parameters. A detailed study is in progress.

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A Polyester and Polyurethane of Diphenyl C_{61}: Retention of Fulleroid Properties in a Polymer

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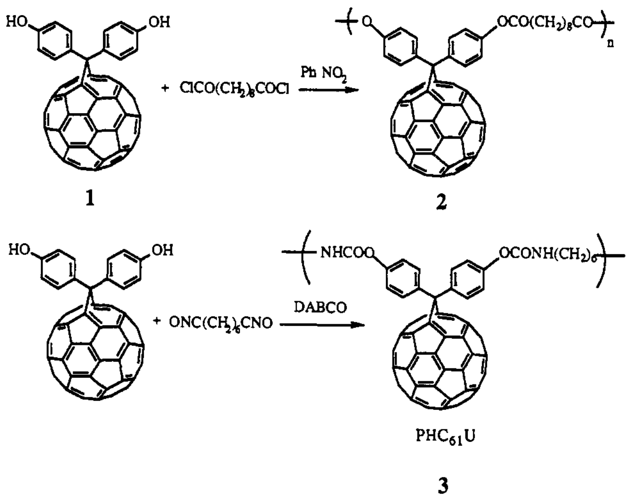
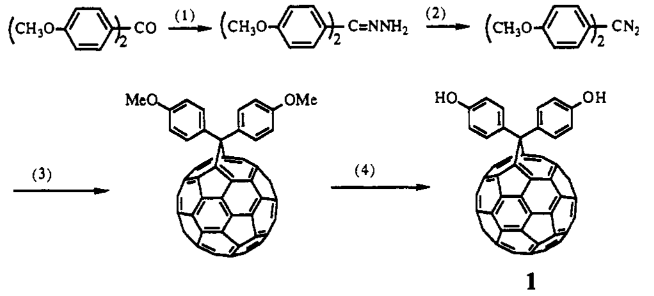
Buckminsterfullerene, C_{60},[1] and its unusual chemical properties,[1b,2] in particular the fulleroid synthesis,[1b,3] prompted us to investigate the possibility of preparing polymers[4] containing the C_{60} moiety as either a member of the backbone ("pearl necklace") or a pendant group ("charm bracelet").[5] We describe herein the syntheses and characterization of two charm-bracelet-type polymers containing C_{61} molecules dangling from the polymer backbone.

The polymers were prepared according to Scheme I, and the monomer synthesis is shown in Scheme II.

Scheme I



Scheme II[a]



[a] (1) NH_2NH_2/ethanol, reflux,[6] 86%; (2) HgO/petroleum ether, room temperature; (3) C_{60}/toluene, room temperature, 73%; (4) BBr_3/*o*-dichlorobenzene, 0 °C to room temperature, 94%.

$(HOC_6H_4)_2C_{61}$ (**1**) is very stable in pyridine, partially soluble in ether, tetrahydrofuran, or *o*-dichlorobenzene, and only very sparingly soluble in benzene or toluene.

Polymerization of **1** and sebacoyl chloride in dry nitrobenzene at 143 °C (22 h), using equimolar amounts of the monomers and no catalyst,[7] produced poly(4,4′-diphenyl-C_{61} sebacate), **2**, in 61% yield as a brown powder[8] which was sparingly soluble in THF but soluble in nitrobenzene and benzonitrile. Infrared spectroscopy of a KBr pellet of the polymer showed the presence of sp^3 C—H (2920, 2850 cm^{-1}) and ester C═O (1760, 1725 cm^{-1}) stretching vibrations. The ^1H NMR spectrum in THF-d_8 had peaks at 10.83 ppm (suggesting the presence of an OH end group), 6.8–8.55 ppm (several sets of sharp peaks: multiplets, phenylene protons), and 1.2–2.6 ppm (several peaks; multiplets, hexamethylene protons).

Comparative thermogravimetric analysis (TGA) results for **1**, poly(biphenol A sebacate) (PBAE), and **2** revealed that, as is the case with most C_{61} fulleroids, **1** is moderately thermally stable. It gradually loses weight upon heating, retaining ~90% of its original mass at 500 °C and ~83% at 700 °C. PBAE exhibits a rapid weight loss from 360 to 480 °C (95% of its initial mass). Similar to PBAE, the TGA of **2** also reveals a weight loss between 360 and 480 °C. Only about 9% (calculated 15.5%) weight loss for the decomposition of **2** was observed in that temperature range.[9] Apparently decomposition to volatile fragments is far from quantitative.

