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Polimerização de propeno com catalisadores metalocênicos via suportação *in-situ* utilizando SMAO como suporte

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SIGLAS E ABREVIATURAS:

MAO - metilaluminoxano
SMAO - MAO suportado em sílica
TMA - trimetilalumínio
TEA - trietilalumínio
TIBA - triisobutilalumínio
DEAC - cloreto de dietilalumínio
$Et(Ind)_2ZrCl_2$ - dicloreto de rac-etilbis(indenil)zircônio
$Et(Ind)_2ZrMe_2$ - dimetil-rac-etilbis(indenil)zircônio
$Me_2Si(Ind)_2ZrCl_2$ - dicloreto de rac-dimetilsililenobis(indenil)zircônio
$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ - dicloreto de rac-dimetilsililenobis(2-metil-indenil)zircônio
Cp_2ZrCl_2 - dicloreto de bis(ciclopentadienil)zircônio
Cp_2HfCl_2 - dicloreto de bis(ciclopentadienil)háfnio
$[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$ - dicloreto de [(tetrametilciclopentadienil)(N-t-butilamido) dimetilsilil]titânio
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ - dicloreto de pentametileno bis(ciclopentadienilindenil)zircônio

RESUMO:

Os catalisadores metalocênicos $Me_2Si(Ind)_2ZrCl_2$ e $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ foram suportados in-situ sobre SMAO e empregados na polimerização de propeno na presença de alquilalumínios tais como TEA, IPRA ou TIBA. Os resultados obtidos demonstraram que o tipo e a concentração de alquilalumínio presente no meio reacional influenciaram tanto a atividade catalítica quanto as propriedades dos polímeros gerados. Os polímeros obtidos com o catalisador suportado in-situ apresentaram propriedades distintas das obtidas no polímero gerado através da polimerização homogênea, além de morfologia controlada, confirmando que de fato a polimerização ocorreu sobre a superfície do SMAO. Através da deconvolução das curvas de GPC foi constatado o aumento do número de tipos de sítios ativos no sistema catalítico suportado in-situ, resultado que também confirmou a heterogeneização do catalisador sobre o suporte. Com o auxílio de cálculos teóricos e da deconvolução das curvas de GPC foi possível propor estruturas para os sítios ativos dos sistemas homogêneo metaloceno/MAO e heterogêneo (suportado in-situ) metaloceno/SMAO/alquilalumínio. Quando eteno foi utilizado como monômero, o comportamento do sistema catalítico metaloceno/SMAO/alquilalumínio suportado in-situ foi distinto do obtido com propeno. O catalisador $Me_2Si(Ind)_2ZrCl_2$ suportado ex-situ sobre SMAO através de técnicas convencionais de suportação foi avaliado por EXAFS e foi constatado que a vizinhança eletrônica do zircônio é influenciada pela razão Zr/SMAO. Os resultados obtidos por EXAFS foram correlacionados com a variação na atividade catalítica na polimerização de eteno em função da alteração na razão Zr/SMAO.

ABSTRACT:

The metallocene catalysts $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ were in-situ immobilized onto SMAO and employed to polymerize propylene in the presence of common alkylaluminums such as TEA, IPRA, or TIBA. The polymerization results showed that the alkylaluminum type and concentration influenced the catalyst activity and the polymer properties as well. The polymers prepared with the in-situ supported catalytic system showed different properties and morphology comparing to the polymers obtained under homogeneous polymerization conditions. These results confirm that the polymerization indeed took place onto SMAO surface. Through the GPC curves deconvolution it was showed that the in-situ immobilized catalytic system had more types of active sites than the homogeneous catalytic system. This result also confirms the heterogeneization of the catalyst onto the support. Using theoretical calculations and GPC curves deconvolution it was possible to propose the structure of the active sites for both catalytic systems, the homogeneous metallocene/MAO system and the heterogeneous (in-situ supported) metallocene/SMAO/alkylaluminum system. The behavior of the catalytic system metallocene/SMAO/alkylaluminum in-situ immobilized was different when ethylene was used as monomer. The EXAFS characterization of the catalyst $Me_2Si(Ind)_2ZrCl_2$ ex-situ supported onto SMAO, i.e., immobilized onto SMAO using conventional immobilization techniques, showed that zirconium electronic neighborhood is dependent on the Zr/SMAO ratio. The EXAFS structure features were correlated to the catalyst activity in ethylene polymerization.

ÍNDICE:

1. INTRODUÇÃO:

Um dos maiores desafios da química de organometálicos moderna é sua aplicação em novas tecnologias e novos materiais. Com este propósito, novos tipos de complexos têm sido sintetizados, modificados e aplicados em novos processos catalíticos e novas aplicações. Uma área de grande importância é a dos complexos metalocênicos com metais do grupo IV, a qual nas duas últimas décadas propiciou avanços significativos no campo da polimerização de poliolefinas, iniciada nos anos 50 com os catalisadores Ziegler-Natta e Phillips[1].

Catalisadores metalocênicos consistem, basicamente, de um complexo entre um dicloreto metálico e dois sistemas de anéis aromáticos de cinco membros[1], os quais podem estar ligados por uma ponte (complexo *ansa* metalocênico) ou não. Os dois ligantes aromáticos podem ser do tipo ciclopentadienila, indenila ou fluorenila. A introdução de substituintes em determinadas posições dos ligantes aromáticos e/ou o tipo de ponte modifica não somente as condições estéricas e eletrônicas na molécula, mas também a simetria no complexo metalocênico. Outro parâmetro importante que pode ser variado é o metal, que pode ser Ti, Hf ou Zr, por exemplo. Tanto os substituintes nos anéis aromáticos quanto o metal têm influência significativa sobre a atividade catalítica e sobre as propriedades do polímero[2-5].

Catalisadores metalocênicos podem ser ativados com organoaluminoxanos, em especial por MAO, o qual permite obter o máximo de atividade[6-12]. A reação de ativação, isto é, o papel do cocatalisador, consiste, em primeiro lugar, da metilação do átomo metálico central e, em segundo lugar, da abstração de um carbânion para produzir um cátion monometilmetalocênico, que é de fato a espécie catalítica[13-18]. Outra função do MAO é a reativação de complexos catalíticos inativos formados por reações de transferência de hidrogênio[19]. Ao contrário do MAO, boratos, especialmente derivados tri- ou tetraarilperfluorados, podem ser utilizados em proporção estequiométrica com o átomo metálico, alcançando atividades comparáveis às obtidas com o emprego de MAO. Entretanto, a desvantagem desta classe de cocatalisador é seu alto preço e a incorporação de flúor ao polímero, o que pode causar problemas ambientais se a poliolefina for decomposta termicamente. Além disto, boratos são muito sensíveis a contaminações e decompõem facilmente, necessitando do uso de pequenas quantidades de alquilalumínio[1].

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[1] Catalisadores do tipo $CpTiCl_3$ também são considerados metalocênicos, embora tenham apenas um anel de 5 membros, sendo que alguns autores distinguem estes sistemas classificando-os como "semi-metalocênicos".

Além do catalisador e do cocatalisador, outros parâmetros também desempenham papel significativo durante a reação de polimerização. A polimerização pode ser conduzida em solução ou em condições heterogêneas como processo suspensão, fase gás ou massa (*bulk*). Como a separação do par iônico catalisador (cátion) ↔ cocatalisador (ânion) é determinante na atividade do catalisador, o solvente desempenha papel importante na reação, pois interage com ambos. Além disto, a solubilidade do monômero e, conseqüentemente, sua concentração são dependentes do solvente usado. Por fim, também devem ser mencionados o efeito da temperatura e pressão de reação e a presença de hidrogênio, parâmetros que afetam significativamente a massa molar, a distribuição de massa molar e a estereosseletividade do catalisador[1].

O desenvolvimento de catalisadores metalocênicos representou um novo passo no campo da polimerização de olefinas, sendo que os polímeros produzidos com tais catalisadores apresentam arquitetura diferenciada quando comparados com aqueles obtidos com catalisadores Ziegler-Natta convencionais. As vantagens do uso dos catalisadores metalocênicos são amplamente conhecidas e descritas na literatura[1-5], podendo ser destacadas:

- alta atividade em solução, podendo ser 100 vezes mais ativo que catalisadores Ziegler-Natta ou Phillips; o complexo *ansa* bis(fluorenila) ($(C_{13}H_8\text{-}C_2H_4\text{-}C_{13}H_8)ZrCl_2$), por exemplo, produz 300 t PE/g Zr.h a 70°C após ativação com um cocatalisador[20];
- potencial para polimerizar olefinas proquirais, tais como propeno, gerando polímeros estereoespecíficos (polipropileno isotático, sindiotático e hemitático);
- habilidade de atuar como catalisador de sítio único e, assim, produzir resinas com distribuição de massa molar estreita;
- capacidade de incorporação uniforme de comonômero, produzindo poliolefinas com distribuição homogênea de ramificações longas e curtas ao longo da cadeia polimérica;
- produção de polímeros e copolímeros com baixíssima quantidade de frações de baixa massa molar (ceras); a quase ausência destas frações fornece excelentes propriedades organolépticas ao produto final[21];
- após heterogeneização do catalisador, sítios ativos diferentes daqueles presentes em solução podem ser produzidos, causando grande efeito sobre a atividade catalítica e sobre as propriedades da poliolefina gerada em termos de massa molar, ramificações e estereoespecificidade.

Embora os catalisadores metalocênicos apresentem maior atividade em condições de polimerização homogênea, a dificuldade no controle da morfologia do polímero, a grande quantidade de MAO necessária à ativação do sistema (razões molares Al/metal = 1.000 a 20.000 podem ser necessárias) e a necessidade de adaptá-los a maioria dos processos existentes atualmente torna necessária a sua heterogeneização[22-23]. A heterogeneização de catalisadores metalocênicos tem sido extensivamente pesquisada e descrita na literatura técnica[24-35] e em patentes[36-40] e proposta como uma alternativa para sobrepor estes problemas.

Para a substituição dos catalisadores Ziegler-Natta utilizados nas plantas atualmente em operação, os catalisadores metalocênicos devem ser imobilizados sobre suportes insolúveis como, por exemplo, sílica, alumina ou cloreto de magnésio, entre outros. O tipo de suporte e a técnica usada para imobilização do catalisador metalocênico e do MAO têm influência crucial sobre o desempenho do catalisador. A escolha apropriada das condições de imobilização pode aumentar a estéreo- e a regiosseletividade do catalisador e as condições de transferência podem ser minimizadas com conseqüente produção de polímeros com estereorregularidade melhorada e maior massa molar. A heterogeneização do catalisador pode também afetar o controle estereoquímico do catalisador. Dependendo da técnica de imobilização e do tipo de cocatalisador, catalisadores que são sindioespecíficos em condições homogêneas de polimerização podem produzir polipropileno essencialmente isotático quando suportados sobre sílica [23].

Existem basicamente três rotas principais para a heterogeneização de catalisadores metalocênicos[41,42]:

(1) imobilização do MAO sobre o suporte com subseqüente adição do catalisador metalocênico em um segundo passo - este procedimento foi um dos primeiros métodos utilizados para a heterogeneização de catalisadores de sítio único e é o mais empregado. Durante a polimerização, o catalisador é utilizado em combinação com MAO externo ou outro alquilalumínio;

(2) imobilização do catalisador metalocênico, seguida da adição do MAO - em função da proximidade do catalisador há forte interação do centro catiônico com o suporte e, deste modo, o polímero formado apresenta características diferenciadas daquelas obtidas em condições homogêneas, normalmente apresentando maior massa molar. Cabe salientar que no

caso da utilização do procedimento (1), onde o MAO é imobilizado inicialmente, o catalisador apresenta comportamento mais semelhante ao verificado na polimerização homogênea;
(3) preparação de um aduto entre o MAO e o catalisador e posterior imobilização do complexo formado - usualmente, MAO e o catalisador são misturados em tolueno e depois de determinado tempo de pré-contato são adicionados ao suporte. Este procedimento permite maximizar o número de sítios ativos através da ativação do componente metálico na solução e não imobilizado sobre o suporte, bem como favorece a utilização de menores razões Al/Zr. Neste caso, o tempo de pré-contato apresenta papel fundamental sobre a reação de polimerização e sobre as propriedades finais do polímero.

Uma alternativa para a heterogeneização de catalisadores metalocênicos é a modificação do suporte, antes ou após a adição do MAO, através da adição de um espaçador. Após a ligação covalente do espaçador com o suporte, o catalisador metalocênico é suportado[43-45].

A redução geralmente drástica da atividade catalítica é a principal desvantagem apresentada pelos sistemas heterogêneos em relação aos homogêneos. Entre as possíveis causas para esta redução na atividade catalítica com a heterogeneização do catalisador, são citadas a geração de aproximadamente apenas 1 % de espécies ativas para a polimerização após a imobilização do catalisador sobre o suporte e o impedimento estérico da superfície do suporte, normalmente sílica, a qual desempenha o papel de um ligante volumoso[42]. Além disto, a lixiviação do catalisador metalocênico da superfície do suporte pelo MAO tem sido apontada como uma desvantagem que deve ser sobreposta, para que o catalisador de fato atue de forma heterogênea. Algumas alternativas têm sido propostas para sobrepor tais problemas, tal como o uso de espaçadores de superfície, os quais mantêm os sítios ativos mais afastados da superfície[43], o uso de espaçadores horizontais, os quais reduzem as reações de desativação bimolecular mantendo os sítios ativos mais afastados entre si[44, 45], e a síntese direta do catalisador metalocênico sobre sílica híbrida inorgânica-orgânica[46].

Todos os procedimentos descritos anteriormente apresentam vantagens e desvantagens e podem levar a catalisadores capazes de produzir polímeros com diferentes propriedades. Entretanto, todas as rotas propostas consomem tempo e envolvem etapas de reação e de lavagem[42]. Para contornar estes problemas, uma metodologia alternativa, denominada imobilização in-situ, foi proposta e usada para avaliar reações de homo- e copolimerização de eteno[47-52]. Este procedimento consiste em adicionar simultaneamente o suporte (sílica previamente tratada com MAO - SMAO), a solução do catalisador e o cocatalisador ou ativador (alquilalumínio) diretamente ao reator, sem a necessidade de MAO externo ou pré-contato das espécies envolvidas antes da polimerização.

A proposta mecanística do procedimento de imobilização in-situ de catalisadores metalocênicos foi publicada em 2000 na avaliação da polimerização de eteno com os catalisadores $Et(Ind)_2ZrCl_2$ e $Et(Ind)_2ZrMe_2$ empregando TMA como ativador[47]. Como descrito na Figura 1, o mecanismo de atuação do catalisador suportado in-situ consiste de cinco etapas:

(1) contato inicial entre o suporte e o catalisador solubilizado no meio reacional;
(2) ativação dos sítios catalíticos;
(3) exposição e ativação de novos sítios catalíticos formados pela fragmentação do catalisador;
(4) reativação dos sítios catalíticos desativados por catalisador em solução;
(5) estado estacionário.

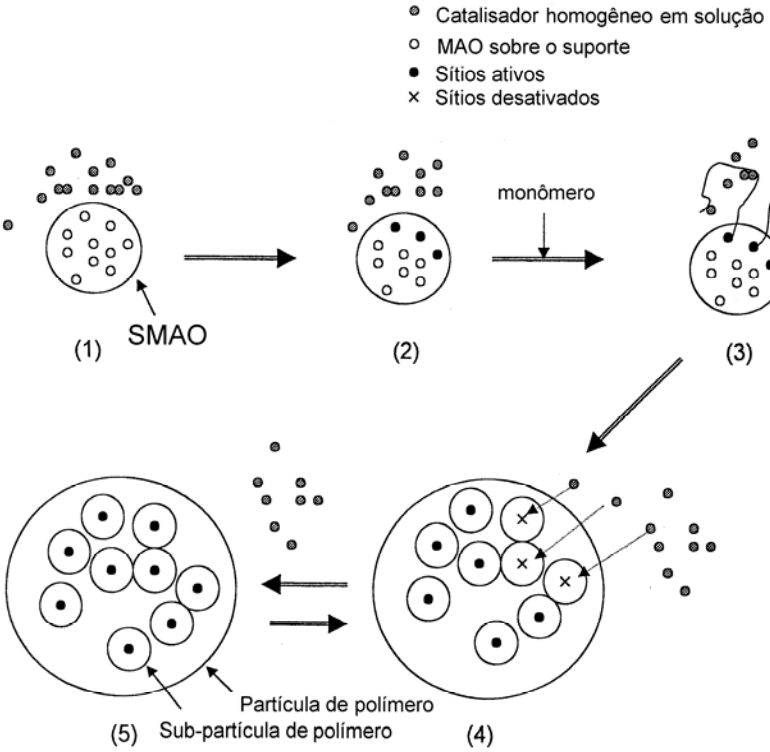


Figura 1. Proposta de mecanismo de atuação do catalisador metalocênico suportado *in-situ*.

Conforme proposta dos autores, inicialmente os sítios ativos são formados através da complexação do catalisador metalocênico e do MAO que está suportado sobre a sílica (etapas 1 e 2). A polimerização inicia com a injeção de eteno, causando a fragmentação e o crescimento da partícula. É suposto que moléculas adicionais de MAO suportado serão expostas durante esta etapa e, assim, serão ativadas por moléculas remanescentes de catalisador em solução (etapa 3). Para explicar as taxas de polimerização estáveis observadas com os catalisadores imobilizados in-situ, ou seja, a ausência de decaimento na taxa de polimerização ao longo do tempo, foi proposto que os sítios desativados na superfície do SMAO são reativados pela complexação com catalisador solúvel e, possivelmente, com TMA, levando ao equilíbrio dinâmico ilustrado nas etapas 4 e 5. Embora o mecanismo seja claramente especulativo, o mesmo explica adequadamente os resultados experimentais obtidos.

O polímero obtido com o catalisador $Et(Ind)_2ZrCl_2$ suportado in-situ apresentou massa molar e distribuição de massa molar semelhantes às obtidas com o catalisador homogêneo e suportado através de métodos convencionais (suportação ex-situ). A análise por microscopia eletrônica de varredura mostrou que o polímero formado com o catalisador suportado in-situ era esférico, replicando o formato do suporte (SMAO), e as esferas apresentavam diâmetro médio de aproximadamente 100 μm, com morfologia semelhante a do polímero obtido com o catalisador suportado ex-situ.

Além disto, na ausência de TMA o catalisador $Et(Ind)_2ZrCl_2$ mostrou-se inativo, enquanto o catalisador $Et(Ind)_2ZrMe_2$ apresentou baixa atividade, demonstrando que o TMA apresenta diferentes funções: eliminador de impurezas, agente alquilante e ativador do catalisador metalocênico imobilizado in-situ.

Em outro artigo, também publicado em 2000, foi avaliado o efeito das condições de polimerização sobre a atividade do catalisador $Et(Ind)_2ZrCl_2$ imobilizado in-situ na polimerização de eteno, bem como sobre a massa molar e a distribuição de massa molar do polietileno formado[48].

A concentração de catalisador não teve efeito sobre a atividade catalítica, ao contrário do que ocorre com o sistema homogêneo que apresenta diminuição da atividade com o aumento da concentração de catalisador devido à dimerização de sítios ativos, com formação de sítios inativos[53, 54], nem sobre a massa molar e a distribuição de massa molar.

O aumento da razão molar Al_{SMAO}/Zr causou aumento da atividade catalítica sem apresentar influência sobre a massa molar e a distribuição de massa molar. Este resultado, ou seja, o fato da massa molar não ser influenciada pela razão Al_{SMAO}/Zr indica que as moléculas de MAO do SMAO não atuam como agentes de transferência de cadeia.

O aumento da temperatura de reação até $80^{o}C$ causou aumento da atividade catalítica, mas após este valor houve acentuada queda da atividade do catalisador. Como possíveis explicações para a desativação do catalisador com o aumento da temperatura foram citadas a lenta dissociação da espécie ativa e/ou a eliminação de hidrogênio β formando hidreto metalocênico, espécie inativa para a polimerização[55]. A massa molar diminuiu e a distribuição de massa molar não foi influenciada pelo aumento da temperatura.

A pressão de eteno não influenciou a atividade catalítica, indicando que a reação de polimerização é de $1^{\underline{a}}$ ordem em relação à pressão de eteno, nem a massa molar e a distribuição de massa molar.

O tipo de cocatalisador ou ativador empregado apresentou influência sobre a atividade do catalisador e sobre as propriedades do polietileno formado. A atividade catalítica diminuiu na ordem TMA > TEA > TIBA > DEAC. Com TIBA foi obtida maior massa molar e com TEA maior distribuição de massa molar.

Posteriormente, foi descrito o efeito da adição de hidrogênio na polimerização de eteno empregando os catalisadores $Et(Ind)_2ZrCl_2$ e Cp_2ZrCl_2 imobilizados in-situ, na presença de TMA como ativador[49].

Ao contrário do observado com catalisadores metalocênicos em condições homogêneas de polimerização, com a adição de hidrogênio foi observado aumento da atividade dos catalisadores $Et(Ind)_2ZrCl_2$ e Cp_2ZrCl_2 imobilizados in-situ. Entretanto, com o catalisador Cp_2ZrCl_2, houve aumento da atividade até determinada pressão de hidrogênio e, após este valor, ocorreu redução. Conforme descrito na literatura, hidretos metálicos imobilizados sobre suportes inorgânicos apresentam aumento de atividade devido ao aumento do número de sítios ativos, o que poderia explicar o resultado obtido com os catalisadores Et(Ind)$_2$ZrCl$_2$ e Cp$_2$ZrCl$_2$ suportados sobre SMAO[56].

Por outro lado, o efeito do hidrogênio sobre a massa molar foi o esperado: com a adição de hidrogênio houve diminuição da massa molar, confirmando o forte efeito de agente de transferência de cadeia do hidrogênio, como observado em reações homogêneas[57, 58].

O catalisador Cp$_2$ZrCl$_2$ apresentou maior resposta ao hidrogênio que o Et(Ind)$_2$ZrCl$_2$. Isto é, para a mesma pressão parcial de hidrogênio, foi obtida menor massa molar com Cp$_2$ZrCl$_2$ que com Et(Ind)$_2$ZrCl$_2$. Com os dois catalisadores, a adição de hidrogênio causou alargamento da distribuição de massa molar, passando de uma distribuição monomodal para bimodal.

