# Polyethene with pendant fullerene moieties†

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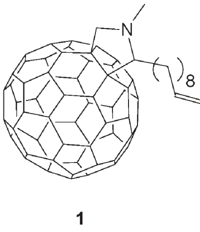
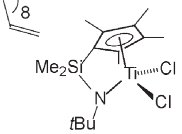
**Polyethene with fullerene moieties pendant on short-chain branches was prepared by the catalytic copolymerisation of ethene and a fullerene-containing vinylic comonomer, yielding polyethene copolymers containing up to 25 wt% of $C_{60}$.**

Materials containing fullerene moieties have been of recent interest due to their wide spectrum of electro-optical properties.[1] Polymers containing such functionalities can give access to a relatively simple means to apply fullerene-containing layers, *e.g.* for use in photovoltaic devices, provided they can be solution-processed *via* spin coating.[2–5] Efforts to obtain such materials through catalysed (co)polymerisation of fullerene-bearing monomers involved norbornene ROMP[6] and acetylene polymerisation[7] processes. To our knowledge, the preparation of fullerene-containing polyolefins by catalytic copolymerisation of ethene or simple 1-alkenes with fullerene-bearing comonomers has not been reported. Nevertheless, such an approach could give access to a new class of functional polymers. Here we describe the synthesis of polyethene containing pendant fullerene moieties by the catalytic copolymerisation of ethene with a fullerene-containing 1-alkene comonomer.

A convenient way to connect reactive groups to $C_{60}$ is the Prato reaction.[8] Using this approach, compound **1** was prepared by reaction of $C_{60}$ with ω-undecylenic aldehyde and sarcosine. The resulting olefinic substrate **1** contains an amine functionality that could potentially interfere with Lewis acidic transition-metal based olefin polymerisation catalysts. Nevertheless, the steric demand of the fullerene moiety, and the long spacer between the amine and the olefin functionality, should minimise these problems. For comparison, the amino-alkene i-$Pr_2N(CH_2)_3CH{=}CH_2$ is known to be readily (co)polymerised using standard group 4 metal-based polymerisation catalysts.[9,10] For the present study we employed the $(C_5Me_4SiMe_2NBu^t)TiCl_2$ (**A**)/methylalumoxane (MAO) catalyst system, well-known for its favourable copolymerisation characteristics,[11] that was used previously by us for the copolymerisation of ethene with 3-(pentenyl-1)-thiophene.[12]



**1**



**A**

The copolymerisation experiments were performed in a 50 ml glass mini-autoclave at 50 °C in toluene solvent and 2.0 bar ethene pressure, with $[Ti] = 5.3.10^{-5}$ mol $l^{-1}$ and Al : Ti = 2000. Catalyst and comonomer can be dissolved together prior to the admission of ethene, as **A**/MAO was found to be unable to effect homopolymerisation of **1**. The results for the copolymerisations at various comonomer concentrations are listed in Table 1. Productivities of around 2000 kg (mol Ti)$^{-1}$ h$^{-1}$ were obtained, and up to 32 wt% incorporation of the comonomer was achieved. By DSC it is seen that the polymer melting point (peak top at 2nd melting) decreases and the melting curve broadens with increasing monomer content. GPC analysis showed that the polydispersities of the copolymers are around 2, indicating normal single-site catalyst behaviour. It may be noted that $M_w$ determination by GPC of polymers bearing fullerene substituents have been seen to be rather unreliable, yielding values that may be underestimated by up to a factor of 2.[13]

In the $^1H$ NMR spectrum of the copolymer (Fig. 1, $C_2D_2Cl_4$ solvent), the resonances of the NMe (δ 2.97 ppm) group, the $NCH_2$ group (δ 4.79 and 4.18 ppm, $^2J_{HH}$ = 9.9 Hz) and the $NCHCH_2$ proton (δ 3.96 ppm, $^3J_{HH}$ = 6.0 Hz) are well-resolved, and can be used to determine the degree of conomomer incorporation. Olefinic resonances are absent, indicating that the polymer is free of residual comonomer. In the $^{13}C$ NMR spectrum, resonances of the functionalised $C_{60}$ moiety, as well as those belonging to the main and side chain carbon atoms adjacent to the branch points, can be clearly distinguished (for representative spectra, see the electronic supplementary information†).

With increasing comonomer content, the IR spectra of the copolymers show a gradual increase of the absorptions associated with the fullerene moiety (Fig. 2). Especially sigificant is the absorption at 527 cm$^{-1}$ due to the $C_{60}$ framework vibration.

The copolymers were subjected to thermogravimetric analysis (TGA) under nitrogen atmosphere. The TGA weight loss curves of the PE-co-**1** copolymers and of pristine linear polyethene are shown in Fig. 3. The incorporation of **1** leads to a slight increase of the weight loss onset temperature (440 °C for PE, 460 °C for PE-co-**1**). Whereas PE is fully evaporated when the temperature approaches 510 °C, the PE-co-**1** copolymers leave a residue after thermolysis that increases with increasing comonomer content.

