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Nickel(II) catalysed co-polymerisation of CO and ethene: Formation of polyketone vs. polyethylene – The role of co-catalysts

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ABSTRACT

The square planar Ni complex (SP-4-3)-[Ni(2-tol)(PPh_3)(N,O)] (N,O = (Z)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyrrolidine-2-ylidene)-hexanenitrile) is an active catalyst for the co-polymerisation of CO and ethene yielding aliphatic polyketone. Addition of Lewis acids like BPh_3 or $B(C_6F_5)_3$ as co-catalyst accelerates the polymerisation but not the lifetime of the catalyst and leads to a mixture of polyethylene and polyketone. Addition of the Lewis base triphenylphosphane (PPh_3) completely suppresses the formation of polyethylene. The polymers formed were characterised by IR spectroscopy, ^{13}C cross polarisation (CP) magic angle spinning (MAS) solid state NMR spectroscopy, differential scanning calorimetry (DSC) and size exclusion chromatography (SEC).

1. Introduction

Aliphatic polyketones are a relatively young class of polymers gaining growing interest [1–3]. They are synthesised in a homogeneous, transition metal-catalysed reaction of CO and olefins and exhibit outstanding properties, e.g. photodegradability through Norrish type I and II mechanisms [1,4]. Industrially, palladium complexes [5–7] are used but since the metal remains in the polymer we focus on cheaper alternatives. Nickel turned out to be a promising candidate [8–13]. The most efficient nickel complex to date [14,15] catalysing the co-polymerisation of CO and ethene is shown in Fig. 1. It is already structurally characterised [14].

We are interested in the mechanism of the co-polymerisation reaction and used the complex shown in Fig. 1 to study the influence of several co-catalysts on the reaction products and the kinetics of the co-polymerisation reaction of CO and ethene.

2. Results and discussion

The catalytically active nickel complex according to Fig. 1 was prepared by literature methods. It catalyses the formation of a strictly alternating polyketone from ethene and CO as is shown in Fig. 2.

A twofold insertion of CO is not favoured for thermodynamic reasons [16] and a twofold insertion of ethene is kinetically too slow. The co-polymerisation reaction was carried out in dry toluene solution (ca. 2–3 mM) at 60 °C and 50 bar (CO partial pressure: 10 bar, C_2H_4 partial pressure: 40 bar) in a glass insert immersed in a standard 100 mL steel autoclave.

In a run over 10 h (see Table 1, catalytic run #1) the resulting polymer exhibits an IR spectrum (KBr disc) showing the typical bands evoked by a strictly alternating aliphatic polyketone with the C=O valence vibration at 1695 cm^{-1} and the C—H valence vibrations around 2910 cm^{-1}. The polymer is completely soluble in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). In the $^{13}C\{^1H\}$ NMR spectrum the methylene signal appears at 35.7 ppm (2.6 ppm ^{1}H, resp.) and the carbonyl signal at 212.7 ppm, respectively (125 MHz, HFIP/$CDCl_3$).

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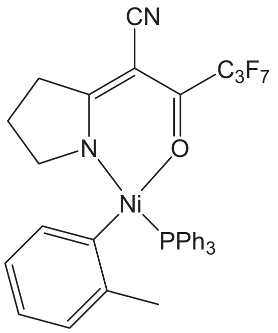

Fig. 1. The most efficient nickel complex (*SP*-4-3)-[Ni(2-tol)(PPh_3)(*N,O*)] (*N,O* = (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyrrolidine-2-ylidene)-hexanenitrile) for the co-polymerisation of ethene and CO to date.

Table 1
Catalytic runs with and without added cocatalyst and resulting efficiency in polymer formation. Dry toluene catalyst solution at 60 °C and 50 bar (CO partial pressure: 10 bar, C_2H_4 partial pressure: 40 bar) in a glass insert immersed in a standard 100 mL steel autoclave. Catalytic run time is 10 h unless otherwise stated.