Em função dos resultados obtidos, foram feitas as seguintes propostas para explicar o aumento da atividade e a bimodalidade com a adição de hidrogênio na polimerização de eteno com os catalisadores Et(Ind)$_2$ZrCl$_2$ e Cp$_2$ZrCl$_2$ imobilizados in-situ sobre SMAO:

- o hidrogênio ativa um tipo de sítios que estava inativo na sua ausência e também aumenta a taxa de polimerização dos sítios originais;
- existem dois tipos de sítios ativos que na ausência de hidrogênio geram a mesma massa molar, mas que têm resposta ao hidrogênio diferente, gerando a bimodalidade no polímero formado.

Em outros três artigos foram descritos os resultados dos testes realizados na copolimerização de eteno e 1-hexeno utilizando a técnica de imobilização in-situ do catalisador[50, 51, 52].

O primeiro artigo[50] descreve os resultados da copolimerização de eteno e 1-hexeno utilizando o catalisador Et(Ind)$_2$ZrCl$_2$ em condições homogêneas, suportado ex-situ sobre sílica e in-situ sobre SMAO. Como cocatalisador, foi utilizado MAO/TMA, nos dois primeiros casos, e apenas TMA, com o catalisador suportado in-situ. Foram comparadas a atividade e a capacidade de incorporação de 1-hexeno dos três catalisadores e a microestrutura (massa molar, distribuição de massa molar e distribuição de ramificações de cadeia curta, ou seja, do comonômero) dos polímeros obtidos.

A maior atividade catalítica foi verificada com o catalisador homogêneo e as razões para a diminuição da atividade do catalisador com a suportação foram atribuídas (1) ao significante impedimento estérico causado pelo suporte ao redor dos sítios ativos e (2) pela desativação dos sítios ativos ou ineficiente produção de sítios ativos durante a suportação, seja ela ex-situ ou in-situ.

Dos três catalisadores avaliados, o homogêneo apresentou a maior capacidade de incorporação de comonômero (3,0 mol %), sendo que os catalisadores suportados ex-situ (2,0 mol %) e in-situ (2,2 mol %) apresentaram resultados semelhantes.

O polímero obtido em condições de polimerização homogêneas teve a maior massa molar e a menor distribuição de massa molar e o polimerizado com o catalisador imobilizado in-situ apresentou a menor massa molar e a maior distribuição de massa molar.

A distribuição de ramificações de cadeia curta do polímero obtido com o catalisador suportado in-situ foi a mais larga, sendo que nos outros dois casos a distribuição de comonômero ao longo da cadeia foi mais estreita.

O fato do copolímero eteno/1-hexeno preparado com o catalisador $Et(Ind)_2ZrCl_2$ imobilizado in-situ sobre SMAO, na presença de TMA como ativador, ter apresentado maior distribuição de massa molar e maior distribuição de ramificações de cadeia curta é um indicativo da presença de duas ou mais espécies ativas, ou seja, de dois ou mais tipos de sítios ativos no catalisador in-situ.

No artigo subseqüente[51] foi comparado o comportamento dos catalisadores $Et(Ind)_2ZrCl_2$, Cp_2HfCl_2 e $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$ (CGC - *constrained geometry catalyst*, produzido pela Dow) na copolimerização de eteno com 1-hexeno em condições homogêneas e de suportação in-situ, bem como foram avaliadas combinações destes catalisadores suportados in-situ, com o objetivo de comparar a microestrutura dos polímeros formados.

A exemplo do realizado nos trabalhos anteriores, nas polimerizações em que os catalisadores foram suportados in-situ, foi adicionado apenas TMA como cocatalisador externo. As polimerizações em condições homogêneas foram conduzidas na presença de MAO e TMA.

Os catalisadores suportados in-situ apresentaram diferente incorporação de comonômero e os polímeros produzidos tiveram massa molar, distribuição de massa molar e de ramificações de cadeia curta diferente do observado nos polímeros produzidos com os respectivos catalisadores em condição de polimerização homogênea.

Para os três catalisadores, com a suportação in-situ, houve diminuição da quantidade de comonômero incorporado, com aumento da cristalinidade, e alargamento da distribuição de ramificações de cadeia curta. O catalisador CGC apresentou o resultado mais surpreendente, pois quando empregado em condições homogêneas produziu apenas polímero amorfo, enquanto o catalisador imobilizado in-situ levou à formação de uma mistura de polímero amorfo e cristalino, ou seja, com distribuição de ramificações de cadeia curta mais larga e bimodal. O catalisador Cp_2HfCl_2 apresentou a mais larga distribuição de ramificações de cadeia curta, nas duas condições de polimerização, indicando a existência de mais de um tipo de sítio ativo.

O efeito da imobilização do catalisador sobre SMAO sobre a massa molar e sobre a distribuição de massa molar foi diferente para cada um dos catalisadores avaliados. A suportação in-situ causou pequena diminuição da massa molar do polímero obtido com $Et(Ind)_2ZrCl_2$, mas aumento significativo com Cp_2HfCl_2 e $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$. Já a distribuição de massa molar diminuiu com o catalisador Cp_2HfCl_2 e aumentou com os catalisadores $Et(Ind)_2ZrCl_2$ e $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$.

Em função da diferença na resposta ao hidrogênio (formação de diferente massa molar com cada catalisador) e ao comonômero (diferente incorporação de 1-hexeno e distribuição de ramificações de cadeia curta) de cada catalisador, a utilização de mistura de catalisadores permitiu obter polímeros com distribuição de massa molar e de ramificações de cadeia curta mais larga. Como cada catalisador da mistura apresentou comportamento como se estivesse sendo utilizado sozinho no reator, isto é, independente da presença do outro catalisador, foi possível predizer as propriedades do polímero final considerando as propriedades dos polímeros formados com cada catalisador individualmente.

Por fim, no último artigo sobre copolimerização entre eteno e 1-hexeno[52], foi avaliado o efeito do tipo de alquilalumínio empregado como ativador com o catalisador $Et(Ind)_2ZrCl_2$ suportado in-situ sobre SMAO sobre a massa molar e sobre a distribuição de cadeias curtas.

Foram avaliados TMA, TEA e TIBA e, conforme o alquilalumínio empregado, foram verificadas diferenças nos resultados de atividade catalítica, massa molar e distribuição de massa molar, quantidade de comonômero incorporada e distribuição de ramificações de cadeia curta.

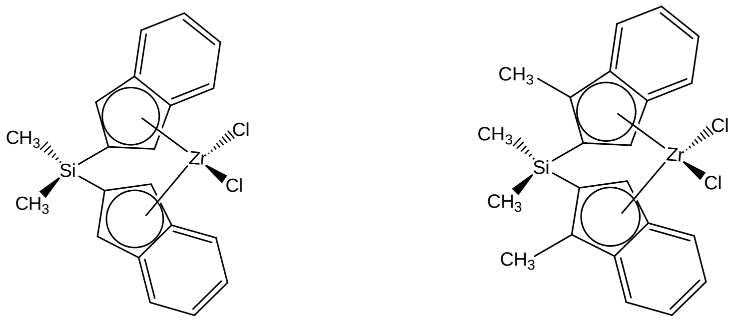
Com o uso de TMA, o catalisador apresentou atividade catalítica cerca de 5 vezes superior àquela obtida na presença de TEA, que por sua vez apresentou atividade 2,5 vezes maior que à verificada com o uso de TIBA como ativador. Os autores propuseram que a maior atividade com o emprego de TMA se deva ao maior poder alquilante deste alquilalumínio e/ou à diferença de tamanho em relação ao TEA e ao TIBA. O maior tamanho destes dois ativadores poderia dificultar seu acesso ao catalisador sobre o suporte, reduzindo o número de sítios ativos.

Em relação à massa molar, foi obtida a seguinte ordem: TIBA > TMA > TEA. A maior massa molar do copolímero de eteno com 1-hexeno obtido com a utilização de TIBA foi explicada em função deste alquilalumínio ser mais volumoso e, assim, possivelmente diminuir as reações de transferência de cadeia para o alumínio, fato também observado por outros autores e descrito na literatura[59-64]. Por outro lado, a maior distribuição de massa molar foi obtida com TMA, enquanto com TEA e TIBA foram verificados resultados semelhantes.

A maior quantidade de comonômero foi incorporada com o uso de TMA, cerca de 4,0 %, enquanto com TEA e TIBA o teor de 1-hexeno ficou em torno de 3,0 %. Além disto, com TMA foi obtida distribuição de ramificações de cadeia curta monomodal, enquanto com TEA e TIBA a distribuição verificada foi bimodal, indicando incorporação de comonômero mais heterogênea. Em função deste comportamento diferenciado em relação à distribuição de ramificações de cadeias curtas ao longo da cadeia, foram realizadas polimerizações na presença de misturas de TMA/TEA e TMA/TIBA, o que permitiu controlar a bimodalidade do polímero quanto à incorporação de comonômero.

Mais recentemente, o procedimento de imobilização in-situ também foi empregado em reações de homo-[65] e copolimerização[66] de eteno usando um novo catalisador zirconoceno binuclear com ponte de pentametileno. Os resultados obtidos demonstraram que o polímero gerado via imobilização in-situ do catalisador metalocênico sobre SMAO apresenta morfologia controlada, replicando o formato do suporte utilizado e, portanto, confirmando a suportação. Assim como descrito nos trabalhos resumidos anteriormente, o tipo de alquilalumínio empregado mostrou influência sobre a atividade do catalisador e sobre as propriedades dos polímeros formados: independente do catalisador utilizado, as maiores atividades foram obtidas com o uso de TMA. Em relação à massa molar, os maiores resultados foram obtidos com TIBA, com o catalisador Cp_2ZrCl_2, e com TMA, com os catalisadores $Et(Ind)_2ZrCl_2$ e $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$. Além disto, a distribuição de massa molar e o tamanho de partícula do polímero formado também foram influenciados pelo tipo de ativador, demonstrando que é possível selecionar uma combinação apropriada de catalisador e ativador para a obtenção de um polímero com as propriedades desejadas.

Ao nosso conhecimento, até o início do trabalho descrito nesta tese, não havia sido avaliada a possibilidade de polimerização de propeno utilizando a metodologia de imobilização in-situ. Deste modo, neste trabalho foram realizadas polimerizações para avaliar a atividade catalítica de catalisadores metalocênicos do tipo bis-indenila com ponte de silício e as propriedades dos polímeros obtidos com a utilização destes catalisadores na polimerização de propeno através do procedimento de suportação in-situ, com a utilização de sílica previamente modificada com MAO (SMAO) como suporte e de um alquilalumínio do tipo AlR_3 como cocatalisador. Os catalisadores I ($Me_2Si(Ind)_2ZrCl_2$) e II ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$), avaliados neste trabalho, são apresentados no Esquema 1.



I

II

Esquema 1

O interesse na utilização de catalisadores com este tipo de estrutura química se justifica porque são semelhantes aos utilizados comercialmente pela Basell e seus licenciados na produção de polipropileno metalocênico (m-PP). Os catalisadores Basell são denominados

Avant M® e as resinas produzidas com estes catalisadores formam a família Metocene®[67]. Tais catalisadores, quando adequadamente suportados, produzem polipropileno com alta massa molar, mesmo em altas temperaturas. As partículas do polímero replicam perfeitamente a distribuição de tamanho de partícula do catalisador apresentando morfologia adequada para utilização em processo fase gás e massa e o polímero obtido apresenta propriedades diferenciadas, tais como baixo teor de extraíveis, característica importante para o uso em embalagens para alimentos e em aplicações medicinais[68].

Salienta-se, contudo, que foram selecionados catalisadores de estrutura mais simples, para serem usados como modelo, por serem mais facilmente acessíveis e mais baratos, apesar de não serem os mais indicados para a polimerização de propeno. Na polimerização de propeno com catalisadores metalocênicos, para obtenção de alta atividade e polímeros com alta massa molar e alta temperatura de fusão, com adequada incorporação de comonômero e distribuição de massa molar, os catalisadores devem possuir substituintes na posição 2 (anel de 5 carbonos) e na posição 4, 6 ou 7 (anel de 6 carbonos) do grupo indenila.

2. OBJETIVO:

O objetivo deste trabalho foi avaliar as potencialidades e limitações do uso de catalisadores metalocênicos suportados in-situ na polimerização de propeno.

Os objetivos específicos do trabalho foram:

- avaliação do efeito da natureza e da concentração do alquilalumínio (TEA, IPRA e TIBA), utilizado como cocatalisador ou ativador, sobre a atividade catalítica de catalisadores metalocênicos suportados in-situ e sobre as propriedades dos polímeros formados;
- comparação dos resultados obtidos na polimerização de propeno via suportação in-situ com resultados de polimerizações de eteno também via suportação in-situ;
- proposição da natureza das espécies catalíticas ou sítios ativos envolvidos na polimerização via suportação in-situ.

3. PARTE EXPERIMENTAL:

3.1. REAGENTES E SOLVENTES:

Os catalisadores dicloreto de rac-dimetilsililenobis(indenil)zircônio ($Me_2Si(Ind)_2ZrCl_2$) (Crompton) e dicloreto de rac-dimetilsililenobis(2-metil-indenil)zircônio ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$) (Boulder Scientific), o suporte sílica modificada com MAO (SMAO, 23 % Al (massa), Crompton) e os cocatalisadores MAO (10 % (massa) em tolueno, Crompton), trietilalumínio (TEA), isoprenilalumínio (IPRA) e triisobutilalumínio (TIBA) (todos da Akzo) foram utilizados sem purificação prévia. Propeno e eteno foram utilizados conforme recebidos do craquer (Copesul), sem purificação prévia. Tolueno e hexano, utilizados, respectivamente, para solubilização do catalisador e como meio reacional, foram secos sob refluxo com sódio metálico e benzofenona e destilados sob atmosfera de nitrogênio.

3.2. DETERMINAÇÃO DA ISOTERMA DE ADSORÇÃO:

Diferentes teores de zircônio foram colocados em contato com SMAO a 60^oC durante 1 h utilizando tolueno como solvente. O tolueno foi removido sob pressão reduzida, o sólido resultante foi lavado com 15 x 2 mL de tolueno, seco a vácuo e o teor de zircônio no catalisador suportado foi determinado por Espectroscopia de Retroespalhamento Rutherford.

3.3. PREPARAÇÃO DE CATALISADORES VIA SUPORTAÇÃO CONVENCIONAL (EX-SITU):

Determinada quantidade de catalisador foi dissolvida em tolueno, adicionada sobre o suporte na razão Zr/suporte desejada e mantida durante 30 minutos à temperatura ambiente sob agitação. O tolueno foi removido sob pressão reduzida e seco a vácuo.

3.4. POLIMERIZAÇÕES:

As reações foram realizadas em reator de bancada de aço inox de 1,5 L e todos os reagentes foram manipulados utilizando a técnica de Schlenk. O procedimento utilizado nas polimerizações via suportação in-situ do catalisador iniciou com a adição do SMAO (Al_{SMAO}/Zr = 500) diretamente ao reator, sob leve fluxo de nitrogênio; a seguir foram adicionados 0,75 L de hexano, 10 mL de solução catalítica (10^{-5} móis) e a quantidade estipulada de alquilalumínio. Após atingir 60°C, o reator foi pressurizado com 6,0 bar de monômero (propeno ou eteno) e esta pressão parcial de monômero foi mantida durante 1 h. O polímero resultante foi precipitado com etanol acidificado (HCl 1 %), lavado com água e etanol e seco em estufa a vácuo a 80°C por 2 h. Todas as reações foram realizadas em duplicata (no mínimo) e os resultados apresentados representam a média obtida em cada condição. O procedimento utilizado nas polimerizações via suportação ex-situ do catalisador foi o mesmo descrito acima, entretanto, no lugar do SMAO e da solução do catalisador em tolueno foi adicionado, ao reator, o catalisador suportado.

3.5. ESPECTROSCOPIA DE RETROESPALHAMENTO RUTHERFORD (RBS):

As análises de RBS foram realizadas no Instituto de Física da UFRGS conforme procedimento descrito na literatura[69, 70]. As análises foram realizadas em amostras na forma de pastilhas, com um feixe de energia de 2 MeV.

3.6. ESPECTROSCOPIA DE ESTRUTURA FINA DE ABSORÇÃO DE RAIOS-X (EXAFS):

As análises de EXAFS foram realizadas no Laboratório Nacional de Luz Síncroton, em Campinas. As medidas na borda K do zircônio foram feitas na linha XAS, dotada de monocromador de silício (220). As amostras foram preparadas em câmara de luvas, cobertas com fita Kapton e medidas no modo de fluorescência.

3.7. MICROSCOPIA ELETRÔNICA DE VARREDURA (SEM):

As análises de SEM foram realizadas no equipamento DSM-940 Zeiss, operando entre 3 e 5 kV. As amostras foram prensadas e recobertas com ouro ou carbono (20 μm de espessura).

3.8. CALORIMETRIA DE VARREDURA DIFERENCIAL (DSC):

As análises de DSC, para determinação da cristalinidade (χ) e das temperaturas de fusão (Tf) e de cristalização (Tc) dos polímeros obtidos, foram realizadas no equipamento da TA Instruments, modelo 2920, com velocidade de aquecimento de 10°C/min, na faixa de 30 a

220^{o}C, sob atmosfera de nitrogênio, conforme normas ASTM D 3417/97 e ASTM D 3418/97. Somente os resultados da segunda corrida de aquecimento foram empregados.

3.9. CROMATOGRAFIA DE PERMEAÇÃO EM GEL (GPC):

As análises de GPC para determinação das massas molares numérica média (M_n) e mássica média (M_w), bem como da polidispersão (M_w/M_n) dos polímeros foram realizadas no cromatógrafo modelo 150 C da Waters equipado com 4 colunas GMHXL-HT (TosoHaas), calibrado com 18 padrões de poliestireno e 3 de polietileno, a 138^{o}C, utilizando 1,2,4-triclorobenzeno como solvente.

3.10. RESSONÂNCIA MAGNÉTICA NUCLEAR DE CARBONO 13 (^{13}C-NMR):

As análises de ^{13}C-RMN para determinação da microestrutura dos polímeros foi realizada no equipamento Varian Inova 300, a 75 MHz e 135^{o}C. As amostras foram preparadas em soluções de o-diclorobenzeno (ODCB) e benzeno-d6 (20 % v/v) em tubos de 5 mm. Os espectros foram obtidos com ângulo de 74^{o}, tempo de aquisição de 1,5 s e tempo de relaxação de 4,0 s.

3.11. ADSORÇÃO DE NITROGÊNIO:

As análises de adsorção de nitrogênio foram realizadas no equipamento Micrometrics Gemini. As amostras foram pré-aquecidas a 80^{o}C durante 12 h sob vácuo antes de cada medida. A área superficial foi determinada através do método de Brunauer-Emmett-Teller (BET) a 196^{o}C, no intervalo de pressão parcial de $0{,}01 < P/P_o < 0{,}25$. O volume total dos poros foi obtido das isotermas de adsorção de nitrogênio.

3.12. DECONVOLUÇÃO DAS CURVAS DE GPC:

As deconvoluções das curvas de distribuição de massa molar dos polímeros foram realizadas utilizando o programa Excel. Para obter o melhor ajuste entre a curva de GPC real e a curva de GPC ajustada (soma das curvas da deconvolução), foi utilizada a ferramenta Solver do Excel de modo a minimizar o parâmetro $\Sigma\Delta^2$, o qual representa a diferença entre pontos da curva real e da curva ajustada. Para cada curva de GPC, o processo de deconvolução foi realizado considerando 1, 2, 3, 4 ou 5 curvas ou picos. Em todos os casos, buscou-se obter o menor valor possível para o parâmetro $\Sigma\Delta^2$, sem que houvesse sobreposição das curvas ou picos.

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5. ARTIGOS PUBLICADOS:

O trabalho realizado como parte desta Tese de Doutorado gerou cinco artigos, sendo que quatro foram publicados entre 2003 e 2006 e um foi submetido à publicação e está em fase de revisão. Os artigos completos são apresentados a seguir, com um breve resumo de cada trabalho.

5.1. ARTIGO 1:

Polypropylene obtained with in situ supported metallocene catalysts
Journal of Molecular Catalysis A: Chemical, **2003**, *202* (1-2), 127-134

O catalisador $Me_2Si(Ind)_2ZrCl_2$ foi imobilizado sobre sílica previamente modificada com MAO (SMAO) através da técnica de imobilização in-situ e utilizado na polimerização de propeno. A avaliação da isoterma de adsorção do catalisador sobre SMAO indicou que o nível de saturação é alcançado com 2,0 % Zr/SMAO. O sistema catalítico foi ativo na ausência de MAO externo, ou seja, somente com a presença do MAO contido no SMAO, sendo, contudo, necessária a adição de um alquilalumínio do tipo TEA, IPRA e TIBA. Foram avaliados o efeito da natureza e o efeito da concentração do cocatalisador sobre a atividade do sistema catalítico e sobre as propriedades do polímero resultante, as quais foram avaliadas através das seguintes técnicas: GPC, DSC, ^{13}C-NMR e SEM. A maior atividade catalítica foi obtida com o uso de IPRA como cocatalisador (1,4 kg PP/g cat h).

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Polypropylene obtained with in situ supported metallocene catalysts

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Abstract

Propylene homopolymerization was carried out with $Me_2Si(Ind)_2ZrCl_2$ immobilized on commercial MAO-modified silica by the in situ supporting technique. Adsorption isotherm determination for this metallocene on silica indicated that the saturation level is reached at 2.0 wt.% Zr/SMAO. Catalyst systems were shown to be active in the absence of external MAO, being activated by common alkylaluminum cocatalysts, namely triethylaluminum (TEA), isoprenylaluminum (IPRA) and triisobutylaluminum (TIBA). The effect of the nature and concentration of cocatalyst on catalyst activity and on polypropylene (PP) properties was evaluated. Best catalyst activity was observed in low concentration of IPRA (1.4 kg PP/g cat h). The resulting polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and scanning electronic microscopy (SEM).

Keywords: Supported zirconocenes; Polypropylene; MAO; Silica

1. Introduction

The development of metallocene catalysts represented a new step in the polymerization field. Polymers produced by metallocene catalysts have a different architecture compared to conventional polymers obtained by Ziegler–Natta catalysts. Among the advantages of these systems are the unique properties of the new resins, such as narrow molecular weight and uniform comonomer distributions. Moreover, the adaptability of metallocene catalysts to existing plants, the potential for product/property modifications through rational catalyst manipulations, and an increasing pace of discovery through new research methodologies are also very attractive features of these catalysts (see, for example [1]).

