacuum at room temperature.

Purification of Solvents. Dimethyl sulfoxide (DMSO) was distilled over sodium chloride and calcium hydride using a column packed with glass helixes. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over phosphorus pentoxide. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation over calcium hydride. Toluene was washed twice with sulfuric acid, water, 5% aqueous hydrogen carbonate, and then with water. It was dried over calcium sulfate and then phosphorus pentoxide and distilled over sodium.

Preparation of monomer[16] (Scheme 1). The reaction between 4,4′-difluorodiphenyldiazomethane and C_{60} was carried out in freshly distilled toluene under nitrogen for 1 h at room

---

® Abstract published in *Advance ACS Abstracts,* September 15, 1994.

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163.

(2) Kroto, H. W. *Science* **1988**, *242*, 1139–1145.

(3) Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017–1022.

(4) Krätschmer, W.; Lamb, L. D.; Fostiropolous, K.; Huffman, D. R. *Nature* **1991**, 347–354.

(5) Wudl, F.; Hirsch, K. C.; Khemani, T.; Suzuki, T.; Allemand, A.; Koch, H.; Echert, G.; Srdanov, G.; Webb, H. M.; *ACS Symp. Ser.* **1992**, *481* (Fullerenes), 161.

(6) Eguchi, S.; Ohno, M. *Kikan Furaren*, **1993**, *1* (3), 99.

(7) Douglas, A. L.; Roger, A. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977–3978.

(8) Shi, S.; Khemani, K. C.; Li, Q. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656–10657.

(9) Patil, A. O.; Schriver, G. W.; Carstensen, B.; Lundberg, R. D. *Polym. Bull.* **1993**, *30*, 187–190.

(10) Geckeler, K. E.; Hirsch, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850–3851.

(11) Geckeler, K.; Pillai, V. N. R.; Mutter, M. *Adv. Polym. Sci.* **1981**, *39*, 65.

(12) Geckeler, K.; Bayer, E.; Spivakov, B. Ya.; Shkinev, V. M.; Vorobeva, G. A. *Anal. Chim. Acta* **1986**, *189*, 285.

(13) Snyder, H. R.; Rowland, R. L.; Sampson, H. J., Jr. *Org. Synth.* **1955**, *3*, 351.

(14) Adamson, J. R.; Bywood, R.; Eastlick, D. T.; Gallagher, G.; Walker, D.; Wilson, E. M.; *J. Chem. Soc., Perkin 1* **1975**, 2030.

(15) Motobe, T.; Hashimoto, Y.; Yamamoto, H.; Watanabe, T.; Miyata, S.; *Polym. Prepr. Jpn.* **1993**, *42*, No. 9.

(16) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö *Science* **1991**, *254*, 1186.

0897-4756/94/2806-2023$04.50/0

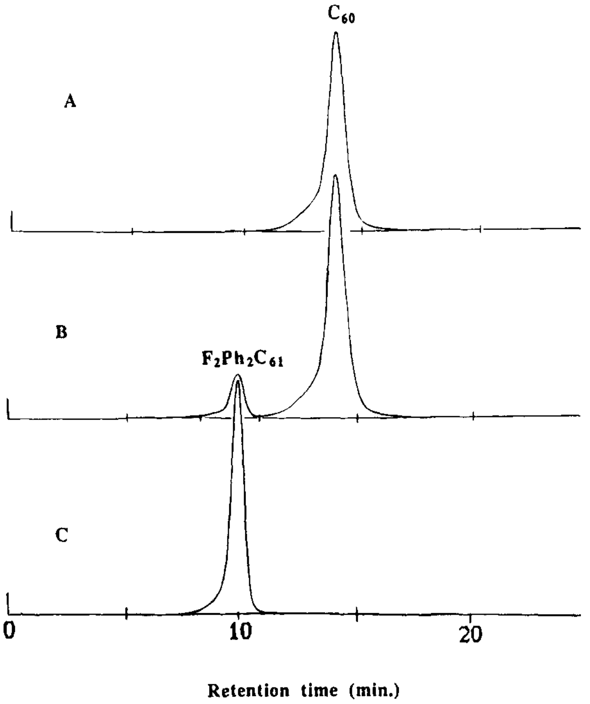
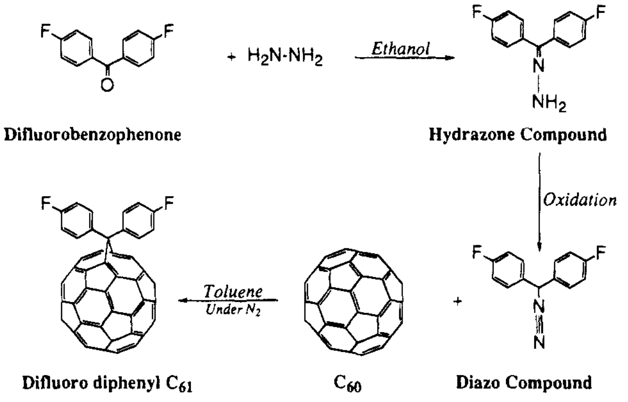


