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Polyethene with pendant fullerene moieties

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Supporting material to:

“Polyethene with pendant fullerene functionalities”

by X. Zhang, A. B. Sieval, J. C. Hummelen and B. Hessen.

Experimental details:

Chemicals.

(C₅Me₄SiMe₃N^tBu)TiCl₂ (**A**) was prepared following literature procedures.¹ Methylalumoxane (MAO, 10 wt % solution in toluene, Witco GmbH) was used as received. [60]Fullerene (>99%) was obtained from Bucky USA. Toluene (Aldrich anhydrous) was passed over an alumina column under nitrogen atmosphere before use. Chloroform was distilled under nitrogen from calcium hydride. Ethene (AGA Polymer grade) was passed over columns of BASF R3-11 oxygen scavenger and molecular sieves (4Å) before being passed to the reactor. Other solvents and reagents were obtained commercially and were used as received.

Co-monomer synthesis: 2'(RS)-dec-9-enyl-2',5'-dihydro-1'-methyl-1'H-pyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene.

A mixture of 7.20 g (10.0 mmol) of C₆₀, 3.80 g of sarcosine (40 mmol) and 3.38 g (20 mmol) of undecylenic aldehyde in 200 ml of o-dichlorobenzene (ODCB) was heated under nitrogen to 85 °C for 5 h.

The reaction mixture was cooled down and concentrated in vacuo to ~75 ml. This solution was placed on a short silica gel column and the unreacted C₆₀ was removed using CS₂. Subsequently, the mono-adduct was obtained using cyclohexane/toluene = 1:1 (v/v). HPLC analysis showed that the obtained product was not yet free from side products, therefore it was further purified by a second column chromatography (silica gel, cyclohexane/toluene = 1:1 (v/v)). The fractions containing the desired product (>99.5% purity (HPLC analysis, remainder C₇₀-adduct)) were combined and concentrated in vacuo. HPLC analyses were performed on a Hewlett Packard HP LC-Chemstation 3D

(HP 1100 series) using an analytical Cosmosil Buckyprep[®] column (4.6 x 250 mm) using toluene/cyclohexane = 1 : 1 (v/v) as eluents.

The resulting material was redissolved in 40 ml of ODCB. The fullerene was precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 55 °C. This gave 2.40 g (2.60 mmol, 26%) of 2'(RS)-dec-9-enyl-2',5'-dihydro-1'-methyl-1'H-pyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene as a brown solid.

The ¹³C NMR spectrum of the monomer was measured both as a ¹H-decoupled spectrum and in a *J*-modulated spin-echo experiment (APT spectrum); measurements were done in CS₂ (at 192.3 ppm relative to TMS) using D₂O (at 4.79 ppm) as an external lock

¹H NMR (300 MHz; CDCl₃): 5.87–5.73 (m, 1H); 5.01–4.90 (m, 2H); 4.81 (d, 1H, *J* = 9.5 Hz); 4.17 (d, 1H, *J* = 9.5 Hz); 3.91 (br. s, 1H); 3.00 (s, 3H); 2.60–2.46 (m, 1H); 2.43–2.30 (m, 1H); 2.06–1.96 (m, 2H); 1.96–1.82 (m, 2H); 1.52–1.22 (br. m, 10H). ¹³C NMR (75 MHz; CS₂/D₂O): 156.33; 154.24; 154.16; 153.30; 146.97; 146.95; 146.52; 146.29; 146.15; 146.07; 146.03; 145.94; 145.86; 145.81; 145.74; 145.56; 145.32; 145.26; 145.13; 145.03; 144.97; 144.56; 144.40; 144.19; 144.14; 142.99; 142.86; 142.48; 142.46; 142.42; 141.99; 141.89; 141.63; 141.52; 141.47; 140.11; 140.04; 139.64; 139.41; 138.36; 137.08; 136.18; 135.68; 135.35; 114.49; 77.97; 76.06; 70.20; 69.87; 39.69; 34.11; 31.18; 30.69; 29.84; 29.45; 29.30; 27.65.

FT-IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer:

IR (KBr, cm⁻¹): 3073 (w); 2923 (m); 2850 (m); 2779 (m); 2327 (w); 1639 (w); 1462 (m); 1429 (m); 990 (w); 906 (m); 526 (m).

General polymerisation procedure.

