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Copolymerization of propene with low amounts of ethene in propene bulk phase

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Abstract

Propene homopolymers and propene–ethene copolymers with small amount of ethene were synthesized using three catalyst systems [*p*-$CH_3OPh_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]ZrCl_2/Me_2HNPh][B(C_6F_5)_4]$ (**Cat I**), [*p*-$CH_3OPh_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]ZrCl_2/[Ph_3C][B(C_6F_5)_4]$ (**Cat II**) and [*p*-$CH_3OPh_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]ZrCl_2/MAO$ (**Cat III**) in propene bulk phase. The activity of the catalyst was dependent on the formed ion pair: **Cat I** showed the highest activity, up to 96,000 kg_{pol}/mol_{Zr} h, at the used polymerization conditions. The produced homo- and copolymers have high molecular weights, between 400 and 600 kg/mol. The ethene incorporation rate was nearly the same with the different catalyst systems; the amount of ethene in the copolymer was increasing linearly with the amount of ethene in feed. The syndiotacticity of the homopolymer was highest, $[rrrr] > 90\%$, with **Cat I** when it was 81.4 with **Cat II** and 80.8 with **Cat III**. The small amount of ethene in the copolymer allows the control of the melting and crystallization behavior. Also the crystallization temperatures of the copolymers were found to depend on the used catalyst system.

Keywords: Bulk polymerization; Metallocene; Propene–ethene copolymers

1. Introduction

The development of *Cs*-symmetric metallocenes by Ewen and Razavi [1] in 1988 opened the opportunities to synthesize syndiotactic polypropene (sPP). *Cs*-symmetric catalysts follow an enantiomorphic site control mechanism. Two enantiotopic coordination sites enable an alternating, enantiofacial orientation of the propene insertion thus forming a syndiotactic polypropene chain. sPP is a crystalline thermoplastic polymer with high melting point. The recent modifications of *Cs*-symmetric metallocenes are capable to produce highly syndiotactic polypropene with good activity and high molecular weight [2].

Copolymerizing a small amount of ethene into the sPP chain enables a modification of the material to be more elastic and simultaneously also allows the control of the crystallization process. Copolymers of sPP with small amounts of ethene have lower melting points, lower glass transition temperatures and higher impact strengths than pure sPP [3]. These copolymers form a new class of thermoplastic elastomers.

Besides methylalumoxane (MAO), borate cocatalysts together with metallocenes are widely used in olefin polymerizations. Activity and stability of the catalyst, the chain transfer processes, and in some cases, the syndiotacticity of the formed polymer is sensitive to the nature of the ion pair formation. Very typically the propene polymerization experiments in laboratory scale are carried out either in solution or slurry and therefore the polymerization behavior in a solvent media is studied a lot and hence well known [4]. Though in industrial processes bulk polymerizations are widely used, the polymerization behavior in the bulk phase is significantly less known. To our knowledge, there are no publications available about propene–ethene copolymerizations in bulk phase by syndiotactic working catalysts. This work focuses on bulk polymerizations of propene and particularly on copolymerizations of propene with low amount of ethene.

Molecular weight is one of the main factors determining the mechanical properties of the polymer. Sufficient high molecular weight, over 300 kg/mol, is needed to attain good tensile and creep properties. The zirconocene complex

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[p-CH_3OPh_2C(2,7-di-^{tert}BuFlu)(Cp)]$ZrCl_2$ produces highly syndiotactic polypropene with good polymerization activity and high molecular weight [2,5]. Homopolymerizations and copolymerizations with small amounts of ethene were performed in liquid propene media using the catalyst systems [p-CH_3OPh_2C(2,7-di-^{tert}BuFlu)(Cp)]$ZrCl_2$/Me_2HNPh][B(C_6F_5)$_4$] (**Cat I**), [p-CH_3OPh_2C(2,7-di-^{tert}BuFlu)(Cp)] $ZrCl_2$/[Ph_3C][B(C_6F_5)$_4$] (**Cat II**) and [p-CH_3 OPh_2C(2,7-di-^{tert}BuFlu)(Cp)]$ZrCl_2$/MAO (**Cat III**). Tri-isobutyl aluminium (TIBA) was used as alkylating agent and scavenger in the borate cocatalyzed systems.

