Macromol. Symp. ***193****, 45–56 (2003)*

^{13}C NMR Studies of Olefin Copolymer Microstructure: A Tool for Understanding Active Center Behavior in *ansa*-Zirconocene-Based Catalysis

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SUMMARY: In the present paper the effects of the solvent, a Lewis base and of non-polymerizable olefin on copolymerization of propene with higher α-olefins performed with isospecific *ansa*-zirconocene catalysts are investigated. A wide range of solvents with increasing polarity, donor character and steric hindrance has been tested, and their effects on copolymer yield, composition and microstructure thoroughly analyzed. Our results demonstrate that the solvent can have a significant influence on the copolymer composition, even though the solvent polarity is not the relevant factor. Polymerizations carried out in coordinating solvents, e.g. aromatic solvents, lead to the formation of products with considerably decreased higher α-olefin content. The reduced incorporation of the higher α-olefin is explained in terms of competition between the nucleophilic medium and the olefin monomer for coordination to the active polymerisation site. The dependence of polymer microstructure on the solvent nucleophilicity is further elucidated by copolymerization studies performed in the presence of diisopropyldimethoxysilane as a Lewis base. The addition of the non-polymerizable olefin, 2-methyl-1-pentene, which does not significantly affect comonomer composition, seems to slightly modify comonomer distribution. The sum of the results obtained give us valuable information regarding the mechanism of polymerisation at the active centers.

Introduction

In contrast to conventional multisite Ziegler-Natta catalysts, single site metallocene-based catalysts produce very uniform homo- and copolymers. As a function of metallocene structure it is possible to control polymer microstructure, molecular mass and molecular mass distribution, and chain-end groups.[1] A further distinctive feature of this type of catalyst, no inexperienced with heterogeneous Ziegler-Natta catalysts, is the strong influence of the reaction conditions and of the other components of the catalytic system on the polymer properties.[2] An example of this

CCC 1022-1360/00/$ 17,50+.50/0

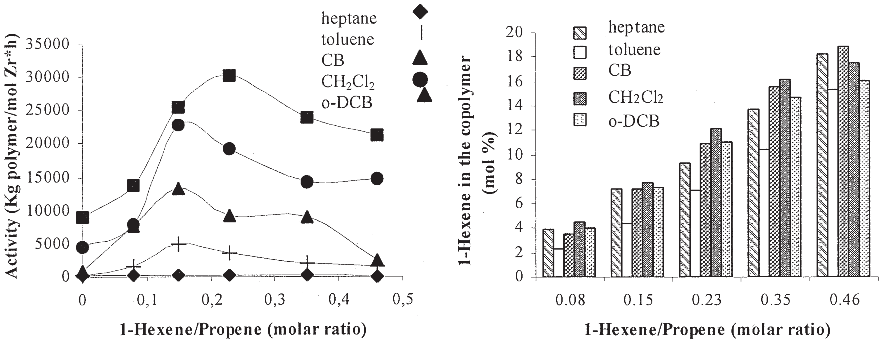
is the dependence of stereospecificity on the monomer concentration. In fact, decreasing monomer concentration significantly decreases the syndiospecificity of the Cs-symmetric *i*Pr(Flu)(Cp)$ZrCl_2$/methylaluminoxane (MAO) catalyst.[2a] The propene concentration also greatly affects the isospecificity of a number of C_2-symmetric ansa-zirconocenes.[2b,c,d,] A case is also reported in which the catalyst stereoselectivity is dependent on the cocatalyst. The same metallocene precursor Me_2Si-(Flu)(N-*t*-Bu)$ZrCl_2$ yields an atactic polymer when MAO is used as a cocatalyst, and a partially syndiotactic polymer when using a boron anion is used.[2e] Another relevant example of the dependence of metallocenes on the polymerization conditions is given by the solvent. Experimental data have shown that the solvent has a strong effect on catalyst activity[3] and in a few cases on catalyst stereospecificity.[4] Indeed the solvent polarity induces a decrease in the syndiospecificity of *i*Pr(Flu)(Cp)$ZrCl_2$/MAO catalyst and a deviation from the hemiisotactic structure is also observed in the presence of *i*Pr(3-MeCpFlu)$ZrCl_2$/MAO.