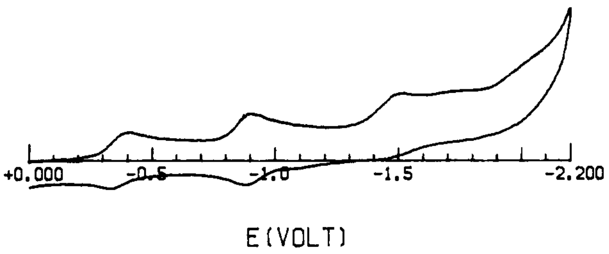


Figure 1. Cyclic voltammetry of polymer **2** in THF with 0.1 M $TBABF_4$ as supporting electrolyte: Pt working and counter electrodes; Ag/AgCl, reference electrode; scan rate, 100 mV/s.

The UV-vis spectrum of a THF solution of **2**, while showing broad bands, is reminiscent of other C_{61}'s[3] with bands at 690, 475, 430, 330, 275, and 250 nm. Solution cyclic voltammetry of the polymer in THF is shown in Figure 1. The presence of the first three characteristic reduction waves[3] of all diphenyl C_{61}'s clearly shows that the polymer retained the electronic properties of diphenyl fulleroids.

When an equimolar amount of hexamethylene diisocyanate and **1** in *o*-dichlorobenzene was heated in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO), an insoluble, brown powder was obtained in 60% yield.[10]

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(4) (a) Polymers containing a C_{60} unit in the backbone of a poly(*p*-xylylene) have recently been reported by Loy, D. A., and Assink, R. A., presented at the Materials Research Society Meeting, Boston, Dec 1991. (b) A "fullerenated" poly(styrene) was prepared by Prakash and Olah: Prakash, S.; Olah, G. *J. Am. Chem. Soc.*, in press.

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(7) HCl was removed by bubbling nitrogen through the reaction mixture.

(8) Contrary to **2**, **3** did not produce good, reproducible combustion analysis results. Attempts are being made to correct this problem. Other analytical data are in accord with the proposed structure. Both polyesters had low M_w. GPC (polystyrene standard) M_w 4000; [η] = 0.2 ± 0.1 dL/g (0.9 g/dL).

(9) The weight loss between 200 and 360 °C is typical of diphenyl fulleroids and has not been assigned to any particular fragmentation.

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When the infrared spectra of **1**, poly(bisphenol A hexamethyleneurethane) (PBAU), and **3** are compared, the IR spectrum of **3** is essentially superimposable with that of PBAU. Since the band intensities of the C_{61} moiety are very weak, they are overwhelmed by the absorptions of the aliphatic hydrocarbon and urethane vibrations of the polymer.

Comparative thermogravimetric analysis (TGA) results for **1**, PBAU, and **3** shows that PBAU exhibits a rapid weight loss (90%) from 180 to 300 °C. The weight loss observed in almost all polyurethanes is attributed to "unzipping" to its original monomers. Similar to PBAU, the TGA of **3** also reveals a weight loss between 180 and 340 °C. The latter is consistent with the urethane structure of **3**. The nonquantitative weight loss of about 9.5–10% (calculated for 100% loss of diisocyanate = 15.5%) for the unzipping of **3** is unexplained at this time.[11]

While PBAU displays an endothermal peak at about 88 °C, which is believed to be the glass transition temperature, the differential scanning calorigram of **3** shows no transitions.[12]

We have shown above that polymers containing fulleroid units[3] can be prepared and characterized. While the polyurethane is insoluble, the polyester is much more tractable. The remarkable retention of the electronic structure of the C_{60} moieties as witnessed by UV–vis spectroscopy and cyclic voltammetry is a very encouraging result which augurs well for observation of unusual fullerene-type properties of products fabricated from these polymers.

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Supplementary Material Available: UV–vis and IR spectra, comparative thermogravimetric analysis, and cyclic voltammetry (5 pages). Ordering information is given on any current masthead page.

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(10) Anal. Calcd for $(C_{81}H_{22}N_2O_4)_n$: C, 89.50; H, 2.03; N, 2.58. Found: C, 88.23; H, 2.91; N, 2.47. Other analytical data are in accord with the proposed structure. M_w could not be determined due to insolubility.

(11) It could be attributable to the thermal stability of the fulleroid moieties and their trapping of "nascent" diisocyanate.

(12) This observation and the insolubility of the polymer could imply cross-linking during urethane formation, but a control experiment (dimethoxyphenyl fulleroid + hexamethylene diisocyanate) showed no reaction, indicating no cross-linking reaction between C_{61} and the isocyanate function.

Synthesis and Structural Characterization of a Layer-Segregated Platinum–Ruthenium Cluster Complex That Exhibits Selective Coordination and a High Activity for the Catalytic Hydrogenation of Diphenylacetylene

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The unique reactivity observed for certain metal alloy catalysts may be produced by preferential interactions of the substances at selected metal sites.[2] In recent studies we have observed a tendency of the metal atoms in high-nuclearity platinum–ruthenium and platinum–osmium carbonyl cluster complexes to segregate into layers of the pure elements.[3] We have now prepared a new member of this family and found that the alkyne PhC_2Ph exhibits a coordination preference for a triruthenium site in the monoalkyne derivative and also displays a high activity for the catalytic hydrogenation of PhC_2Ph to (*Z*)-stilbene, Ph(H)C=C(H)Ph.