Catalytic run #	Catalyst (mmol)	Co-catalyst (mmol)	PE formed	Productivity[a]
1	30	–	×	3000
2[b]	34	–	×	0
3[b]	35	162 BPh_3	×	550
4	30	30 BPh_3	✓	3200
5	25	55 BPh_3	✓	3100
6	31	260 BPh_3	✓	3200
7	29	195 PPh_3	×	3300
8	30	2000 PPh_3	×	2300

[a] g polymer/g Ni.
[b] Catalyses were stopped after 45 min.

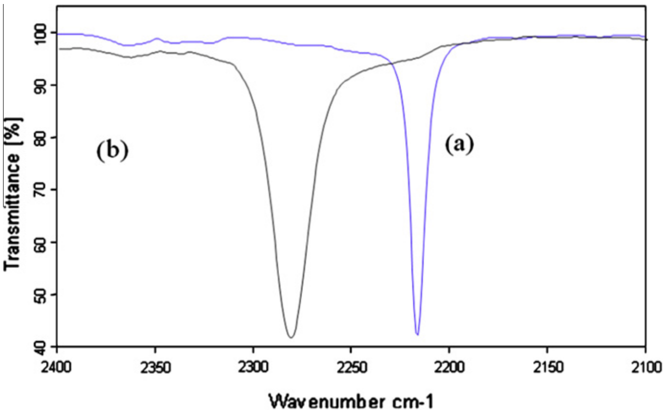

Fig. 3. IR spectra between 2100 cm^{-1} and 2400 cm^{-1} in toluene solution, *d* = 0.1 mm. (a) (*SP*-4-3)-[Ni(2-tol)(PPh_3)(*N,O*)]; (b) (*SP*-4-3)-[Ni(2-tol)(PPh_3)(*N,O*)] + BPh_3 (molar ratio 1:2).

The formation of polyethylene does not take place in the first hours of catalysis. Apparently, during that time, (SP-4-3)-[Ni(2-tol)(PPh_3)(N,O)] does not catalyse the polymerisation of ethylene under our reaction conditions in the presence of CO, nor it does in absence of CO. We assume that during the first hours of catalysis the nickel species slowly generates an active catalyst for the polymerisation of ethylene.

We assume for thermodynamic reasons that the initial step of polyketone formation consists in CO coordination to the nickel center followed by insertion of CO into the nickel–arylcarbon bond of the catalytically active complex (see Fig. 1). This could in principle follow either an associative or a dissociative way: CO could add to the nickel centre forming a fivefold coordinated transition state (associative), or a coordinated ligand could dissociate off, opening a coordination site for CO (dissociative).

We were interested to see if the triphenylphosphane ligand was involved in this initial step. If the first step involves a reversible dissociation of PPh_3, addition of free PPh_3 in solution should impede the CO–ethylene co-polymerisation. We added PPh_3 to the reaction mixture in a 5–70-fold stoichiometric excess (see Table 1, catalytic runs #7 and #8, respectively) but observed no influence on the catalytic activity. Remarkably, in runs over at least 20 h, the resulting polymer contains no polyethylene. Apparently, PPh_3 in the catalytic mixture inhibits the formation of the species which catalyses the polymerisation of ethene.

We investigated not only the influence of added *Lewis bases* such as PPh_3, but also the use of *Lewis acids* like BPh_3 or $B(C_6F_5)_3$, as co-catalysts in the reaction mixture (see Table 1, catalytic runs #4 and #6, respectively). Lewis acids in general could act as triphenylphosphane scavengers and thus favour the dissociation of PPh_3. In long-term catalytic runs (>20 h) we observed no difference in catalytic productivity regardless if a Lewis acid was added or not. In both cases the respective mass of polymer mixture was formed, not differing significantly in the polyketone/polyethylene ratio.

