

Living random and block copolymerization of ethene and propene on a tailor-made phenoxyimine catalyst and characterization of the resulting high molecular weight PE-*block*-P(E-*co*-P) block copolymers

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Abstract

The phenoxyimine catalyst (bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) was tailored to enable random and block copolymerisation of propylene and ethylene with compositions covering the entire feasible composition range. Well-defined high molecular weight diblock copolymers of the type PE-*block*-P(E-*co*-P), consisting of a semi-crystalline polyethylene and a soft P(E-*co*-P) block, were prepared and evaluated with respect to propylene content and the block lengths. The characterisation by means of AFM, CRYSTAF data and high temperature chromatographic elution provided the experimental evidence that no homo-polyethylene and less than 5% of the random copolymer are formed as by-products.

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1. Introduction

Group IV metal catalysts have proven to be excellent reagents for the preparation of polyolefines of high stereoselectivity at very high activities [1]. Post-metallocene group IV metal complexes as catalysts for living olefin polymerisation have been of great research interest in recent years [2,3]. Living polymerisation enables the access to very high molecular weight polymers with low molecular weight distributions, controlled reaction conditions and the sequential synthesis of block copolymers [4,5]. Recently Fujita et al. at Mitsui Chemicals, Inc.® found a new class of catalysts for living olefin polymerisation, the so-called FI catalysts [3,6,7]. The living effect in polymerisation was achieved by a weak attractive interaction of the fluorine atoms in the ligands with a β -hydrogen atom of the growing polymer chain, resulting in preventing termination [8]. These catalysts opened the way to the synthesis of ethylene—1-olefin—block copolymers and

a variety of new polymer architectures. High molecular weight random copolymers of the type P(E-*co*-P) as well as diblock copolymers of the types PE-*block*-sPP, PE-*block*-P(ethene-*co*-propene), sPP-*block*-P(ethene-*co*-propene) as well as triblock-copolymers of the type PE-*block*-P(ethene-*co*-propene)-*block*-sPP and PE-*block*-P(ethene-*co*-propene)-*block*-PE have been synthesised [9–11].

In the group of Fujita only few data on the analysis and morphologies of the obtained block copolymers have been reported [3,12,13]. Coates et al. have studied morphology and thermodynamic behaviour of block copolymers prepared by living olefin polymerisation. They used differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMS) and transmission electron microscopy (TEM) as analytical methods. Flory–Huggins interaction parameters in sPP-*block*-P(E-*co*-P) have been analysed by mean field theory [14]. In this paper, we report the studies on the synthesis of well-defined diblock copolymers of the type PE-*block*-P(E-*co*-P) with low ethylene content of the rubbery block. A systematic variation of the block lengths and the propylene content has been performed. The block copolymers were fully characterised using atomic force microscopy (AFM) to investigate morphologies, dynamic mechanical analysis (DMA) and DSC for determination of the glass transition and melting

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temperatures as well as crystallisation analysis fractionation (CRYSTAF) and high temperature chromatographic elution to prove the presence of block copolymers.

2. Experimental

2.1. Solvents and chemicals

Toluene was distilled from sodium/potassium, heptane was distilled from sodium. Both were kept under argon. All other solvents were lab-grade and used as received. Ethylene (3.0) and propene (2.5) were obtained from Messer-Griesheim. Irganox 1010 was obtained from Ciba and used as a stabilizer. Methylaluminoxane was purchased as solution in toluene (10% g/v; 5.24 wt% Al) from Crompton GmbH. The synthesis and characterisation of the catalyst precursor bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride (**1**) have been reported before [15]. Bis-(*N*-(3'-*tert*-butyl-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride (**2**) was purchased from MCat GmbH.

2.2. Characterisation

NMR spectra were recorded by Dr M. Kowalski (macromolecular institute of the Albert-Ludwigs-Universität Freiburg) on a Bruker ARX 300 spectrometer (299.87 MHz) using the solvent peaks as reference for ^1H spectra and ^{13}C spectra. High temperature NMR spectra were recorded at 120 °C. Elemental analysis was carried out in the institute for organic chemistry and biochemistry of the Albert-Ludwigs-Universität Freiburg by Hickl using a Vario EL. High temperature size exclusion chromatography was carried out by Westphal on a PL-220 using a triple column set (PLgel mixed-bed) and 1,2,4-trichlorobenzene stabilized with 2 mg/mL of Irganox 1010 as solvent at 145 °C. Molecular weight distributions were analysed by light scattering, viscosimetry and refractive index. Calibration was carried out against linear PS standards using a calibration transfer for polyethylene or polypropylene samples, respectively. Glass transition temperatures and melting points of the obtained polymers were detected using a Seiko 6200.

Samples for DMA were prepared using approximately 4 g of the block copolymers, which had been dissolved in xylene at 140 °C and re-precipitated in methanol for purification. Sample specimens (40 mm × 6 mm × 1–1.2 mm, using 0.3 g of the block copolymer) have been prepared using a Collin press at 190 °C (vacuum). Of each sample at least six sample specimens have been prepared and measured. Measurements were performed using a Rheometrics Solid Analyzer RSA II in 'Film Fixture'-geometry and 'Dynamic Temperature Default Step'-programme. The following parameters were used: length on strain of the sample 22 mm; frequency 1.0 Hz, initial temperature -90 °C, final temperature 120 °C, strain 0.1% (0.3% above 20 °C). Storage modulus E' and loss modulus E'' as well as $\tan \delta$ were recorded versus temperature.