Polyethylene, polypropylene (PP) and copolymers with higher α-olefins are already produced industrially

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by metallocene catalysts but still on small scale, since there are still some drawbacks that have to be overcome, such as difficulty in controlling polymer morphology and the large amount of MAO necessary to achieve high activity and keep catalyst stability. The heterogeneization of metallocenes has been researched extensively and proposed as an alternative to overcome such problems. There are many routes described in the literature employing different supports, immobilization procedures (grafting, wet impregnation), surface chemical modification (alkylaluminum, organosilicon), just to mention a few [2].

Although heterogeneous systems present some advantages over the homogeneous ones, the activity of supported metallocenes is generally reduced in comparison to those of homogeneous systems. Many reasons have been attributed to this decreased activity, such as the generation of only 1.0% of the total grafted content as active species [3] and steric effects of the silica surface, which plays the role of a huge ligand. Moreover, zirconocene extraction from the silica surface by MAO has been pointed out as a disadvantage that must be overcome if supported catalysts are to be used successfully. Some alternatives have been proposed to overcome these problems, such as the use of surface spacers which keep the zirconocene centers farther from the surface [4], the use of horizontal spacers which reduce bimolecular deactivation reactions [5], and the direct synthesis of metallocenes on inorganic–organic hybrid silica [6].

All the proposed supported procedures are time demanding, involving reaction and washing steps and final catalyst characterization. Soares et al. proposed an alternative methodology (in situ supporting) which uses a commercial immobilized cocatalyst [7]. This approach consists in the direct addition of the catalyst solution to the MAO-supported silica inside the reactor, just before pressurizing with monomer. No additional MAO is required since common alkylaluminum cocatalysts can activate in situ supported catalysts. Therefore, this procedure avoids time consuming steps or addition of external MAO. Supported catalysts prepared by this in situ immobilization technique have been evaluated for ethylene homo- and copolymerization [8–11]. In the present work, we studied propylene homopolymerization employing *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) as catalyst and commercial MAO-modified silica (SMAO) support. The effect of common alkylaluminum cocatalysts was evaluated on catalyst activity and polymer properties. Adsorption isotherm measurements were performed to determine the surface saturation content for this metallocene. Resulting polymers were characterized by differential thermal calorimetry (DSC), gel permeation chromatography (GPC), ^{13}C nuclear magnetic resonance (NMR) spectroscopy and scanning electronic microscopy (SEM).

2. Experimental

2.1. Materials

All the experiments were performed under inert atmosphere using Schlenk techniques. The catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (Witco), MAO-supported silica (SMAO, 23 wt.% Al, Witco), triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA) (all from Akzo) were used without purification. Propylene was used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene and hexane were purified by refluxing over sodium and by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

2.2. Adsorption isotherm determination

Several initial catalyst solutions (0.5–5.0 wt.% Zr/SMAO) were contacted with SMAO at 60 °C for 1 h. The resulting slurry was washed with 15 × 2 ml of toluene, vacuum dried, and the final metal content in the resulting solid was determined by Rutherford backscattering spectrometry (RBS), according to the standard procedure described elsewhere [12]. For comparative reasons, polypropylene produced by these catalysts was analyzed by scanning electronic microscopy micrography and compared to those produced by homogeneous and in situ supported catalysts.

2.3. Polymerization

Polymerizations were performed in a 1.5 l stainless-steel reactor equipped with mechanical stirrer, constant temperature circulator and inlets for argon and for propylene. The reactor was filled with SMAO

(Al/Zr = 500 (mol/mol)), 0.75 l of hexane, 10 ml of catalyst solution (10^{-5} mol catalyst in toluene) and alkylaluminum. When the mixture reached 60 °C, the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. The polymer was precipitated by acidified (HCl) ethanol. Homogeneous polymerizations were performed under the same conditions using MAO (Al/Zr = 500 and 2000) as cocatalyst, instead of the alkylaluminum.

2.4. Polymer characterization

Crystallinity (χ), melting (T_m) and crystallization (T_c) temperatures were determined using a TA Instruments 2920 differential scanning calorimeter, according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan were reported. The heating rate was 10 °C/min in the temperature range from 30 to 220 °C. Molecular weight distributions were determined by high temperature gel permeation chromatography using a 150 C Waters instrument equipped with four columns GMHXL-HT (TosoHaas) at 138 °C. 1,2,4-Trichlorobenzene was used as mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards.

Polymer microstructure was determined by ^{13}C NMR. The spectra were obtained at 135 °C in a Varian Inova 300 operating at 75 MHz. Sample solution of the polymer were prepared in *o*-dichlorobenzene (ODCB) and benzene-d_6 (20% (v/v)) in 5 mm sample tubes. Spectra were taken with a 74° flip angle, in an acquisition time of 1.5 s and a delay of 4.0 s.

Scanning electronic microscopy analyses were performed using a DSM-940 Zeiss instrument operating at 3–4 kV. Samples were prepared as films sputter-coated with gold (20 mm thickness). Images magnification was 2000×.

3. Results and discussion

Many catalyst supporting techniques are reported in the literature, differing on the immobilization procedure, as well as the resulting properties and goals of the final catalyst [13]. In the specific case of supported metallocene catalysts, two routes are important, namely grafting and impregnation, since in the present case the maintenance of the coordination sphere is mandatory for the catalyst application. Grafting reaction implies in the chemical reaction between the catalyst and the support, followed by washing steps in order to remove non-reacted, physically adsorbed catalysts. Impregnation is a faster method, in which support and catalyst solution are put into contact. The solvent is removed, but the resulting catalyst is not washed: the initial amount of catalyst might remain totally in the solid, whether chemically reacted or just physically adsorbed. The maximum loading of a surface with a certain catalyst can be obtained by determining its adsorption isotherm, in which different initial catalyst concentrations are put into contact with the support, followed by washing, grafting, and drying steps. Afterwards the final metal content is measured.

We have previously determined Cp_2ZrCl_2, TMA and MAO adsorption isotherms on different commercial silicas [14]. Since in the present approach the catalyst is directly contacted with the support inside the reactor, it is expected that the amount of catalyst impregnated is less than the saturation level of the catalyst on the support. Therefore, we initially determined the adsorption isotherm of $Me_2Si(Ind)_2ZrCl_2$ on the SMAO support.

Fig. 1 shows the adsorption isotherm at 60 °C, the same temperature used for the polymerizations. According to Fig. 1, the saturation level is reached at ca. 2.0 wt.% Zr/SMAO. It is worth mentioning that for initial concentrations lower than the saturation level, almost all the catalyst present in the solution is adsorbed onto the support. Such behavior is typical of strong interaction between the catalyst and the support [15].

The in situ procedure was tested for a ratio of Al/Zr = 500, which is below the saturation level of Al/Zr = 40. It is worth noting that Al/Zr = 500 represents a lower Zr content in comparison to that of Al/Zr = 40, keeping the Al content constant. The effect of the nature and amount of the cocatalyst on catalyst activity is shown in Table 1. Three cocatalysts were evaluated, namely TEA, IPRA, and TIBA, in the range between 0.7 and 20.0 mmol, corresponding to Al/Zr comprised between 70 and 2000 (mol/mol) of external aluminum.

Among the three cocatalysts investigated, IPRA led to the highest activity system. The activity was roughly two or three times higher than those observed for the two other systems. In the case of IPRA, catalyst

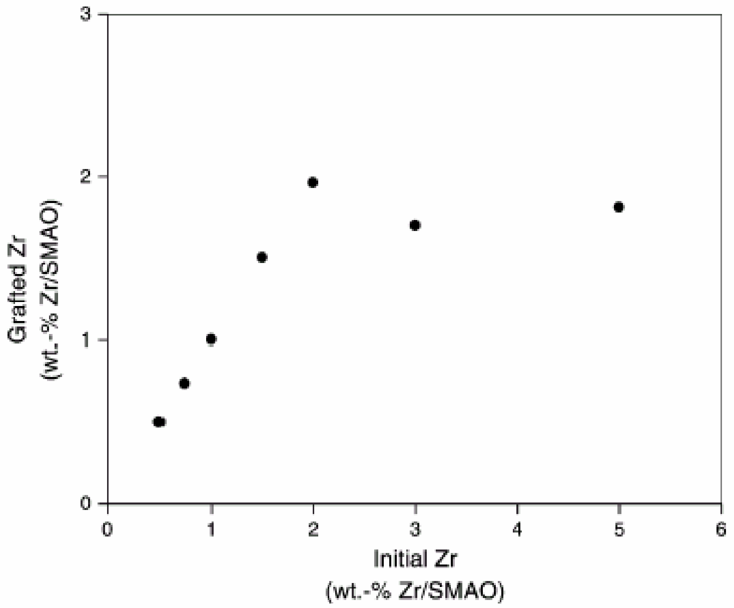


Fig. 1. Adsorption isotherm of $Me_2Si(Ind)_2ZrCl_2$ on SMAO (Witco). Grafting reaction performed in toluene at 60 °C.

activity decreased as the cocatalyst amount increased. For TEA and TIBA, the catalytic activity was almost constant for the different amounts of cocatalyst, decreasing for values higher than 5.0 mmol. A plausible polymerization mechanism explaining the role of alkylaluminium as scavenger, alkylating agent and cocatalyst activator with in situ supported metallocenes has been reported [10]. Lower catalyst activity in the ethylene polymerization with in situ supported $EtInd_2ZrCl_2$ was also reported in the case of TEA and TIBA cocatalysts [11]. Polymerization tests with ex situ catalysts, using TIBA as cocatalyts showed similar results.

Table 1
Catalyst activities of $Me_2Si(Ind)_2ZrCl_2$/SMAO system in the presence of different alkylcocatalysts

Alkylaluminum, Al/Zr[a] (mol/mol)	Activity (kg PP/g cat h)		
	TEA	IPRA	TIBA
70	0.3	1.4	0.5
130	0.4	0.8	0.4
250	0.4	0.1	0.6
500	0.3	0.2	0.2
1000	0.1	0.1	0.2
2000	0.2	np	np

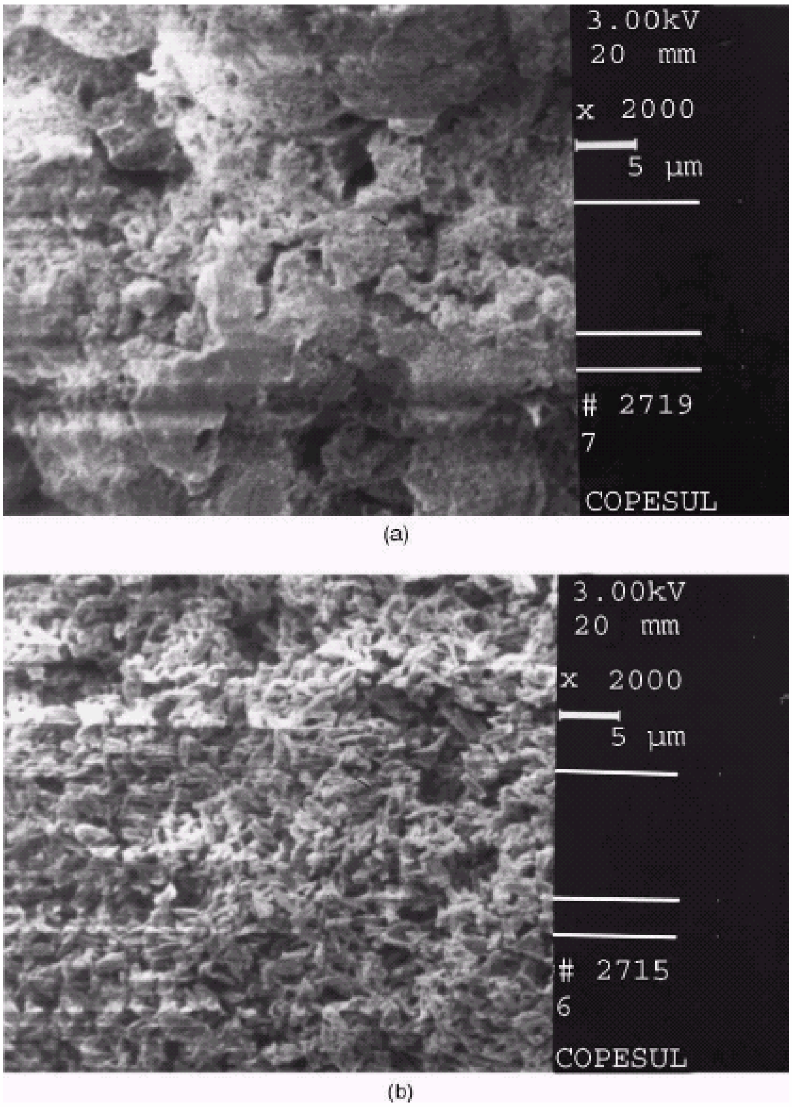
np: not performed; homogeneous reactions using MAO as cocatalyst (Al/Zr = 500) produced 4.6 kg PP/g cat h.

[a] External aluminum.

For comparative reasons, homogeneous reactions using MAO as cocatalyst (Al/Zr = 500) were also performed producing 4.6 kg PP/g cat h, i.e. almost three times higher than the highest activity observed in the case of IPRA and in situ supported catalyst. Higher Al/Zr ratio (Al/Zr = 2000) led to more active systems, producing 13.0 kg PP/g cat h.

This behavior, has been reported several times in the literature. The decrease in catalyst activity has been attributed to generation of inactive species on the support surface and/or to diffusion limitations during polymerization [3]. Considering both homogeneous systems, the increase in activity from Al/Zr = 500 to 2000 was already observed in the literature for similar cocatalyst ranges and might be attributed to the various roles of MAO during polymerization. The role of MAO as cocatalyst is not still clearly elucidated, and many roles have been attributed to this compound, such as alkylation of the catalyst, stabilization of the cationic metallocene alkyl by acting as a counter-ion, and the prevention of bimolecular reduction of the catalyst. Moreover, MAO can scavenge impurities such as water and oxygen from the reaction milieu (see, for example [16]).

The resulting polymers were characterized by DSC, GPC and ^{13}C NMR (Table 2). DSC results show that the polymers obtained with the in situ supported catalyst system have a lower melting temperature (T_m), crystallization temperature (T_c) and crystallinity, than those made with the homogeneous systems. On the other hand, the polymers produced via in situ supported catalyst exhibited higher MW than those obtained with the homogeneous system using Al/Zr = 500. This behavior has already been observed [17] and attributed to blocking of one of the sides of polymerization active sites by the support, hindering the deactivation step. In other words, β-elimination transfer between two metallocene centers is hindered,



(a)

(b)

Fig. 2. Micrographs of SEM (2000×) of the polymers obtained with $Me_2Si(Ind)_2ZrCl_2$: (a) homogeneous, (b) in situ supported catalysts system, and (c) ex situ supported catalysts system.

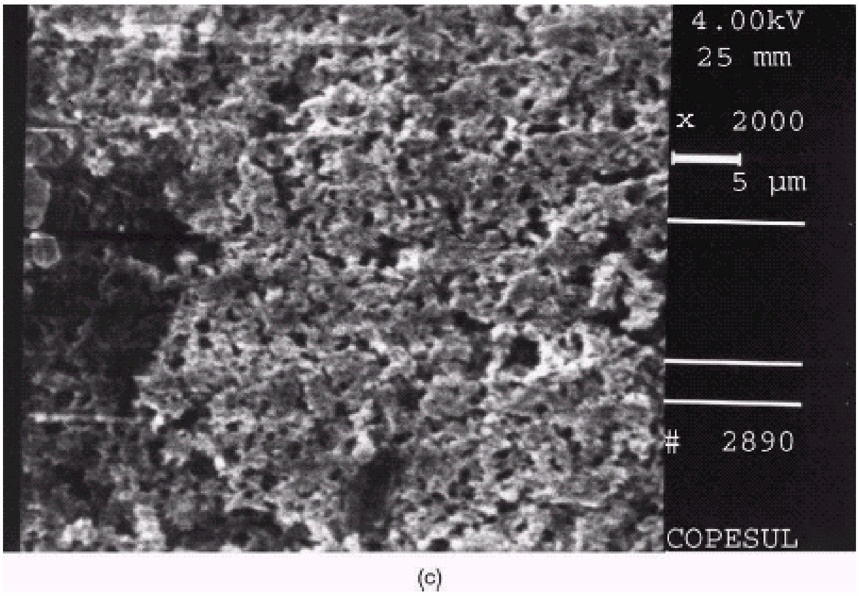


Fig. 2. (*Continued*).

resulting in a larger growth of the polymer chain, and therefore in higher molecular weight [18]. Since polymers with high average molecular weights show better mechanical properties than those with low average molecular weights, this is an attractive feature of supported metallocene catalysts in general, and in situ supported catalysts in particular.

Molecular weight depends on alkylaluminum type, decreasing in the following order: TIBA > IPRA > TEA. Similar results were observed in the case of polyethylenes produced with in situ supported $EtInd_2ZrCl_2$ [11].

The polymers produced with in situ supported catalyst had a polydispersity index only slightly higher than the polymers made with homogeneous systems, suggesting that the single-site character of $Me_2Si(Ind)_2ZrCl_2$ is kept in the in situ immobilization.

The tacticity of polypropylene was calculated by ^{13}C NMR. The percentage of dyads (m) is also presented in Table 2. All the polymers were highly isotactic ($m = 94.0\%$) and the stereoregularity seems not to be affected by the nature of the cocatalyst or by the supporting procedure. The control of stereoregularity of polypropylene is very important because it is directly related with properties such as mechanical strength, hardness, impact resistance and transparency of the polymer.

Table 2
Polymer properties of PP obtained with homogeneous and supported $Me_2Si(Ind)_2ZrCl_2$/SMAO system

System	T_m (°C)	T_c (°C)	χ (%)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	m (%)
TEA (in situ)[a]	139	106	29	18600	40000	73000	2.2	94.0
IPRA (in situ)[a]	137	108	42	20100	44000	84000	2.2	92.7
TIBA (in situ)[a]	140	105	36	29800	67000	117000	2.2	94.0
IPRA (ex situ)[a]	135	102	39	19800	41000	73000	2.1	–
Homogeneous (Al/Zr = 500)	142	110	53	16400	34000	55000	2.1	–
Homogeneous (Al/Zr = 2000)	142	110	52	21300	44000	70000	2.1	94.0

[a] Al/Zr = 130 (external aluminum).

The morphology of the polymers obtained by both homogeneous and supported catalysts was examined by SEM. According to Fig. 2, a micrograph of the polymer made with the homogeneous catalyst shows a conglomerate of crystalline polypropylene without any morphological control (Fig. 2a). On the other hand, the polymer obtained using SMAO-in situ immobilization (Fig. 2b), presented the same homogeneity in porosity showed by the polymer produced with the ex situ supported catalyst, i.e. prepared by conventional grafting procedure (Fig. 2c), suggesting that the polymerization took place effectively on the silica support. Besides, the polymers obtained with the in situ and the ex situ supporting procedure presented similar properties, as shown in Table 2.

4. Conclusions

In situ supported $Me_2Si(Ind)_2ZrCl_2$ prepared by direct contact of metallocene with SMAO in the reactor generates a catalyst system that is active for propylene polymerization in the presence of simple alkylaluminum cocatalysts such as TEA, TIBA, and IPRA. Considering that the saturation level of $Me_2Si(Ind)_2ZrCl_2$ on SMAO is reached with 2.0 wt.% Zr/SMAO, the employed Al/Zr ratio of 500 (mol/mol) enhances the likelihood that the metallocene catalyst might have grafted on the support surface or at least will not be significantly extracted during polymerization.

Polymers obtained with the in situ supported catalyst had lower T_m, T_c, and crystallinity than those made with the homogeneous catalyst. On the other hand, polymers produced by the in situ supported systems had higher molecular weights than those synthesized with the homogeneous catalyst at the same Al/Zr ratio. Tacticity does not vary with the catalytic system, showing that the stereoselectivity of the catalyst was not affected by the support. Besides, SEM micrographs showed that polymers obtained with the in situ and conventionally supported systems presented a defined morphology, conversely to polymers obtained with the homogeneous system, confirming that there is no significant extraction of the catalyst from the silica support during polymerization of propylene.

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5.2. ARTIGO 2:

Polypropylene made with in-situ supported $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ catalysts: Properties comparison

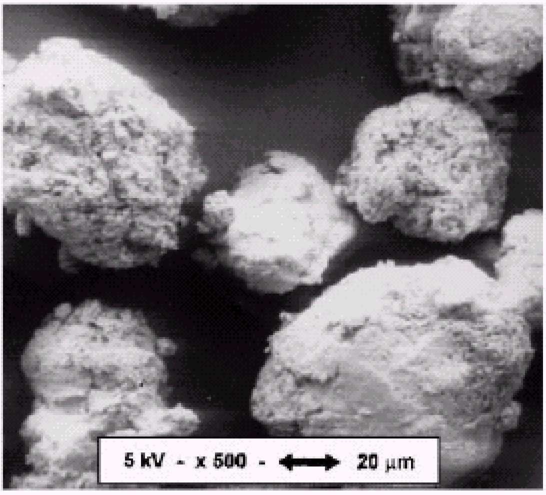
Macromolecular Chemistry and Physics, **2004**, *205*, 1525-1529

Foram realizadas homopolimerizações de propeno empregando os catalisadores $Me_2Si(Ind)_2ZrCl_2$ e $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, os quais foram suportados in-situ sobre SMAO. Como cocatalisadores foram empregados alquilalumínios convencionais. Foram investigados o efeito do tipo e o efeito da concentração do alquilalumínio na polimerização de propeno utilizando TEA, IPRA e TIBA como cocatalisadores. Os polímeros foram analisados por GPC, DSC e SEM. O efeito do tipo e da concentração de alquilalumínio sobre a temperatura de fusão e sobre a massa molar do polipropileno foi o mesmo para os dois catalisadores. Os polímeros obtidos com o catalisador suportado in-situ apresentaram menor temperatura de fusão e, em quase todas a condições de polimerização, maior massa molar do que os produzidos em condições homogêneas. O polipropileno produzido com o catalisador $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ apresentou maior temperatura de fusão e maior massa molar em comparação com o polipropileno obtido com $Me_2Si(Ind)_2ZrCl_2$. As micrografias obtidas por SEM mostraram que os polímeros obtidos através da suportação in-situ do catalisador sobre o SMAO apresentam morfologia bem definida, confirmando que a polimerização de fato acorreu sobre a superfície do suporte.