In short-term runs we determined the yield of the total polymer mass after 45 min. If no Lewis acid was added, no polymer was formed during the first 45 min (see Table 1, catalytic run #2). Upon repeating the experiment with the addition of a 2–4-fold stoichiometric excess of BPh_3 or $B(C_6F_5)_3$ to the reaction mixture, about 1/3 of the polymer mass obtained in the respective long-term run was already formed during the first 45 min (see Table 1, catalytic run #3).

In order to elucidate possible exchange interactions of the Lewis acids with the nickel complex, we recorded IR spectra in solution. Fig. 3 shows the spectrum of (SP-4-3)-[Ni(2-tol)(PPh_3)(N,O)], as well as a 1:2 mixture of the nickel complex with BPh_3 in toluene solution in the range between 2100 and 2400 cm^{-1}. The wave number of the CN valence stretch in the complex (2216 cm^{-1}) is shifted by about 66 cm^{-1}–2282 cm^{-1} upon coordination of BPh_3 to the ligand's CN nitrogen. Similar results were achieved by using the stronger $B(C_6F_5)_3$ as Lewis acid. Antibonding electron density is withdrawn from the CN moiety, resulting in a stronger bond and a corresponding higher CN stretching frequency. This also results in a lower electron density at the nickel centre. We conclude that monomer insertion is facilitated by an electron deficient nickel centre, resulting in decreased reaction times and thus a faster product formation. Ziegler et al. showed for similar systems comprising N,O chelate ligands that a decreased electron density on the nickel centre resulted in a decreased insertion barrier for ethene [17].

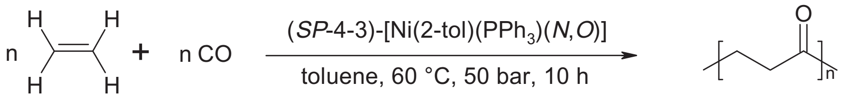

Fig. 2. Strictly alternating aliphatic polyketone from the catalysed co-polymerisation of ethene with CO (*N,O* = (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyrrolidine-2-ylidene)-hexanenitrile).