Atomic force microscopy (AFM) experiments were performed with a Nanoscope III scanning probe microscope.

Images were taken at the fundamental resonance frequency of the Silicium cantilever (300 MHz) in phase mode. The flat surfaces that were examined were obtained by cutting the sample with a Diatome diamond knife at -45 °C using a ultramicrotome (Ultracut E, Reichert and Jung) equipped with a cryochamber.

A CRYSTAF apparatus, model 200 from PolymerChar S. A., was used for fractionation. Samples (20 mg) were dissolved in 30 mL of distilled 1,2-dichlorobenzene at 160 °C. After dissolution, the temperature was decreased at a rate of 0.1 °C/min.

The prototype of a high temperature gradient HPLC system PL XT-200 (Polymer Laboratories) was used. The stationary phase was Nucleosil 500, column size 25 × 0.46 cm, average particle diameter 5 μm (Macherey Nagel). The column outlet was connected with a customized evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories) working at a nebulization temperature of 160 °C, an evaporation temperature of 270 °C and with an air velocity of 1.5 L/min. The eluent flow rate was 1 mL/min. A robotic sample handling system PL-XTR (Polymer Laboratories) was applied for sample preparation and injection. The column compartment was set to 140 °C, the injection port and transfer line between the chromatograph and the auto sampler was set to 150 °C, while the temperature of the sample block and the tip of the robotic arm was 160 °C. For data collection and processing the software package 'WinGPC-Software' (Polymer Standards Service GmbH) was used [16].

2.3. General procedure for the synthesis of random copolymers of ethylene and propene

P(E-co-P) was synthesised in a 1600 mL Parr polymerisation reactor (Multi-purpose polymerisation reactor) from Labeq AG using a constant flow of the monomer gas mixture to insure constant conditions for the preparation of the first block (random copolymer of ethylene and propene). Polymerisation was carried out at 25 °C, in 600 mL of toluene at 2 bar. MAO was used as cocatalyst, using a ratio Ti/Al = 1:2500. The reactor was filled with toluene and a part of the amount of cocatalyst. Then the atmosphere was saturated with 2 bar of the desired gas mixture of ethylene and propylene and the reactor was thermostated to 25 °C. Fifteen micromoles (16.3 mg) of the catalyst were dissolved in few millilitre of toluene and activated by the remaining amount of MAO. The solution of the activated catalyst was injected by syringe using a slight argon over-pressure. After a certain period of time, the reactor was depressurised and the reactor content was drained and the polymer was precipitated by pouring the reaction mixture in methanol/aq HCl (5% v/v)/few mg of Irganox 1010. The polymer was filtered, washed with methanol and dried in vacuo over night at 60 °C.

2.4. General procedure for the block copolymerisation

The polymerisation was carried out using a semi-automated 600 mL Parr polymerisation reactor (Multi-purpose polymerisation reactor) from Labeq AG. Polymerisation was carried out at 25 °C, in 250 mL of toluene at 2 bar. MAO

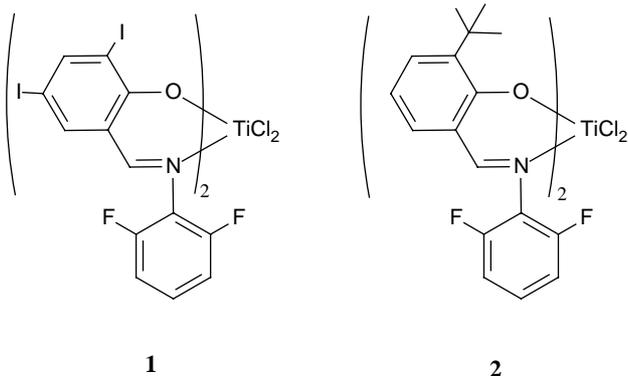
was used as cocatalyst, using a ratio Ti/Al=1:2500. The reactor was filled with toluene and half the amount of cocatalyst. Then the atmosphere was saturated with 2 bar of ethylene (gas feed 150 g/h) and the reactor was thermostated to 25 °C, 7.5 μmol (8.15 mg) of **1** were dissolved in few millilitre of toluene and activated by the remaining amount of MAO. The solution of the activated catalyst was injected by syringe using a slight argon over-pressure. After a certain period of time the atmosphere in the reactor was evaporated to 0.2 bar for several times and the reactor was fed with propene (100 g/h). The polymerisation proceeded in presence of little ethylene left in the atmosphere at 2 bar for another period of time. Then the reactor was depressurised and the reactor content was drained and the polymer was precipitated by pouring the reaction mixture in methanol/aq HCl (5% v/v)/few milligram of Irganox 1010. The polymer was filtered, washed with methanol and dried in vacuo over night at 60 °C.