Full Paper

Macromolecular Chemistry and Physics

Summary: Propylene homopolymerizations were carried out using $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, MAO-modified silica, and common alkylaluminum cocatalysts. Supported catalysts were prepared by the in-situ immobilization technique. The effect of the type and concentration of alkylaluminum on propylene polymerization was evaluated using TEA (triethylaluminum), IPRA (isoprenylaluminum), and TIBA (triisobutylaluminum) as cocatalysts. The polymers were analyzed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and scanning electronic microscopy (SEM). The effect of the type and concentration of alkylaluminum on the melting temperature and the molar mass of the polypropylene was the same for both catalysts. The polymers made with in-situ supported catalyst had lower melting points and, in almost all polymerization conditions, higher molar masses than those produced by homogeneous polymerization. Polypropylene samples made with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ had higher melting temperatures and molar masses than those made with $Me_2Si(Ind)_2ZrCl_2$. SEM micrographs showed that the polymers obtained with in-situ supported systems had a well-defined morphology, confirming that the polymerization indeed took place onto the silica support.



SEM micrographs of polypropylene particles obtained with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ in the presence of IPRA.

Polypropylene Made with In-Situ Supported $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ Catalysts: Properties Comparison

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Introduction

The structure of metallocene catalysts, the so-called sandwich compounds, in which a π-bonded metal atom is situated between two aromatic ring systems is known since the 50's.[1,2] Nevertheless, only in the 70's with the discovery and application of methylaluminoxane (MAO) as cocatalyst it was possible to reach high activities with metallocene catalysts for the polymerization of olefins.[3,4] In the 80's, other milestones were reached: chiral bridged metallocene complexes were synthesized[5] and it was shown that suitable titanocene catalysts were able to make partially isotactic polypropylene.[6] The first decisive step concerning the production in large scale of metallocene polypropylene happened in the early 90's when bridged bis-indenyl zirconocenes with substitution in 2-position of the indenyl ligand were developed. For the first time, polypropylene with industrially relevant molar masses, molar mass distributions, tacticities, and comonomer incorporations could be obtained.[7–9]

Homogeneous metallocene catalysts are unsuitable for the production of isotactic polypropylene on an industrial scale, considering the main existing polymerization processes used nowadays, i.e., gas-phase and bulk polymerization conditions. In order to use them as a drop-in technology in the place of conventional Ziegler-Natta catalysts, metallocene catalysts have to be supported on a insoluble particulate substrate. One way to do so is to support them on silica, alumina, magnesium dichloride, or other supports.[10]

We have recently shown that the new metallocene catalyst in-situ immobilization technique on MAO-modified silica used to polymerize ethylene[11,12] could also be employed to obtain polypropylene with the catalyst $Me_2Si(Ind)_2ZrCl_2$.[13,14] In the present investigation, we compare the effect of the type and concentration of alkylaluminum cocatalyst on propylene polymerization using the in-situ immobilization technique with the catalysts $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$. The polymers were characterized by differential thermal calorimetry (DSC), gel permeation chromatography (GPC), and scanning electronic microscopy (SEM).

Experimental Part

Materials

All the experiments were performed under inert atmosphere using Schlenk techniques. The catalysts *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) (Crompton) and *rac*-dimethylsilylenebis(2-methyl-indenyl)-zirconium dichloride ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$) (Boulder Scientific), the support MAO-modified silica (SMAO, 23 wt.-% Al, Crompton), and the cocatalysts MAO (10 wt.-% in toluene, Crompton), triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA) (all from Akzo) were used without purification. Propylene was used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene and hexane were purified by refluxing over sodium followed by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

Polymerization

Polymerizations were done in a 1.5-L stainless steel reactor equipped with a mechanical stirrer, a constant temperature circulator, and inlets for nitrogen and propylene. The reactor was filled with SMAO ($Al_{SMAO}/Zr = 500$ (mol/mol)), 0.75 L of hexane, 10 mL of catalyst solution (10^{-5} mol catalyst in toluene), and alkylaluminum. When the mixture reached 60 °C, the stirring rate was set at 750 rpm and the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The polymer product was filtered, washed with distilled water, washed with ethanol, and dried at 80 °C under vacuum. The mass of dry polymer was measured to determine product yield. Each polymerization reaction was repeated at least twice, and all results presented in this paper are the average of these values. The homogeneous polymerizations were carried out in the same way, but only MAO ($Al_{MAO}/Zr = 500$) was added into the reactor with the catalyst.

Polymer Characterization

Melting temperatures (T_m) were determined using a TA Instruments 2920 differential scanning calorimeter (DSC), according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan are reported here. The heating rate was 10 °C/min in the temperature range from 30 to 200 °C, and the analysis was done under nitrogen atmosphere. Molar mass distributions were determined by high-temperature gel permeation chromatography (GPC) using a 150C Waters instrument equipped with four columns GMHXL-HT (TosoHaas) at 138 °C. 1,2,4-Trichlorobenzene was used as mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. Scanning electronic microscopy (SEM) analyses were performed using a DSM-940 Zeiss instrument operating at 5 kV. Samples were prepared as films sputter-coated with carbon (20-μm thickness). Image magnifications varied from 200 to 500.

Results and Discussion

Table 1 shows the catalytic activity and the average polymer properties for the polymerizations done in this investigation. Data from homogeneous polymerizations with both catalysts using MAO ($Al_{MAO}/Zr = 500$) as cocatalyst were also included for comparison.

As expected, the supported metallocene complexes had lower activities than the corresponding homogeneous metallocene catalysts. The reasons for this poor catalytic activity might be (1) significant steric hindrance around the active site due to the large support surface, and (2) deactivation of catalytic sites or inefficient production of active sites during the supporting process.[11]

In homogeneous polymerization conditions, the catalyst $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ showed activity almost 8 times higher than the catalyst $Me_2Si(Ind)_2ZrCl_2$. Contrarily, both catalysts had similar activities when the in-situ supporting technique was used.

The catalysts had maximum activity with IPRA, at an Al/Zr molar ratio of 100. Nevertheless, when the concentration of IPRA increased, the catalytic activity decreased substantially. Similar behavior was observed with TEA and the system $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO, i.e., increasing the alkylaluminum amount in the reaction medium caused the activity to drop swiftly. On the other hand, for polymerizations carried out with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO in the presence of TIBA, and with $Me_2Si(Ind)_2ZrCl_2$/SMAO in the presence of TIBA or TEA, the catalytic activity was practically the same for all Al/Zr ratios

Table 1. Catalytic activity of the systems $Me_2Si(Ind)_2ZrCl_2$/SMAO and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO in the presence of TEA, TIBA or IPRA and properties of the polymers obtained with homogeneous and in-situ polymerization.

Alkylaluminum		Activity	T_m	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Type	Concentration mol/mol[a]	kg PP/g cat.h	°C	kg/mol	kg/mol	
$Me_2Si(Ind)_2ZrCl_2$						
homogeneous polymerization[b]		4.6	142	16	34	2.1
TEA	100	0.4	141	21	45	2.1
	250	0.3	141	20	42	2.1
	500	0.3	140	16	30	1.9
TIBA	100	0.5	140	26	58	2.2
	250	0.6	141	30	63	2.1
	500	0.2	140	33	68	2.1
IPRA	100	1.4	141	21	45	2.1
	250	0.1	nd	nd	nd	nd
	500	0.2	139	28	61	2.2
$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$						
homogeneous polymerization[b]		38	147	48	93	1.9
TEA	100	1.0	134[c]/145	69	128	1.9
	250	0.1	127[c]/142	33	61	1.9
	500	0.1	134[c]/145	17	50	2.9
TIBA	100	0.3	132[c]/146	56	116	2.1
	250	0.3	137[c]/145	67	131	2.0
	500	0.3	131[c]/146	102	255	2.5
IPRA	100	1.5	135[c]/142	52	123	2.4
	250	0.3	128[c]/143	100	218	2.2
	500	0.2	128[c]/143	155	247	1.6

nd: not determined.

[a] $Al_{alkylaluminum}/Zr$ ratio.

[b] $Al_{MAO}/Zr = 500$ mol/mol. Without external alkylaluminum.

[c] Small shoulder in the melting endotherms of the polymers.

evaluated. It is worth mentioning that both catalysts were not active in the absence of alkylaluminums, as it was also observed for the ethylene polymerization using in-situ supported $Et(Ind)_2ZrCl_2$.[11]

All polymers produced with in-situ supported catalysts showed lower melting temperature (T_m) than the polymers synthesized in homogeneous conditions. As expected, polymers prepared using $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ showed higher T_m, due to the effect of the 2-substitution on the indenyl five-membered ring.[15,16]

As shown in Table 1, all polymers prepared with the system $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO had double melting temperatures. Besides, it is worth to mention that the homogeneous polymer had only one T_m. For comparison, Figure (1) shows the melting endotherms of polymers obtained with both catalysts using TEA as cocatalyst and an Al/Zr molar ratio of 100. One possible reason for the low T_m shoulder in the melting endotherms (peak ranging from 127 to 135 °C) may be the occurrence of regioirregularities during the growth of the polymer chain. According to Brintzinger et al., the irregularities introduced into a polypropylene chain by 1,3- and/or 2,1-misinsertions decrease its melting point considerably, and their frequency seems to depend mainly on the steric demands of the substituents on the C_5 ring.[17] As the polymer synthesized with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ in homogeneous conditions did not show the lowest T_m peak, one might suppose that the support in

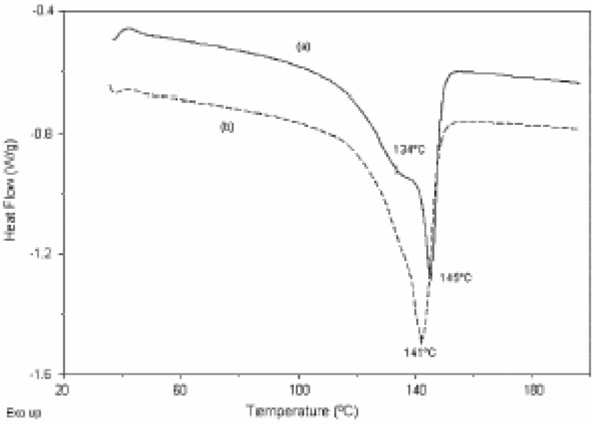

Figure 1. Melting endotherms of polymers produced in the presence of TEA ($Al_{MAO}/Zr = 100$) with (a) $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ and (b) $Me_2Si(Ind)_2ZrCl_2$.

the heterogeneous polymerizations might play the role of a bulky ligand that, together with the 2-methyl substituent, would facilitate monomer misinsertions.

According to the GPC results, the polymers obtained via in-situ immobilization of both catalysts in the presence of an alkylaluminum showed higher molar mass than the polymers prepared in homogeneous polymerizations. The only exceptions were the polymers produced using TEA as cocatalyst with $Al_{alkylaluminum}/Zr \geq 250$ mol/mol. As also expected, the catalyst with 2-methyl substituent on the C_5 ring produced polymers with higher molar mass than the catalyst without substituents on the indenyl ring.[15–18]

The effect of the type of alkylaluminum cocatalyst on the molar mass of the polymer was similar for both catalysts: with the bulkier alkylaluminums TIBA and IPRA, the molar mass increased as the amount of cocatalyst increased; on the other hand, it decreased with increasing amounts of TEA. With $Me_2Si(Ind)_2ZrCl_2$, polymer with the highest molar mass was produced using TIBA, while the same was observed when $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ was combined with IPRA. In both cases, the lowest molar mass was obtained when the cocatalyst was TEA. Similar results were already mentioned in the literature.[19,20] It seems that alkylaluminums having bulkier ligands may reduce the occurrence of terminations by chain transfer to cocatalyst, resulting in polymer with higher molar mass.[21]

The morphology of the polymers was evaluated by SEM. For example, Figure (2) shows the micrographs of the polymers prepared with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$. It is apparent that the polymer particles obtained with the in-situ supported metallocene catalyst (Figure (2c) and (2d)) have spherical shapes, resembling that of the support (replication phenomenon). On the other hand, the polymer prepared in homogeneous conditions (Figure (2a) and (2b)) has no well-defined morphology. Similar results were also described in the literature for polyethylenes prepared with in-situ supported catalysts.[11,22] Thus, as we have already discussed in a previous study,[13] SEM micrographs confirm

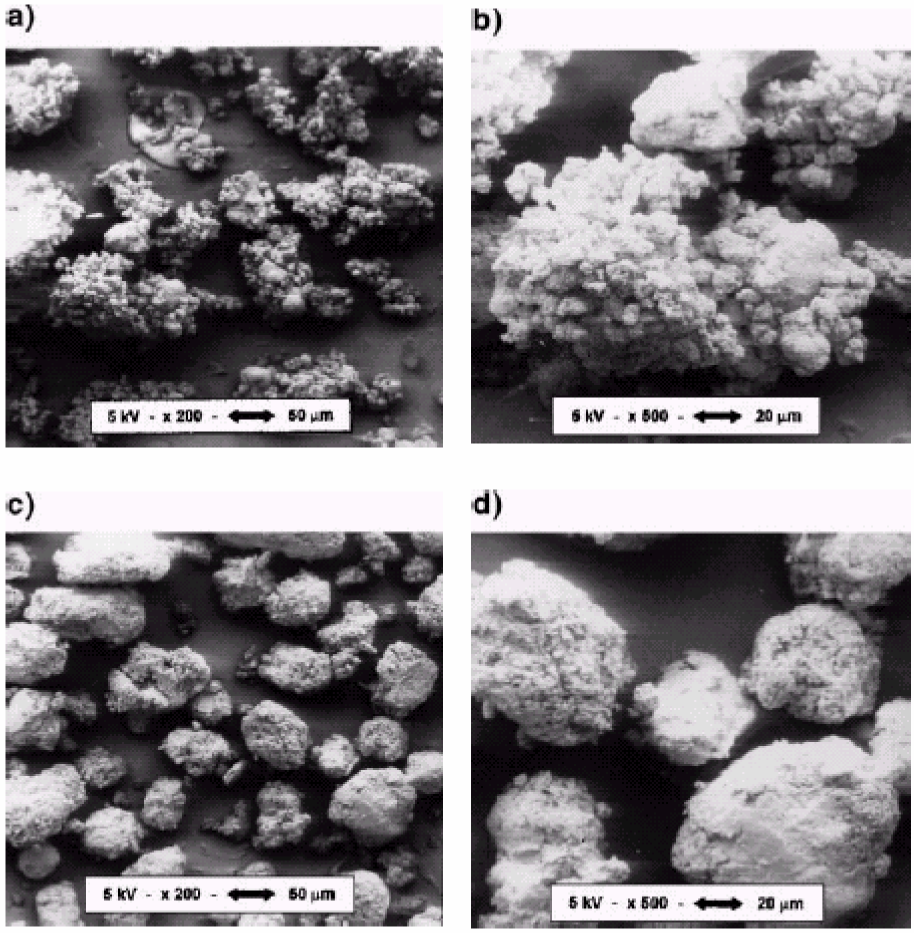

Figure 2. SEM micrographs of polymer particles obtained with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$: (a) homogeneous (×200), (b) homogeneous (×500), (c) in the presence of IPRA with $Al_{IPRA}/Zr = 100$ (×200), (d) in the presence of IPRA with $Al_{IPRA}/Zr = 100$ (×500).

that the polymerization took place effectively on the support and that the catalyst was immobilized onto the surface of SMAO during the in-situ supporting procedure. Metallocene catalyst leaching does not seem to be a problem with this supporting technique.

Conclusions

Both catalysts investigated, $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, had lower activities when in-situ immobilized than in homogeneous polymerizations. The highest activities were observed when IPRA was used as a cocatalyst, especially in low Al_{IPRA}/Zr molar ratios (100 mol/mol). Interestingly, their activities were similar when supported, even though $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ has a higher activity in homogeneous polymerizations.

Polypropylenes prepared with in-situ supported metallocene catalysts had lower melting temperatures and higher molar masses (except when TEA was used with $Al_{TEA}/Zr \geq 250$ mol/mol) than the polymers made with the equivalent homogeneous catalyst.

The system $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO produced polypropylene with the highest molar mass. The effect of the alkylaluminum used as cocatalyst on the molar mass was the same for both catalysts: increasing amounts of TEA decreases the molar mass but the opposite effect was observed with TIBA and IPRA. In this case, the molar mass increased as the concentration of alkylaluminum increased. We speculate that this is related to the presence of bulkier ligands in IPRA and TIBA.

Polymers prepared with $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ had higher melting temperatures than the ones made with $Me_2Si(Ind)_2ZrCl_2$. Surprisingly, all polypropylenes synthesized with in-situ immobilized $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO showed a shoulder in the DSC melting endotherms ranging from 127 to 135 °C. We propose that these lower melting temperatures might be related to regioirregularities, i.e., 1,3- and/or 2,1-misinsertions of the comonomer during the chain growing. Since neither the polypropylene prepared with homogeneous $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, nor the polypropylene made with $Me_2Si(Ind)_2ZrCl_2$ (both homogeneous and supported) showed double melting temperatures, one might suppose that the presence of the methyl substituent on the C_5 ring as well as the presence of the support in the neighborhood of the active sites might favor monomer misinsertions.

SEM micrographs showed that the polymer particles obtained with in-situ supported metallocene complexes had spherical shape and replicated the shape of the support. This result confirms that the polymerization took place onto the surface of SMAO under negligible catalyst leaching.

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5.3. ARTIGO 3:

Effects of the type and concentration of alkylaluminum cocatalysts on the molar mass of polypropylene made with in situ supported metallocene catalysts
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Foram realizadas homopolimerizações de propeno com o catalisador $Me_2(Ind)_2ZrCl_2$ suportado in-situ sobre SMAO utilizando TEA, TIBA ou IPRA como cocatalisador. O efeito do teor e do tipo de alquilalumínio foi avaliado variando a relação $Al_{alquilalumínio}/Zr$ entre 40 e 1000 mol/mol. A massa molar do polipropileno obtido variou de acordo com a natureza do alquilalumínio na seguinte ordem: TIBA > IPRA > TEA > sem alquilalumínio (homogênea). Os polímeros obtidos com o sistema catalítico suportado in-situ apresentaram menor cristalinidade e ponto de fusão que o obtido com o sistema homogêneo. A isotaticidade do polipropileno não foi influenciada pelas condições de polimerização empregadas. De acordo com a deconvolução das curvas de GPC, os catalisadores suportados in-situ apresentaram maior número de sítios ativos distintos do que o catalisador homogêneo, confirmando que o catalisador estava de fato imobilizado sobre o suporte. A massa molar do polímero produzido em cada tipo de sítio ativo diminuiu com o aumento da relação Al/Zr até 250 mol/mol, sendo observada uma relação linear entre o inverso da massa molar ($1/M_n$) e a concentração de cocatalisador. Acima desta razão molar, esta correlação não foi mais válida.

Effects of the Type and Concentration of Alkylaluminum Cocatalysts on the Molar Mass of Polypropylene Made with *In Situ* Supported Metallocene Catalysts

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ABSTRACT: Propylene homopolymerizations were carried out with *rac*-dimethylsilylenebis(indenyl)zirconium dichloride, methylaluminoxane-modified silica, and common alkylaluminum cocatalysts. Supported catalysts were prepared by the *in situ* immobilization technique. The effects of the type and concentration (Al/Zr = 40–1000) of alkylaluminum on the propylene polymerization were evaluated with triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA) as cocatalysts. The polymers were analyzed by gel permeation chromatography, differential scanning calorimetry, and ^{13}C-NMR. The polypropylene molar mass varied according to the nature of the alkylaluminum in the following order: TIBA > IPRA > TEA > no alkylaluminum. The polymers made with an *in situ* supported catalyst had lower crystallinities and melting points than the ones produced by homogeneous polymerization. The isotacticity was not affected by the polymerization conditions examined in this investigation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1050–1055, 2005

Key words: catalysts; molecular weight distribution/molar mass distribution; poly(propylene) (PP)

INTRODUCTION

The advantages of using metallocene catalysts are well known and fully reported in the scientific literature.[1–4] These unique catalysts have the ability to produce polymers with narrow molar mass distributions and uniform comonomer incorporation. Therefore, polymers and copolymers produced by metallocenes can have significantly lower contents of low-molar-mass, waxlike fractions, providing excellent organoleptic properties. Besides, the molar masses, terminal groups, stereochemistry, and short-chain and long-chain branching can be controlled as functions of the metallocene structure.[5]

Although metallocene catalysts have higher activity under homogeneous polymerization conditions, they need to be heterogenized to be adapted to most existing polymerization processes.[6] There are four main methods of heterogeneization:[7]

1. Impregnation of the metallocene onto the support surface, which effectively means physisorption or chemisorption of the metallocene.
2. Adsorption of the metallocene/methylaluminoxane (MAO) adduct onto the support surface.
3. Initial impregnation of MAO onto the support followed by adsorption and simultaneous activation of the metallocene.
4. Covalent bonding of the metallocene by its ligand environment to the support, followed by activation of the metallocene with external MAO.

All these procedures have advantages and disadvantages and may lead to catalysts that produce polymers with different properties. Nevertheless, all the proposed routes are time-demanding, involving reaction and washing steps.[8] To overcome these problems, an alternative methodology (*in situ* immobilization) has been proposed and used to evaluate ethylene homopolymerization and copolymerization.[9–14] This approach consists of simultaneously adding the sup-

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port [commercial methylaluminoxane-treated silica (SMAO)], the catalyst solution, and the cocatalyst (alkylaluminum) directly into the polymerization reactor, without the need of either external MAO or precontact among the species before polymerization. More recently, the *in situ* immobilization procedure has also been used in ethylene homopolymerization[15] and copolymerization[16] with a newly synthesized pentamethylene-bridged dinuclear zirconocene catalyst. Once again, the polymers had good morphology and replicated the morphology of the support.

