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Polyethene with pendant 3-thienyl functionalities†

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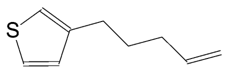
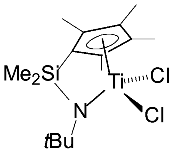
Polyethene with 3-thienyl functionalities pendant on short-chain branches was prepared by catalytic random copolymerisation of ethene and 3-(penten-1-yl)thiophene; the functionalities can be used to graft poly(3-hexylthiophene) onto the polyethene surface.

Incorporating functionalities into polyolefin materials to improve surface-related properties, such as dyeability, printability, adhesion, wettability and compatibility, has been the subject of considerable research both in academia and industry. This can be realised by metal-catalysed copolymerisation of ethene or propene with functional comonomers (*e.g.* containing amine, ester, alcohol or borane groups[1–5]), but compatibility of the (Lewis acidic) transition-metal catalyst with the (often Lewis basic) functionalities is an important issue. Here we describe the copolymerisation of ethene with 3-(penten-1-yl)thiophene (3-PT), an olefin with a very soft Lewis basic functionality, to give random PE-*co*-PT copolymers with pendant 3-thienyl groups on the short-chain branches. Through these functionalities, this copolymer can readily be grafted with the conjugated polymer poly(3-hexylthiophene).

In previous work we observed that both neutral and cationic Lewis acidic group 3 and group 4 metal-based ethene polymerisation catalysts are compatible with thiophenes, allowing ethene to be polymerised by these catalysts even in neat thiophene.[6,7] This prompted us to investigate copolymerisations of ethene with thienyl-functionalised 1-alkenes to obtain polyethene copolymers with thienyl side-groups. As comonomer we employed 3-(penten-1-yl)thiophene (3-PT). This was prepared by reaction of 3-bromothiophene with the Grignard reagent derived from 5-bromopent-1-ene, catalysed by [1,3-bis-(diphenylphosphino)propane]$NiCl_2$, following the procedure of Zimmer *et al*. for the synthesis of 3-substituted thiophenes.[8] As polymerisation catalyst we used the well-known copolymerisation catalyst system ($C_5Me_4SiMe_2NBu^t$)$TiCl_2$ (**A**)/MAO (MAO = methyl alumoxane).[9]



3-PT



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Initial copolymerisation experiments were performed in a 50 ml glass mini-autoclave at 80 °C in toluene solvent (Al : Ti = 2000) and 2.5 bar ethene pressure. Results for the copolymerisations at various comonomer concentrations are listed in Table 1. Productivities up to 4000 kg (mol Ti)$^{-1}$ h^{-1} were obtained, and up to 20.8 mol% incorporation of the comonomer. The polymer melting point decreases with increasing monomer content and the polydispersities of the copolymers are typically around 2, indicating normal single-site catalyst behaviour.

The copolymers were also characterised by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum, the resonances of the three protons on the 3-thienyl functionality are observed at δ 6.95 and 7.25 ppm (in a ratio of 2 : 1), and the adjacent methylene group as a triplet ($^3J_{HH}$ = 7.6 Hz) at δ 2.67 ppm. The aliphatic region of the ^{13}C NMR spectrum of the copolymer with 3.2 mol% comonomer incorporation is shown in Fig. 1. The resonance of the methine carbon is observed at δ 37.9 ppm and the resonances of the α-, β- and γ-carbons along the backbone at δ 34.4, 27.1, and 30.3 ppm, respectively. The α′-, β′- and γ′-carbons resonances belonging to the short chain branch connecting to the thienyl group are found at δ 34.0, 28.1, and 31.0 ppm, respectively. Besides the above-mentioned resonances, additional resonances were identified (indicated by an asterisk in Fig. 1) that are associated with sequential comonomer incorporation.[10,11] All characterisation data thus far indicate that the conomomer is readily and randomly copolymerised with ethene.

The PE-*co*-PT copolymer was prepared on a larger scale (10 g) in a 1 l autoclave (200 ml toluene solvent, 2 bar ethene, 8.75 mM comonomer) with a productivity of 41.10^3 kg (mol Ti)$^{-1}$ h^{-1}, M_w = 184 000 and M_w/M_n = 2.5. The comonomer content was 2.5 mol % (12.4 wt %) by NMR, with T_m = 113 °C. For comparison, ethene homopolymerisation under the same conditions yielded HDPE with a productivity of 39.10^3 kg (mol Ti)$^{-1}$ h^{-1}, M_w = 192 000 and M_w/M_n = 2.3 (T_m = 133 °C). The copolymerisation thus appears to be readily scaled up, and the presence of the Lewis basic comonomer has no detrimental effect on catalyst productivity or polymer molecular weight.