The homo- and co-polymerisations were performed in a 50-ml glass Mini-clave (Büchi AG, Switzerland) with a magnetic stirrer. Before use, the reactor was dried at 80 °C in a vacuum oven for 2 hours. A typical reaction procedure was as follows: In a nitrogen-filled glove-box, the mini-clave was sequentially charged with 15 ml of toluene, the desired amount of **1** (for copolymerisations), 0.9 g of MAO solution (10 wt % in toluene) and 0.815 μmol of (C₅Me₄SiMe₃N^tBu)TiCl₂ (0.3 ml of a 2.72 mM stock solution in toluene). The reactor was taken out of the glove-box, put into an oil-bath of 50 °C and charged with 2.0 bar of ethene. The ethene pressure was kept constant during reaction by

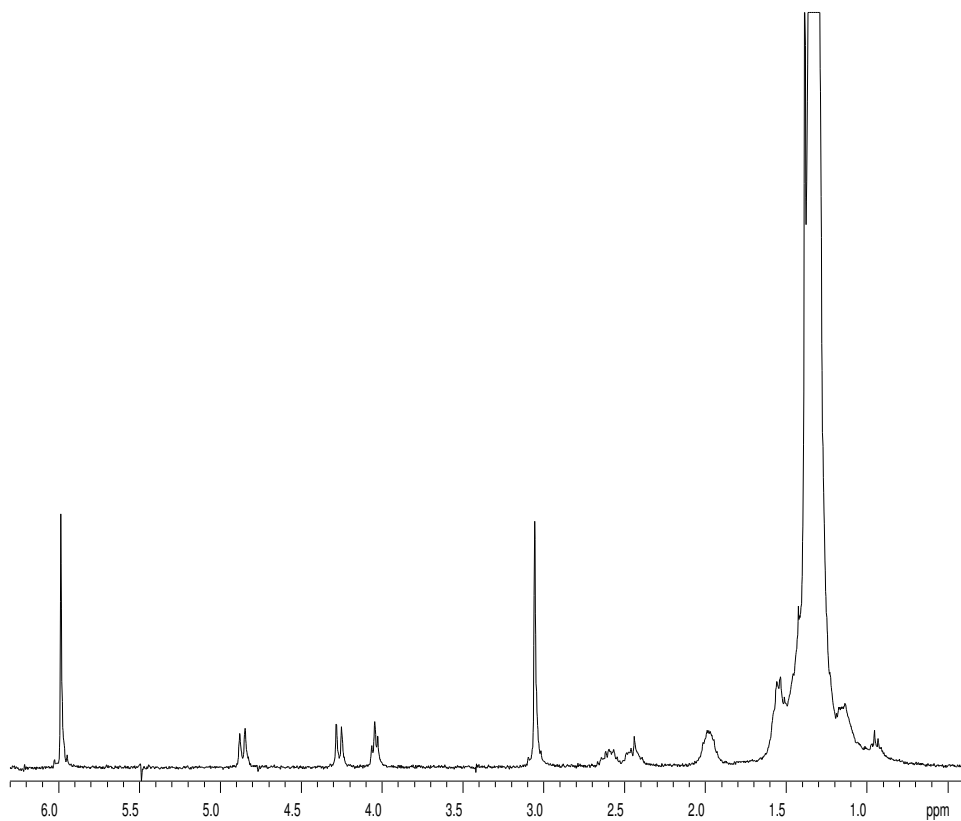
replenishing flow. After 0.5 hour, the (co)polymerisation was terminated by addition of methanol containing HCl. The reaction mixture was stirred in acidified methanol at 50 °C for 2 hours, then the product was filtered, washed with methanol. To remove the unreacted comonomer, the product was extracted with chloroform in Soxhlet extractor for 5 hours, and dried in vacuum at 80 °C overnight. The copolymers were obtained as powders with colours ranging from white, pale brown to dark brown with increasing comonomer incorporation.

Polymer characterisation.