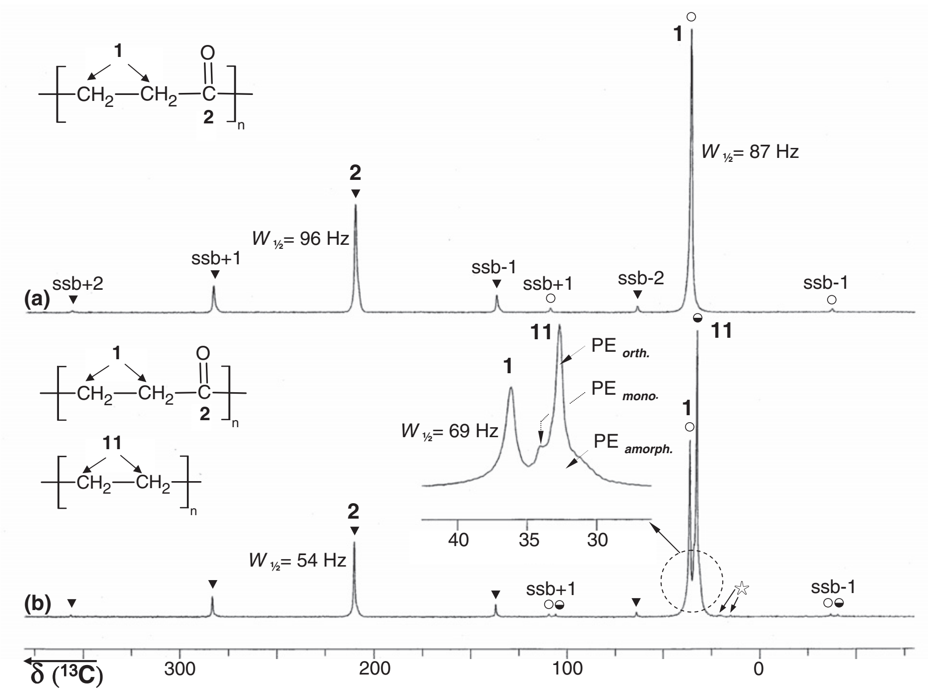

Fig. 4. 75 MHz-^{13}C-CP/MAS-solid state-NMR-spectra (δ in ppm, T = 301 K, Ro = 5.52 kHz, (a) NS = 4290, (b) NS = 2916): (a) pure polyketone, (b) mixture (*ca.* 37%:63%) of polyketone and polyethylene (PE). Isotropic chemical shifts are marked by numbers. Spinning side bands (ssb, +: shift to higher frequencies, –: shift to lower frequencies) and the main signal of the carbonyl C atom are denoted by ▼, those of the CH_2-atoms by ○ (polyketone) and by ◒ (polyethylene). The insert of trace (b) shows the spectrum between 42.5 and 26.0 ppm. Signals of the different crystalline and amorphous forms of polyethylene are marked by arrows. Small signals in trace (b) (arrows and ☆) at δ = 20.2 and 15.0 ppm (nonexistent in trace (a)) might origin from terminating groups of polyethylene.

More information concerning the structure and morphology of the polyketone of catalytic run #1 (see Table 1) was obtained by ^{13}C-CP/MAS-solid state-NMR (see Figs. 4, trace a and 5, traces a–c). The chemical shifts of the main signals at δ = 36.1 and 210.1 ppm do not differ significantly from the values obtained for the polymer in HFIP solution. From that we conclude that the structure in solution and in solid state is similar. The carbonyl signal (δ = 210.05 ppm) is accompanied by several spinning side bands, as expected. Therefore, less anisotropy of the sp^3-hybridised C atoms in the CH_2 groups (compared to the sp^2 hybridisation of the carbonyl groups) leads to weak first order side bands. With respect to the intensities of the side bands, integration of the signals affords a ratio of 1.9: 1 (CH_2 vs. $C{=}O$) suggesting the co-polymerisation of one ethene per CO and thus the formation of a strictly alternating polyketone. The isotropic chemical shifts are similar to those found for polyketone produced by palladium/alumoxane catalysed reactions [18].

Even after an extended number of scans the spectrum contains no further lines besides the above mentioned. If a twofold insertion of CO would have happened, ^{13}C NMR signals of the carbonyl moiety should appear around 200 ppm. A twofold ethene insertion would lead to signals of the CH_2-groups around 41–45 ppm. There are neither hints of a "side" insertion of ethene in the spectra nor of a polyspiroketal structure. All findings of the solid state NMR therefore indicate an alternating, uniform composition of the polymer.

In general, the ^{13}C NMR spectra of dissolved polymer samples usually show characteristic small signals, typical for terminating groups. For example, a terminating carbonyl group exhibits a characteristic resonance at 217.1 ppm [19]. Similar chemical shifts are then expected in the solid-state NMR-spectra as well, since the ends of the chains are more flexible fragments of the polymers and should therefore be more easily detectable by solid state NMR. Missing of such signals, as in our case, could be a hint of a high molecular weight of the polymer. This is supported by SEC analyses of the polymer samples showing molecular weights >10^5 (see Fig. I, Supplementary material).

The MALDI-TOF mass spectra of the polymer show that it is a strictly alternating polyketone, but it seems that MALDI-TOF-MS is not a suitable means of characterisation to determine the molecular weight distribution (compare Figs. I and II in Supplementary material). Only low molecular polyketones are detected showing the characteristic mass difference of 56 Da (see Fig. II, Supplementary material). We have not been able to identify the end groups.

