Supplementary data

Experimental details:

Chemicals. 3-n-Hexylthiophene (3-HT) was synthesized from 1-bromohexane and 3-bromothiophene following the procedure described by Zimmer et al.\textsuperscript{1} (C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{3}N\textsubscript{t}Bu)TiCl\textsubscript{2} (A) was prepared following literature procedures.\textsuperscript{2} Methylalumoxane (MAO, 10 wt % solution in toluene, Witco GmbH) and (dppp)NiCl\textsubscript{2} (Aldrich, dppp = 1,3-bis(diphenylphosphino)ethane) were used as received. Toluene (Aldrich anhydrous) was passed over an alumina column under nitrogen atmosphere before use. For the polymerisation experiments in the 1 l autoclave (see below), toluene (Aldrich anhydrous) was passed over columns of alumina, molecular sieves (4Å) and BASF R3-11 oxygen scavenger 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.

3-(Pentenyl-1)thiophene (3-PT). This procedure is based on that published by Zimmer et al. for the synthesis of various 3-substituted thiophenes.\textsuperscript{1} Under nitrogen atmosphere, a solution of 5-bromo-pentene-1 (15.96 g, 0.11 mol) in 20 ml of diethyl ether was added dropwise to a suspension of magnesium (2.4 g, 0.10 mol) in 20 ml of diethyl ether. After disappearance of the metallic magnesium, a solution of 3-bromothiophene (17.9 g, 0.11 mol) in 20 ml of diethyl ether was added, followed by 60 mg of (dppp)NiCl\textsubscript{2}. The mixture was warmed to 35°C and stirred at that temperature for 15h. The reaction mixture was poured into a mixture of crushed ice and 2N hydrochloric acid, and extracted three times with 100 ml of diethyl ether. The combined ether layers were dried over MgSO\textsubscript{4}. After removal of the solvent, the residue was vacuum distilled, yielding 8.5 g (0.056 mol, 56% on Mg) of 3-PT (b.p. 89°C at 2.5 mbar). NMR (300 MHz, CDCl\textsubscript{3}): δ 7.28 (m, 1H, thienyl CH), 7.0 (m, 2H, thienyl CH), 5.92 (m, 1H, -CH=), 5.1 (m, 2H, =CH\textsubscript{2}), 2.72 (t, 7.7 Hz, CH\textsubscript{2}), 2.17 (m, 2H, CH\textsubscript{2}), 1.81 (qui, 7.7 Hz, CH\textsubscript{2}). \textsuperscript{13}C{\textsuperscript{1}H} NMR (75 MHz, CDCl\textsubscript{3}): δ 140.2 (thienyl C), 136.1, 126.0, 122.9 (thienyl CH), 117.8 (-CH=), 112.4 (=CH\textsubscript{2}), 31.0, 27.4, 27.3 (CH\textsubscript{2}).
Small scale polymerisations. 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 charged with 15 ml of toluene, the desired amount of comonomer (for copolymerisations), 0.27 ìmol of catalyst A (0.1 ml of a 2.7 mM stock solution in toluene) and 0.3 g of MAO solution (10 wt % in toluene). The reactor was taken out of the glove-box, put into an oil-bath of 80 °C and charged with 2.5 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, and dried in vacuum at 80 °C overnight.

Polymerisations in a 1-litre autoclave. These polymerisations were performed in an automated autoclave setup, fully temperature and pressure controlled, and with inert atmosphere handling equipment for the addition of solvent and reagents. In a nitrogen-filled glove-box, solutions of 2.72 ìmol of catalyst A (1.0 ml of a 2.7 mM stock solution in toluene) in 10 ml of toluene, and of 6.0 g of MAO solution in toluene (10 wt %) with the desired amount of comonomer (when applicable) were prepared in separate vials, sealed with a septum. Before use, the autoclave (1 l stainless steel, Premex®, Switzerland) was dried at 100 °C under reduced pressure (< 9.9 x 10⁻² bar). Subsequently the reactor was charged with 200 ml of dry toluene and thermostated at 80 °C. After pressurising with ethene (2.0 bar) and equilibration, the MAO solution (also containing comonomer in the copolymerisation experiment) was injected into the reactor. Polymerisation was started by injection of the catalyst solution. During polymerisation, the pressure of ethene was kept constant by replenishing flow. After 5 min, the polymerisation was stopped by addition of acidified methanol. The work-up of the (co)polymers was the same as that described for the small scale experiments.

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.
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.

**Graft copolymerisation.** The graft polymerization of poly(3-hexylthiophene) onto PE-co-3PT was carried out using the procedure described by Pomerantz et al for the polymerisation of 3-alkylthiophenes.³ In a 100 ml 3-necked flask, equipped with a magnetic stirring bar, condenser and dropping funnel, 3-hexylthiophene (1.0 g, 6.5 mmol) was placed, together with a solid piece (0.2182 g) of PE-co-3PT (3.2 mol% comonomer content). A solution of 1.2 g of anhydrous FeCl₃ in 50 ml of chloroform was added dropwise into the flask over 20 min. Upon completion of the addition, the mixture was warmed to 55 °C and kept at that temperature for 24 hours. Subsequently the green solid polymer material was recovered, extracted with chloroform to remove free poly(3-hexylthiophene) homopolymer, and de-doped by rinsing with a mixture of concentrated ammonia solution and chloroform. Drying the product under vacuum at 80 °C resulted in 0.2300 g of orange-brown material (5.4% weight increase). Performing the same procedure with a piece of polyethene homopolymer (0.1681 g) resulted in the recovery of 0.1689 g of slightly off-white material (0.5% weight increase).

**Fluorescence spectrum.** The fluorescence spectrum of poly(3-hexylthiophene) grafted on the PE-co-3PT copolymer was recorded on a Perkin-Elmer LS 50B instrument from a pressed solid sample of 13 mm diameter and 2 mm thickness at ambient temperature. The excitation wavelength was 450 nm, with excitation and emission widths of 10 nm and a scan rate of 100 nm/min.

**References**

2. 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 PbCl\(_2\) instead of AgCl was used in the oxidation step.