Over the last few years our investigation has been aimed at verifying whether the polymerization conditions and the other components of the catalytic systems also affect copolymerization, that is, copolymer composition and comonomer distribution and, accordingly, exploring the possibility of modulating copolymer microstructure and properties by acting on these factors.[5] In the present paper the effects of the solvent, of a Lewis base and of a non-polymerizable olefin on copolymerization have been focused upon. Most experiments were conducted with propene and 1-hexene (1-H) comonomers with the now “classical” isospecific *rac*-Et(Ind)$_2$$ZrCl_2$/MAO catalyst. A few selected experiments with a different catalyst and a different comonomer were also conducted, to check the general validity of the results obtained.

Results and Discussion

Effect of solvent. A series of propene/1-H copolymers with different compositions was been prepared by using a wide range of solvents characterized by different polarity, nucleophilicity and structure, in the presence of the isospecific *rac*-Et(Ind)$_2$$ZrCl_2$/MAO catalyst. Fig.1a shows the effect of solvent polarity on copolymerization activity for different 1-H/propene molar ratio in solution. According to increasing polarity the solvents are: heptane ($\varepsilon = 1.92$), toluene($\varepsilon = 2.38$), chlorobenzene (CB) ($\varepsilon = 5.68$), methylene chloride($\varepsilon = 8.93$) and o-dichlorobenzene (ODCB) ($\varepsilon =$

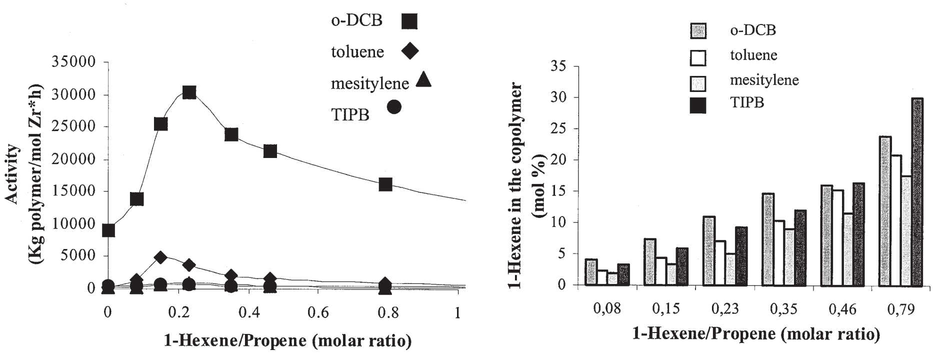
10.12). It is apparent that the homo- and copolymerization activity sharply increases along with the medium polarity.



a) b)

Figure 1. Effect of solvent polarity on activity (a) and on 1-H content (b). Catalyst: *rac*-Et(Ind)$_2$ZrCl$_2$/MAO. Polymerization conditions: solvent = 100 ml; [Zr] = $20 \cdot 10^{-6}$ mol/L; MAO/Zr =3000 (mole ratio); propene pressure = 1.12 bar; T = 0 °C; time = 30 min.

Fig.1b shows the effect of solvent polarity on 1-H content. No correlation is observed between 1-H content and solvent polarity since very close 1-H contents are obtained with the polar solvents and with heptane for almost all the compositions. The only exception is represented by toluene, in which the comonomer content is remarkably lower than that in the other solvents for all the compositions, especially at the lowest comonomer concentrations. These data suggest that activity and selectivity versus the more hindered comonomer are governed by different factors: the lower 1-H content in toluene seems to be related to toluene's donor character rather than to polarity. Such an hypothesis was verified by comparing the variations of activity and copolymer compositions in a series of solvents characterized by increasing donor character. In the order of nucleophilicity they are: o-DCB, toluene, mesitylene (MES) and 1,3,5-triisopropylbenzene (TIPB). Fig.1a shows that low and very similar activities are obtained in the highly coordinating MES and TIPB. Fig.2b shows the effect of increasing donor character on 1-H content in the copolymers. As expected, the 1-H content decreases by passing from o-DCB to toluene and to MES, for almost all the compositions. 1-H insertion is particularly disfavoured in MES, where the decrease of 1-H content is 30-50% with respect to o-DCB. A correlation between the 1-H content and donor character for these three solvents is made apparent: the higher the donor character of the solvent, the lower the comonomer content. However, such a tendency is reversed in the most nucleophilic solvent TIPB, where the 1-H content increases again and even exceeds that in o-DCB for the highest 1-H concentrations.