A lineshape analysis of the ^{13}C solid-state NMR signals offers insights into the morphology of the solid. A close look into the lineshape of the carbonyl resonance (see Fig. 5, trace a–c) reveals that the sharp main signal is accompanied by a broad shoulder at higher field. Deconvolution analysis using GLINFIT reveals two equally sized narrow lines (δ = 210.4 ppm, $W_{1/2}$ = 67 Hz and δ = 210.0 ppm, $W_{1/2}$ = 63 Hz) and a broad line (δ = 208.8 ppm, $W_{1/2}$ = 120 Hz). Similar analysis of the spectrum in the range of the CH_2 signals affords consistent results. Two equally shaped, narrow Lorenz lines (δ = 36.2 ppm, $W_{1/2}$ = 61 Hz and δ = 35.9 ppm, $W_{1/2}$ = 57 Hz) and a significantly broader line (δ = 36.8 ppm, $W_{1/2}$ = 194 Hz) comprising about 24% of the total intensity. Narrow lines in a solid state spectrum indicate an ordered assembly of the solid whereas broad lines indicate a disordered solid. This said, the spectra indicate that the sample mainly consists of a pure, strictly alternating polyketone in the crystalline modification (>75%). Only about 25% of the sample consists of amorphous fragments. The presence of an amorphous fraction in the sample has been proven by determining the relaxation times using the Torchia pulse sequence [20,21].

Ethene/CO copolymers are literature-known to comprise two crystalline modifications, α [18,22–24] and β [25,26], which orthorhombic unit cells are similar to the crystalline, orthorhombic unit cell of polyethylene. In the presence of palladium catalysts both modifications form during polymerisation, the amount of the α modification being strongly dependent on the reaction conditions. Upon heating (T > 110 °C) the α modification merges into the β