2.5. Preparation of blend of PE and P(E-co-P)

A mixture of 30% (g/g) polyethylene ($M_n=930$ kg/mol, $M_w/M_n=1.70$) and a random P(E-co-P) copolymer (80 mol-% propylene content, $M_n=1200$ kg/mol, $M_w/M_n=1.33$) prepared by living olefin polymerisation were dissolved in xylene at 140 °C. Irganox 1010 was added and after 10 min the viscous solution was poured into three times the amount of methanol for re-precipitation of the polymer blend. The obtained polymer was dried in vacuo for 1.5 days at 60 °C.

3. Results and discussion

Upon activation of **1** with MAO living polymerisation of ethylene and propylene is achieved to form linear polyethylene and atactic polypropylene as has been reported before [15]. A series of high molecular weight random copolymers of ethylene and propylene were synthesised on **1**/MAO. Three additional random copolymers were synthesised on **2**/MAO for comparison of propylene incorporation and chain lengths. The structures of the catalyst precursors **1** and **2** are displayed in Scheme 1. The results of these experiments are summed up in Table 1 (see separate document).



Scheme 1. Phenoxyimine catalysts used for random and block copolymer synthesis.

Only in case of copolymerisation of ethylene and propylene on **1**/MAO high molecular weight polymers ($M_n > 500$ kg/mol) with high incorporation of propylene (up to 93 mol-%) were obtained. Fig. 1 shows the dependence of the propene incorporation into the copolymer on the propene concentration in the monomer gas mixture in case of copolymerisation on **1**/MAO. Due to substitution with iodine atoms instead of more bulky organic substituents in the 3'-position of the salicylidene ring, incorporation of the comonomer was significantly improved in comparison to copolymerisation on **2**/MAO (Fig. 2). Furthermore, a higher activity of the catalyst is observed, when the propene content within the monomer gas mixture is raised, compared to the activity of the catalyst during ethylene polymerisation when using **1**/MAO as the catalyst (Fig. 3). Especially at high propene concentration (83 mol-%) a dramatic loss of activity was determined during copolymerisation of ethylene and propylene on **2**/MAO.

A series of block copolymers were prepared by means of sequenced ethylene and ethylene/propylene feed on **1**/MAO and varying the polymerisation times for the ethylene and the rubbery block. The results are shown in Table 2 (see separate document). The catalytic system **1**/MAO shows extremely high activity for ethylene homopolymerisation (1000 kg PE/mol Ti·h), but marginal activity for propylene homopolymerisation (24 kg PP/mol Ti·h). Therefore, long polymerisation times have been applied for the synthesis of the second P(E-co-P) block. Furthermore due to the evaporation and gas exchange process, some ethylene was left in the gas atmosphere to promote the reaction because of the comonomer effect. This amount cannot be controlled and therefore, is varying from run to run. This can be seen as in run VII more propene is incorporated although polymerisation time for the second block is longer in run VIII.

Polydispersity increases with time of propylene polymerisation. When the rubbery block is formed, chain transfer to MAO becomes more likely due to the lower catalyst activity. Therefore, molar masses of the block copolymers seem to be limited to $M_n < 1200$ kg/mol except for very long PE blocks. After chain transfer, the catalyst can start new insertions leading to few polymer chains of random copolymer P(E-co-P). By chromatographic techniques and CRYSTAF (see below) we have been able to show that the content of the random copolymer P(E-co-P) is lower than 5% (g/g), observed only for very long polymerisation time.

Melting temperatures of the polyethylene block are only weakly affected by the propylene content. Melting temperatures decrease by few degrees in comparison to pure PE synthesised within the same conditions ($T_m=134.9$ °C). Nevertheless, the melting enthalpy and, therefore, crystallinity are significantly lower due to incomplete phase separation. Glass transition temperature (T_g) of the (E-co-P)-block is dependent on its ethylene content. As no more ethylene is delivered into the reactor after the gas exchange, a gradient copolymer block is formed at long reaction times. That is why samples, which have the same overall composition like in run II and run VI or in runs III, VII and VIII show different values for the T_g .

Table 1
Synthesis of random copolymers of ethylene and propylene on phenoxyimine catalysts/MAO

Run	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11
Catalyst	1	2	2	2							
Activity (g polymer/mmol Ti×h)	1000	900	1000	930	720	240	190	120	300	285	47
mol-% Propene (gas)	25	37.5	50	67	83	91	95	97	50	67	83
mol-% Propene (polymer) ^a	11	20	24	43	57	67	76	93	4	9	28
M_n /(kg/mol)	1700	2200	1600	950	1000	1100	1150	220	345	400	230
M_w/M_n	1.8	1.9	1.7	1.8	1.5	1.9	1.5	1.9	1.4	1.6	1.8
T_g /(°C)	-39	-48	-46	-52	-45	-37	-29	-15	n.d.	-51	-48
T_m /(°C)	72	35	33	None	None	None	None	None	135	115	111

25 $\mu\text{mol/L}$ catalyst, 600 mL toluene, MAO: Al/Ti=2500:1, 25 °C, 2 bar, 30 min. n.d., not determined.

^a Propene content determined by ¹H NMR spectroscopy.

DMA curves have been measured of several samples to check for phase transitions of the block copolymer. Fig. 4 shows an representative tan δ curve of run V.