2. Experimental section

2.1. Materials

Monomers propene and ethene (Messer Griesheim) were purified by passing through columns containing Cu catalyst (BASF R3-11) and 3 Å molecular sieves. The commercial MAO solution (Crompton Corporation) was filtered and the trimethyl aluminum (TMA) and toluene were removed by distillation in vacuum. Tri-isobutyl aluminum (TIBA) was purchased from Aldrich and used as delivered. The metallocene complex [p-CH_3OPh_2C(2,7-di-^{tert}BuFlu)(Cp)]$ZrCl_2$ was synthesized in the group of professor Kaminsky [2]. The borate cocatalysts [Me_2HNPh][B(C_6F_5)$_4$] and [Ph_3C][B(C_6F_5)$_4$] were purchased from Boulder Scientific.

2.2. Polymerizations

The polymerizations were carried out in 1-l Büchi stainless steel autoclave equipped with an additional internal cooling system. The monomer feed was kept constant with a Peteric 3002 press-flow controller. The monomer consumption was monitored using the Büchi data system bds 488. The evacuated reactor was cooled down to −20 °C and charged with 400 ml liquid propene. There after 20.4 mmol MAO, dissolved in a small amount (1–2 ml) of toluene, or 13.6 mmol TIBA was fed into the reactor. The reactor was warmed up to 0 °C. The pressure in the reactor was 4.7–4.8 bars. In copolymerizations the desired amount of ethene (0.05, 0.24 or 0.48 bar corresponding the propene/ethene feed ratios of ca. 270, 80 and 40 in feed) was added. In borate-cocatalyzed polymerizations, the metallocene complex, dissolved is toluene, was fed into the reactor and let to be alkylated for 15 min. After that, feeding the borate cocatalyst solution started the polymerization. In MAO-cocatalyzed polymerizations, feeding the metallocene complex, dissolved in toluene, started the polymerization. The pressure was kept constant by supplying ethene into the reactor (semi-batch process). Because of the high propene/ethene molar ratio in the reactor and the quite low polymer yield, supplying ethene during the polymerisation did not change the propene/ethene ratio significantly. In homopolymerizations propene was not constantly added. Injecting 5 ml ethanol to the reactor and letting the gaseous monomer slowly out stopped the polymerization. The reactor was washed with toluene and the toluene–polymer mixture was poured into 400 ml acidic (1% hydrochloric acid) ethanol. The polymer was stirred in acidic ethanol overnight, washed with pure ethanol and dried in vacuum at 60 °C. In the copolymerizations the conversion of propene was kept low and it can be assumed that the propene/ethene ratio remained nearly constant throughout the polymerization.

2.3. Characterization of the homo- and copolymers

^{13}C NMR spectra were measured with Bruker Ultrashield 400 NMR-spectrometer (100.62 MHz) at 100 °C using pulse angle 30°; delay time 5 s and at least 1000 scans. 2.0 ml 1,2,4-trichlorobenzene and 0.5 ml 1,1,2,2-tetrachloroethane-d2 were used as solvents in the measurements.

Weight average molecular weight (M_w) and molecular weight distribution (MWD) were measured with Waters GPCV2000 containing HT3, HT4 and HT6 styragel columns. Mark–Houwink constants $K = 0.0019$ and $\alpha = 0.725$ were used.

Differential scanning calorimetric (DSC) curves were measured with a Mettler Toledo 821e instrument. Glass transition temperatures (T_g) and melting temperatures (T_m) were measured from the second heating cycle and crystallization temperatures (T_c) from the first cooling. Heating and cooling rate was 10 °C/min.

3. Results and discussion

3.1. Activity of the catalyst

The activity of the catalyst is largely dependent on the polymerization conditions and the nature of the formed ion pair. It is commonly accepted that cocatalysts like MAO, [Me_2HNPh][B(C_6F_5)$_4$] and [Ph_3C][B(C_6F_5)$_4$] together with metallocenes form $[L_2M\text{–}R]^+[X]^-$ type active species. (L, ligand; M, metal; and X, counter anion). The degree of interactions is dependent on the nature and structure of the ion pair and on the polymerization conditions. The structure of the cocatalyst is highly important with respect to its behavior and activating mode. Nucleophility, coordinating ability and bulkiness of the cocatalyst affect the activity of the catalyst. Borate anions are less bulky, more polar and have better coordinating ability than MAO [6]. Consistently the activity and the rate of catalyst site epimerization should decrease in the case of $[B(C_6F_5)_4]^-$ compared to MAO. According to our previous work, [Me_2HNPh][B(C_6F_5)$_4$] as cocatalyst give higher activities than [Ph_3C][B(C_6F_5)$_4$] or MAO in toluene at low polymerization temperatures [7]. The formation of active species is rather inefficient at low temperatures in the case of MAO [8,9] and hence the formation of inactive species, like alkylidene complexes $L'_2MCH_3(\mu\text{-}Cl)Al(Me_2)_2$ and $L'_2M{=}CH_2$ or [$L'_2M(Me)OAl(Me)$][MAO] (L′, cyclopentadienyl based ligand; M, Ti, Zr) is possible [6,10]. Also the M–(CH_3)CH_2–Al species are inactive in polymerization, but they can further react with MAO to form the active species [6]. In this study **Cat I** shows up to100 times higher activities than **Cat II** or **Cat III**, as can be seen from Table 1 and Fig. 1. The counter anion in the case of **Cat I** and **Cat II** is the same