In our previous publication, we showed that *rac*-dimethylsilylenebis(indenyl)zirconium dichloride [$Me_2Si(Ind)_2ZrCl_2$] prepared by *in situ* immobilization on SMAO polymerized propylene in the presence of common alkylaluminums such as triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA). The polymers obtained with the *in situ* supported catalyst had lower values of the melting temperature (T_m), crystallization temperature, and crystallinity (χ) than those made with the homogeneous catalyst. On the other hand, polymers produced with the *in situ* supported systems had higher molar masses than those synthesized with the homogeneous catalyst at the same Al/Zr ratio. The tacticity did not vary with the catalytic system, and this showed that the stereoselectivity of the catalyst was not affected by the support. Scanning electron micrographs showed that the polymers obtained with *in situ* and conventionally supported systems had a well-defined morphology, unlike the polymers made with the homogeneous system, and this confirmed that there was no significant extraction of the catalyst from the silica support during the polymerization of propylene. Moreover, the concentration of the catalyst used was below the saturation level (2.0 wt % Zr/SMAO), and this indicated that all or almost all of the catalyst present in the solution was adsorbed onto the support.[17]

In this investigation, we evaluated the effect of the type and concentration of the alkylaluminum cocatalyst on propylene polymerization with *in situ* supported $Me_2Si(Ind)_2ZrCl_2$. The polymer products were characterized with differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). To estimate the number of active site types present in the catalytic system and to evaluate the alkylaluminum effect on the polymer generated by each active center type, we deconvoluted GPC curves into Flory's most probable distributions.

EXPERIMENTAL

Materials

All the experiments were performed under an inert atmosphere with Schlenk techniques. The catalyst $Me_2Si(Ind)_2ZrCl_2$ (Witco, Bergkamen, Germany), MAO-modified silica (SMAO, 23 wt % Al; Witco, Bergkamen, Germany), and TEA, IPRA, and TIBA (all from Akzo, Chicago, IL) were used without purification. Propylene was used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene (Merck, São Paulo, Brazil) and hexane were purified via refluxing over sodium and distillation. Hexane (Conoco Phillips, Borger, TX) was degassed with bubbling nitrogen before each reaction.

Polymerizations

The polymerizations were performed in a 1.5-L stainless reactor equipped with a mechanical stirrer, a constant-temperature circulator, and inlets for nitrogen and propylene. The reactor was filled with SMAO (Al/Zr = 500 mol/mol), 0.75 L of hexane, 10 mL of a catalyst solution (10^{-5} mol of the catalyst in toluene), and alkylaluminum. When the mixture reached 60°C, the stirring rate was set at 750 rpm, and the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The polymer product was filtered, washed with distilled water, washed with ethanol, and dried at 80°C *in vacuo*. The mass of the dry polymer was measured to determine the product yield. Each polymerization reaction was repeated at least twice, and all the results presented in this article are the averages of these values.

Polymer characterization

χ and T_m were determined with a TA Instruments 2920 (New Castle, DE) differential scanning calorimeter according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan were reported here. The heating rate was 10°C/min from 30 to 220°C, and the analysis was performed under a nitrogen atmosphere. The molar mass distribution was determined by high-temperature GPC with a Waters model 150C instrument (Milford, MA) equipped with four GMHXL-HT columns (TosoHaas, Tokyo, Japan) at 138°C. 1,2,4-Trichlorobenzene was used as the mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. The deconvolution of the polymer molar mass distribution was performed with an Excel spreadsheet.

The polymer microstructure was determined by ^{13}C-NMR. The spectra were obtained at 135°C in a Varian Inova 300 (Palo Alto, CA) operating at 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in 5-mm sample tubes. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s.

RESULTS AND DISCUSSION

The catalytic activities and average polypropylene properties are shown in Table I. For comparison,

TABLE I
Catalytic Activity of the $Me_2Si(Ind)_2ZrCl_2$/SMAO System in the Presence of TEA, TIBA, or IPRA and the Properties of the Polypropylenes Obtained with Homogeneous and *in situ* Polymerization

Alkylaluminum							
Type	Concentration (mol/mol)[a]	Activity (kg of PP/g of catalyst h)	T_m (°C)	χ (%)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
Homogeneous polymerization[b]		4.6	142	53	16	34	2.1
TEA	70	0.3	142	41	22	45	2.1
	250	0.4	141	27	20	42	2.1
	500	0.3	140	25	16	30	1.9
	1000	0.1	140	18	14	26	1.8
TIBA	40	0.4	140	31	24	58	2.4
	70	0.5	139	42	24	53	2.2
	130	0.4	140	35	28	62	2.2
	250	0.6	141	33	30	63	2.1
	500	0.2	140	26	33	68	2.1
	1000	0.2	141	29	34	69	2.0
IPRA	130	0.8	141	44	22	47	2.2
	500	0.2	139	36	28	61	2.2

[a] $Al_{alkylaluminum}/Zr$ ratio.
[b] $Al_{MAO}/Zr = 500$ mol/mol, without external alkylaluminum.

data from a homogeneous polymerization with MAO as the cocatalyst were included. As previously reported,[9,10] all reactions performed via *in situ* immobilization were less active than the homogeneous polymerization.

Alkylaluminum cocatalysts have been thought to act as scavengers, alkylating agents, and cocatalyst activators with *in situ* supported metallocenes.[9] The activity of $Me_2Si(Ind)_2ZrCl_2$/SMAO was practically independent of the type of alkylaluminum used in the polymerization (Table I), but the catalyst system had maximum activity with IPRA at an Al/Zr ratio of 130. For all systems (TEA, TIBA, and IPRA), the activity decreased as the cocatalyst concentration increased.

According to the DSC results, the polymers obtained via *in situ* immobilization of the catalyst in the presence of an alkylaluminum showed lower T_m and χ values than the polymer produced in the homogeneous polymerization. It seems that the heterogeneous nature of the surface species generated in the case of the *in situ* supported $Me_2Si(Ind)_2ZrCl_2$ might have led to a reduction in χ of the resulting polypropylene.

The tacticity of some samples, including the polymer obtained in the homogeneous polymerization, was calculated with ^{13}C-NMR. All of them were highly isotactic ($m = 92.7$–94.0%), and this indicated that the stereoregularity was influenced neither by the type of the cocatalyst nor by the immobilization procedure.

Except for the polymers produced with $Al/Zr \geq 500$ mol/mol with TEA, all the others had higher molar masses than that of polypropylene produced with the homogeneous catalyst. This behavior is typical of supported zirconocenes and has been attributed to the blocking of the polymerization active sites by the support, which probably reduces β-elimination transfer reactions.[18]

The molar mass was influenced by the concentration and type of alkylaluminum. The molar mass decreased with increasing amounts of TEA. On the other hand, it increased with increasing amounts of TIBA or IPRA. This result clearly indicated that chain transfer to alkylaluminum was more relevant with TEA than with TIBA and IPRA, probably because of the intrinsic steric effects played by the two latter alkylaluminum cocatalysts.

For the same concentration of alkylaluminum, the polymer molar mass decreased in the following order: TIBA > IPRA > TEA. Similar results were obtained for polyethylenes produced with *in situ* supported rac-ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$.)[14] Alkylaluminums with bulkier ligands, such as TIBA and IPRA, may reduce the occurrence of terminations by chain transfer to cocatalyst, leading to polymers with higher molar masses.[19] These results support the idea that the alkylaluminum not only acts as a scavenger but also has some influence on the formation of active centers.

The influence of alkylaluminums used as cocatalysts on the molar mass of polypropylene has already been reported in the literature for homogeneous and heterogeneous polymerizations. For propylene homopolymerizations and 1-hexene copolymerizations with $Et(Ind)_2ZrCl_2$ with TIBA/MAO mixtures, the molar mass of the polymers increased with the addition of TIBA, without any change in the isotacticity or in the concentration of the comonomer incorporated.[20] The molar mass of the polypropylene prepared with $Et(Ind)_2ZrCl_2$ or $Me_2Si(Ind)_2ZrCl_2$ in the presence of $TEA/Ph_3CB(C_6F_5)_4$ decreased when the amount of TEA increased. However, when $TIBA/Ph_3CB(C_6F_5)_4$ was used as cocatalyst, the molar mass did not change. Moreover, comparing the polymers obtained with

TABLE II
GPC Deconvolution Curves of M_n and the Fraction of the Polymer Generated by Each Active Center Type with TEA, TIBA, or IPRA as the Cocatalyst

Alkylaluminum		Peak/active center I		Peak/active center II		Peak/active center III	
Type	Concentration (mol/mol)[a]	M_n (kg/mol)	Fraction (%)	M_n (kg/mol)	Fraction (%)	M_n (kg/mol)	Fraction (%)
Homogeneous polymerization[b]		8.1	23	19	77	—	—
TEA	70	8.6	16	23	78	57	6
	250	7.4	18	21	69	41	13
	500	9.7	44	20	56	—	—
	1000	9.7	74	22	26	—	—
TIBA	40	10	22	26	57	54	21
	70	9.6	19	23	52	42	29
	130	7.7	7	21	37	40	56
	250	5.7	4	18	29	38	67
	500	9.8	11	32	63	47	26
	1000	11	8	33	84	70	8
IPRA	130	11	26	23	63	59	11
	500	9.8	16	30	76	79	8

[a] $Al_{alkylaluminum}/Zr$ ratio.
[b] Al_{MAO}/Zr = 500 mol/mol, without external alkylaluminum.

both catalysts, we found that the ones prepared in the presence of TIBA/$Ph_3CB(C_6F_5)_4$ had a molar mass higher than or equal to that of polymers prepared with TEA/$Ph_3CB(C_6F_5)_4$.[21] Polypropylenes obtained with the heterogeneous system rac-ethylenebis(tetrahydroindenyl)zirconium dichloride ($Et(IndH_4)_2ZrCl_2$)/MAO/SiO_2 in the presence of TMA, TEA, or TIBA had higher molar masses than those synthesized in the absence of alkylaluminum. The molar mass of the polymers decreased according to the following order: TIBA > TEA ≥ TMA.[22]

The polydispersity index of the polymers made in the presence of TEA or TIBA decreased when the concentration of the alkylaluminum increased. With IPRA, this effect was not observed, but it should be taken into account that only two Al/Zr ratios were examined with this cocatalyst.

To estimate the number of active centers present in the catalytic system and to evaluate the alkylaluminum effect on the polymer generated by each active center type, we deconvoluted the GPC curves into Flory's most probable distributions.[23,24] The results are shown in Table II. Catalyst–surface interactions might have led to the formation of sites of different types. Although the GPC curves of polymers produced with the homogeneous (unsupported) catalyst were deconvoluted into two peaks (indicating the presence of two active center types), the GPC curves of almost all the polymers prepared via *in situ* immobilization required three peaks. The only exceptions were the polymers produced with Al/Zr ratios of 500 and 1000 mol/mol of TEA, for which the best fit was obtained with only two peaks. Figures 1 and 2 show examples of GPC curves and their respective deconvolutions into Flory's most probable distributions.

The polymer molar mass assigned to each active center type decreased with increasing Al/Zr ratio until a value of 250 mol/mol was reached. When this

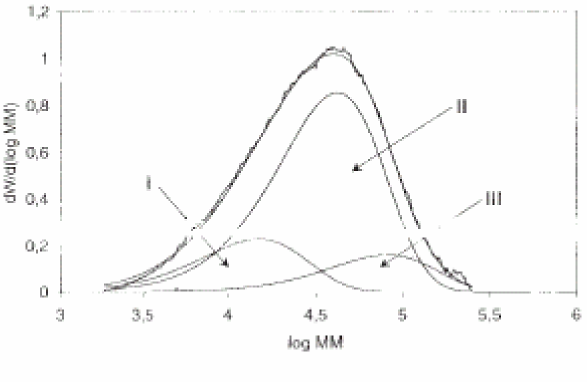

Figure 1 Molar mass distribution deconvolution of the polymer prepared with 250 mol/mol of TEA as a cocatalyst.

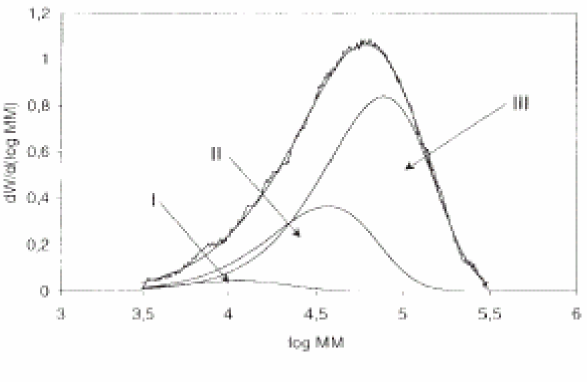

Figure 2 Molar mass distribution deconvolution of the polymer prepared with 250 mol/mol of TIBA as a cocatalyst.

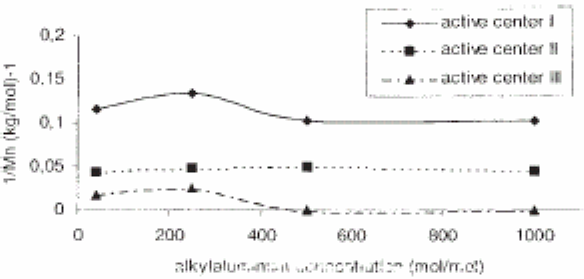

Figure 3 Effect of the TEA concentration on $1/M_n$ of the polymer formed by each active center type.

ratio was further increased, the molar mass per active site type started increasing (Table II).

Comparing the polymerizations carried out with TEA or TIBA at the same concentration of alkylaluminum, we found that the amount of polymer generated by active center I with TEA was higher than that with TIBA. On the other hand, the amount of polymer formed by active center III was higher when TIBA was used. This suggested that TEA might have caused a selective deactivation of active center III that was responsible for the highest molar mass population.

The reciprocal of the number-average molar mass ($1/M_n$) of the polymer chains made on each active center may be related to the τ parameter, the ratio of the chain transfer rates to the chain propagation rate:[25–27]

$$\frac{1}{M_n} = \tau = \frac{k_m}{k_p} + \frac{k_\beta}{k_p\,[\mathrm{M}]} + \frac{k_{\mathrm{Al}}\,[\mathrm{Al}]}{k_p\,[\mathrm{M}]} + \frac{k_{\mathrm{H_2}}\,[\mathrm{H_2}]}{k_p\,[\mathrm{M}]} \qquad (1)$$

where k_m is the rate constant of chain transfer to the monomer, k_β is the β-hydride elimination rate constant, k_{Al} is the rate constant of chain transfer to alkylaluminum, k_{H2} is the rate constant of chain transfer to hydrogen, k_p is the chain propagation rate constant, [M] is the monomer concentration, [Al] is the alkylaluminum concentration, and [H_2] is the hydrogen concentration.

As in all polymerizations carried out in this investigation, the monomer concentration was kept constant, and hydrogen was not used, we could assume that eq. (1) could be simplified to

$$\frac{1}{M_n} = k' + \frac{k_{\mathrm{Al}}\,[\mathrm{Al}]}{k_p\,[\mathrm{M}]} = k' + k''\,[\mathrm{Al}] \qquad (2)$$

This simplification assumed that k_p was independent of the alkylaluminum concentration. This assumption could not be proved with the data presented in this work and could, at least partially, explain the deviations observed between the mathematical model and the experimental data discussed later.

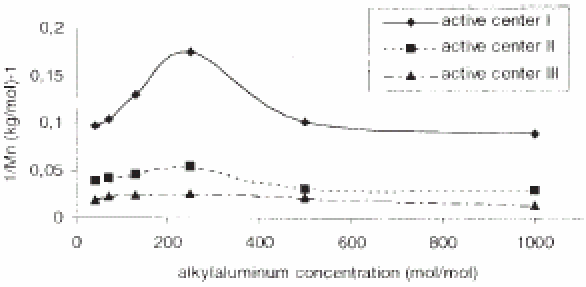

Figure 4 Effect of the TIBA concentration on $1/M_n$ of the polymer formed by each active center type.

Figures 3 and 4 show the effects of the concentration of TEA or TIBA on the reciprocal of M_n for polymers made by each active center type; they are based on the molar mass deconvolution results.

The same behavior was observed for both alkylaluminums: up to approximately Al/Zr = 250 mol/mol, $1/M_n$ increased as the TEA or TIBA concentration increased, according to the predictions of eq. (2). However, for higher amounts of alkylaluminum, $1/M_n$ decreased with increasing Al/Zr ratios. These results indicated that eq. (2) was valid only when low concentrations of the alkylaluminum were used (0–250 mol/mol), not being valid for higher concentrations.

A simple empirical correlation could be derived for the dependence of M_n on the Al/Zr ratio when the molar mass of the whole polymer was considered (Table III).

Figure 5 shows that there was a linear relationship between $1/M_n$ of the total polymer and the TEA concentration:

$$\frac{1}{M_n} = k_1 + k_2\,[\mathrm{TEA}] \qquad (3)$$

On the other hand, $1/M_n$ was proportional to the reciprocal of the square root of the TIBA concentration, as shown in Figure 6 and quantified here:

TABLE III
Effect of the Alkylaluminum Concentration on the Reciprocal of M_n of the Total Polymer Prepared with TEA or TIBA as the Cocatalyst

	Alkylaluminum	
Type	Concentration (mol/mol)[a]	$1/M_n$ (kg/mol)$^{-1}$
TEA	70	0.045
	250	0.050
	500	0.063
	1000	0.071
TIBA	40	0.042
	70	0.042
	130	0.036
	250	0.033
	500	0.030
	1000	0.029

[a] $\mathrm{Al_{alkylaluminum}}/\mathrm{Zr}$ ratio.

$$\frac{1}{M_n} = k_3 + \frac{k_4}{\sqrt{[\mathrm{TIBA}]}} \qquad (4)$$

CONCLUSIONS

Polypropylene prepared with *in situ* supported $Me_2Si(Ind)_2ZrCl_2$ through the direct contact of the catalyst with SMAO in the presence of TEA, TIBA, or IPRA had, in comparison with the polymer obtained with a homogeneous catalyst at an Al_{MAO}/Zr ratio of 500, lower χ and T_m values, similar isotacticities and polydispersity indices, and higher molar masses.

The catalytic activity decreased when the alkylaluminum concentration increased, almost independently of the cocatalyst type. Catalysts with IPRA had slightly higher activities for all the systems studied.

The polymer molar mass was influenced by the type and concentration of the alkylaluminum. When the concentration of TEA increased, the molar mass decreased. On the other hand, with TIBA and IPRA, the molar mass increased as the alkylaluminum concentration increased. For the same alkylaluminum concentration, the polymer prepared with TIBA had the highest molar mass, whereas the one obtained with TEA had the lowest.

Although the difference in the values could be considered small, the polydispersity decreased with increasing amounts of TEA or TIBA. The polydispersity did not change with various amounts of IPRA in the limited range of this investigation.

According to the GPC curve deconvolution, the *in situ* supported catalysts seemed to present a larger number of distinct active centers than the homogeneous one, and this suggested that the catalyst was in fact heterogenized onto the support surface.

The molar mass of the polymer made on each active center type decreased as the Al/Zr ratio increased up to 250 mol/mol. Up to this concentration, there was a linear relationship between the reciprocal of M_n and the alkylaluminum concentration. When the cocatalyst concentration was further increased, this relationship was no longer observed.

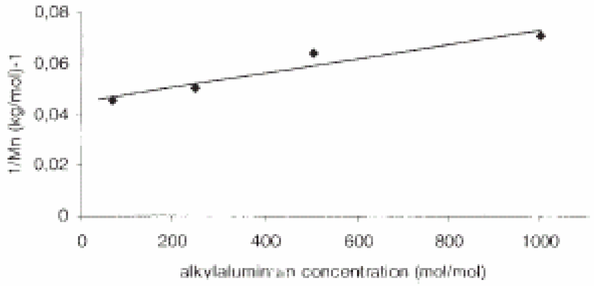

Figure 5 Effect of the TEA concentration on $1/M_n$ of the total polymer.

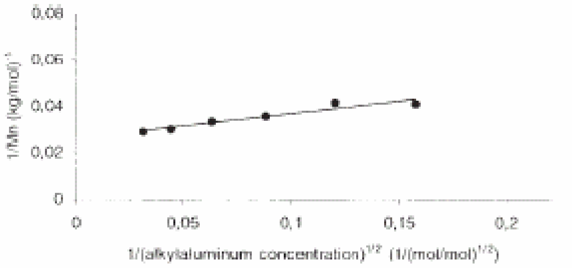

Figure 6 Effect of the TIBA concentration on $1/M_n$ of the total polymer.

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5.4. ARTIGO 4

Ethylene and propylene polymerization using in situ supported $Me_2Si(Ind)_2ZrCl_2$ catalyst: Experimental and theoretical study

Macromolecular Materials and Engineering, **2006**, *291*, 279-287

O catalisador $Me_2(Ind)_2ZrCl_2$ foi imobilizado in-situ sobre SMAO e utilizado em reações de homopolimerização de eteno ou propeno na presença de TEA ou TIBA como cocatalisador. O sistema catalítico $Me_2(Ind)_2ZrCl_2$/SMAO exibiu diferente comportamento dependendo da quantidade e da natureza do alquilalumínio empregado e do monômero. A atividade catalítica foi aproximadamente 0,4 kg polímero/g cat h com os dois cocatalisadores na polimerização de propeno. Atividades similares foram observadas na polimerização de eteno em presença de TIBA. Quando eteno foi polimerizado utilizando TEA em razão molar Al/Zr de 250, a atividade foi 10 vezes maior. Os polietilenos obtidos apresentaram praticamente a mesma temperatura de fusão. Por outro lado, os polipropilenos produzidos com o catalisador suportado in-situ apresentaram temperatura de fusão levemente superiores a do polipropileno obtido em condições homogêneas. A natureza e a quantidade de alquilalumínio presente no meio reacional influenciaram a massa molar dos polímeros produzidos. A massa molar do polipropileno foi maior quando TIBA foi utilizado como cocatalisador. Comportamento oposto foi verificado para os polietilenos. Em relação à concentração de alquilalumínio, a massa molar diminuiu com o aumento da quantidade de TEA. Na presença de TIBA, a massa molar dos polietilenos foi praticamente a mesma, independente do teor de alquilalumínio adicionado, e a massa molar dos polipropilenos aumentou com o aumento da quantidade de cocatalisador. A deconvolução das curvas de GPC mostrou a presença de dois picos para os sistemas homogêneos e três picos para os sistemas heterogêneos suportados in-situ. A única exceção foi observada quando TEA foi empregado em razão molar de 500, onde também foram obtidos dois picos. Baseado nos resultados das deconvoluções das curvas de GPC e de modelagem teórica foi possível apresentar propostas para a estrutura dos sítios ativos nos sistemas catalíticos homogêneos e heterogêneos.