All block copolymers show the same phase behaviour in DMA analysis. The T_g was determined at $-28.1\text{ °C} \pm 1.3\text{ °C}$ (average value from 8 measurements) and is in good consistence with the T_g -value obtained by DSC (-35.7 °C) or by the minimum of the E'' -plot (-31.5 °C). The T_{β} -

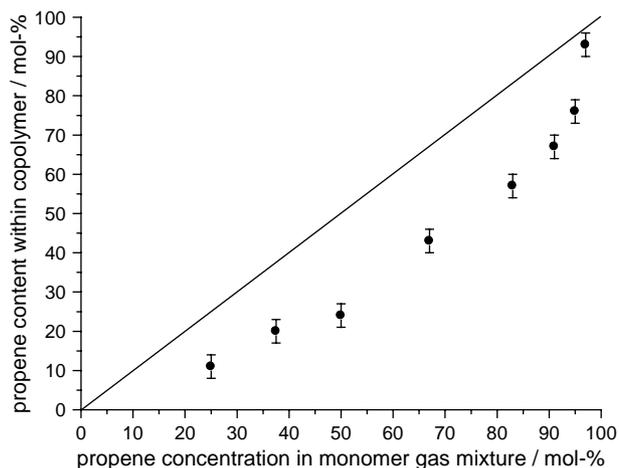


Fig. 1. Dependency of the propene incorporation into the copolymer on the propene concentration in the monomer gas mixture in case of copolymerisation on **1**/MAO (25 $\mu\text{mol/L}$ **1**, 600 mL toluene, MAO: Al/Ti=2500:1, 25 °C, 2 bar, 30 min).

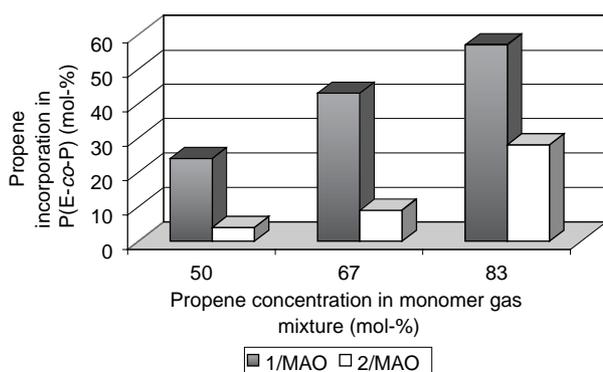


Fig. 2. Propene incorporation into P(E-co-P) depending on phenoxyimine catalyst and propene concentration in the monomer gas mixture.

transition of the polyethylene block is described in literature [17] to be between -100 and -120 °C and was not accessible by the temperature region of the apparatus. Only the start of the expected peak could be detected at -80 to -90 °C .

Between -60 and -80 °C a plateau can be detected derived from order-disorder transitions due to molecular rearrangements in the phase-separated polymer. As the block copolymer cannot be molten entirely, heterogeneous samples were obtained when being prepared under pressure within the vacuum press. Therefore the same samples were mixed using a mini-compounder, so that more uniform samples could be prepared. New measurements showed no significant change neither in T_g -value (-27.2 °C) nor in the course of the DMA curve itself.

At 30 °C the values of the storage modulus E' and the loss modulus E'' of the rubbery plateau were determined: E' (30 °C) = $3.4 \times 10^6 \pm 0.3 \times 10^6\text{ Pa}$; E'' (30 °C) = $8.0 \times 10^5 \pm 0.6 \times 10^5\text{ Pa}$.

AFM images were measured in phase mode of block copolymer samples with varying propylene content. Furthermore one image of a blend of 30% PE and 70% P(E-co-P) has been measured for comparison. They are shown in Figs. 5 and 6.

The AFM images show a change in morphology from a rather micellar domain of the soft 'rubbery' phase in image (a)

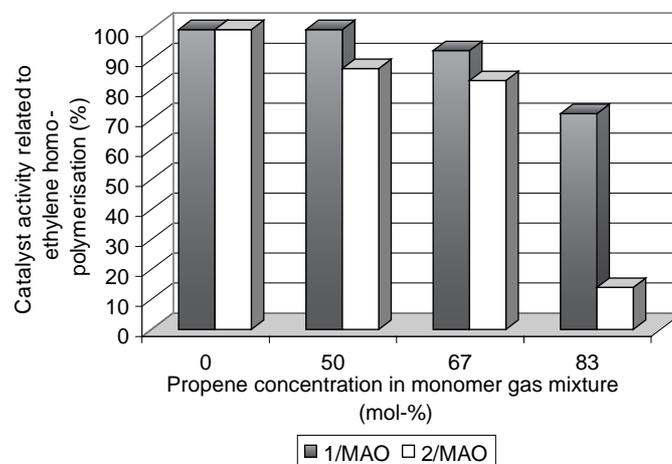


Fig. 3. Catalyst activity during copolymerisation of ethylene and propylene depending on amount of propene in the monomer gas mixture compared to ethylene homopolymerisation (100%).