Table 1
Polymerization experiments conducted in 400 ml liquid propene at 0 °C with different catalyst systems

Run	Catalyst	xE (p%)	$p(E)$ (bar)	n (cat) (µmol)	n (borate) (µmol)	n (TIBA/MAO) (mmol)	t_p (min)	Yield (g)	Activity[a]	$X(E)$ (%)	M_w (kg/mol)	MWD	$T_m(1)$ (°C)	$T_m(2)$ (°C)	T_g (°C)	T_c (°C)	Tacticity (% [*rrrr*])
1	**Cat I**	0	0	0.4	0.8	13.6	5	1.56	46800	0	640	1.8		144.8	0.6	99.3	90.1
2	**Cat II**	0	0	0.4	1.2	13.6	30	0.12	600	0	500	3.1	139.9	146	−4	98.6	81.4
3	**Cat III**	0	0	0.6		20.4	30	0.22	700	0	570	2.3	131.5	142.3	0	88.7	80.8
4	**Cat I**	1	0.05	0.3	0.6	13.6	2	0.66	66000	0.9	630	1.8	138.7	145.9	−1.5	93.8	
5	**Cat II**	1	0.05	0.3	0.9	13.6	15	0.32	4300	1.3	630	1.9	135.5	142.5	−0.8	90.7	
6	**Cat III**	1	0.05	0.3		20.4	30	0.23	1500	2.6	590	2.3	121.1	133.6	−4.3	76.5	
7	**Cat I**	5	0.24	0.3	0.6	13.6	5	0.65	70000	3.2	560	1.9	124.6	128.3	−2.3	68.8	
8	**Cat II**	5	0.24	0.5	1.5	13.6	30	0.17	700	4.2	370	3.6	119.1		−3.7	50.7	
9	**Cat III**	5	0.24	0.5		20.4	30	0.50	2000	4.9	540	2.3	110.9	121.2	−5.1	60.5	
10	**Cat I**	10	0.48	0.2	0.4	13.6	2.5	0.80	96000	6.3	430	2.0	105.6	112.9	−6.9	53.4	
11	**Cat II**	10	0.48	0.5	1.5	13.6	15	0.41	3300	6.2	420	2.5	107.2	112.6	−7.8	36.3	
12	**Cat III**	10	0.48	0.6		20.4	30	1.03	3400	7.4	410	3.0	104.4	110.9	−9.4	47.6	

$X(E)$ is the amount of ethene in polymer. $T_m(1)$ is the first and $T_m(2)$ the second melting peak in the DCS-curve.

[a] Kg PP/(mol$_{Zr}$ h).

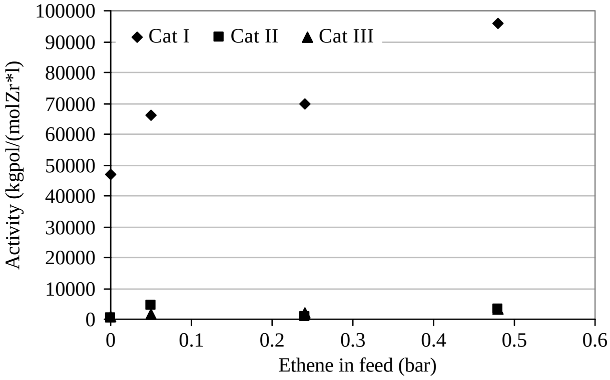
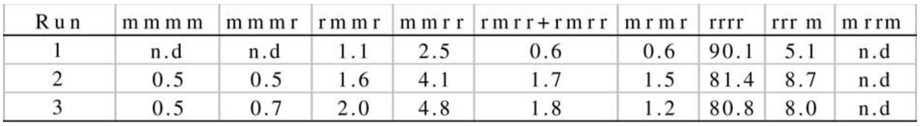


Fig. 1. The effect of the different catalyst systems **Cat I**, **Cat II** and **Cat III** on the polymerization activity.