The characterisation data of the polymers show that they have all the features of normal ethene/1-alkene copolymers. In the catalytic polymerisation, the catalyst productivity is not adversely affected to a significant extent by the comonomer. Polyethene copolymers with pendant fullerene moieties are thus readily available using a well-known olefin polymerisation catalyst system and a comonomer prepared in a straightforward manner using the Prato reaction. The present copolymers show solubilities typical of polyethene copolymers with low levels of comonomer

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† Electronic supplementary infirmation (ESI) available: Experimental details. See http://www.rsc.org/suppdata/cc/b4/b417249c

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**Table 1** Copolymerization of ethene with **1** by **A**/MAO at 50 °C[a]

| **1**/mmol | Yield/g | Productivity/ × $10^3$ kg (PE) mol(Ti)$^{-1}$hr$^{-1}$ | $M_w$ [c] × $10^{-3}$ | $M_w/M_n$ [c] | $T_m$/°C[d] | mol (wt)% of **1**[e] |
|---|---|---|---|---|---|---|
| 0.0 | 0.29[b] | 2.1 | 100 | 2.1 | 134.7 | 0.0 |
| 0.06 | 0.70 | 1.7 | 54 | 2.0 | 128.7 | 0.26 (7.6) |
| 0.13 | 0.84 | 2.0 | 70 | 2.4 | 125.7 | 0.38 (10.7) |
| 0.17 | 0.90 | 2.2 | 70 | 2.1 | 125.9 | 0.57 (15.3) |
| 0.23 | 0.47 | 1.2 | n.d. | n.d. | 120.7 | 0.90 (22.1) |
| 0.35 | 0.60 | 1.5 | 64 | 1.8 | 118.9 | 1.48 (32.3) |

[a] conditions: 0.81 μmol Ti, MAO cocatalyst [Al]/[Ti] = 2000, *P*(ethene) = 2.0 bar, toluene solvent (15 ml), 50 °C, run time 30 min. [b] run with 0.17 μmol Ti. [c] by GPC. [d] by DSC, heating rate = 10 °C/min, peak top temperature. [e] by $^1$H-NMR.

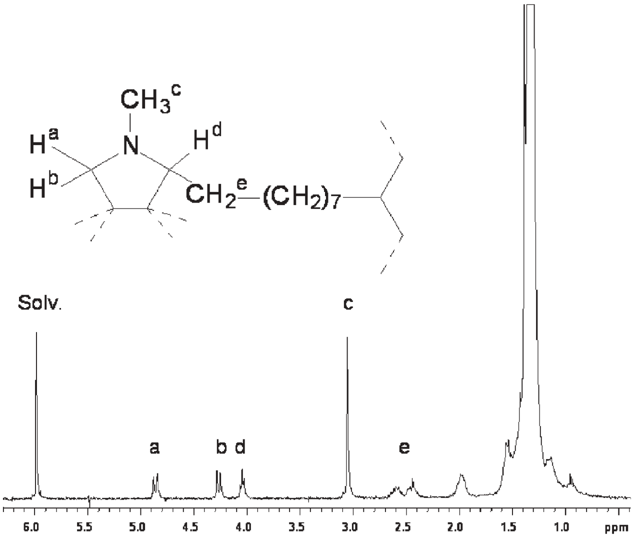

**Fig. 1** $^1$H NMR spectrum of the PE-co-**1** copolymer (1.48 mol% of comonomer. $C_2D_2Cl_4$ solvent, 120 °C).

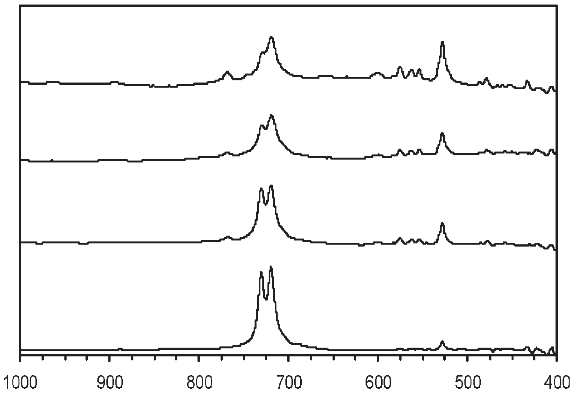

**Fig. 2** IR absorption spectra of PE-co-**1** with increasing content of **1** (bottom to top: 0.26, 0.57, 0.90 and 1.48 mol%; horizontal scale in cm$^{-1}$, vertical scale absorbance, arbitrary units).

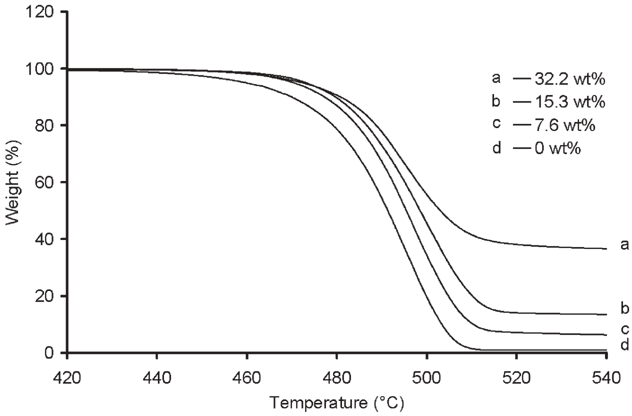

**Fig. 3** TGA weight loss curves (for heating under $N_2$ atmosphere) of PE-co-**1** copolymers with varying comonomer content (7.6, 15.3 and 32.2 wt%) compared to that of linear polyethene.

incorporation. They are sufficiently soluble in solvents like 1,1,2,2-tetrachloroethane and *o*-dichlorobenzene at elevated temperatures (>100 °C) for NMR spectroscopy and GPC analysis, but insufficiently soluble at ambient temperature for convenient use in spin-coating processing. Nevertheless, the present results suggest that more soluble derivatives, *e.g.* ethene/1-octene/**1** terpolymers or atactic propene/**1** copolymers, should also be accessible *via* similar protocols. Although no electron transport measurements have been performed as yet on the fullerene-containing copolymers described here, experimental and theoretical results from percolation theory predict a critical percolation density of approximately 16 vol% for randomly packed spheres in 3-D systems.[14,15] Thus the copolymers with relatively high fullerene content, *e.g.* the one with 1.48 mol% of comonomer (25 wt% of $C_{60}$), are expected to contain sufficient fullerene moieties to allow electron transport.

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## Notes and references

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