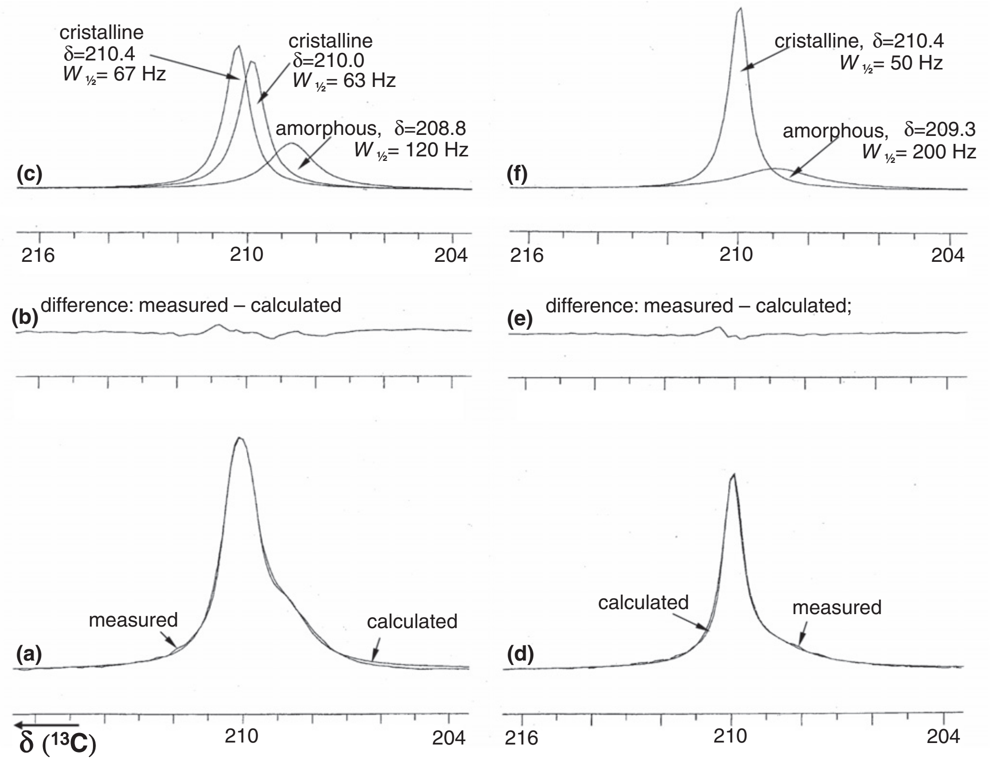

Fig. 5. 75 MHz ^{13}C-CP/MAS solid state NMR (δ in ppm), subspectra around the signal of C=O. (a–c) Spectra of pure polyketone, (d–f) spectra of a polyethylene/polyketone mixture. The experimental lines (traces (a) and (d), "measured") have been simulated using the deconvolution program GLINFIT (Bruker). A Lorenz profile (traces (a) and (d), "calculated") has been simulated to match the experimental curve as close as possible. The difference of experimental and simulated spectra is shown in traces (b) and (e) (error < 4.0%). The simulated spectrum of the polyketone sample consists of three lines (see trace (c)), the one of the polyethylene/polyketone mixture of two lines (see trace (f)). Broad lines can originate from amorphous parts, sharp lines from crystalline parts of the sample. Therefore the sample of the pure polyketone consists of two crystalline modifications (δ = 210.4 ppm, *ca.* 39% and δ = 210.0 ppm, *ca.* 37%) and an amorphous part (δ = 208.8 ppm, *ca.* 24%). The mixed sample consists of polyketone of one crystalline modification (δ = 210.4 ppm, *ca.* 70%) and an amorphous part (δ = 209.3 ppm, *ca.* 30%). A similar analysis has been accomplished for the subspectra in the range of CH_2 (50.0–24.0 ppm, not shown). Results are consistent with the findings afore. For the deconvolution of the spectra of pure polyketone two narrow lines (*ca.* 1:1) and a broad Lorenz line are needed; for the signals of the mixed sample only two lines (one narrow and one broad) are needed for the polyketone part to achieve a fit error less than 4%. The amorphous and crystalline fractions of the polymers are in good accordance with those shown in this figure.

modification. It has to be shown by further experiments if this is also true for our Ni based system. The presented results of the solid state NMR analysis might be a hint that the copolymer obtained from Ni catalysed co-polymerisations has the same structure as the one obtained from Pd catalysed reactions.

When the reaction is carried out for at least 20 h, the IR spectrum of the resulting polymer sample shows an additional sharp band at 720 cm^{-1}. This band is typical for a rocking vibration of a $-[CH_2]_n-$ ($n \geqslant 4$) subunit which is nonexistent in strictly alternating polyketone. An additional band also appears at 2850 cm^{-1}, typical for a symmetrical C—H valence vibration in said subunits. The question arises whether a polyketone has formed, comprising at least two consecutive ethylene units in a regular or statistical manner, or a mixture of strictly alternating polyketone and polyethylene. The polymer formed is not completely soluble in HFIP, leaving an insoluble residue. The IR and NMR spectra of the soluble part are identical to the spectra originating from strictly alternating aliphatic polyketone. The IR spectrum of the insoluble residue shows no band of a C=O valence absorption, but retains the bands at 720 cm^{-1} and 2850 cm^{-1}. These findings indicate a polymer mixture of alternating polyketone and polyethylene rather than statistical polyketone.

To further analyse the polymer, we recorded the ^{13}C{^{1}H} CP/MAS solid state NMR spectrum of the mixed polymer sample which shows the signals of the carbonyl and the methylene carbons of the polyketone and the signal for the methylene carbon of the polyethylene (Fig. 4, trace b).

The isotropic chemical shift of the signals of the copolymer is identical to those of the pure polyketone. The integration of the signals results in an approx. ratio of 1.9:1 (CH_2 vs. C=O). Together with the non-appearance of other signals this is indicative for a strictly alternating ethene/CO copolymer. The molecular weight distribution is probably also similar to the sample of pure polyketone; terminating groups could not be detected even after long accumulation times. Small signals in the aliphatic region (see Fig. 4, trace b); δ = 20.2, 15.0 ppm) are expected for the terminating groups of polyethylene.