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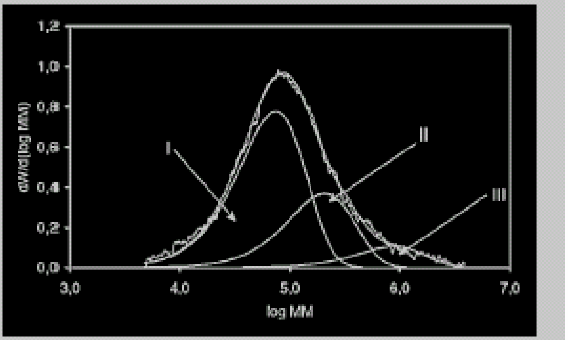
Summary: $Me_2Si(Ind)_2ZrCl_2$ was in situ immobilized onto SMAO and used for ethylene and propylene polymerization in the presence of TEA or TIBA as cocatalyst. The catalytic system $Me_2Si(Ind)_2ZrCl_2$/SMAO exhibited different behavior depending on the amount and nature of the alkylaluminum employed and on the monomer type. The catalyst activity was nearly 0.4 kg polymer · g cat^{-1} · h^{-1} with both cocatalysts for propylene polymerization. Similar activities were observed for ethylene polymerization in the presence of TIBA. When ethylene was polymerized using TEA at an Al/Zr molar ratio of 250, the activity was 10 times higher. Polyethylenes made by in situ supported or homogeneous catalyst systems had practically the same melting point (T_m). On the other hand, poly(propylenes) made using in situ supported catalyst systems had a slightly lower T_m than poly(propylenes) made using homogeneous catalyst systems. The nature and amount of the alkylaluminum also influenced the molar mass. The poly(propylene) molar mass was higher when TIBA was the cocatalyst. The opposite behavior was observed for the polyethylenes. Concerning the alkylaluminum concentration, the molar mass of the polymers decreased as the amount of TEA increased. In the presence of TIBA, the polyethylene's molar mass was almost the same, independent of the alkylaluminum concentration, and the poly(propylene) molar mass increased with increasing amounts of cocatalyst. The deconvolution of the GPC curves showed 2 peaks for the homogeneous system and 3 peaks for the heterogeneous in situ supported system. The only exception was observed when TEA was used at an Al/Zr molar ratio of 500, where the best fit was obtained with 2 peaks. Based on the GPC deconvolution results and on the theoretical modeling, a proposal for the active site structure was made.



Molar mass distribution deconvolution of polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

Ethylene and Propylene Polymerization Using In Situ Supported $Me_2Si(Ind)_2ZrCl_2$ Catalyst: Experimental and Theoretical Study

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Introduction

In situ immobilization of metallocenes is a simple procedure for a catalyst supported directly in the polymerization reactor. A homogeneous metallocene catalyst solution, a MAO-modified silica support (SMAO) and an alkylaluminum are simultaneously added to the reactor, followed by monomer addition. No other preparation steps are involved and no pre-contacting of catalyst, cocatalyst and support is required. This procedure was first described some years ago, and has been used in ethylene homopolymerization and copolymerization with the catalysts

Cp_2ZrCl_2, Cp_2HfCl_2, $Et(Ind)_2ZrCl_2$, $Et(Ind)_2ZrMe_2$, $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$ (CGC catalyst from Dow) and $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, a bridged binuclear catalyst.[1–8]

In our previous publications we have shown that in situ supported metallocenes can also be used to polymerize propylene with $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, with common alkylaluminum as cocatalysts, and SMAO as the support. The maximum catalyst load onto the support, the influence of the nature and concentration of the alkylaluminum on the catalyst activity and on the polymer properties, the polymer morphology and an investigation of the number and types of active sites present on the catalyst based on the deconvolution of the molar mass distribution curves measured by gel permeation chromatography (GPC) have been described.[9–11]

In the present investigation, we compare the behavior of $Me_2Si(Ind)_2ZrCl_2$/SMAO (in situ immobilized) for the polymerization of ethylene and propylene in the presence of TEA or TIBA as cocatalyst. The catalyst activity and the polymer properties were correlated to the type and amount of alkylaluminum present in the reactor. Based on deconvolution results of the GPC curves, possible structures for the active sites were proposed using theoretical modeling.

Experimental Part

Materials

All the experiments were performed under an inert atmosphere using Schlenk techniques. The catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) (Crompton), the support MAO-modified silica (SMAO, 23 wt.-% Al, Crompton) and the cocatalysts MAO (10 wt.-% in toluene, Crompton), triethylaluminum (TEA) and triisobutylaluminum (TIBA) (both from Akzo) were used without purification. Ethylene and propylene were used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene and hexane were purified through refluxing over sodium followed by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

Polymerization

Polymerizations were done in a 1.5 L stainless steel reactor equipped with a mechanical stirrer, an electrical temperature controller and inlets for nitrogen and ethylene or propylene. The reactor was filled with SMAO ($Al_{SMAO}/Zr = 500$ mol/mol), 0.75 L of hexane, 10 mL of catalyst solution (10^{-5} mol catalyst in toluene) and alkylaluminum. When the mixture reached 60 °C, the stirring rate was set at 750 rpm and the reactor was pressurized with ethylene or propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The polymer product was filtered, washed with distilled water and ethanol and dried at 80 °C under a vacuum. The mass of dry polymer was measured to determine product yield. Each polymerization was repeated at least twice. All results discussed in this paper are the average of these duplicate runs. The homogeneous polymerizations were carried out in the same way, but only MAO ($Al_{MAO}/Zr = 500$ mol/mol) was added to the reactor with the catalyst.

Polymer Characterization

Melting temperatures (T_m) were determined using a TA Instruments 2920 differential scanning calorimeter (DSC), according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan are reported here. The heating rate was $10\,°C \cdot min^{-1}$ in the temperature range 30–200 °C under a nitrogen atmosphere. Molar mass distributions were determined by high temperature gel permeation chromatography (GPC) using a 150C Waters instrument equipped with four GMHXL-HT (TosoHaas) columns at 138 °C. 1,2,4-Trichlorobenzene was used as the mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. The deconvolution of the polymer molar mass distribution was performed using an Excel spreadsheet. To obtain the best fit between the measured GPC curve and the fitted GPC curve (sum of the deconvoluted curves), Excel's Solver routine was used to minimize the sum of the squares of the differences between the measured and the fitted GPC curves ($\Sigma\Delta^2$). For each GPC curve, the deconvolution process was carried out considering 1, 2, 3 or 4 curves or peaks. In all results presented in this work the parameter $\Sigma\Delta^2$ had the lowest possible value, without overlapping of curves or peaks.[12]

Theoretical Method

The MM2 calculations to obtain the steric energies were done using the MOPAC section of Chem3D from Cambridge Soft, version 5, taking into consideration the steric energies for different arrangements of SMAO and the catalyst. Since the main interest was to evaluate steric interactions, the electronic structure was not explicitly considered. The distances Zr-indenyl were fixed considering the published literature dealing with structural facts on zirconocenes. The model of SMAO included 1 Al and 2 Si atoms. The Al atoms were saturated with O and the Si atoms with OH, according to previously published works.[13–18]

The zirconocenes were modeled with all their atoms, considering the structural information available, using the method developed by Ferreira et al.[13]. This approach has produced manuscripts describing zirconocene adsorption on SiO_2,[14] MAO adsorption on SiO_2,[15] zirconocene reaction with MAO or SiO_2[16,17] and the presentation of a new model of active site for olefin polymerization.[18,19]

Results and Discussion

Experimental Data

Table 1 shows the catalytic activity and the average polymer properties for the polymerizations carried out in this investigation. Data from homogeneous polymerizations with both monomers using MAO ($Al_{MAO}/Zr = 500$ mol/mol) as cocatalyst were also included for comparison.

Table 1. Catalytic activity of the system $Me_2Si(Ind)_2ZrCl_2$/SMAO in the presence of TEA or TIBA as cocatalyst, and properties of the polymers obtained with homogeneous and in situ polymerization of ethylene and propylene.

Alkylaluminum		Activity	T_m	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Type	Concentration[a] mol/mol	kg polymer · g cat^{-1} · h^{-1}	°C	kg · mol^{-1}	kg · mol^{-1}	
Polyethylene						
Homogeneous polymerization[b]		5.1	133	67	166	2.5
TEA	70	1.3	132	75	191	2.5
	250	4.0	132	66	154	2.3
	500	3.2	132	65	143	2.2
TIBA	70	0.6	133	53	184	3.5
	250	0.5	132	51	164	3.2
	500	0.3	132	53	185	3.5
Poly(propylene)						
Homogeneous polymerization[b]		4.6	142	16	34	2.1
TEA	70	0.3	142	22	45	2.1
	250	0.4	141	20	42	2.1
	500	0.3	140	16	30	1.9
TIBA	70	0.5	139	24	53	2.2
	250	0.6	141	30	63	2.1
	500	0.2	140	33	68	2.1

[a] $Al_{alkylaluminum}/Zr$ ratio.
[b] $Al_{MAO}/Zr = 500$ mol/mol. Without external alkylaluminum as R_3Al, only MAO.

The supported metallocene complexes had lower activities than the corresponding homogeneous metallocene catalysts, as expected and already observed using the in situ immobilization procedure.[5,6] Among the possible reasons for this poor catalytic activity of the supported systems are the significant steric hindrance around the active site caused by the support surface, the deactivation of catalytic sites and the inefficient production of active sites during the immobilization process,[5] generating nearly 1% of total Zr active species after the catalyst immobilization procedure.[20]

In the range of alkylaluminum concentrations ($Al_{alkylaluminum}/Zr = 70-500$ mol/mol) studied, the catalyst activity was almost the same for propylene polymerization using TEA and TIBA (≈0.4 kg polymer · g cat^{-1} · h^{-1}). Similar results were also observed for ethylene polymerization using TIBA as cocatalyst. On the other hand, in the ethylene polymerizations carried out with $Me_2Si(Ind)_2ZrCl_2$/SMAO in the presence of TEA, the catalyst activity was substantially higher. When a molar ratio of Al_{TEA}/Zr of 250 was used, the catalyst activity was 4.0 kg PE · g cat^{-1} · h^{-1}, almost 80% of the activity observed for the equivalent homogeneous ethylene polymerization.

In the copolymerization of ethylene and 1-hexene with $Et(Ind)_2ZrCl_2$ in situ immobilized onto SMAO, higher activities were observed using TMA as cocatalyst than with TEA or TIBA.[4] It was speculated that this decrease in activity could be linked to the reduction ability of the cocatalysts or to steric hindrance. Due to the increasing bulkiness of the alkylaluminums TEA and TIBA, it is possible that the access to the catalyst molecules on the support is limited, reducing the number of active sites and, as a consequence, reducing the activity of the catalyst.

A similar phenomenon might explain the lower activity of the $Me_2Si(Ind)_2ZrCl_2$/SMAO for the ethylene polymerization using TIBA, since TIBA is bulkier than TEA. On the other hand, catalyst activity for propylene polymerization was independent of alkylaluminum type. Thus, one can speculate that, in the presence of propylene, the difference in molecular sizes between TEA and TIBA is not so relevant.

While the polyethylenes had almost the same melting temperature (T_m), all poly(propylenes) produced with the in situ supported catalyst showed lower T_ms than the polymer synthesized in homogeneous conditions. This may be due to the formation of regioirregularities during the growth of the poly(propylene) chain on the supported catalyst such as 1,3- and/or 2,1-misinsertions.[20] Besides, it demonstrates that the support plays a significant role on propylene insertion.

All polyethylenes had higher molar masses than the poly(propylenes). According to Brintzinger et al., isospecific metallocene catalysts usually polymerize ethylene at rates four to five times faster than those for propylene.[21] This increase in polymerization rate will be reflected in a higher molar mass, provided that the chain transfer rates do not increase at the same rate. The polydispersity of the polyethylenes was higher than that of the poly(propylenes).

In the range of alkylaluminum concentrations evaluated, the effect of the nature of the cocatalyst type on the polydispersity of the polymers was different depending on the monomer. As can be seen in Table 1, the polyethylenes produced with TIBA had higher polydispersities than those obtained using TEA, while all poly(propylenes) had basically the same polydispersity.

The type and the concentration of the alkylaluminum influenced the molar mass of the polymers in different ways. Poly(propylenes) prepared with the in situ supported catalyst had a higher molar mass when TIBA was used. It has been suggested that alkylaluminums having bulkier ligands may have a lower rate of chain transfer to cocatalyst, resulting in polymers with higher molar masses.[22] Nevertheless, polyethylenes had exactly the opposite behavior: resins made with TEA had higher molar masses than those made with TIBA.

The molar mass of poly(propylenes) increased as the concentration of TIBA increased, while in the case of the polyethylenes, the molar mass was essentially independent of the concentration of TIBA in the reactor. Interestingly, the molar masses of polyethylene and poly(propylene) always decreased with increasing concentration of TEA.

In order to estimate the number of active site types present in the catalytic system, the GPC curves were deconvoluted into Flory's most probable distributions,[12,23] and the results are shown in Table 2. Although the polydispersity of the polyethylenes produced in the presence of TEA and with the homogeneous system, as well as of the poly(propylenes), was almost the same, the result of the mathematical deconvolution was not the same for all polymers. The GPC curves of the polymers produced with the homogeneous (unsupported) catalyst were deconvoluted into only two peaks, indicating the presence of two active site types. The GPC curves of almost all polymers prepared via in situ immobilization of the catalyst were best fitted into three peaks, indicating the presence of three kinds of active sites. The only exceptions were the polymers produced with Al/Zr = 500 mol/mol of TEA, in which the best fit was obtained with two peaks. Up to now it is not clear why in the presence of a high amount of TEA (Al/Zr = 500 mol/mol) active sites 3 do not generate polymer, while using TIBA at the same concentration 3 peaks are obtained in the GPC deconvolution, i.e., sites 3 are still active. It should be speculated that under this condition active sites 3 are completely deactivated due to the higher alkylation power of TEA in comparison to TIBA. Besides, as shown in our previous work, it should also be mentioned that in the polymerization of propylene using Al_{TEA}/Zr = 1 000 mol/mol, the best fit was also achieved with only 2 peaks. Nevertheless, with Al_{TIBA}/Zr = 1 000 mol/mol 3 peaks are still obtained in the mathematical deconvolution of the GPC curve.[11] Figure 1 to 6 show examples of GPC deconvolution curves.

All the above results confirm that the alkylaluminum is not just acting as a scavenger. In fact, it should be playing a significant role with the catalyst, affecting the activity of the system and the properties of the polymers.

Theoretical Modeling

Figure 7 shows the proposed structures for the active sites on the homogeneous $Me_2Si(Ind)_2ZrCl_2$/MAO system, following the ideas previously presented by Ferreira

Table 2. GPC curves deconvolution. Molar mass ($\overline{M}_n$) and fraction of the polymer generated by each active site type using TEA or TIBA as cocatalyst.

Alkylaluminum		Peak/active site 1		Peak/active site 2		Peak/active site 3	
Type	Concentration[a)]	$\overline{M}_n$	Fraction	$\overline{M}_n$	Fraction	$\overline{M}_n$	Fraction
	mol/mol	$kg \cdot mol^{-1}$	%	$kg \cdot mol^{-1}$	%	$kg \cdot mol^{-1}$	%
Polyethylene							
Homogeneous polymerization[b)]		57	70	159	30	–	–
TEA	70	46	58	126	33	287	9
	250	41	57	89	30	191	13
	500	42	59	109	41	–	–
TIBA	70	37	57	89	33	360	10
	250	36	55	89	37	370	8
	500	37	62	103	30	445	8
Poly(propylene)							
Homogeneous polymerization[b)]		8.1	23	19	77	–	–
TEA	70	8.6	16	23	78	57	6
	250	7.4	18	21	69	41	13
	500	9.7	44	20	56	–	–
TIBA	70	9.6	19	23	52	42	29
	250	5.7	4	18	29	38	67
	500	9.8	11	32	63	47	26

[a)] $Al_{alkylaluminum}$/Zr ratio.
[b)] Al_{MAO}/Zr = 500 mol/mol. Without external alkylaluminum as R_3Al, only MAO.

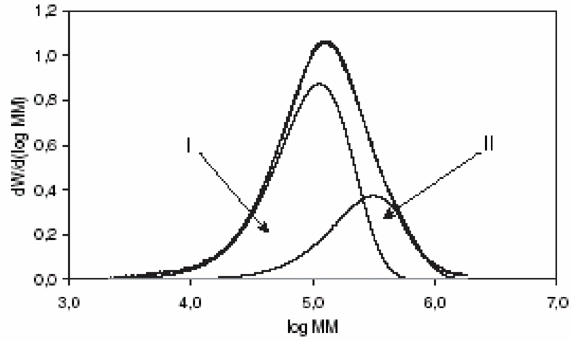

Figure 1. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/MAO.

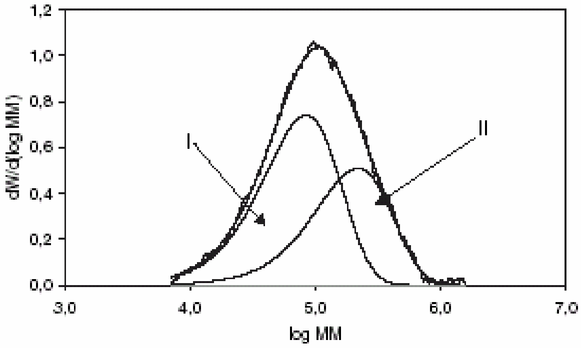

Figure 2. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TEA with 500 mol/mol of alkylaluminum as cocatalyst.

et al.[18,19]. The monomer used was ethylene, but the proposal is also valid for propylene. Several facts are relevant when the structures of Figure 7 are analyzed. Two active site types are proposed and:

(a) Structures 7(a) and 7(b) are equivalent, as well as structures 7(c) and 7(d).

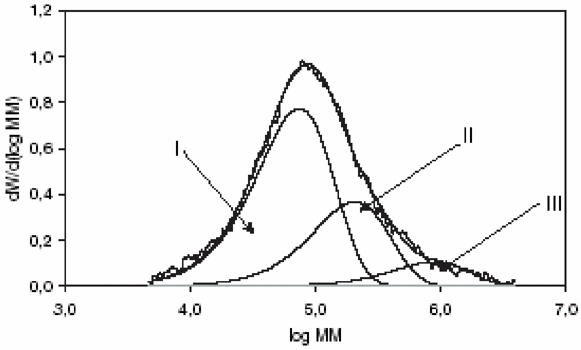

Figure 3. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

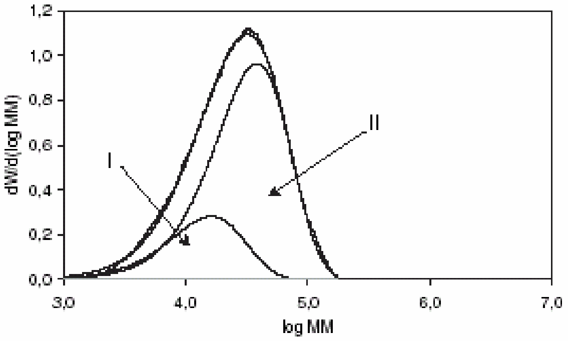

Figure 4. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/MAO.

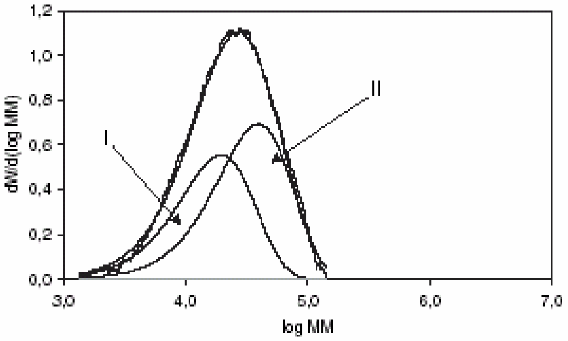

Figure 5. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TEA with 500 mol/mol of alkylaluminum as cocatalyst.

(b) The difference between structures 7(a)–7(b) and 7(c)–7(d) is the distribution of the ligands around the Zr, i.e., the MAO position related to the bis-indenyl rings. The MAO and bis-indenyl rings are in the same plane in structure 7(c) and 7(d) and in different planes in structures 7(a) and 7(b).

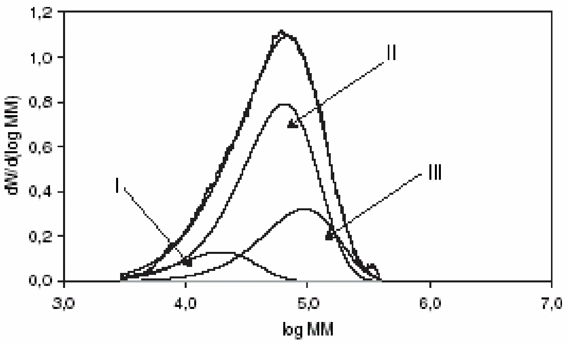

Figure 6. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

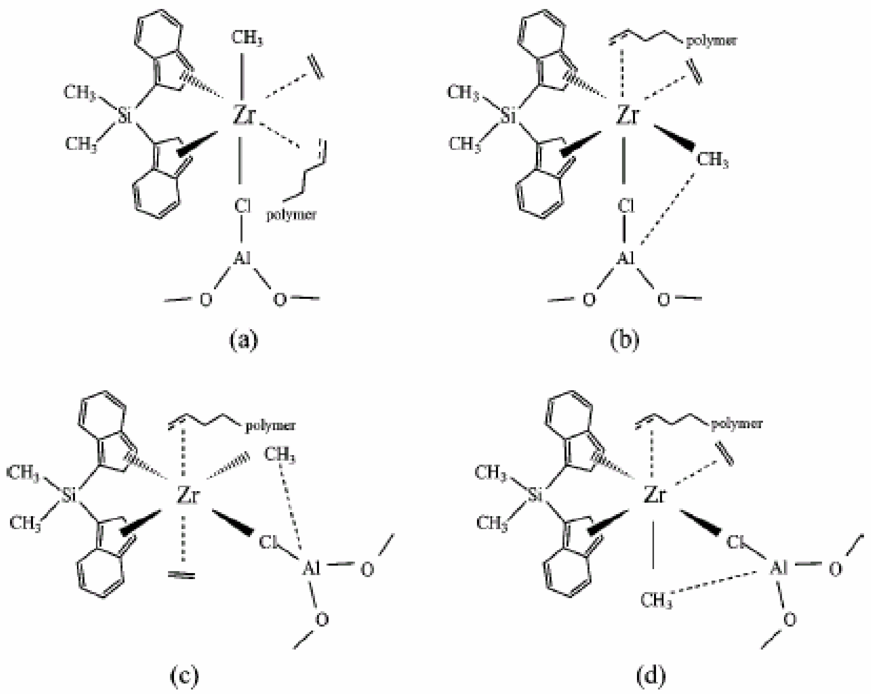

Figure 7. Proposed structures for the active site types in the system $Me_2Si(Ind)_2ZrCl_2$/MAO: (a) and (b) active site 1; (c) and (d) active site 2.