Figure 1. Chromatograms for the separation of C_{60} and $F_2Ph_2C_{61}$. C_{60} before the addition of diazomethane derivative (A) as well as after the addition (B). The chromatogram of purified $F_2Ph_2C_{61}$ is shown in (C). Experimental conditions: copoly(styrene–divinylbenzene) column (30 × 0.8 cm), eluent toluene, flow rate 1 mL min^{-1}, detection at 330 nm.

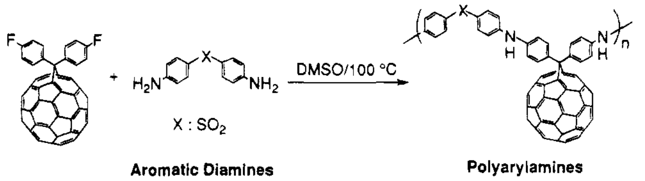
Scheme 1. Synthesis of Monomer



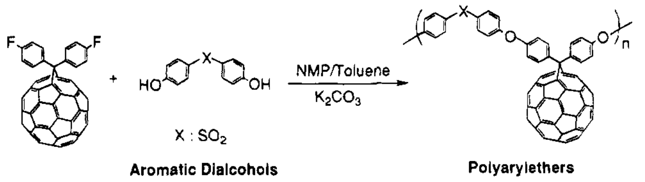
temperature. The product thus obtained was a mixture of 4,4'-difluorodiphenyl fulleroid, $(FPh)_2C_{61}$, and of untransformed C_{60}. A purple solution was formed, which turned to red-brown after 20 min. Toluene was evaporated, and the black product was dried under vacuum at room temperature. To purify the crude product, which contains about 80% of unreacted C_{60} (as checked by HPLC, see Figure 1), we used the chromatography technique with a column filled with silica gel, using benzene/hexane (1/10 by volume) as an eluent. The monomer is less soluble in benzene than C_{60} and thus was obtained in low yields. The product was dissolved in a small amount of benzene, precipitated into hexane, and dried under vacuum at room temperature for 24 h.

Preparation of Polymers. *Synthesis of Poly(4,4'-diphenyl-C_{61} amines) (Scheme 2).* Poly(arylamine sulfones) were prepared by reacting stoichiometric quantities of the $(FPh)_2C_{61}$ monomer with an aromatic diamine sulfone in DMSO. The mixture was stirred at 100 °C under nitrogen. The solution became viscous after about 5 h. The solution was then diluted with hot DMSO and kept overnight at 100 °C. The crude polymer was precipitated into water, filtered off, washed with hot water and methanol, and then dried at 50 °C in vacuum. The polymer thus obtained was a brown powder, yield 70–80%.

Scheme 2. Synthesis of Poly(4,4'-diphenyl-C_{61} amines)



Scheme 3. Synthesis of Poly(4,4'-diphenyl-C_{61} ethers)



Synthesis of Poly(4,4'-diphenyl-C_{61} ethers) (Scheme 3). The following procedure was used for the synthesis of poly(aryl ether sulfones) via nucleophilic aromatic substitution in a polar aprotic solvent. 4,4'-Dihydroxydiphenyl sulfone (27 mg, 1.08 × 10^{-4} mol) and potassium carbonate (15 mg, 1.1 × 10^{-4} mol) were dissolved in 25 mL of NMP in a 250 mL four-neck flask equipped with a stirrer, Dean Stark trap, condenser, nitrogen inlet, and thermometer. Toluene (25 mL) was added as an azeotropic agent. The reaction mixture was heated to 140 °C for 3 h to dehydrate the solution and then up to 170 °C. At this temperature, 100 mg (1.08 × 10^{-4} mol) of $(FPh)_2C_{61}$ fulleroid were added and the solution was stirred 8 h at 170 °C. The solution was then cooled to room temperature and diluted with 50 mL of tetrahydrofuran. The polymer was precipitated into methanol/water (80/20 by volume), filtered off, and dried in vacuum. The polymer was obtained as a powder; yield 75–90%.