Table 2
Results of the block copolymerisation using 1/MAO

Exp. no.	I	II	III	IV	V	VI	VII	VIII	IX	X
Time/min (ethylene)	3	3	3	3	3	6	6	6	10	20
Time/h (propylene)	0.25	0.5	1	5	16	1	5	16	1	1.67
mol-% Propene	14	39	55	70	75	38	57	52	8	12
M_n (kg/mol)	550	1100	1200	950	900	880	960	870	2000	> 3000
M_w/M_n	1.4	1.8	1.8	1.8	1.9	1.6	1.8	2.0	1.6	n.d.
1st Block (kg/mol)	400	400	400	400	400	620	620	620	1100	n.d.
2nd Block (kg/mol)	150	700	800	550	500	260	340	250	900	n.d.
T_m (°C)	134	132	132	128	129	130	128	130	133	122
T_g (°C)	-43	-34	-37	-30	-36	-53	-47	-53	< -60	-50

25 $\mu\text{mol/L}$ 1, 250 mL toluene, MAO, Al/Ti=2500:1, 2 bar, 25 °C. n.d., not determined as M_n value was outside calibration of the SEC column. Block lengths were calculated according to polymers obtained from ethylene homopolymerisation as ethylene content of second block cannot be determined: polymerisation time: 3 min, $M_n=400$ kg/mol, $M_w/M_n=1.33$. Polymerisation time: 5 min, $M_n=625$ kg/mol, $M_w/M_n=1.34$. Polymerisation time: 10 min, $M_n=1100$ kg/mol, $M_w/M_n=1.33$.

at low propene content towards the inverse phase with micellar polyethylene structure at 70 mol-% propene content in image (d) (diameter of polyethylene micelles in range below 100 nm). Due to the phase separation the crystallisation in sample a) is disturbed. Therefore, a non-regular distribution of the P(E-co-P) micelles within the semi-crystalline matrix seems to occur. The domain size is about 150–300 nm. At 39 mol-% propylene content a lamellar structure is visible in image (b) (The horizontal lines are artefacts from cutting the sample and due to the high molecular weight of the polymer). The size of the polyethylene lamella is between 200 and 400 nm. In image (c), a slightly distorted cylindrical morphology with average diameter of 400–500 nm can be seen. It can clearly be seen from Fig. 6, that in the blend non-regular morphology is present with large domain sizes ($>1.5 \mu\text{m}$). So the AFM images in Fig. 5 plead for the existence of block copolymers.

CRYSTAF analyses were performed on several block copolymers and the prepared blend for comparison. The plots of concentration and change in concentration versus temperature are shown in Figs. 7 and 8. The rectangular peak at the end of the measurement (temperature <30 °C) is the detector signal for the soluble part of the sample.

For CRYSTAF analysis the polymer is dissolved in 1,2-dichlorobenzene at 120 °C and slowly cooled down to room

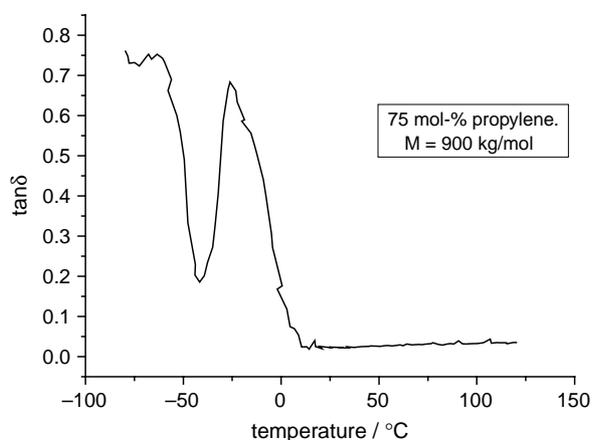


Fig. 4. Plot of $\tan \delta$ vs. temperature of block copolymer obtained from run V showing a T_g at (-28.1 ± 1.3) °C.

temperature (6 K/h). At a distinct temperature a crystallisation of the polymers takes place. For PE the crystallisation is expected at 87–88 °C.

In the CRYSTAF plots of the blend the polymers of run IX and X one peak of crystallisation is present. For the block copolymer samples the concentration at this point drops to a value about 0% (a slight amount of each polymer stays in solution, also for pure PE samples) whereas the concentration in the blend drops down to 70%. This indicates that in case of the blend only the PE is precipitating from the solution whereas in the block copolymer samples a full crystallisation takes place. When polymers with high propylene content (more than 50 mol-%) are investigated, no peak of crystallisation can be detected. The block copolymer is soluble enough to stay in solution. These results give strong evidence of for the existence of block copolymers.

The crystallisation peak would be expected at slightly lower temperature for the block copolymer samples than for PE. The maximum of the dc/dT -plot for the blend is at 87.3 °C, showing the crystallisation of PE. The corresponding maxima for the polymer of run IX is at 87.6 °C, the one for the block copolymer X is at 81.6 °C. The polymer from run IX has a very low propylene content (8 mol-%) within the second block. The precipitation of this block copolymer does not seem to be affected by the P(E-co-P)-block. After further increase of the propylene content to 12 mol-% (run X) a significant shift in the precipitation temperature to 81.6 °C can be observed. Here, it can also be seen that no homopolyethylene is present in the sample.