(c) The position occupied by the coordinated olefin could be taken by another MAO molecule without important changes in the electronics because the new coordinating MAO would act as a Lewis base.

(d) The structures that include the interaction of MAO and methyl groups (7(b), 7(c) and 7(d)) are favored.

(e) The active sites for ethylene and propylene polymerization are the same, although with different k_p (chain propagation rate constant) and k_{ter} (chain termination rate constant) values.

Catalyst activities might be similar in ethylene and propylene polymerization with the homogeneous system because no steric and/or electronic effects are expected for both monomers. This can be assumed because there is no substitution in the indenyl ligands of the catalyst. The molar mass of the poly(propylene) samples is far lower than those of the polyethylenes produced and the amount of polymer produced by each site type is different, showing that the propagation reactions and the concentration of each site type are different depending on the monomer. For propylene, the polymer produced in the major percentage is the one with the highest molar mass. The opposite is observed in the case of ethylene, i.e., a higher amount of polymer with low molar mass is formed.

As can be seen in Figure 7(a) and 7(b), active sites 1 have the growing chain and the coordinated olefin placed side by side. Due to this proximity, it might be supposed that active sites 1 are more prone to producing low molar mass fractions than active sites 2, since chain transfer to monomer could take place more easily. Figure 7(c) and 7(d) show that in active sites 2 the coordinated olefin is not as available to chain transfer reactions as in active sites 1, and it can be expected that active sites 2 will produce polymer with higher molar mass.

For each active site type, the reciprocal of the number average molar mass of the polymer chains can be related to the parameter τ in Flory's distribution:[24]

$$\frac{1}{M_n} = \tau = \frac{k_m}{k_p} + \frac{k_\beta}{k_p[M]} + \frac{k_{MAO}[MAO]}{k_p[M]} + \frac{k_{H_2}[H_2]}{k_p[M]} \qquad (1)$$

where k_m is the chain transfer to monomer rate constant, k_β is the β-hydride elimination rate constant, k_{MAO} is the chain transfer to MAO rate constant, k_{H_2} is the chain transfer to hydrogen rate constant, k_p is the chain propagation rate constant, $[M]$ is the monomer concentration, $[MAO]$ is the MAO concentration and $[H_2]$ is the hydrogen concentration.

As it is supposed that the polymer produced in active sites 1 is more influenced by the transfer reaction to monomer, one might assume that

$$\frac{1}{M_n} = \tau \simeq \frac{k_m}{k_p} \gg \frac{k_\beta}{k_p[M]} + \frac{k_{MAO}[MAO]}{k_p[M]} + \frac{k_{H_2}[H_2]}{k_p[M]} \qquad (2)$$

Thus, when carrying out polymerizations with different monomer partial pressures, it is expected that the molar

Table 3. GPC curve deconvolution: Molar mass ($\bar{M}_n$) and fraction of the polyethylene generated by each active site type in homogeneous conditions.

Ethylene pressure	Peak/active site 1		Peak/active site 2	
	$\bar{M}_n$	Fraction	$\bar{M}_n$	Fraction
bar	$kg \cdot mol^{-1}$	%	$kg \cdot mol^{-1}$	%
5.0	54	56	155	44
7.0	47	64	120	35

Table 4. Steric energy of the proposed active site types.

Catalytic system	Figure	Steric energy
		$kcal \cdot mol^{-1}$
Homogeneous Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO	7(a)	−145.3
	7(b)	−142.6
	7(c)	−136.9
	7(d)	−138.2
Heterogeneous Me$_2$Si(Ind)$_2$ZrCl$_2$/SMAO/AlR$_3$	8(a)	−142.2
	8(b)	−143.0
	8(c)	−142.8
	8(d)	−138.9
	8(e)	−121.8
	8(f)	−141.8

mass of the polymer produced by active sites 1 will either not change or will show a lower change compared to the polymer made by active sites 2. The deconvolution results of the GPC curves of polyethylenes produced under homogeneous conditions with ethylene partial pressures varying between 5.0 and 7.0 bar are shown in Table 3. The molar mass of the polyethylene produced with active sites 1 decreased by 13% while that of the polymer made with active sites 2 decreased by 23% when the ethylene partial pressure was changed from 5.0 to 7.0 bar, confirming the previous assumptions. It should be emphasized that, according to Equation (1), an increase in the molar mass of the polymer made by active sites 2 was expected with increasing ethylene pressure. Nevertheless, similar results have already been described for ethylene polymerization carried out using Et(Ind)$_2$ZrCl$_2$ in the absence of hydrogen and for low hydrogen concentrations.[25] This result is yet to be explained.

Figure 8 shows the proposed structures for the supported system Me$_2$Si(Ind)$_2$ZrCl$_2$/SMAO. As mentioned for Figure 7, the monomer used was ethylene, but the proposal is also valid for propylene. Considering the same ideas previously discussed for the homogeneous system, four different structures, sites 1 through 4, are proposed. Two of the four structures (active sites 1 and 2 - Figure 8(a) to 8(d)) are similar to those proposed to the homogenous system, but the presence of the support and the possibility of TEA or TIBA coordination, replacing the monomer, makes the overall electronics on Zr different. The alkylaluminum probably decreases the electrophilicity of the metal because of the strength of the coordination, and the MAO at the SiO$_2$ surface is not the same compared to that of the homogeneous system, Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO.

Active sites 3 and 4 are supposed to coordinate the alkylaluminum, i.e., it is assumed that the alkylaluminum is chemically bonded to the Zr. As the homogeneous polymerizations were carried out using no external alkylaluminum such as TEA or TIBA, but MAO, active sites 3 and 4 are not present in the homogeneous system.

As the deconvolution of the GPC curves of the polymers produced using the heterogeneous catalyst showed 3 peaks (except for the polymers prepared in the presence of TEA with Al/Zr = 500 mol/mol) it might be supposed that one of the structures proposed in Figure 8(e) and 8(f) does not generate an active site for polymerization. Due to the bulkiness of the support, of the bis-indenyl rings and of the group AlR$_2$ present in both structures, it might be assumed that structure 8(f) shows higher steric hindrance than structure 8(e) and therefore it is probably inactive for ethylene and propylene polymerization.

Table 4 shows the steric energy calculated for each structure in Figure 7 and 8. Although structure 8(f) (site type 4) has smaller steric energy than structure 8(e) (site type 3), i.e., −141.8 against −121.8 $kcal \cdot mol^{-1}$, the site type represented by structure 8(f) does not polymerize due to the higher steric hindrance. It must be emphasized that the more stable structures during the coordination step are not always the ones with the lowest activation energy for the insertion step.[26] Taking into account the steric hindrance and the step of olefin coordination, it can be speculated that the most probable structures should be 8(a)–8(b) (site type 1), 8(c)–8(d) (site type 2) and 8(e) (site type 3).

Conclusion

The in situ immobilized system Me$_2$Si(Ind)$_2$ZrCl$_2$/SMAO showed lower activity for propylene polymerization in the presence of TEA or TIBA, and for ethylene polymerization in the presence of TIBA than the homogeneous system Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO. However, when ethylene was polymerized using Me$_2$Si(Ind)$_2$ZrCl$_2$/SMAO with TEA as cocatalyst, almost 80% of the homogeneous system activity was reached.

The poly(propylenes) prepared using the in situ supported catalyst system had a slightly lower melting point than the poly(propylenes) made using the homogeneous catalyst system. On the other hand, the polyethylenes made using in situ supported catalyst and by homogeneous catalyst systems showed practically the same melting point.

The nature and the amount of the alkylaluminum used as cocatalyst influenced the molar mass of the polymers prepared when using the in situ immobilization of the metallocene catalyst onto SMAO. The poly(propylene) molar mass was higher when TIBA was used as the

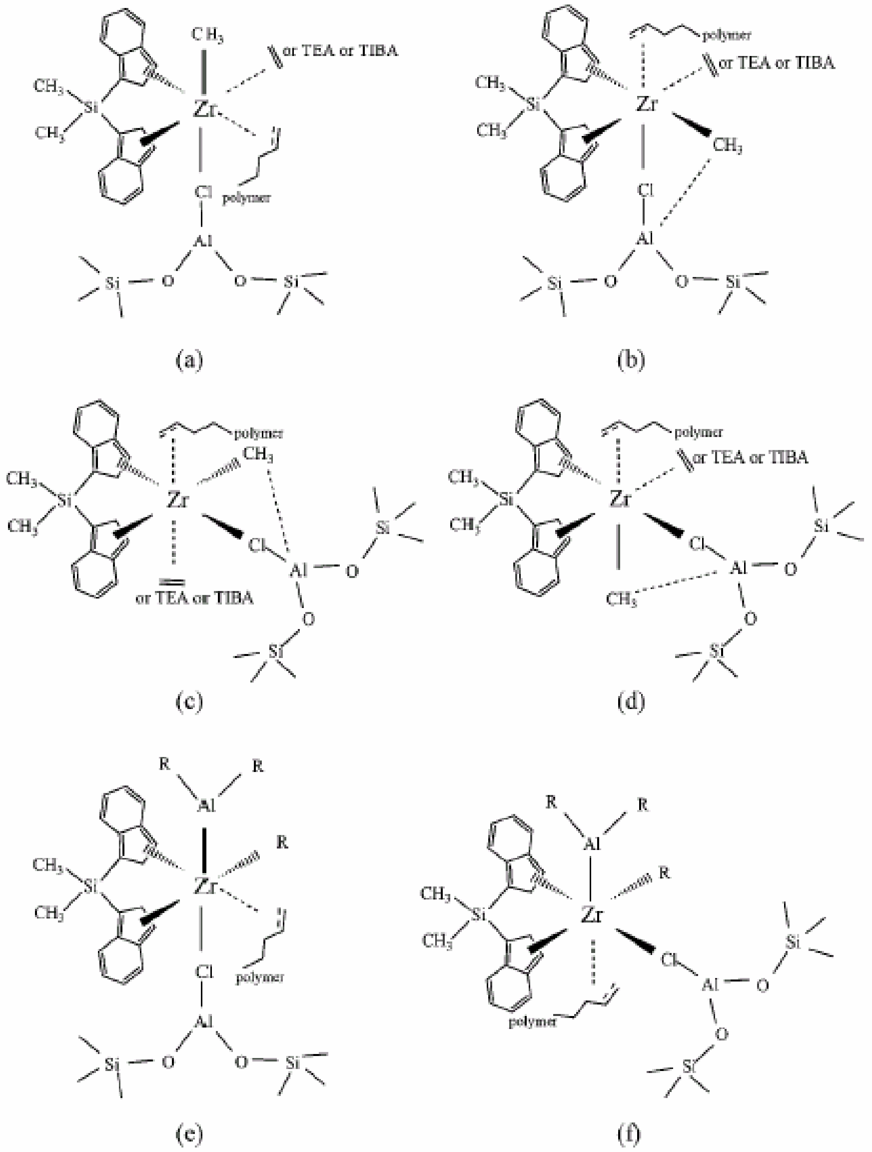

Figure 8. Proposed structures for the active site types in the system $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$: (a) and (b) active site 1; (c) and (d) active site 2; (e) active site 3; (f) active site 4.

cocatalyst, but the opposite behavior was observed for the polyethylenes. As the amount of TEA increased, the molar mass of the polymers decreased. In the presence of TIBA, the polyethylene molar mass was almost the same, independent of the alkylaluminum concentration, and the poly(propylene) molar mass increased with increasing amounts of cocatalyst. The polyethylenes had a higher polydispersity when TIBA was used as a cocatalyst. These results confirm that the cocatalyst acts not just as a scavenger, but also plays an important role on the catalyst.

The GPC curve deconvolution showed 2 peaks for the homogeneous systems and 3 peaks for almost all heterogeneous in situ systems, indicating the presence of 2 and 3 different types of active sites, respectively. The only exception was observed when TEA was used at an Al/Zr molar ratio of 500, where the best fit was obtained with 2 peaks. Based on these results and on theoretical modeling, it was possible to propose the structure of the active sites.

The results presented in this paper confirm the importance of the alkylaluminum used as a cocatalyst in the generation of a different type of active sites when SMAO is used as support, and the role of the olefin in the generation and stabilization of the active sites.

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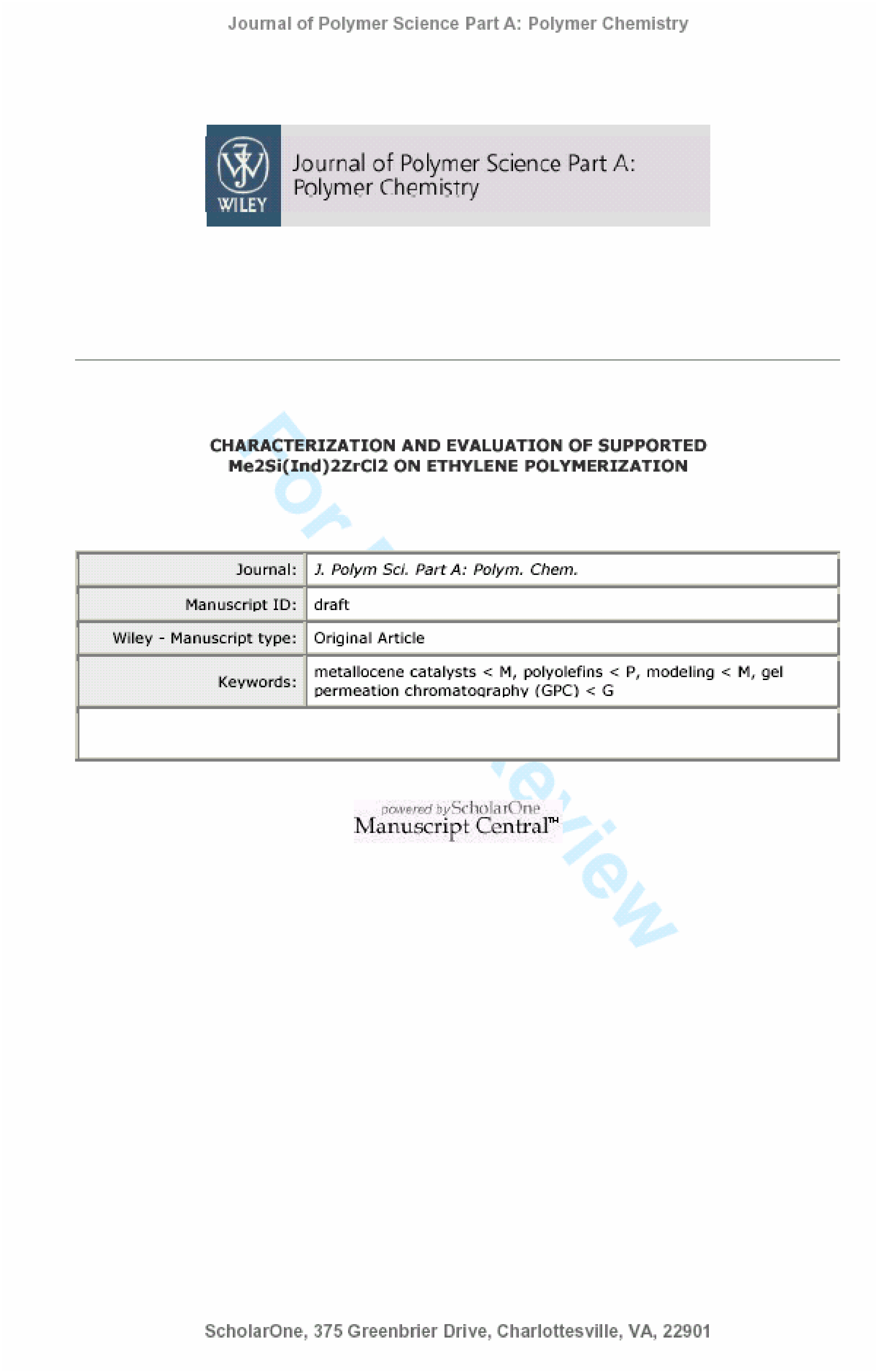
5.5. ARTIGO 5

Characterization and evaluation of supported $Me_2Si(Ind)_2ZrCl_2$ *on ethylene polymerization*
Submetido para publicação ao Journal of Polymer Science Part A: Polymer Chemistry (2006)

O catalisador $Me_2Si(Ind)_2ZrCl_2$ foi imobilizado sobre SMAO variando a razão mássica Zr/SMAO entre 0,1 e 1,5 % e avaliado na polimerização de etileno utilizando IPRA como cocatalisador. A caracterização de dois catalisadores suportados contendo 0,3 % e 0,8 % Zr/SMAO por EXAFS indicou que o número e a intensidade dos picos além da camada de coordenação, associados com os vizinhos mais próximos, depende da concentração de Zr. Para o catalisador com maior teor de Zr, somente um pico a 2,8 Å foi observado. O catalisador contendo 0,3 % de Zr/SMAO apresentou dois pequenos picos, um a 2,8 e outro a 3,8 Å. Os polímeros produzidos com os catalisadores suportados apresentaram menor cristalinidade e maior massa molar e polidispersão em comparação aos produzidos em condições homogêneas. A deconvolução das curvas de GPC indicaram a presença de quatro sítios distintos para os sistemas catalíticos suportados.



Journal of Polymer Science Part A: Polymer Chemistry

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Polymer Chemistry

CHARACTERIZATION AND EVALUATION OF SUPPORTED Me2Si(Ind)2ZrCl2 ON ETHYLENE POLYMERIZATION

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CHARACTERIZATION AND EVALUATION OF SUPPORTED $Me_2Si(Ind)_2ZrCl_2$ ON ETHYLENE POLYMERIZATION

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ABSTRACT

$Me_2Si(Ind)_2ZrCl_2$ was grafted onto commercial MAO-modified silica (SMAO) at different loadings (between 0.1 and 1.5 wt.% Zr/SMAO). Supported catalyst were evaluated in ethylene polymerization having isoprenylaluminum (IPRA) as cocatalyst. Characterization of two supported catalysts bearing 0.3 and 0.8 wt.% Zr/SiO_2 by Extended X-ray Absorption Fine Structure (EXAFS) indicated that the number and the intensity of the peaks beyond the coordination shell, associated with the next nearest neighbors, depend on the Zr concentration. For the catalyst with higher Zr content only one peak (2.8 Å) was observed. The catalyst with 0.3 wt.% Zr/SMAO presented two

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small peaks at 2.8 and 3.8 Å. Polymers produced with the supported catalysts presented lower crystallinity and higher molar mass and polydispersity in comparison to that produced by the homogenous one. Gel permeation chromatography (GPC) chromatogram deconvolution suggests the presence of four catalyst sites for the supported systems.

Keywords: supported zirconocenes, polyethylene, MAO, silica, EXAFS

INTRODUCTION

A great part of the literature devoted to metallocene in polymerization catalysts has dealt with studies concerning the heterogeneization of such catalyst systems. A solution polymerization process requires separation of the polymer, and removal, recovery and purification of the solvent. On the other hand, gas phase processes have lower cost and energy consumption. As most of the existing polymerization plants run slurry- and gas-phase process with heterogeneous systems, the homogeneous metallocenes must be heterogenized on a support if application to those processes is aimed. Moreover, the heterogenization of metallocene is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology.

In the last decade many attempts have been done in the heterogeneization of metallocene compounds. Different preparatory routes are described in the literature aiming at developing supported metallocene catalysts which could replace without larger costs, the heterogeneous catalysts Ziegler-Natta in the industrial plants.[1] Silica is the most used carrier. Nevertheless other supports have also been evaluated such as MCM-41, SBA-15,[2] polymer, [3], silica chemically modified with agents such as MAO or perfluorophenylborate [4], just to mention a few. Zirconocene systems synthesized *in situ* [5] or on hybrid silica [6-7] are also examples of the preparation of supported metallocene catalysts.

Another approach to produce supported metallocene resides in the so-called *in situ* immobilization, in which the components (catalyst and support) are directly contacted in the reactor. Supported metallocene prepared by the *in-situ* immobilization technique have been evaluated for ethylene homo- and copolymerization [8-11]. In previous works we studied propylene homopolymerization employing in situ immobilized $Me_2Si(Ind)_2ZrCl_2$ as catalyst and commercial MAO-modified silica as support. The effect of common alkylaluminum cocatalysts was evaluated on catalyst activity in propylene polymerization and on polymer properties.[12-14] The use of common alkylaluminum, such as TEA or TIBA, reduces the possibility of leaching the catalyst from the surface, as reported for supported metallocenes.[15] Besides, considering that the determination of the isotherm adsorption allows one to know the maximum surface loading regarding these complexes,[12] the use of very low concentration, far from the saturation level, guarantees that there should be enough available sites on the surface for zirconocene grafting. Support morphology replication phenomena were also observed for polymers produced by these in situ-supported catalysts.[14]

In the present work, we prepared supported $Me_2Si(Ind)_2ZrCl_2$ systems grafted on MAO-modified silica, bearing different Zr content, which were evaluated in ethylene polymerization. Two systems were characterized by extended X-ray absorption fine structure (EXAFS) in the Zr-edge and structure features were correlated to catalyst activity and polymer properties. The results were discussed according to a theoretical model based on the Ziegler group work and the application of a MM2 calculation to a model of MAO-zirconocene interaction.

EXPERIMENTAL

Materials

All the experiments were performed under inert atmosphere using the Schlenk technique. The catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$, Witco), MAO-modified silica (SMAO, 23 wt.% Al/SiO_2, Witco) and isoprenylaluminum (IPRA) (Akzo) were used without purification. Ethylene was used as received from the cracker (Copesul, Triunfo, Brazil), without any further purification. Toluene and hexane were purified by refluxing over sodium and by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

Preparation of the supported catalysts.