a b

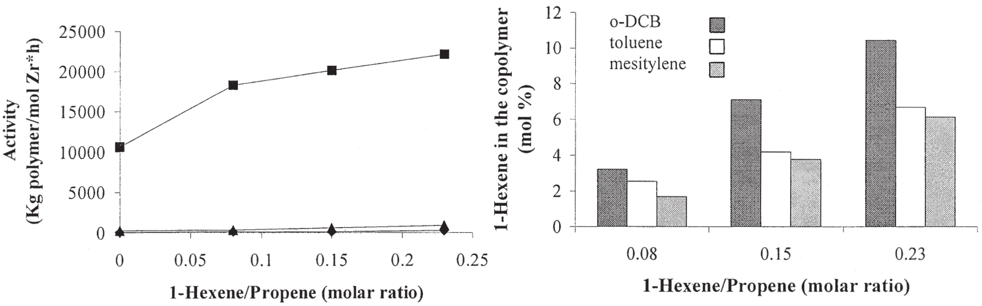
Figure 2. Effect of solvent donor character on activity (a) and on 1-H content (b). Catalyst: *rac*-Et(Ind)$_2$ZrCl$_2$/MAO. Polymerization conditions: solvent = 100 ml; [Zr] = $20\cdot10^{-6}$ mol/L; MAO/Zr =3000 (mole ratio); propene pressure = 1.12 bar; T = 0 °C; time = 30 min.

A statistical analysis of the copolymerizations with all four solvents was performed, on the basis of the quantitative tetrad comonomer distributions determined from ^{13}C NMR spectra, aimed at investigating the influence of the solvent on the kinetics of copolymerization. The first-order Markovian model was applied using the procedure described in literature.[6] The reactivity ratios r_P and r_H (where $r_P = k_{PP}/k_{PH}$ and $r_H = k_{HH}/k_{HP}$) for all the four solvents are given in Tab.1. The reactivity ratio products indicate an almost random distribution ($0.75<r_Pr_H<1.57$), however a clear difference is apparent among the solvents. The value of r_P increases by increasing the nucleophilicity of the solvent, by passing from o-DCB to toluene to MES. This is in line with the analogous decrease of 1-H incorporation in these solvents at the same comonomer composition. When TIPB is used a r_P value of 2.3 is obtained, close to the value observed in o-DCB, even if the nucleophilicity of this solvent is higher than that of MES. The gradual increase in reactivity ratio shows that the nucleophilic solvent, besides significantly affecting the copolymer composition, also moderately affects the comonomer distribution.

Table 1. Reactivity ratios obtained by statistical elaboration of tetrad values from experimental ^{13}C NMR data.

Solvent	r_p	r_H	r_pr_H
o-DCB	2.1	0.34	0.71
Toluene	2.9	0.43	1.26
MES	3.9	0.36	1.41
TIPB	2.3	0.66	1.57

In order to check if the observed solvent effect is a general effect, a few experiments have also been conducted with a different catalyst and with a bulkier comonomer by using three selected solvents: o-DCB, toluene and MES, which greatly differ to each other as to their nucleophilicity. The experiments have been performed at the three comonomer compositions, where the solvent effect were more evident.



a)

b)

Figure 3. Effect of solvent on activity (a) and on 1-H content (b). Catalyst: *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO. Polymerization conditions: solvent = 100 ml; [Zr] = $20 \cdot 10^{-6}$ mol/L; MAO/Zr =3000 (mole ratio); propene pressure = 1.06 bar; T = 0 °C; time = 30 min.

Figures 3a and 3b, show the effect of the solvent on propene/1-H copolymerization activity and 1-H copolymer content with *rac*-$Me_2Si(Ind)_2ZrCl_2$ catalyst respectively. Here the increases in the activities at low comonomer concentrations are more moderate than with *rac*-$Et(Ind)_2ZrCl_2$, especially in toluene. The trends in comonomer contents, when passing from o-DCB to toluene and to MES are, however, almost identical.