Extraction of the block copolymer samples with *n*-heptane does not lead to separation of a fraction of aPP. Solutions of the block copolymers obtained by run IV, V and VII have been separated on high temperature gradient HPLC column [18]. The samples were dissolved in 1-decanol (stabilized with 1 g/L 2,6-di-*tert*-butyl-4-methylphenol) at 160 °C for 6 h. Starting eluent is ethylene glycol mono butyl ether (EGMBE). Starting at 100% EGMBE for 2 min, the volume fraction of 1,2,4-trichlorobenzene (TCB) was increased linearly to 100% within the following 3 min and then kept constant for another 3 min. Finally, the initial chromatographic conditions are

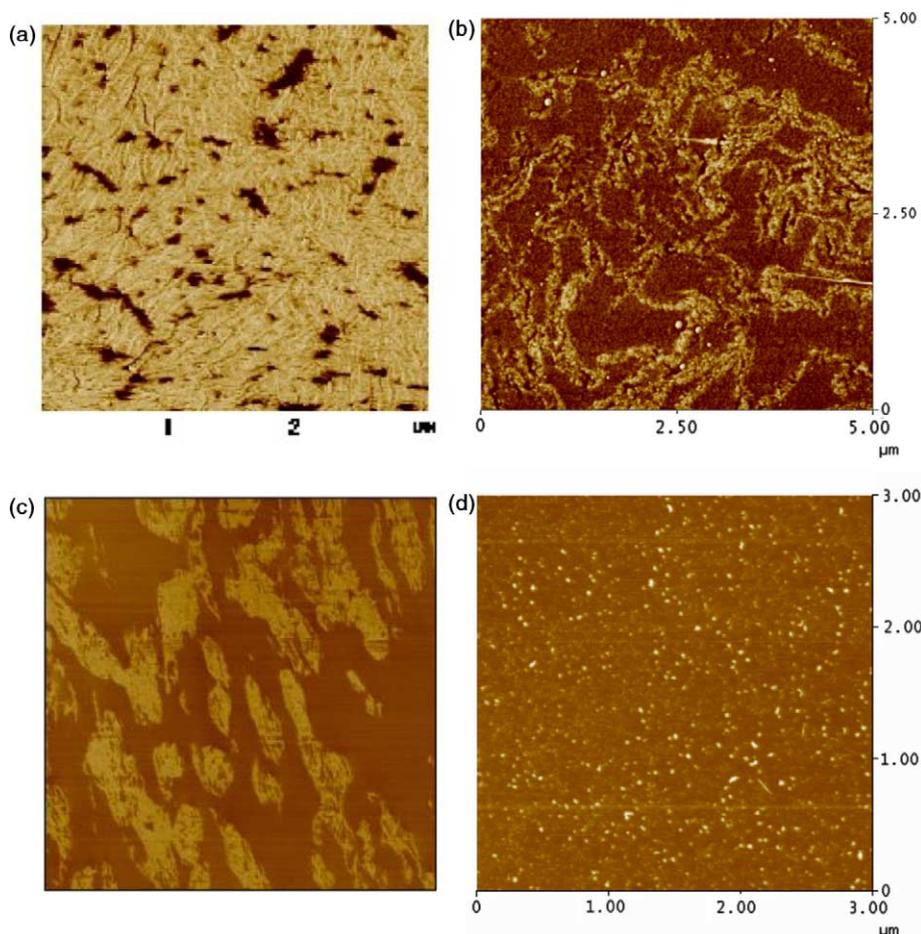


Fig. 5. AFM images of PE-*block*-P(E-*co*-P) with varying propene content (a) 8 mol-%, scale 3 μm ; (b) 39 mol-%, scale 5 μm ; (c) 55 mol-%, scale 5 μm ; (d) 70 mol-%, scale 3 μm .

re-established. The corresponding solvent gradient profile is shown in Fig. 9.

In gradient HPLC experiments carried out, the samples were dissolved in a good solvent (1-decanol) and then injected into a mobile phase of low solvent strength for polyethylene (EGMBE). EGMBE is a good solvent for PP and a non-solvent for PE. This causes a part of the sample to precipitate on the column. By continuously increasing the solvating power of the eluent (linear gradient of EGMBE/TCB), the precipitate

is redissolved and separated by adsorptive or solubility effects. These adsorptive or solubility effects correlate with the chemical composition of the sample and a separation according to chemical composition can be achieved [18]. In this

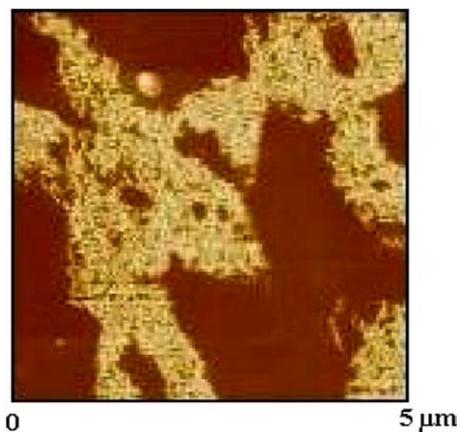


Fig. 6. AFM image of blend of 30% PE and 70% P(E-*co*-P), scale 5 μm .