$[B(C_6F_5)_4]^-$. The difference in activity between the two borates could result from the reaction of $[Ph_3C][B(C_6F_5)_4]$ with TIBA [11], even though we could diminish this reaction by alkylating the complex first with TIBA and feeding $[Ph_3C][B(C_6F_5)_4]$ after the alkylation. The conditions in polymerizations are complex involving many variables. $[Me_2HNPh][B(C_6F_5)_4]$ reacts with $[Ph_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]Zr(^iBu_2)$ to form the ion-pair $[[Ph_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]Zr(^iBu)]^+[B(C_6F_5)_4]^-$, CH_4 and Me_2NPh. The Lewis basic amine Me_2NPh might interact with the zirconium centre stabilizing the formed ion pair, while $[Ph_3C]^+$ reacts forming a less interacting Ph_3C^iBu [12]. The influence of the amine is dependent on the polymerization conditions and the used complex. The amine can possible displace propene from the vacant site leading to lower activity and M_w [13,14].

3.2. Microstructure and molecular weight of the homo- and copolymers

The stereoerror formation mechanisms of *Cs*-symmetric *ansa*-metallocenes have been extensively reviewed in literature [4,15]. There are three generally considered stereoerror formation mechanisms: site epimerization producing [*m*] stereodefects, enantiofaciale misinsertions producing [*mm*] stereodefects and chain epimerization giving either [*m*] or [*mm*] stereo defects, depending on the stereochemistry at the metal centre [2]. The stereoerror formation is assumed to be cocatalyst sensitive, though it is not very well understood and only few studies are reported [16,17]. According to the previous study, [5] the stereoselectivity of **Cat III** is rather insensitive to the polymerization temperature, the syndiotacticity remains nearly at the same level even at higher polymerization temperatures. Analysis of the polymers by ^{13}C NMR spectroscopy reveal that both **Cat II** and **Cat III** produce polymers with nearly equal syndiotacticities, %[*rrrr*] = 80.8–81.4%. Interestingly, the polymer produced with **Cat I** have markedly higher syndiotacticity, %[*rrrr*] > 90%, as can be seen from Table 1. **Cat I** produces no detectable [*mmmm*] and [*mmmr*] pentads, as shown in Fig. 2. Marks et al. [18] have suggested that more tightly bounded, stereochemically immobile anions, could depress epimerization



Run	mmmm	mmmr	rmmr	mmrr	rmrr+rmrr	mrmr	rrrr	rrr m	mrrm
1	n.d	n.d	1.1	2.5	0.6	0.6	90.1	5.1	n.d
2	0.5	0.5	1.6	4.1	1.7	1.5	81.4	8.7	n.d
3	0.5	0.7	2.0	4.8	1.8	1.2	80.8	8.0	n.d

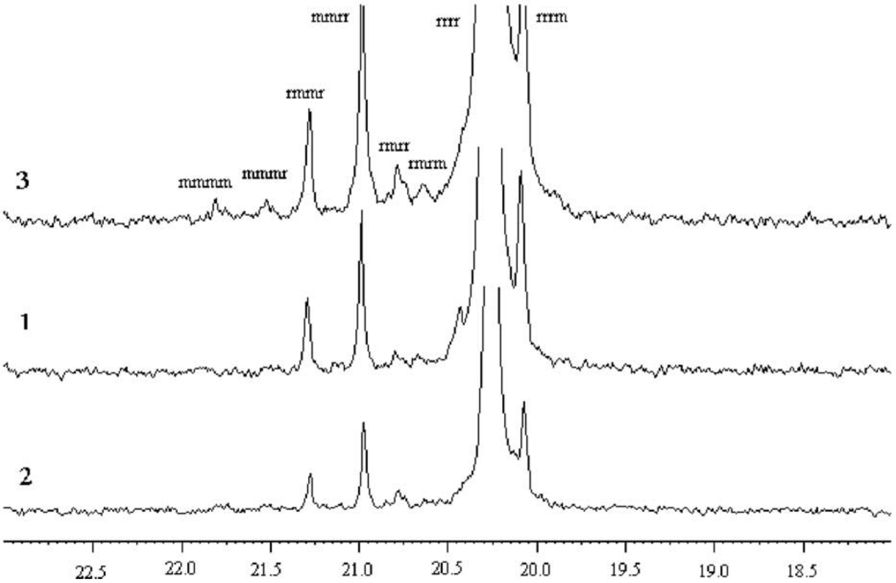


Fig. 2. Pentad distributions in percentage for the propene polymerizations with **Cat I**, **Cat II** and **Cat III**.

