

Polymer-Bound C₆₀

Kurt E. Geckeler* and Andreas Hirsch*

Institute of Organic Chemistry
University of Tuebingen
Auf der Morgenstelle 18
DW-7400 Tübingen, Germany

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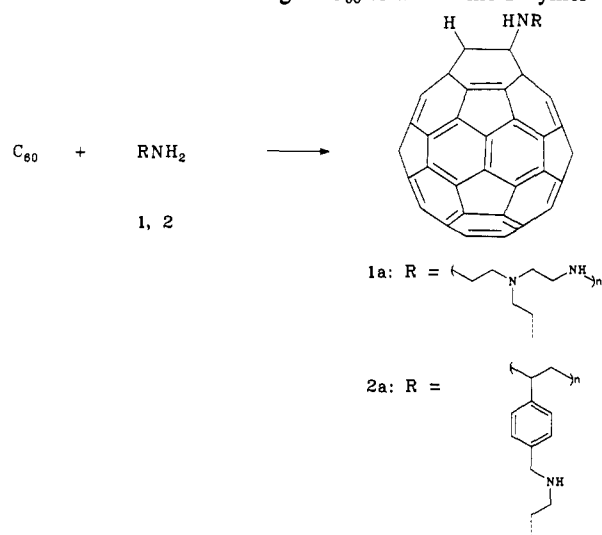
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Buckminsterfullerene (C₆₀)^{1,2} and its n-doped derivatives exhibit a variety of outstanding electronic,³ conducting,⁴ and magnetic⁵ properties. It is obvious that the combination of the advantages of this molecule with the properties of other materials like polymers is very challenging. In order to realize this interesting concept two principal approaches can be envisaged: (a) macromolecules with pendant fullerene (on-chain, "fulleroplastic"), or (b) polymer materials with fullerene units incorporated into the main chain (in-chain, "polyfullerene"). The "on-chain" (polymer-bound) fullerenes have several intrinsic advantages over polyfullerenes which are mainly due to the defined, stereochemical arrangement of the C₆₀. In this paper we report for the first time a study of polymer-bound C₆₀ using soluble amino polymers capable of adding to fullerene double bonds. Defined C₆₀-on-chain polymers were obtained by allowing these polymers to react with C₆₀ under very mild conditions at room temperature.

So far, only two attempts to prepare polymeric fullerene derivatives are known in the literature. A highly cross-linked polymeric derivative based on polystyrene was mentioned in 1991 briefly but not described in detail.⁶ Very recently, a copolymeric product, which was obtained by using flash thermolysis of paracyclophane, was reported.⁷ Apart from the extreme reaction conditions (650 °C, under vacuum, then -78 °C), this approach suffers from the major disadvantage that no defined and cross-linked products were obtained. As stated in this paper, there are no reports of polymers derived from C₆₀.

Soluble polymers have been shown to be very useful supports and reagents for a variety of applications.^{8,9} Among these, poly(alkylene imine)s are known to be an interesting class of macromolecular compounds.¹⁰ We prepared the C₆₀-on-chain polymers (Scheme I) by titrating toluene solutions of C₆₀ with the aminopolymers **1** and **2** (Table I). The coupling to the polymer chain proceeded according to the well-known amine addition to fullerene double bonds.^{11,12} The consumption of fullerene can be regarded as a "buckyball fishing" process.

In the case of the completely insoluble polymer **1a**, the titration with **1** can be followed quantitatively by the determination of the consumption of fullerene-60 with UV/vis spectroscopy. Toward this end, 20 mg (0.027 mmol) of fullerene-60 was dissolved in 20

Scheme I. Covalent Binding of C₆₀ to an Amino Polymer

mL of toluene in a centrifuge vial. To this solution was added **1**, dissolved in toluene (28 g/L), in steps of 100 μL at room temperature. Upon the addition of the precursor polymer, polymer-bound C₆₀ (**1a**) precipitated immediately. To determine the consumption of fullerene-60, the suspension was centrifuged, 100 μL of the solution was removed, and then 2 mL of *n*-hexane was added for the determination of the absorption at 598 nm. In this way, a linear decrease of the fullerene-60 concentration upon precursor polymer addition was detected (see supplementary material). When the titration reached the point at which about 60% of the fullerene-60 was consumed, the addition of the precursor polymer **1** was stopped. In summary, a total of 1500 μL of a toluene solution of **1** was added. After centrifugation and decanting from the toluene solution, polymer **1a** was washed with toluene and chloroform (2 times) and dried at 80 °C under vacuum for 24 h.

The yield of **1a** (49.0 mg) in combination with the amount of C₆₀ consumed (11.3 mg) allows one to determine the capacity (Table I). This can also be done in the case of polymer **2a**, which does not completely precipitate upon precursor polymer addition. In this case, the titration itself (conditions: 7.4 mg (0.010 mmol) of C₆₀ in 10 mL of toluene titrated with **2** in toluene (16 g/L) in steps of 100 μL at room temperature) can be followed relatively by UV/vis spectroscopy since only a part of **2a** precipitates upon precursor polymer addition. For the quantitative determination of the capacity of the polymer-bound C₆₀, **2a** was precipitated by the addition of hexane subsequent to the titration. Thus, the amount of remaining C₆₀ (4.1 mg) as well as the yield of **2a** (17.0 mg) could be obtained, which allows one to calculate the capacity (Table I). The capacity values were also determined by thermogravimetry.

The solid-state ¹³C MAS NMR spectra of the products exhibited the only two expected distinct peaks at 47.2 ppm (CH₂ groups) and 147.2 ppm (quaternary fullerene carbons). The polymer **2a** can be dissolved in toluene and carbon disulfide, thus being the first soluble fullerene-containing polymer. The UV/vis spectrum of its golden brown solution in toluene shows peaks at 308 (sh), 326, and 435 nm, which are characteristic absorptions for monofunctionalized organofullerenes.^{13,14} The FT-IR spectra confirmed the monofunctionalization of the C₆₀ units by showing the typical band pattern in the region between 580 and 514 cm⁻¹. The splitting in this region is characteristic due to the lowering

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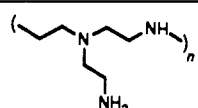
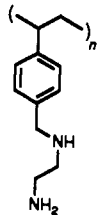

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Table I. Experimental Data of Polymer-Bound Fullerenes

no.	name of precursor polymer	repetitive structural unit of the precursor polymer	molar mass ^a (g mol ⁻¹)	molar ratio (polymer:C ₆₀)	capacity (mg g ⁻¹)
1a	poly(ethylene imine) ^b		35 000	18:1	230
2a	poly[4-[(2-aminoethyl)imino]methyl]styrene] ^{c,d}		20 000	19:1	180
3	poly(propylene imine)		no reaction		

^a Referred to the precursor polymer. ^b Reference 10. ^c K. E. Geckeler and R. Zhou, unpublished results. ^d Amino group containing comonomer unit of a copolymer with styrene (1:1).

of the local symmetry in monoaddition products of fullerene.^{13,15,16} Comparative spectra of analogous compounds confirmed this observation.

In conclusion, we have discovered that it is possible to prepare covalently polymer-bound C₆₀. It is the first time that a characterized polymer derivative of fullerene has been described. The concept presented here opens access to a new class of interesting polymers.¹⁷ It also allows the design of soluble

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fullerene-containing polymers that are suitable for the processing of advanced materials.

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Supplementary Material Available: UV/vis and FT-IR spectra, simultaneous TG-DT analysis, ¹³C MAS NMR spectrum, and titration curves (21 pages). Ordering information is given on any current masthead page.

(17) German Patent Application pending.