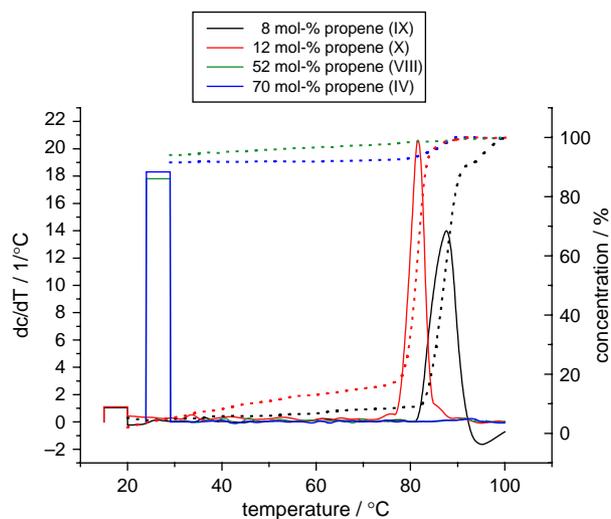


Fig. 7. CRYSTAF plots of concentration c (in % of the starting concentration, right Y-axis, dots) and dc/dT (in $1/^\circ\text{C}$, left Y-axis, lines) for representative samples of block copolymers with varying amount of propene.

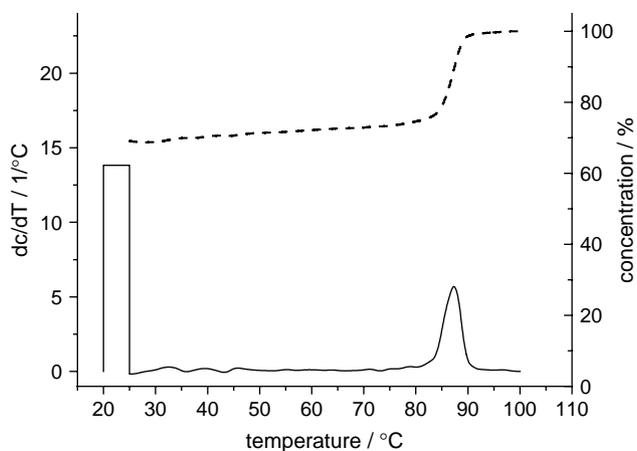


Fig. 8. CRYSTAF plot of concentration c (in % of the starting concentration, right Y-axis, dots) and dc/dT (in $1/^\circ\text{C}$, left Y-axis, lines) for blend of PE (30%) and P(E-co-P) (70%).

separation, system isotactic and atactic PP are eluted in size exclusion mode, while polyethylene and copolymers of ethene and propene are not soluble in the starting eluent EGMBE and are eluted with the gradient. Standards of aPP and HDPE ($M_n=290$ kg/mol, $M_w/M_n=1.26$) have been studied for a validation of the elution volume. The chromatograms are shown in Fig. 10. Chromatograms of the polymers obtained by run IV, V and VII are shown in Fig. 11.

As can be seen from Fig. 10 all atactic polypropylene is eluted at an elution volume below 2.3 mL in SEC mode. Polyethylene is eluted between 8.0 and 8.2 mL with a slight dependence on molar mass. At elution volumes of 2.3–8.0 mL copolymers of ethylene and propylene of different chemical composition are eluted.

As shown in Fig. 11 the chromatograms of the synthesised block copolymers showed two peaks, a small one at 2.4–2.5 mL elution volume and a fairly larger one at 7.6–7.8 mL elution volume. The small peak is detected at the elution volume of the 1-decanol solvent. It is possible that a small amount of the sample is eluted with the solvent volume, used at injection. This phenomenon is described as a ‘breakthrough peak’ [19]. When 1-decanol was used for dissolution of the homopolymers, no breakthrough peak could be detected [18].

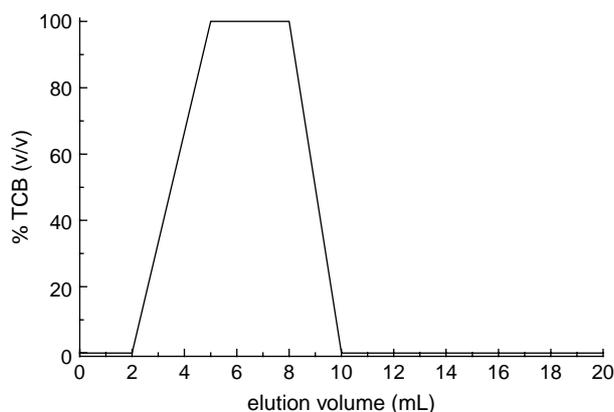


Fig. 9. Solvent gradient (EGMBE/TCB) for chromatographic elution on high temperature gradient HPLC column.