One difference between the pure polyketone and the polyketone in the mixed sample is obviously shown in its morphology. The comparison of the half width of signals 1 and 2 (see Fig. 4) in both samples indicates a more uniform polyketone if it is formed besides polyethylene. If polyketone is the sole polymer formed, its morphology is much more heterogeneous. Lineshape analysis (see Fig. 5, trace d–f) is consistent with this: only one signal for the crystalline modification (*ca.* 70% of the polyketone) and one broad line for the amorphous fragments are necessary to simulate the spectrum with a very small error. The analysis of the CH_2 signal is consistent with this.

Also, the results of determining the relaxation time are consistent with a higher ordered structure of the polyketone. The T_1 relaxation times of the CH_2 and C=O signals are higher in the mixed sample compared to the sample of the pure polyketone.

Besides polyketone, the sample consisted of approx. 2/3 of polyethylene which shows a typical distribution of modifications: the

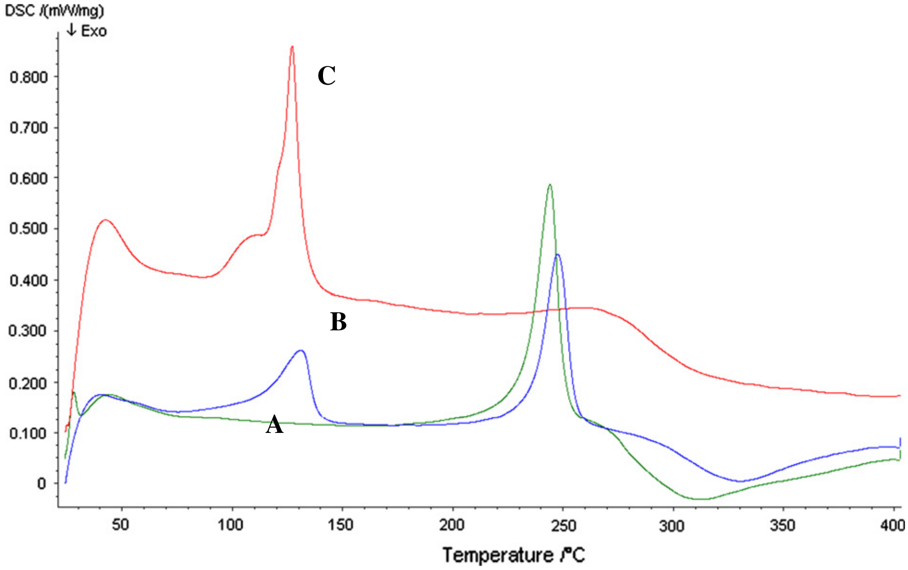

Fig. 6. DSC curves of polymer samples. **A**: polymer completely soluble in HFIP – melting point 240 °C (polyketone). **B**: polymer not completely soluble in HFIP – melting points 240 °C and 125 °C (mixture of polyketone and polyethylene). **C**: in HFIP insoluble fraction of **B** – melting point 125 °C (pure polyethylene).

crystalline modifications (orthorhombic and monoclinic) are dominant, the amorphous modification consists of about 30%. This is the typical composition of polyethylene formed by homo-polymerisation of ethylene. This might be a hint that after long reaction times during the nickel-catalysed co-polymerisation, pure polyethylene is formed besides polyketone. For a block copolymer one would expect additional signals for the linking groups, but there are not hints in the spectra for this. The soluble part of the polymer does not show any signals for polyethylene indicating that no block copolymer was formed.

In addition we characterised the polymer by differential scanning calorimetry. The DSC curve shows two peaks at 240 °C (polyketone) and 125 °C (polyethylene), respectively. We confirmed this assignment by separating the two polymers by their solubility behaviour in HFIP, determined their individual DSC curves and compared them to standard samples of strictly alternating aliphatic polyketone and polyethylene, respectively (Fig. 6).