rates leading to a lower number of [*m*] stereodefects and to a more stereospecific polymerization. In this study all three catalytic systems produce both isolated [*m*] and [*mm*] stereodefects as a consequence of skipped insertions (site epimerization) as well as of monomer insertion with the wrong enantioface [19]. The average propene sequence syndiotacticities for the copolymers (runs 4–12) were decreasing with the increasing amount of ethene in copolymer. For **Cat I** the sequence syndiotacticities were 89% (run 4), 82% (run 7) and 79% (run 10), for **Cat II** 81% (run 5), 72% (run 8), and 75% (run 11) and for **Cat III** 79% (run 6), 73% (run 9) and 73% (run 12), respectively.The molecular weight of a polymer depends on the rate of propagation to the rate of chain transfer reactions. With the used catalyst systems, chain transfer to monomer is the main chain termination process [7]. When the amount of ethene is increased, β-hydrogen transfer to the smaller ethene monomer takes place easier than β-hydrogen transfer to the bulkier propene monomer, which can be seen as a decrease in molecular weight. Though the molecular weights remain still at a high level, as can be seen from Table 1. The molecular weights of the homo- and copolymers made with **Cat I** are slightly higher than those made with **Cat II** or **Cat III**. The molecular weight distributions are somewhat broader in the less active experiments (runs 2, 8 and 12). Even then the molecular weight distributions are monomodal.

3.3. Ethene incorporation

There are rather little data available about the solubility of ethene in liquid propene in normal laboratory conditions and unfortunately the solubility for ethene in liquid propene under the condition of interest was not available. According to Mizan et al. [20] the solubility of ethene in liquid propene at 25 °C is approximately 0.8 kmol/m^3. At 25 °C and an ethene partial pressure of 1 bar, the solubility is 0.5 kmol/m^3. In our experiments 0.05 bar ethene fed in 400 ml liquid propene at 0 °C corresponds to 0.9–2.6 mol% ethene in polymer, as shown in Table 1. The amount of ethene in polymer is increasing almost linearly with increasing amount of ethene in feed, proving that the ethene is dissolved in the liquid propene. There is no significant difference in the ethene incorporation rate between the different cocatalysts, as can be seen from Fig. 3. Ethene is randomly distributed in the polymer chain; no EEE triads are observed in the ^{13}C NMR spectra, as depicted in Table 2. Also the number of alternating EPE triads is low.

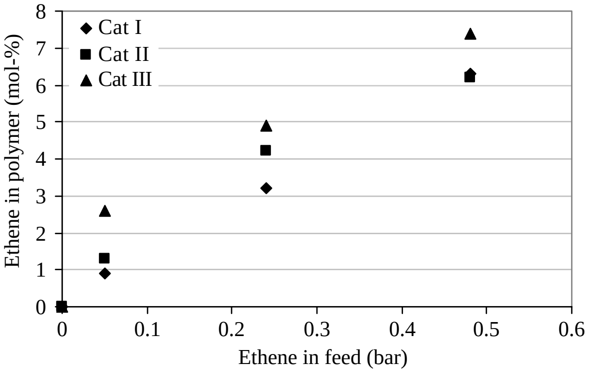


Fig. 3. Ethene incorporation with **Cat I**, **Cat II** and **Cat III**.

Table 2
Triad distributions in percentage for the *P*/*E* polymerizations with **Cat I**, **Cat II** and **Cat III**

Run	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
4	0	3.3	0.3	0	4.0	92.5
5	0	3.2	0.8	0	5.0	91.0
6	0	3.7	1.7	0.1	6.9	88.0
7	0	3.5	2.2	0.5	7.5	86.7
8	0	3.9	2.8	0.5	9.0	84.2
9	0	3.1	3.8	0.6	9.6	83.0
10	0	4.5	4.9	0.8	13.1	76.9
11	0	4.9	4.8	0.7	13.6	76.5
12	0	4.6	5.8	1.4	13.6	75.1