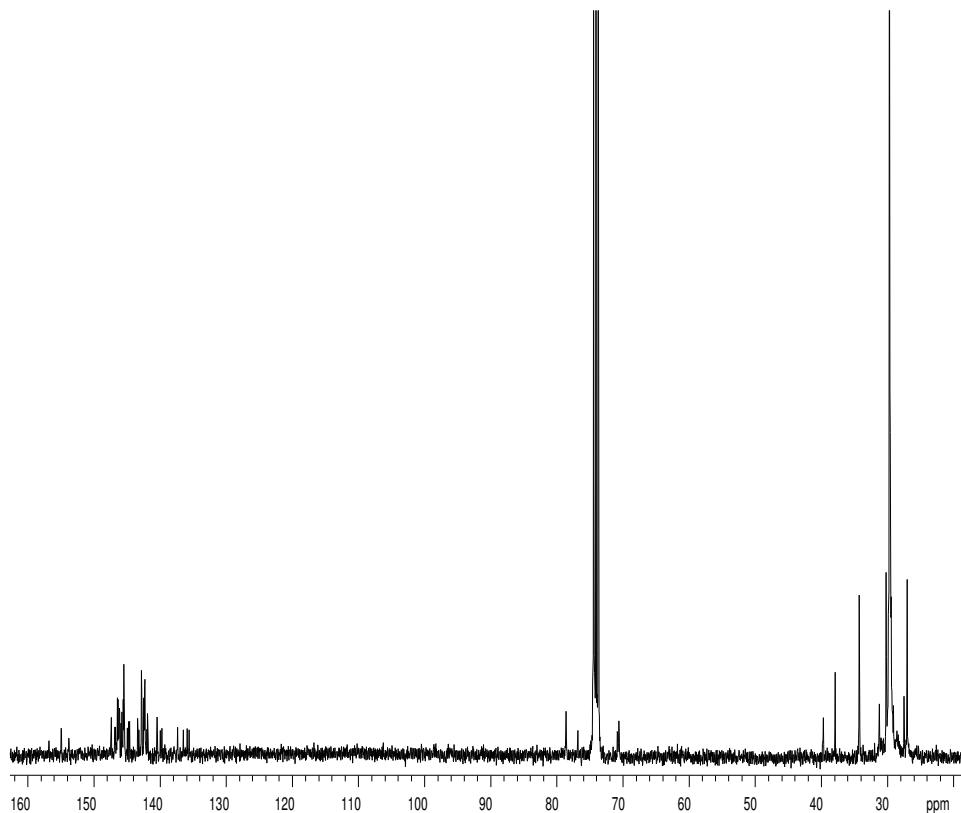
¹H NMR and ¹³C NMR spectra of the polymers (in 1,1,2,2-tetrachloroethane at 120 °C) were recorded with a Varian VXR-300 spectrometer. FT-IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer. Samples were measured as dispersions in KBr powder in diffuse reflection mode, using a Smart Collector DRIFT set-up. Molecular weight and polydispersity of the polymers were determined with a PL-GPC 210 (Polymer Laboratories) at 150 °C, 1,2,4-trichlorobenzene as eluent, calibrated with narrow molecular weight distribution polystyrene standards. The melting points were measured with a Perkin-Elmer DSC 7 under nitrogen from the second melting, heating rate = 10 °C/min. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 using a heating rate of 10°C/min in a nitrogen atmosphere.

Reference:

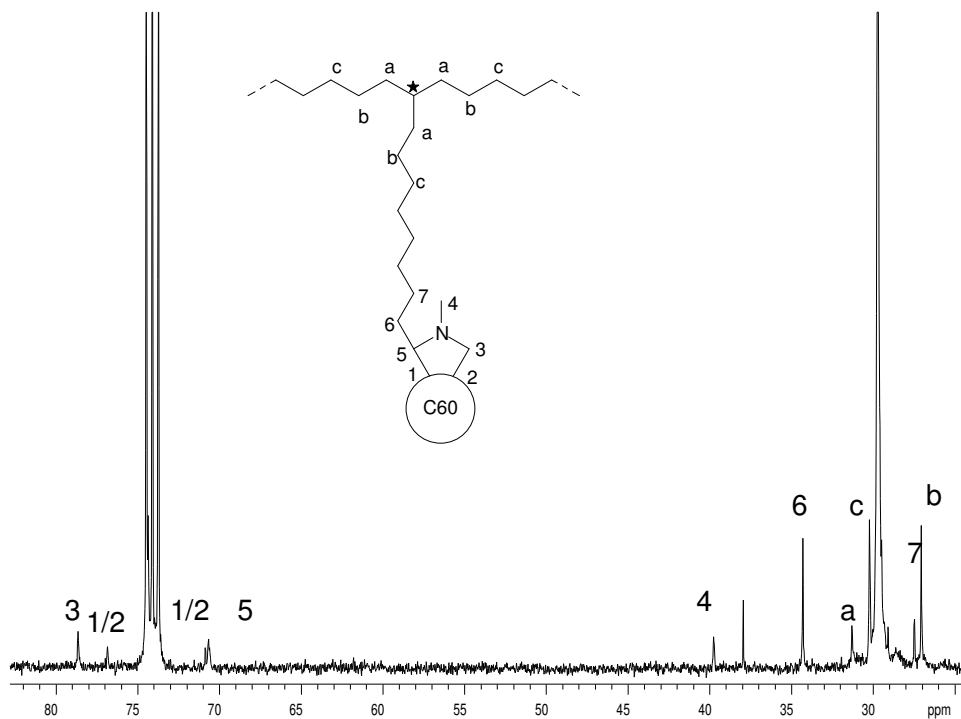
1. The procedure was followed as described in J. C. Stevens, F. J. Timmers, R. D. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S. Lai, EP 0416815 (1990), except that PbCl₂ instead of AgCl was used in the oxidation step.



¹H NMR spectrum (300 MHz, C₂D₂Cl₄ solvent, 120°C) of copolymer with 1.48 mol% comonomer incorporation.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$ solvent, 120°C) of copolymer with 1.48 mol% comonomer incorporation. Full width spectrum. The copolymer (70 mg) was dissolved in 0.7 mL of $\text{C}_2\text{D}_2\text{Cl}_4$ solvent. At 120°C , 7920 transients were acquired with a 10 s recycle delay (pw = 7).



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$ solvent, 120°C) of copolymer with 1.48 mol% comonomer incorporation. Expansion of the aliphatic region of the spectrum with assignment of resonances.