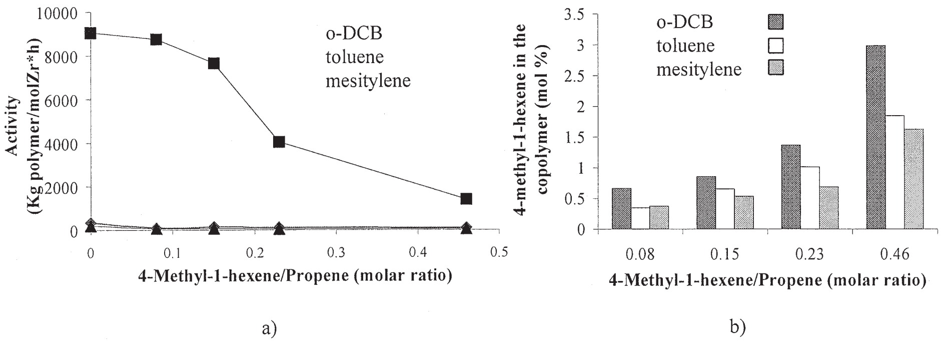


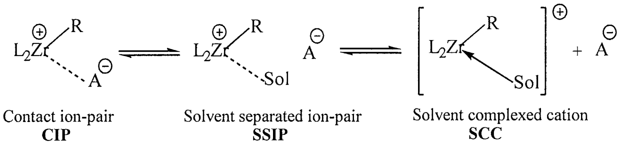
Figure 4. Effect of solvent on copolymerization activity (a) and comonomer content (b). Catalyst: *rac*-$Et(Ind)_2ZrCl_2$/MAO. Polymerization conditions: solvent = 100 ml; [Zr] = $40 \cdot 10^{-6}$ mol/L; MAO/Zr = 1500 (mole ratio); propene pressure = 1.12 bar; T = 0 °C; time = 30 min.

Figures 4a and 4b show the effect of the solvent on copolymerization activity and comonomer content, respectively, when 4-methyl-1-hexene (4M1H) is used instead of 1-H with *rac*-$Et(Ind)_2ZrCl_2$/MAO catalyst. The first observation is that here the maximum activity, the so called "second monomer effect", does not appear and the activities progressively decrease with increasing comonomer concentrations. As to the comonomer content, in general, at the same feed composition much lower amounts of 4M1H than of 1-H are incorporated: one sixth, or one seventh with respect to 1-H. However, the trends of comonomer contents, when passing from one solvent to another, are the same with 4M1H as with 1-H .

All these observations show that the solvent effect on copolymer compositions is quite a general effect, and independent of the catalyst and the comonomer.

We will now attempt to rationalize all the above data in the light of the now settled picture of the equilibria established among the ionic species present in solution, in the absence of the olefin (Scheme 1).

Scheme 1



The contact ion pair (CIP), produced due to activation of the precatalyst by the cocatalyst, can interact with a molecule of the solvent, which repels away the anion, to form the solvent separated ion pair (SSIP), in which the solvent is located between the cation and the anion. Once produced, the SSIP can undergo further solvation, which leads to the formation of a solvent-complexed cation (SCC) where the anion, which is far away, can no longer interact with the cation. Studies conducted by Eisch on $Cp_2TiMeCl/MeAlCl_2$ in the presence of ethylene[7] have demonstrated that the relative reactivity of these species in polymerization can be ordered as: SSIP»CIP>SCC, that is, polymerization activity greatly increases in polar non-coordinating solvents, when SSIP prevails over CIP, and decreases with the donor character of the solvent, when SCC is formed.

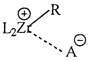
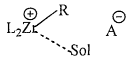
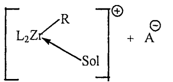
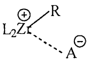
Under the hypothesis that with the *rac*-$Et(Ind)_2ZrCl_2$/MAO catalyst similar equilibria arise among the three kinds of ionic pairs, and taking into account that different solvents influence the relative populations of these species in different ways, we can make a few comments regarding the solvation effect on copolymerization behavior (Scheme 2).

i) In non polar solvents (e.g. heptane) the dominant species is CIP (Scheme 2a), while a solvent with a higher dielectric constant facilitates charge separation and thus will favour the formation of SSIP (Scheme 2b). Extremely different activities, but the same copolymer compositions, are observed in the two cases. This means that, although the active centers are more accessible to the incoming monomer in SSIP than in CIP, the relative insertion and propagation rates of the two comonomers are the same in both cases.