Results and Discussion

p,p'-Disubstituted diphenyl fulleroids are easily prepared because the raw materials, substituted benzophenones, are either commercially available or easy to prepare and they are readily converted to stable diazomethanes through the hydrazones. Extended reaction time (more than 2 h) using different stoichiometries gives the following difluorodiphenyl fulleroids: C_{62}, C_{63}, and C_{64}. For the latter, 24 h and large excess (over 2 equiv of diphenyldiazomethane) were used to obtain the product.

Fulleroid was identified by ^1H NMR (JEOL FX-400) spectra. The ^1H NMR spectrum in CS_2–acetone-d_6 indicates the presence of biphenyl substituted by fluoride atoms in the product; δ 6.93 (4H, meta H–Ar), δ 8.12 ppm (4H, ortho H–Ar). It is interesting to note that, in the case of $(FPh)_2C_{61}$ fulleroid, the ortho and meta protons are shifted. In the former, ortho hydrogen atoms are the closest atoms to the surface of the sphere, they appear at 8.12 ppm, considerably deshielded relative to the latter as they appear at 7.85 ppm.[16] The UV–visible absorption of the monoadduct is virtually identical to that of C_{60} (see Figure 2).

The fast-atom-bombardment (FAB) mass spectra were recorded on a VG 70-250 HF spectrometer (xenon 7–8 keV; matrix was *m*-nitrobenzyl alcohol). FABMS: Several cluster fragmentations among 1300 and 720 (stronger, C_{60}) and the parent weak peak at 922 ($(FPh)_2C_{61}$). The amount of carbon found by elemental analysis does not agree with the calculated one. It is well-known that most of the elemental analyses of C_{60} derivatives give consistently low carbon values. The fact that the

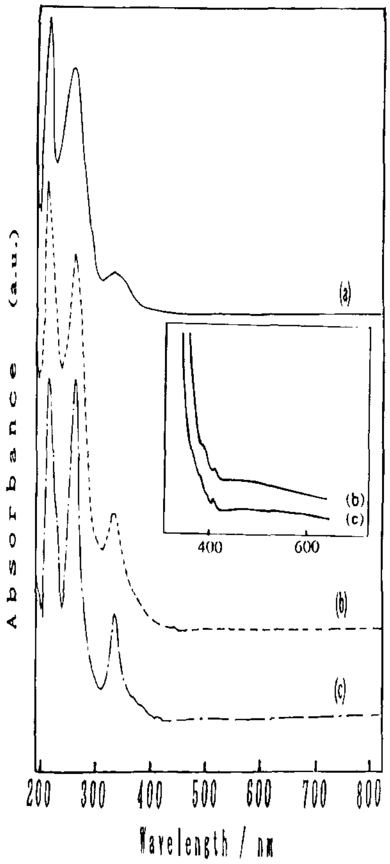


Figure 2. Comparative ultraviolet–visible absorption spectra of C_{60}, monomer and polymer, from top to bottom: (a) poly-(4,4′-diphenyl-C_{61} amine); (b) $F_2Ph_2C_{61}$; and (c) C_{60}. The inset is the 700–380 nm at 3 times the gain. The absorbance of two spectra has not been normalized.

hydrogen content of C_{60} molecules is increased, would indicate a more complete combustion than in the case of $(FPh)_2C_{61}$.