Soluble poly(3-alkylthiophenes) are well-known (semi)conducting polymers, that find application *e.g.* in light-emitting diodes and nonlinear optical materials.[12] They can be prepared

Table 1 Copolymerization of ethene with 3-(penten-1-yl)thiophene (3-PT) at 80 °C^a

3-PT amount/ mmol	Yield/g	Productivity ×10^3 kg (PE) mol (Ti)$^{-1}$ h^{-1}	$M_w{}^b$×10^{-3}	$M_w/M_n{}^b$	T_m/°C^c	3-PT content mol%^{d}
0	0.22	1.6	86	2.06	134.0	0
0.13	0.50	3.7	82	1.97	125.0	0.5
0.33	0.50	3.7	73	1.84	123.4	1.7
0.66	0.54	4.0	64	1.92	118.4	3.2
0.99	0.52	3.9	56	1.81	112.4	5.6
1.98	0.35	2.6	nd	nd	54.7	20.8

^{a} Conditions: [Ti] = 1.8 × 10 $^{-5}$ mol/l, [Al]/[Ti] = 2000, P(ethene) = 2.5 bar, toluene solvent (15 ml), run time 30 min. ^{b} By GPC. ^{c} By DSC, heating rate = 10 °C min^{-1}. ^{d} By ^{13}C-NMR.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b209885g/

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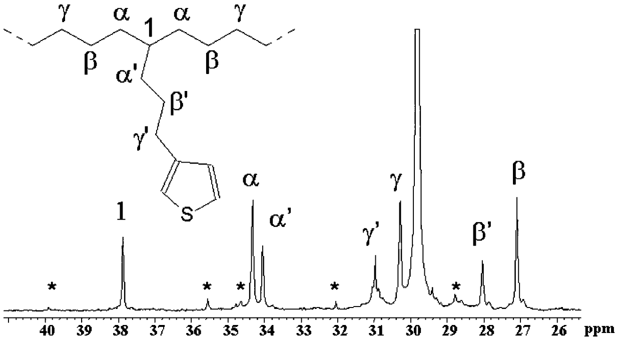


Fig. 1 Aliphatic region of the ${}^{13}C$ NMR spectrum of the PE-*co*-PT copolymer.

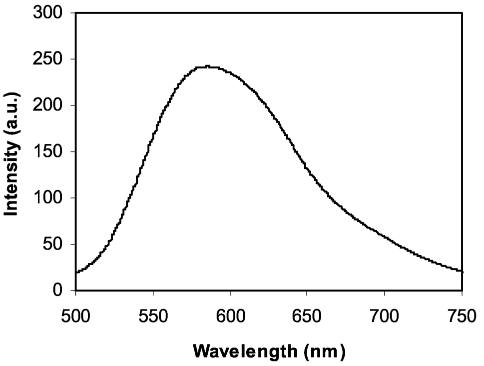
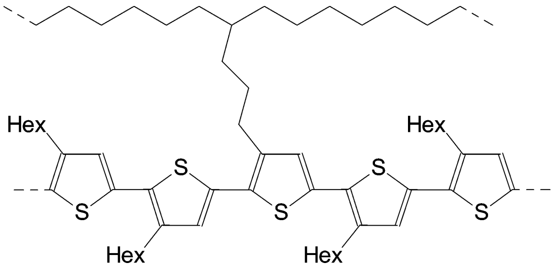


Fig. 2 Fluorescence spectrum (excitation wavelength 450 nm) of the PE-*co*-PT copolymer grafted with poly(3-hexylthiophene).

by $FeCl_3$-mediated polymerisation of 3-alkylthiophenes through the thiophene 2- and 5-positions in $CHCl_3$ solvent at moderate temperatures.[13,14] Subjecting a solid sample of PE-*co*-PT copolymer (with 3.2 mol% comonomer content) to these conditions with 3-hexylthiophene monomer yielded a highly coloured material with the green colour typical of Fe-doped poly(3-alkyl)thiophenes. Extraction with chloroform to remove non-grafted soluble poly(3-hexylthiophene) homopolymer, and by de-doping through rinsing with ammonia solution and chloroform, yielded a brown–red polymer that fluoresces bright orange under a UV lamp (λ 365 nm), typical of undoped poly(3-alkylthiophenes). The emission spectrum of this material (Fig. 2, excitation wavelength 450 nm) shows a broad band with λ_{max} of 585 nm, comparable with the fluorescence of normal poly(3-hexylthiophene).[15]

The modest weight increase of the sample (5%) indicates that under these conditions the copolymer hardly swells and is mainly grafted on the surface of the macroscopic sample (as could be confirmed by a colour gradient observed upon cutting the solid sample). Similar treatment of polyethene homopolymer resulted in a very small weight increase of the sample (0.5%) to yield material that is barely coloured, and that does not show visible fluorescence under UV irradiation. From these data we infer that the pendant 3-thienyl functionalities in the PE-*co*-PT copolymer allows this material to be grafted with the conjugated poly(3-hexylthiophene) by incorporation of these pendant 3-thienyl functionalities into the polythiophene backbone (schematically shown in Scheme 1).

This straightforward approach provides an interesting comparison with the multi-step sequence for the formation of polythiophene surface-functionalised polyethene published recently by Bergbreiter *et al.*, where polyethene was first oxidised with CrO_3, followed by sequential reaction with ethyl chloroformate, poly(*tert*-butylacrylate) and 2-(3-thienyl)ethanol, followed by $FeCl_3$-mediated thiophene polymerisation.[16]



Scheme 1 Representation of poly(3-hexylthiophene) grafted on the pendant thienyl groups of the PE-*co*-PT copolymer.

In conclusion, we have prepared a new polyethene copolymer with heteroatom-containing functionalities, poly[ethene-*co*-3-(penten-1-yl)thiophene], that can be prepared in quantity using a readily available polymerisation catalyst. The copolymer can be directly grafted with poly(3-alkylthiophene), and should give access to other grafted polyethene materials as well, as the thienyl functionality can also be readily converted to *e.g.* initiators for anionic polymerisation. The reactive and physical properties of the PE-*co*-PT copolymer and its derivatives are presently under investigation.

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