ii) Coordinating solvents (e.g. aromatic solvents) will favour the formation of SCC (Scheme 2c). Both activity and 1-H content are low and the higher the donor character of the solvent the lower the 1-H content. This means that the complexed solvent is a barrier to the coordination of both incoming olefins, but the coordination of the bulkier comonomer on SCC is more disfavoured than that of propene. Thus the bulkier the comonomer, the less favourable is its coordination.

iii) The above trend is reversed when a bulky coordinating solvent such as TIPB is used (Scheme 2d), where the comonomer content is the same as in a neutral, non-coordinating solvent. Our interpretation is that, since the steric demands of TIPB are excessive for access to the Zr center, the complex cannot be formed and the equilibrium is again shifted towards CIP. So the most coordinating TIPB gives the same activity and composition as heptane. This last consideration is supported by the data by Eish[7], which show that the combination of $Cp_2TiMeCl/MeAlCl_2$ and mesitylene leads to the formation of a complex that can be isolated, while an analogous compound is not formed with hexamethylbenzene due to steric factors.

Scheme 2

	Solvent	Dominant ionic species	Activity	Effect on comonomer content
(a)	non polar, non coordinating (e.g. heptane)	 Contact ion-pair **CIP**	low	no effect
(b)	polar (e.g. o-DCB, CH_2Cl_2)	 Solvent separated ion-pair **SSIP**	high	no effect
(c)	coordinating (e.g. toluene, mesitylene)	 Solvent complexed cation **SCC**	low	decrease
(d)	bulky coordinating (e.g. TIPB)	 Contact ion-pair **CIP**	low	no effect

Effect of a Lewis base. A corroboration for the above hypothesis of competitive complexation between coordinating solvents and a Zr cation is offered by further experiments that we have conducted; we added a Lewis base and the same *rac*- Et(Ind)$_2$ZrCl$_2$/MAO catalyst in toluene to the copolymerizations. The Lewis base used was diisopropyldimethoxysilane. Two series of experiments were performed by utilizing two different silane/Zr ratios (5 and 7.5) and compared to an analogous series performed without a donor. The donor addition produced a remarkable deactivation, even at very low silane/Zr ratios (Fig.5a). At silane/Zr ratio as high as 10, negligible amounts of polymer are produced. In both series a decrease of 1-hexene content is observed for all three comonomer compositions (Fig.5b). Only slight differences in copolymer compositions are appreciable between the two series at different silane/Zr ratios. However, the trend of the 1-H decrease shows that the donor produces an effect similar to that of a coordinating solvent, that is, it gives rise to competition between the nucleophilic agent and the bulkier comonomer.

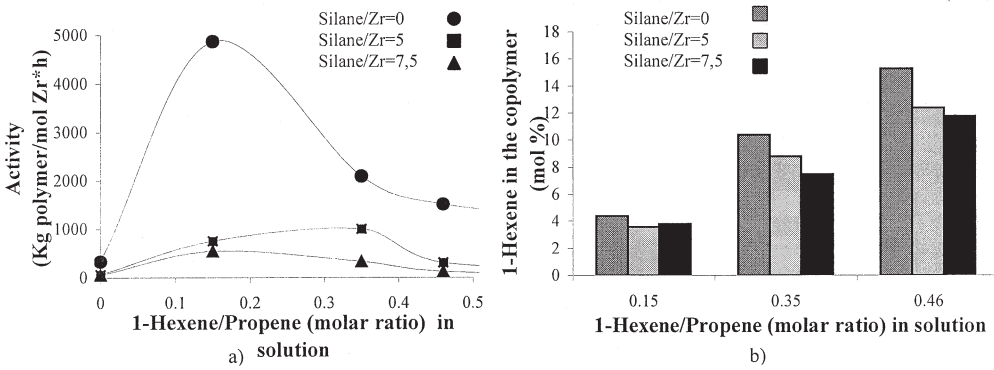
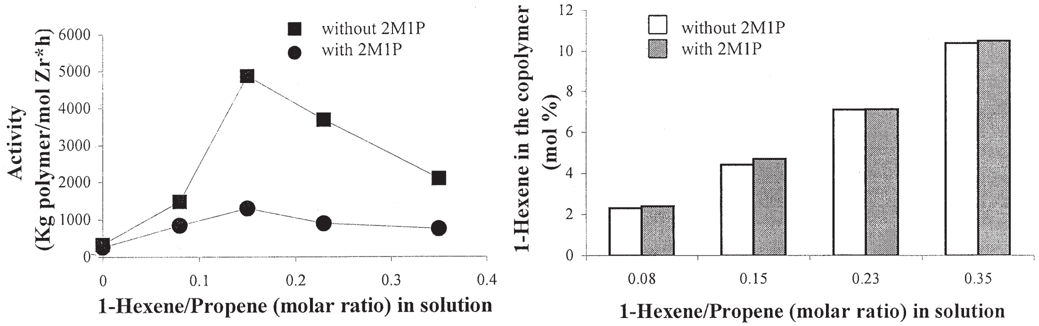