3.4. Thermal behavior

The crystallinity has a strong influence on the mechanical and physical properties of the copolymers. sPP presents a complex polymorphic behavior with four known crystalline forms [21]. The crystallization behavior of the propene–ethene copolymers depends on the comonomer content and distribution, stereoregularity, as well as M_w and MWD. De Rosa et al. have extensively studied the influence of the comonomeric ethene units on the polymorphic behavior of sPP [21–23]. The ethene units are partly included in the crystalline regions of the propene–ethene copolymers both in the case of sPP [22] and isotactic PP [24]. The ethene units induce the formation of crystallizable trans-planar sequences and therefore even relatively high amounts, up to 20 mol% of ethene can be copolymerized in sPP chain without the copolymer becoming amorphous. The comonomer distribution is mainly dependent on the catalyst system and the polymerization conditions. It has been demonstrated that regio- and stereoregularity of the propene insertion has an influence on the crystalline lattice [25].

Characteristic for sPP are the multiple melting peaks in DSC melting endotherms. The melting peak at lower temperatures corresponds to the melting of the primary and secondary crystals, formed at corresponding crystallization temperature. The melting peak at higher temperatures represents the melting of the recrystallized crystals, formed during a subsequent heating endotherm [26,27]. The peak intensities and the form of the melting endotherms are dependent on not only the crystallization temperature but also on the cooling rate. In our experiments almost all samples showed double melting peaks. In the homopolymer sample run 1 the first melting peak is only a shoulder and in the copolymer sample run 8, the second melting peak cannot be detected at all, the peak is very broad to the direction of higher temperatures.

The different cocatalysts have an influence on the melting and crystallization behavior of the copolymers. Especially the crystallization temperature is dependent on the catalyst system, as can be seen from Fig. 4. **Cat I** is able to produce a more stereo-regular polymer than **Cat II** or **Cat III**, thus leading to better-organized polymer with higher crystallization temperatures. Surprisingly the copolymers produced with **Cat III** have almost equal crystallization temperatures as the copolymers made with **Cat I**, although the homo- and copolymers made with **Cat III** have lower syndiotacticities. The melting temperatures are less influenced by the cocatalyst; with all the catalyst systems the melting and glass transition temperatures are decreasing nearly linearly with increasing ethene content in the copolymer.

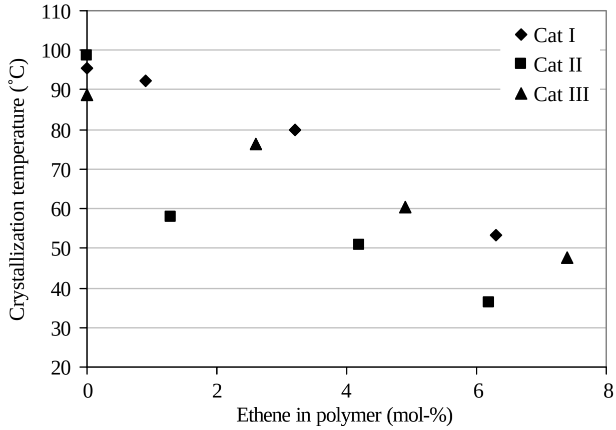


Fig. 4. Crystallization temperatures of the homo- and copolymers made with different catalyst systems.

4. Conclusions

Propene homopolymerizations and propene–ethene copolymerizations with small amount of ethene were performed using the novel *Cs*-symmetric zirconocene *p*-CH_3OPh_2C(2,7-di-^{tert}BuFlu)(Cp)]$ZrCl_2$ and three different cocatalysts in propene bulk phase. With the studied catalyst systems it is possible to produce propene homo- and copolymers with good activity and high molecular weight. The activity and stereoselectivity of the catalyst are dependent on the formed ion pair. **Cat I** showed the highest activity at the used polymerization conditions. Also the syndiotacticitiy of the homopolymer was notably higher; the pentad tacticity of the homopolymers was over 90% in the case of **Cat I**, while it was 81.4 and 80.8 with **Cat II** and **Cat III**. Possibly the amine group can interact with the active site stabilizing the ion pair and diminishing the epimerization reactions. The different catalyst systems have only minor effect on the ethene incorporation rate; the amount of ethene in the copolymer was increasing linearly with the amount of ethene in feed. Small amount of ethene in the copolymer allows the control of melting and crystallization process. The crystallization temperatures were found to be dependent on the used catalyst system.

Acknowledgements

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