3. Conclusion

We have shown that the nickel complex (SP-4-3)-[Ni(2-tol)(PPh$_3$)(N,O)] (N,O = (Z)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyrrolidine-2-ylidene)-hexanenitrile) shown in Fig. 1 is an active catalyst for CO/ethylene co-polymerisation yielding polyketone. In the presence of the Lewis acid BPh$_3$ or B(C$_6$F$_5$)$_3$ co-polymerisation of CO and ethylene yielding polyketone as well as homo-polymerisation of ethene yielding polyethylene is observed. The addition of Lewis acids leads to an increased reaction rate for the polymer formation, but not to longer catalyst lifetime. We have shown that a polymer mixture of strictly alternating aliphatic polyketone and polyethylene rather than non-alternating (statistical) polyketone is formed. Upon addition of PPh$_3$ the formation of polyethylene is completely suppressed. To our knowledge no nickel or palladium complexes are known to date which catalyse the synthesis of different polymers depending on the added co-catalyst.

4. Experimental

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was dried over sodium and distilled in a nitrogen atmosphere. Solution NMR spectra were recorded at room temperature using a Bruker Avance DRX 200 spectrometer for ^{1}H, ^{13}C and using a Bruker Avance DRX 500 spectrometer. The proton and carbon chemical shifts are given in ppm and referenced to the signal of the solvent residual signals [27] (CDCl$_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm; C$_6$D$_6$: ^{1}H 7.16 ppm, ^{13}C 128.1 ppm. Solid state ^{13}C CP/MAS-NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with double bearing probe and a Bruker B-VT 1000 temperature control unit. The ZrO$_2$ rotor (7 mm internal diameter) was charged with the polymer sample und sealed by Kel-F inset. Optimal contact time for ^{13}C CP was 2.5–3.5 ms. The spinning rate (Ro) was between 3 and 6 kHz. The external standard for ^{13}C NMR was adamantene (™(CH$_2$) = 38.40, relative to TMS). Infrared spectra were recorded on a FT-IR Bruker IFS 66 spectrometer. MALDI-TOF MS data were recorded on an Bruker Daltonics Ultraflex I, EI MS data were obtained from a Varian MAT 311 A instrument. Size exclusion chromatography (SEC) spectra were recorded on a Waters GPC instrument equipped with a Shimadzu LC-10AD pump, a WATERS 2414 differential refraction index detector (at 35 °C) and a MIDAS auto-injector (50 μL injection volume). HFIP was used as eluent at a flow rate of 1.0 mL min^{-1}. PSS (2× PFG-lin-XL, 7 μm, 8 × 300 mm, 40 °C) columns were used. Molecular weights and molecular weight distributions were calculated relative to PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. DSC measurements were done with a Netzsch instrument, model STA 449c.

[Ni(2-tol)(PPh$_3$)(N,O)] (N,O = (Z)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyrrolidine-2-ylidene)-hexanenitrile) was prepared according to literature procedures [14,15].

4.1. General procedure for catalyses

All co-polymerisation reactions were carried out in a standard 100 mL stainless steel autoclave under inert gas atmosphere. 20 mg (2.8 mmol) [Ni(2-tol)(PPh$_3$)(N,O)] was dissolved in 10 mL dry toluene. 40 bar (ca. 12 g, 0.4 mol) ethene and subsequently 10 bar (ca. 3 g, 0.1 mol) CO were added with stirring. The reaction mixture was heated to 60 °C while stirring for the desired time. The autoclave was then allowed to cool to room temperature and residual pressure was released. The polymer formed was washed three times with methanol and air-dried.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.08.002.

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[21] Applying this pulse sequence, the intensity of the signal decreases with progressing relaxation and reaches zero at $\tau = 5T_1$. This way, the signal of the amorphous fraction can be suppressed (fast relaxation) and be separated from the resonances of the crystalline fraction (slow relaxation). The spectrum of the amorphous polymer results from the difference spectra, that is spectrum of the sample (crystalline and amorphous, $\tau = 0$) minus spectrum after signal suppression of the amorphous fraction (crystalline, at $\tau = 5T_{1,}$ amorphous). The result obtained this way for the polyketone sample (amorphous copolymer, ca. 26%) is in good accordance with the result of the deconvolution analysis.
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