Polycondensation of Appropriate Monomers. Fullerenes are known to be attacked by nucleophiles, and it has been reported that they react with aliphatic amines but not with aromatic amines.[17] The homopolymerization of 4,4′-difluorodiphenyl fulleroid $(FPh)_2C_{61}$ and 4,4′-diaminodiphenyl sulfone to form poly(arylamine sulfones) was studied in different solvents such as NMP, DMSO, and DMAc. The experiments carried out in DMSO solution at 100 °C give the best polycondensation rate, which is probably due to the similarity of the structures. The presence of sulfonyl group in the polymer increases the solubility. As expected, the rate of polycondensation increases with the time of reaction. A long reaction time, 18 h, was used to obtain a polymer having a reduced viscosity (RV) of 0.325 dL/g. The hydrofluoric acid was removed by bubbling nitrogen through the reaction mixture. This technique allows us to eliminate a number of side reactions and is useful when an accurate dihalide:bisamine stoichiometry has to be controlled. The brown powder polymer is soluble in THF, DMSO, and other solvents; it is characterized by infrared spectroscopy (IR). The spectra shows the presence of amine –NH– (3358, 1650 cm^{-1}), Ar C–H (3080, 1155 cm^{-1}), and Ar C–C (1601, 1493 cm^{-1}) stretching vibrations. The UV–visible spectrum of the polyarylamine biphenyl C_{61} (see Figure 2) has absorption maxima at 212, 250, and 326 nm. The retention of the electronic structure of the C_{60} moieties in this polymer was deduced from the similarities of the electronic spectra. The thermogravimetric analysis (TGA, see Figure 3) shows that the degradation temperature T_d of the polymers is situated near 380 °C, and the weight loss is about 95% at 420 °C. The studied polymer has a low molecular weight, $M_w = 5000$.

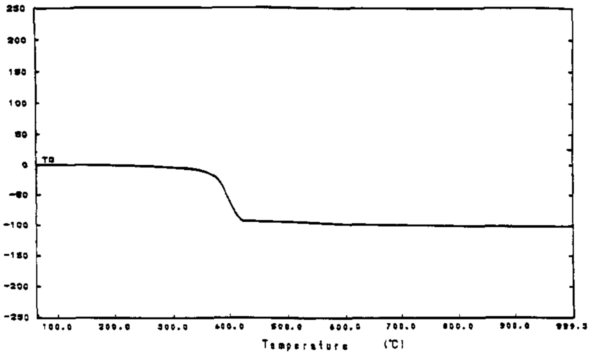


Figure 3. TGA curve of poly(4,4′-diphenyl-C_{61} amine). The heating rate was 10 °C/min.

The polycondensation of 4,4′-dihalogenodiphenyl fulleroid with bisphenoxide sulfones was studied in different solvents. The solvent has an important effect, the preferred solvents are polar and aprotic, such as DMSO and NMP, which are good solvents for both reactants and polymers and give a greater enhancement of the reaction rate than other solvents.[18] The polycondensations are carried out in NMP solution, using a slight excess of a weak base (potassium carbonate) catalyst combined with an azeotropic compound (toluene). The best results are obtained with the couple K_2CO_3/NMP. When the reaction is carried out without K_2CO_3 catalyst, no polymer is obtained. The nucleophilic aromatic displacement of halogen in aromatic compounds is activated by the strongly electron-withdrawing C_{60} group, which leads to high molecular weight, up to $M_w = 2 \times 10^4$. The degradation temperature of this polymer is also near 380 °C and the UV–visible spectrum is identical to that of poly(arylamine sulfones).

Conclusions

It is the first time that classical polymers, such as poly(arylamine sulfones) and poly(aryl ether sulfones), carrying C_{60} side chains have been prepared. Using our precursor polymer, we can develop other new conductible polymers such as poly(4,4′-diphenyl-C_{61} sulfides). The new results presented here open access to a new class of interesting polymers.[19] It also allows the design of soluble fullerenes-containing polymers that are suitable for the processing of advanced materials.

Acknowledgment. We are grateful to Dr. Paras N. Prasad of the Research Foundation of State University of New York for the financial support. This study was partially supported by the Grant-Aid for Scientific Research, 05452109, from the Ministry of Education, Science and Culture.

---

(17) Hammond, G. S.; Kuck, V. J., Ed.; *Fullerenes Synthesis, Properties, and Chemistry of Large Carbon Clusters* **1991**, *161*, 481.

(18) Johnson, R. N.; Farnham, A. G.; Glendenning, R. A.; Hall, W. F.; Merriam, C. N. *J. Polym. Sci.*, A-1 **1967**, *5*, 2375.

(19) German Patent Application pending.