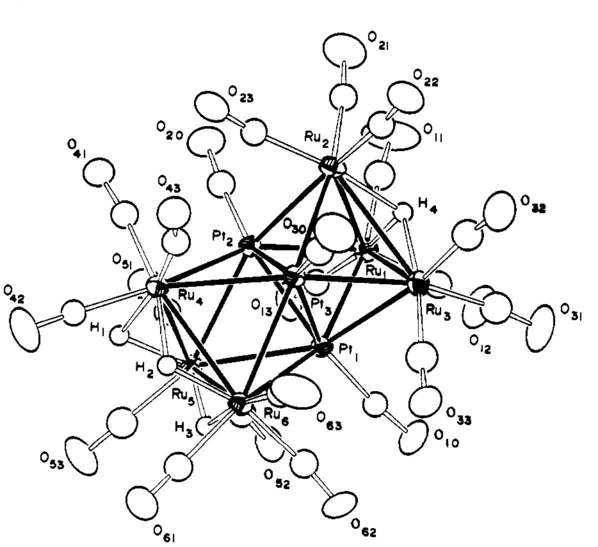

Figure 1. An ORTEP diagram of $Pt_3Ru_6(CO)_{20}(\mu\text{-}H)_3(\mu_3\text{-}H)$, **1**. Selected interatomic distances (Å) are Pt(1)–Pt(2) = 2.629 (1), Pt(1)–Pt(3) = 2.635 (1), Pt(2)–Pt(3) = 2.646 (1), Ru(1)–Ru(2) = 3.084 (2), Ru(1)–Ru(3) = 3.043 (2), Ru(2)–Ru(3) = 3.054 (3), Ru(4)–Ru(5) = 3.002 (2), Ru(4)–Ru(6) = 3.024 (2), Ru(5)–Ru(6) = 3.033 (2), Ru(1)–H(4) = 2.0 (1), Ru(2)–H(4) = 1.9 (2), Ru(3)–H(4) = 1.9 (1).

The new complex $Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_3(\mu_3\text{-}H)$, **1**, was obtained in 83% yield from the reaction of $Ru_4Pt_2(CO)_{18}$ with hydrogen (1 atm) in a refluxing heptane solution. Compound **1** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses,[4] and an ORTEP diagram of its molecular structure is shown in Figure 1.[5] The structure consists of three triangular layers of nine metal atoms arranged in the form of a face-shared bioctahedron. The central layer consists of three platinum atoms while the outer layers are pure ruthenium. Three hydride ligands bridge each edge of the Ru(4)–Ru(5)–Ru(6) triangle while the fourth hydride is a triple bridging ligand across the Ru(1)–Ru(2)–Ru(3) triangle, δ (at –88 °C) –15.84 (s, 3 H), –19.26 (s, 1 H). The platinum–platinum distances are similar to those found in other layered mixed metal clusters,[3] but with ruthenium–ruthenium distances are unusually long due to the presence of the hydride ligands.[6] The molecule also contains 21 carbonyl ligands and obeys the conventional electron counting theories for condensed polyhedra.[7]

When allowed to react with PhC_2Ph in a refluxing hexane solution, **1** was converted to the derivative $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}$

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(4) $Ru_4Pt_2(CO)_{18}$, 25.0 mg, dissolved in 140 mL of heptane was heated to reflux for 12 min in the presence of a slow purge with hydrogen. After cooling, a small amount of dark precipitate was removed by filtration and discarded. The solvent was removed from the filtrate, and the residue was washed with pentane several times to yield pure **1**, 16.1 mg. An additional 3.0 mg of **1** was subsequently obtained from the washings by TLC using 3/1 hexane/CH_2Cl_2 solvent. Total yield: 19.1 mg (83%). IR for **1** (ν_{CO} in CH_2Cl_2): 2081 (w, sh), 2066 (vs), 2052 (m, sh), 2026 (w). ^1H NMR (δ in acetone at –88 °C): –15.84 (s, 3 H), –19.26 (s, 1 H). Anal. Calcd (found): for C, 14.14 (14.49); for H, 0.23 (0.26).

(5) Crystal data for **1**: space group = $P2_1/c$, a = 18.157 (3) Å, b = 11.701 (4) Å, c = 17.580 (4) Å, Z = 4, 2657 reflections, R = 0.033. Diffraction data at 20 °C were collected on a Rigaku AFC6S diffractometer using Mo Kα radiation.

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