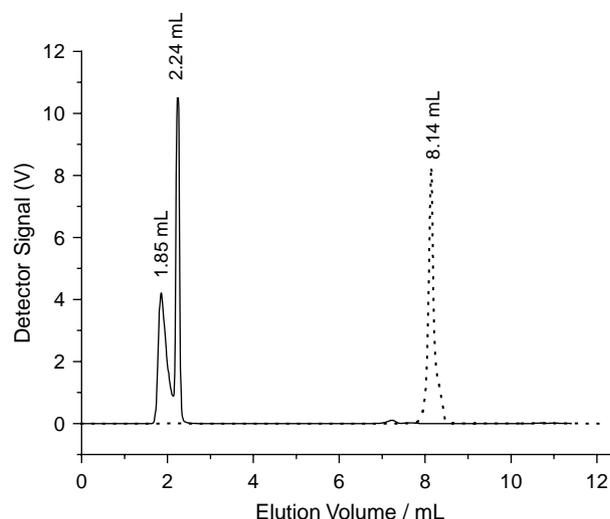


Fig. 10. Chromatograms of aPP (full line) and PE standard ($M_n=290$ kg/mol, $M_w/M_n=1.26$; dotted line) in HT-gradient HPLC (numbers: elution volume for the maximum of the detector signal in millilitre).

Still it could be possible that a small amount of the block copolymer could be eluted with the 1-decanol solvent. It is as well possible that small amounts of P(E-co-P) was formed during polymerisation. This could be due to the long polymerisation times (5 h and more) for the second block. Transfer to MAO might occur after a long period of time leading to the synthesis of small amounts of random copolymer. It is also possible that a small amount of low molar mass polymer is formed by oxidative degradation of the sample during dissolution in 1-decanol at 160°C even in the presence of stabiliser. This might be even more likely and would explain the solubility within the 1-decanol droplet and the mobile phase (EGMBE) and therefore the low elution volume of the peak.

High temperature gradient HPLC showed that neither homo-polyethylene nor homo-polypropylene is formed during

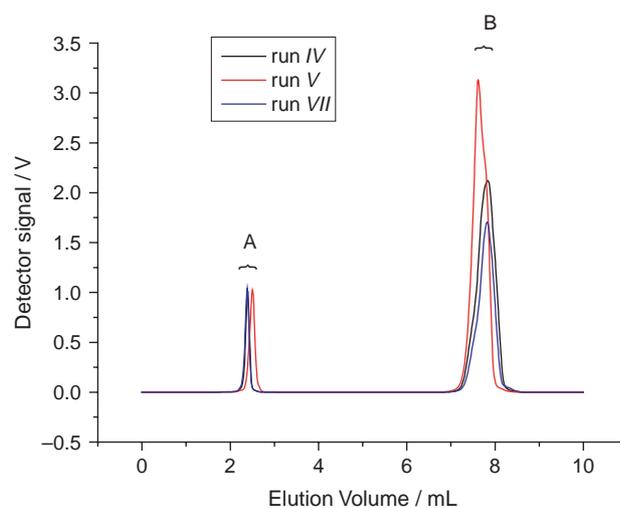


Fig. 11. Chromatograms of the block copolymer from run IV, V and VII in HT-gradient HPLC (run IV, elution volume of the peak maximum A: 2.39 mL and B: 7.83 mL; run V, A: 2.50 mL, B: 7.61 mL; run VII, A: 2.39 mL, B: 7.82 mL).

the synthesis of the block copolymers. This is well in accordance with the CRYSTAF analyses as no crystallisation peak for polyethylene was detected (Fig. 7). The elution volume of the large peak is significantly below the volume expected for homo-PE. This gives a good proof that the block copolymer is present in the sample. A dissolution behaviour quite similar to polyethylene resulting in a large elution volume can be well explained due to the polyethylene block. This is another indication for the existence of block copolymers. A single large peak is observed showing that a uniform block copolymer is obtained during the polymerisation process. As the detector signal is not linear in intensity for different types of polymers without a detector calibration no calculations can be made on the amount of polymer causing a certain peak area. But concerning CRYSTAF experiments the mass of the side product should be definitely below 10% g/g.

4. Conclusions

A series of high molecular weight random P(E-co-P) copolymers throughout the entire feasible composition range were synthesised on (bis-(*N*-(3',5'-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) (**1**)/MAO. Only when **1**/MAO was used as the catalyst high incorporation of propylene and a high catalytic activity in case of high propylene gas concentration were achieved.

In addition, a series of high molecular weight block copolymers of the type PE-*block*-P(E-co-P) have been synthesised by sequential monomer addition via living olefin polymerisation using the phenoxyimine catalyst **1**/MAO. A systematic variation of the block lengths and the propylene content have been performed. Block copolymers with block length in the range between 400 kg/mol $\leq M_n \leq 1100$ kg/mol for the polyethylene block and 150 kg/mol $\leq M_n \leq 900$ kg/mol for the second, rubbery block were obtained. The block copolymers were analysed by NMR, DSC and DMA. AFM morphologies and CRYSTAF experiments give good proof for the formation of block copolymers. HT gradient HPLC showed that neither homopolyethylene nor homopolypropylene is formed during the synthesis of the block copolymers. The single large peak gives a very good hint that a uniform block copolymer is formed during the polymerisation process. One major application of these block copolymers is the role of compatibilizers in polymer blends. Due to their ultra-high molecular weight such high molecular weight thermoplastic elastomers offer new

opportunities for tailoring new polyolefin blends obtained either by melt compounding or reactor blend technology.

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