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A New C_{60} Polymer via Ring-Opening Metathesis Polymerization

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As pointed out in a recent review,[1] there are several reasons for producing polymers that contain C_{60}. The peculiar features of the fullerene are indeed retained in most of its derivatives. Thus, polymeric fullerene materials can be expected to possess the same electronic, optical, and catalytic properties of the parent C_{60}. In addition, polymers can be easily handled, whereas C_{60} and its derivatives give films with much difficulty. Due to low solubility of C_{60}, it is difficult to obtain fullerene-based high molecular weight polymers. In this paper we report the preparation and characterization of a high molecular weight polymer containing C_{60}, obtained via ring-opening metathesis copolymerization (ROMP) with norbornene.

The fullerene monomer for ROMP was prepared by cycloaddition of quadricyclane to C_{60}, purified, and characterized according to our published procedure (Scheme 1).[2]

In our original paper, we have also shown that the double bond of the norbornene moiety in **1** is relatively unhindered and more reactive toward a number of reagents than the fullerene double bonds. We took advantage of this characteristic for subjecting this molecule to ROMP conditions. ROMP is in fact a very mild polymerization procedure which allows good control of the structure and the stereochemistry of the polymer.[3]

Due to the low solubility of **1**, the polymerization was carried out with an excess of norbornene (1% molar of **1**). At room temperature, a 1,2-dichlorobenzene solution of **1** (0.036 mols), norbornene (3.6 mols) and Mo(CH-t-Bu)(NAr) $[OCMe(CF_3)_2]_2$[4] as the catalyst, was stirred overnight under nitrogen (Scheme 2). The mixture was quenched with pyvalaldehyde, and the copolymer precipitated by addition of methanol. Whereas **1** is completely insoluble in chloroform, the copolymer **2** could be easily dissolved in this solvent and purified by precipitation by addition of methanol. The average molecular weight (M_w), measured by GPC using polystyrene as standard, was 103 360, with a polydispersity index of 5.2. A uniform free-standing film of **2** was obtained by peeling off the relatively thick deposit cast from a chloroform solution onto a glass substrate. Thermogravimetric analysis showed that the polymer degraded at 470 °C, indicating that the C_{60}-containing polymer is a robust material, but of lower thermal stability than polynorbornene (Figure 1).

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(1) Hirsch, A. *Adv. Mater.* **1993**, *5*, 859.

(2) Prato, M.; Maggini, M.; Scorrano, G.; Lucchini, V. *J. Org. Chem.* **1993**, *58*, 3613.

(3) Stevens, M. P. *Polymer Chemistry*; Oxford: New York, 1990; p 285.

(4) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Bazan, G. C.; Oskam, J. H.; Cho, H. N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899. (c) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.

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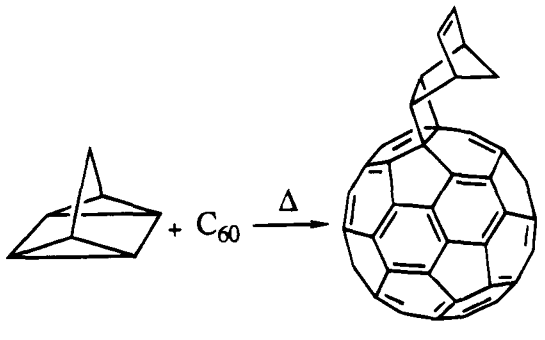
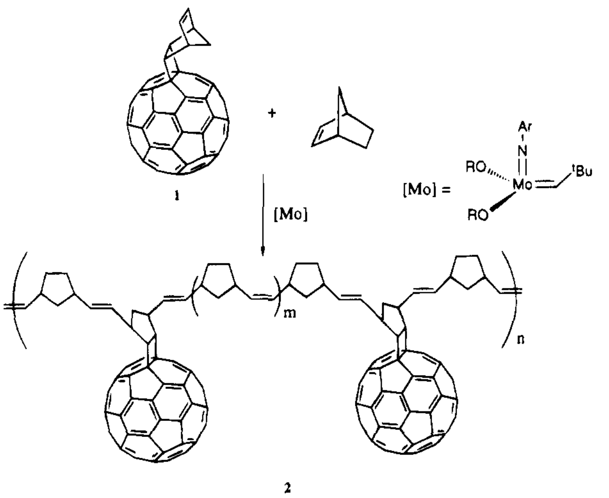
Scheme 1



1

Scheme 2



The proton and carbon NMR spectra show the typical pattern of polynorbornene. The cis/trans isomer ratio is affected by the relative amount of **1** present during the polymerization process. In the absence of **1**, the cis/trans ratio of polynorbornene was ca 3:1. When 0.7 mol% **1** was present, the cis/trans ratio changed to 4.7:1. Raising the amount of **1** up to 1 mol% increased the isomer ratio to 6:1. The visible spectrum of the copolymer containing 1 mol% **1** shows that the electronic configuration of **1** is retained in the polymer, with shoulders at ca. 320–340 nm and the typical absorptions at 430 and 700 nm. The cyclic voltammetry of the copolymer exhibits the usual behavior of C_{60} monoadditon derivatives, thus confirming that the polymer is electroactive.[5]

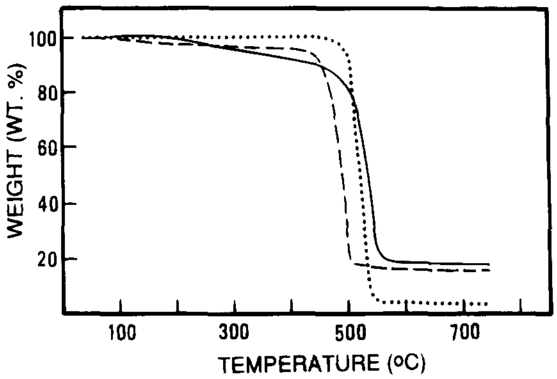


Figure 1. Thermogravimetric analysis of polymer **2** (dashed line), cross-linked **2** (solid line), and polynorbornene (dotted line).

When the C_{60}-containing polymer (1 mol%) was heated to 80 °C for 72 h in the solid state, cross-linking occurred. The resulting polymer was insoluble in all organic solvents, exhibiting the swelling and solvent sorption typical of cross-linked materials. Thermogravimetric analysis showed degradation at 517 °C. Cross-linking also occurred upon heating a sample of pure polynorbornene under the same conditions.

We have shown that a processable film which contains only 1% of a C_{60} derivative exhibits electronic and electrochemical properties which are typical of the carbon cluster.

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Supplementary Material Available: Detailed experimental procedures and spectroscopic characterization of polymer **2** (11 pages). Ordering information is given on any current masthead page.

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(5) (a) See supplementary material. (b) Shi, S.; Khemani, K. C.; Li, Q. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656 found that a polymer incorporating a modified C_{60} also retained the electrochemical properties of methanofullerenes.