Figure 5. Effect of a Lewis base on copolymerization activity (a) and comonomer content (b); Catalyst: *rac*-Et(Ind)$_2$ZrCl$_2$/MAO. Polymerization conditions: solvent toluene = 100 ml; [Zr] = $20 \cdot 10^{-6}$ mol/L; MAO/Zr =3000 (mole ratio); propene pressure = 1.12 bar; T = 0 °C; time = 30 min.

Effect of a non-polymerizable olefin. We have also studied the effect of non-polymerizable olefins on copolymerization. In the present investigation we used 2-methyl-1-pentene (2M1P) as an inactive or slightly active monomer. The choice of this olefin is due to the fact that 2M1P is actually a model olefin of the most common unsaturated terminal formed with metallocene catalysts. Indeed 2M1P is always present in more or less amounts in these systems[8] and thus it could be interesting to evaluate how it affects activity and copolymer microstructure.

We conducted a series of copolymerizations by using a concentration of 2M1P equal to that of 1-H comonomer.

Figure 6a shows that the catalyst activity was greatly depressed for all the compositions. This shows that 2M1P acts as a polymerization inhibitor, but without completely poisoning the catalyst, even at the highest concentration.



a)

b)

Figure 6. Effect of a non-polymerizable olefin on copolymerization activity (a) and comonomer content (b). Catalyst: *rac*-Et(Ind)$_2$ZrCl$_2$/MAO. Polymerization conditions: solvent toluene = 100 ml; [Zr] = $20\cdot10^{-6}$ mol/L; MAO/Zr =3000 (mole ratio), 2M1P/1H = 1; propene pressure = 1.12 bar; T = 0 °C; time = 30 min.

We did not observe any decrease in 1-H content at increasing 2M1P concentrations (Fig. 6b); a slight increase in the bulkier comonomer content was even observed at two compositions. Table 2 shows the reactivity ratios obtained by the statistical treatment of the experimental tetrads deduced from ^{13}C NMR. We can see that, in spite of the almost unvaried composition, the reactivity ratio product surprisingly increases in the presence of 2M1P, due to the increased of r_H. It seems that 2M1P, which strongly affects the activity, can also exert an influence on the comonomer distribution. All these data suggest that the inactive olefins do not simply compete with the comonomers in coordinating to the active centers, like the other coordinating agents, but affect the equilibria present in the polymerization system in a more complicated way that deserves further investigation.

Table 2. Reactivity ratios obtained by statistical elaboration of tetrads values from experimental ^{13}C NMR data.

	r_P	r_H	r_Pr_H
without 2M1P	2.93	0.43	1.26
2M1P/1H = 1	2.99	0.55	1.64

Conclusion

The use of solvents with increasing donor character and steric hindrance has allowed us to determine the origin of the variations in copolymer composition as a function of the solvent.

When a nucleophilic solvent is used, provided that its steric demand is capable of having access to the cationic center, the equilibrium among the ionic species present in solution is shifted towards the formation of a solvent-complexed cation (SCC). Such a solvent-complexed cation has a lower propagation rate, since the incoming monomer must displace the coordinated solvent to form the olefin-complexed cation. The latter is a prerequisite for the olefin insertion. In the competition with the complexed solvent, the bulkier comonomer is disfavoured with respect to propene, and the more stable the complex the more disfavoured the bulkier comonomer insertion.

The addition of increasing amounts of a Lewis base produces the same effect as the increasing coordinating capability of the solvent and thus supports the proposed mechanism.

The addition of a non-polymerizable olefin produces an effect which is different from that of the other coordinating agents; in fact it depresses the activity without sensibly affecting the copolymer composition. An unexpected influence on comonomer distribution is also observed.

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