Several catalyst solutions bearing Zr concentration corresponding to contents between 0.1 and 1.5 wt.% Zr/SMAO were contacted with SMAO at room temperature for 30 minutes. The resulting slurry was washed with 15 × 2 mL of toluene, vacuum dried, and the final metal content in the resulting solid was determined by Rutherford Backscattering spectrometry (RBS).

Catalyst characterization

Rutherford backscattering spectrometry (RBS)

Zirconium loadings in catalysts were determined by RBS using He^+ beams of 2.0 MeV incident on homogeneous tablets of the compressed powder of the catalysts systems. Zr/Si atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and converted to wt.-% Zr/SiO_2.

For an introduction to the method and applications of this technique the reader is referred elsewhere.[16]

Nitrogen Adsorption

A Micrometeritics Gemini equipment was used for nitrogen sorption studies. The samples were preheated at 80 ^{0}C for 12 h under vacuum before each measurement. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method at -196 ^{0}C, in the partial pressure range of $0.01 < P/P_0 < 0.25$. The total pore volume was obtained from the N_2 desorption isotherm.

X-ray absorption fine structure spectroscopy (EXAFS)

The X-ray absorption spectroscopy experiments were performed at the XAS beam line [17] LNLS (Campinas, Brazil) using a Si(220) monochromator and vertical slits of 1.0 mm. Data were recorded at room temperature in transmission mode using two ion chambers filled with argon. Pellets of the catalysts powders were prepared in a glove box and covered with Kapton® tape to avoid air oxidation.

The EXAFS (Extended X ray Absorption Fine Structure) spectra were acquired in the range 17870 - 18440 eV with 2 eV step and 4 sec/pt. Several scans were collected for each catalyst, in the case of the one with lower Zr content 10 scans were averaged to improve the signal to noise ratio.

The EXAFS spectra were analyzed by a standard procedure of data reduction, using the WINXAS code.[18] A linear function was used in the background subtraction and a polynomial function to simulate the atomic absorption. A Fourier transform (FT) in the k range 2.9-9 Å^{-1} was performed using a Bessel window. Structural parameters were obtained from least squares fitting in r-space using theoretical phase shift and amplitude functions obtained from the FEFF code.[19]

In the fit were determined the coordination number (N), interatomic distance (R), Debye Waller factor (σ) and energy shift (E_0). For the coordination shell the passive electron reduction factor (S_0^2) was determined from $Me_2SiInd_2ZrCl_2$ for Zr-C bonds and kept fixed at 0.89 for the catalysts samples. For the next nearest neighbors the S_0^2 value was kept at 1. The analysis was done by keeping the energy shifts ΔE_0 fixed at -2.0 eV for the Zr-C pair and 3.7 eV for the Zr-Al pair. In the fitting procedure, the number of free parameters did not exceed the number of independent data points given by the Nyquist theorem.[20]

Polymerization

Polymerization reactions were performed in a 1.5 L stainless steel reactor equipped with mechanical stirrer, constant temperature circulator and inlets for argon and for ethylene. The reactor was filled with the supported catalyst (Al/Zr = 500 (mol/mol)), 0.75 L of hexane and isoprenylaluminum (IPRA). When the mixture reached 60°C, the reactor was pressurized with ethylene up to 6.0 bar (partial pressure) for 60 min. Homogeneous polymerizations were performed under the same conditions using MAO (Al/Zr = 500) as cocatalyst, instead of IPRA. Polymers were precipitated by acidified (HCl) ethanol and dried under vacuum at 90 °C for 4 h.

Polymer characterization

Crystallinity (χ), melting (Tm) and crystallization (Tc) temperatures were determined using a TA Instruments 2920 differential scanning calorimeter (DSC), according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan were reported. The heating rate was 10°C/min in the temperature range from 30 to 220°C. Molar mass distributions were determined by high temperature gel permeation chromatography (GPC) using a 150 C Waters instrument equipped with four columns GMHXL-HT (TosoHaas) at 138 °C. 1,2,4-trichlorobenzene was used as mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. The deconvolution of the polymer molar mass distribution was performed using an Excel spreadsheet. To obtain the best fit between the measured GPC curve and the fitted GPC curve (sum of the deconvoluted curves), Excel's Solver routine was used to minimize the sum of the squares of the differences between the measured and the fitted GPC curves ($\Sigma\Delta^2$). For each GPC curve, the deconvolution process was carried out considering 1, 2, 3, or 4 curves or peaks. In all results presented in this work the parameter $\Sigma\Delta^2$ had the lowest possible value, without overlapping of curves or peaks.

Theoretical studies using MM2

The software was provided by Cambridge Soft and the MM2 version was incorporated to Chem3D 5.0 (1999), which uses a modified version of Allinger MM2 force field. The main incorporated functions to Allinger´s MM2 force field are charge-dipole interaction term, a quartic stretching term, cutoffs for electrostatic and Van der Waals terms with 5th order polynomial switching function, automatic "pi" system calculations and torsion and non-bonded constraints. The parameters table of Chem 3 D contains many adjustable parameters which allows one to correct many of the potential functions in outlying situations.

RESULTS AND DISCUSSION

Metal loading and catalyst activity

The maximum surface loading for a certain catalyst can be obtained by determining its adsorption isotherm. In a previous work, $Me_2Si(Ind)_2ZrCl_2$ solutions containing between 0.5 and 5.0 wt.-% Zr/SMAO were put in contact with commercial MAO-modified silica (SMAO).[12] The saturation level was reached at ca. 2.0 wt.-% Zr/SMAO. Almost all metallocene present in the toluene solution seemed to have been immobilized on SMAO surface for contents below 2.0 wt% Zr/SMAO. Such behavior suggested strong interaction between the catalyst and the surface.

The effect of variation of Zr content immobilized on SMAO lower than the saturation level was evaluated on ethylene polymerization (Figure 1). The highest catalyst activity was observed for 0.1 wt.% Zr/SMAO. As the grafted content increases, catalyst activity decreases up to 0.8 wt.% Zr/SMAO remaining roughly constant for 1.5 wt.% Zr/SMAO. The decrease in catalyst activity with increasing the catalyst content was already reported in the literature and it was attributed to the possibility of bimolecular deactivation reactions due to greater proximity among catalyst centers in high Zr content.[21] Under the same experimental conditions, homogeneous $Me_2Si(Ind)_2ZrCl_2$ in the presence of MAO as cocatalyst (Al/Zr = 500) produced 5.1 kg PE g $cat^{-1}.h^{-1}$. Homogeneous catalysts usually have higher catalyst activity than supported ones, since in the former all molecules are potentially active. Specifically in the case of immobilized metallocene catalysts, depending on the Brönsted acidity and on the OH groups density, some inactive species such as μ-oxo covalently bonded species or bidentated ones can be formed. It is believed that ca. 1 % of the grafted species are indeed active.[22] Besides, the silica surface itself plays the role of huge ligand in the supported catalysts and this steric hindrance renders difficult the accessibility to the catalyst sites.

The rate of polymerization is often diffused limited. Zirconocene sites near a pore mouth or on the surface would contribute more to the observed rate than the sites inside the pores. Therefore, the reactivity of these catalyst would be higher in the case of lower loading samples, since most of the catalyst species should be grafted on the uttermost surface. Support surface area measured by nitrogen adsorption and calculated by the BET model was 185, 160 and 145 $m^2 g^{-1}$, respectively for SMAO, and for the supported catalyst bearing 0.3 and 0.8 wt.% Zr/SMAO. Indeed the surface area showed a reduction in ca. 22 % comparing the surface area from the support and that of the resulting catalyst with 0.8 wt.% Zr/SMAO. Nevertheless, a reduction of ca. 85 % in catalyst activity is observed, when compared these two catalyst (see Figure 1). Therefore, although diffusion might be influencing as the grafted metal content increases, it cannot thoroughly justify the reduction in catalyst activity. These two catalyst were further analyzed by EXAFS.

EXAFS allows one to get information on the environment around the Zr center by measuring the X-ray absorption in Zr – K edge. EXAFS has already been employed in the characterization of metallocenes. [23-25] In a previous study, EXAFS analysis in the Zr edge showed that for hybrid supported metallocene catalysts, systems bearing Cp_2ZrCl_2 and $(nBuCp)_2ZrCl_2$ in 1:3 molar ratio afforded more disordered system.[26]

The Zr K edge EXAFS spectra of the $Me_2Si(Ind)_2ZrCl_2/MAO/SiO_2$ catalysts with Zr content of 0.8 and 0.3 wt.% Zr/SMAO are quite similar (Figure 2). The shape of the signal is a damped sine function mostly coming from the coordination shell. The beat pattern shoulder observed at about 6 $Å^{-1}$ indicates the contribution of next nearest neighbors to the EXAFS signal.

The Fourier transforms (Figure 3) of both samples display one main peak at about 1.5 Å related to the coordination shell. The number and the intensity of the peaks beyond the coordination shell, associated with the next nearest neighbors depend on the Zr concentration. For the catalyst with higher Zr content only anotuer one peak at about 2.8 Å is observed. The catalyst with 0.3 wt.% Zr/SMAO has 2 small peaks at 2.8 and 3.8 Å. The Fourier transforms were also performed using a different apodization window and *k* extension, the number and shape of the peaks in the FTs was identical, meaning that the one at 3.8 Å corresponds to an interatomic distance and is not an artifact of the data handling.

The quantitative analysis yielded the parameters presented in Table 1. The refinement of the coordination shell was performed considering different possibilities of scattering atoms such as carbon and/or chlorine atoms. The best fits were obtained for both samples considering a single carbon shell as first neighbor atoms and an excellent fit quality was obtained in both cases. Values for Zr-C and Zr-Al bond distance are close to those reported in the literature.[23] Figure 4a shows the fit obtained for the catalyst with higher Zr content.

In the analysis of the next nearest neighbors different atoms were considered. Among the possibilities silicon, aluminum, chlorine and oxygen atoms were examined. Due to the similarity of phase shift and amplitudes [27] of aluminum and silicon atoms, it is practically impossible to distinguish them in an EXAFS fit. The best fit results were obtained for the catalyst with 0.8 wt.-% Zr/SMAO considering a single Al or Si shell (Figure 4b). Nevertheless, considering the saturation level of MAO on silica to be ca. 8-10 wt.% Al/SiO_2,[28] and the fact that commercial SMAO has ca. 23 wt.% Al/SiO_2, it is very likely that the next nearest neighbor atoms are aluminum ones.

In the case of the catalyst with 0.3 wt.-% Zr/SMAO the two peaks beyond the coordination shell were fitted considering two Zr-Al shells and a good fit quality was obtained (Figure 4c).

According to Table 1, the number of neighbors (C and Al) is roughly the same. It is worth noting that the number of C (5) may be resulted from the constructive and destructive interference of the signal, which is a mean. In the case of 0.3 wt.% Zr/SiO_2, two Al shells are detected: One at 3.43 Å and another at 4.12 Å, the latter being absent in the case of 0.8 wt.% Zr/SiO_2 system. The longer Zr-Al distance may guarantee a weaker zirconocenium ion-par ($[SiO\text{-}Al(Me)O^-][R_2ZrMe]^+$ originated from the reaction between the zirconocene and the MAO-modified silica surface and stabilized by the multicoordinative crown aluminoxane species. This weaker interaction rends the system more prone to dissociation during the olefin coordination, letting the propagation reaction to grow further, which in turn affords higher catalyst activity.

Polymer characteristics

The obtained polyethylenes were characterized by GPC and DSC (Table 2). The detected melting temperature (T_m) at 132°C is typical of high-density polyethylene (HDPE). Cristallinity (χ_c) is lower for polyethylenes obtained with supported catalysts and increased as Zr content increased. Polymers obtained with heterogeneous catalysts presented molar mass higher than that obtained with the homogeneous one. This behavior has already been observed and attributed to blocking of one of the sides of polymerization active sites by the support, hindering the deactivation step. In other words, β-elimination transfer between two metallocene centers is hindered, resulting in a larger growth of the polymer chain, and therefore in higher molar mass [29]. Polydispersity (M_w/M_n) lied between 4.0 and 6.9, i.e., the single site nature of metallocene seems not to be kept after grafting. The intrinsic heterogeneity from the support surface might afford different potential catalyst sites.

Molar mass distribution of polymers can be described by Flory's most probable distribution and mathematical models can be useful tools in gaining better understanding of a process or a system.[30-32] Figure 5 shows GPC curves for polymers obtained with homogeneous and supported catalysts. The best deconvolution curves of supported catalysts suggest the presence of four polymeric species, which present different molar mass (Table 3). Such results suggest the presence of more than one catalyst site on the support surface. It is worth noting that polyethylenes with a broad polydispersity show greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques. Many efforts have been done to produce polymers by metallocene catalysts with a broader polydispersity.[1]

A theoretical model was constructed in order to explain the results observed in terms of catalyst activity and data from EXAFS analysis.

Theoretical Model

The employed MAO model was similar to that proposed by Zurek and Ziegler,[32]: A cage with coordinated TMA in which all O atoms are tricoordinated to 3 Al atoms and the cage includes two $AlMe_2$ groups. One $AlMe_3$ molecule is coordinated to the cage (Figure 6).

Figure 7 shows the MAO model reacted with silica surface, considering tetrahedral Si, and the formation of an Al-O-Si bond, with the loss of an H (from the surface) and a methyl group (from MAO model).

According to Zurek-Ziegler model, the interaction of the zirconocene with MAO produces a compound with 2 Cl atoms on the same Al (from the cage) or in two different Al atoms (also from the cage) and a zirconocene with a Zr^+-methyl (Me) bond. Interaction of the zirconocene with MAO was considered to take place through chlorine (from $OAlMe_2Cl$) or through O_2AlMe_2. The interaction of one or two zirconocenes with the same MAO cage (supported) was also taken into account. Then, the zirconocene interacts with the MAO model in sequence, according to the following reactions:

$$\text{Al-Methyl} + ZrCl_2 \rightarrow \text{Al-Cl} + \text{ZrClMethyl} \qquad (1)$$

$$\text{ZrClMethyl} + \text{Al-Methyl-} \rightarrow Zr^+ \text{ -- Methyl} + AlCl^- \text{-- Methyl} \qquad (2)$$

Two possibilities were then explored: Different Al atoms for reactions 1 and 2 or similar Al (and therefore in reaction 2, the second chlorine is transferred to Al-Cl instead to Al-Methyl). The preferred conformation has 2Cl atoms in 2 different Al atoms. Figures 8 and 9 show the two different resulting structures on the MAO model.

The zirconocene can be coordinated through chlorine (conformation 1) or through oxygen (conformation 2), as shown in Figures 10 and 11. When coordinated through O , the zirconocene site is considered to be a dormant site.[33]

Table 4 shows the structural parameters for each of both conformation. Besides a situation in which 2 zirconocenes are considered to be reacted with one cage was also included. This situation is considered to take place with 0.8 wt.-% Zr/SMAO.

Comparing the EXAFS (Table 1) and MM2 data (Table 4), one can see that there is a very good agreement for Zr-Al distance. In the case of 0.3 wt.-% Zr/SMAO, there is a distribution of active and dormant sites, bearing different Zr-Al (and Zr-O) bond distances. For 0.8 wt.-% Zr/SMAO supported system, with higher concentration of zirconocene, the remaining available sites for activation on the supported MAO-cage can react with a second zirconocene. Repulsion between zirconocenes make the Al-Zr distances shorter. In this case, the model must accommodate 2 negative charges and therefore the distances are shorter since two positive charges are involved. Besides steric crowding is higher and probably then propagation constants are lower (Figure 12). Coordination of Zr is high considering the methyl group, the two Cp centroids, the Al and the bridge chlorine or methyl with the Aluminum. In sum, for higher Zr content, no dormant sites would be present, but the steric hindrance is increased due to the interaction of different zirconocenes on MAO-cage surface and the resulting tight ion-pairs bear shorter Al-Zr bond distance. This would explain the lower observed catalyst activity on ethylene polymerization

CONCLUSIONS

Catalyst activity of supported systems, resulting from the grafting of $Me_2Si(Ind)_2ZrCl_2$ on MAO-modified silica seems to be dependent on Al/Zr ratio, decreasing as the Zr content increases. The neighborhood of the resulting grafted species, according to EXAFS measurements, seems to vary with the Zr content: two Zr – Al moieties were found to be present in the case of 0.3 wt.% Zr/SMAO, but only one for 0.8 wt.% Zr/SMAO.

Surface heterogeneity is also reflected on polymer properties, specially in the polymer poydispersity, which shows to be higher than that observed with the homogeneous catalyst.

Theoretical calculation can model the interaction for low and higher metal content: the steric effect among catalyst zirconocene species on the MAO-silica surface must be account for the observed decrease in catalyst activity.

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Figure Captions

Figure 1. Catalyst activity of $Me_2Si(Ind)_2ZrCl_2$ supported on MAO-modified silica.

Figure 2. EXAFS spectra at the Zr K edge: (a) catalyst with 0.8 wt.-% Zr/SMAO; (b) Catalyst with 0.3 wt.-% Zr/SMAO.

Figure 3. Fourier transforms of the EXAFS signal over the k range 2.9-9 $Å^{-1}$: (a) Catalyst with 0.8 wt.-% Zr/SMAO; (b) Catalyst with 0.3 wt.-% Zr/SMAO.

Figure 4. Fitting of the FT modulus and imaginary part , the experimental data are the solid lines and fit the dash dot lines: (a) Fit of the coordination shell considering a Zr-C bond for the catalyst with 0.8 wt.-% Zr/SMAO content; (b) Fit of the next nearest neighbor peak considering a Zr-Al bond for the catalyst with 0.8 wt.-% Zr/SMAO content; (c) Fit of the next nearest neighbor peaks considering two Zr-Al bonds for the catalyst with 0.3 wt.-% Zr/SMAO content.

Figure 5. Molar mass distribution deconvolution of the polymers by the (a) homogenous system; (b) supported system bearing 0.3 wt.% Zr/SMAO and (c) supported system bearing 0.8 wt.% Zr/SMAO.

Figure 6. MAO cage model, according to ref. [33].

Figure 7. MAO cage model reacted with SiO_2 surface.

Figure 8. Counterion with 2 Cl and 1 Al atoms from the supported MAO cage model (steric energy = - 557.4 Kcal/mol)

Figure 9. Counterion with 2 Cl atoms included into the supported MAO cage model (steric energy = - 558.4 Kcal/mol)

Figure 10. Zircocation coordinated through $OAlMe_2Cl$ – Conformation 1 (steric energy = - 579.8 Kcal/mol).

Figure 11. Zircocation coordinated through $OAlMe_2Cl$ – Conformation 1 (steric energy = - 556.2 Kcal/mol).

Figure 12. Two active sites on a supported MAO cage model.

Table 1. Structural parameters obtained from the fitting, the coordination number (N), interatomic distance (R), and Debye Waller factor (σ).

Zr content	Pair	N	R (Å)	σ^2 (Å^2)
0.8%	Zr-C	5.6 ± 1.0	2.22 ± 0.02	0.0106 ± 0.0021
	Zr-Al	0.8 ± 1.0	3.40 ± 0.04	0.0043 ± 0.0009
0.3%	Zr-C	5.1 ± 1.0	2.23 ± 0.02	0.0061 ± 0.0012
	Zr-Al	0.4 ± 1.0	3.43 ± 0.04	0.0081 ± 0.0014
	Zr-Al	0.4 ± 1.0	4.12 ± 0.04	0.0081 ±0.0016

Table 2. Polymer characteristics for the different catalyst systems.

wt.% Zr/SMAO (wt.%)	T_m (°C)	χ_c (%)	$\overline{M}_n$ (kg/mol)	$\overline{M}_w/M_n$
$Me_2Si(Ind)_2ZrCl_2$	133	59	67	2.5
0.1	132	36	71	4.0
0.3	132	37	59	6.9
0.5$^{(*)}$	129	43	69	5.6
0.8	132	41	63	5.9
1.5	132	44	79	4.0

* Polymer did not completely dissolved

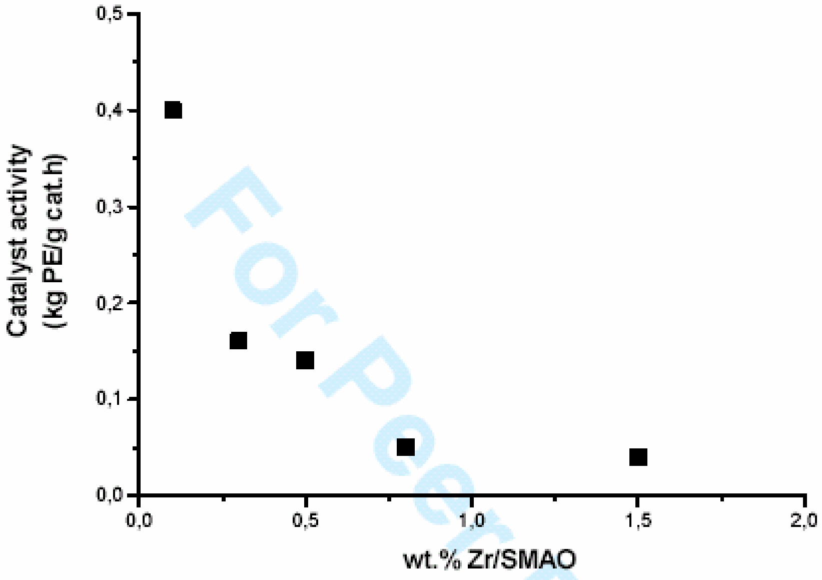
Table 3. Mn values and percentages of the peaks resulting from the deconvolution of GPC chromatograms.

Zr/SMAO	Peak I/Site I		Peak II/Site II		Peak III/Site III		Peak IV/Site IV	
(wt.%)	$\bar{M}_n$(1)	%	$\bar{M}_n$(1)	%	$\bar{M}_n$(1)	%	$\bar{M}_n$(1)	%
0.3	5.5	3	46	45	144	28	605	24
0.8	10	6	49	45	164	27	551	22

(1) kg/mol

Table 4. Structural parameters obtained using MM2 calculations.

	Zr-Al (Å)	Zr-O (Å)	Zr-Coordination
Conformation 1	3.764	5.45	6/7
Conformation 2	4.080	4.041	5/6
Two zirconocenes	3.559/3.50	5.259/4.06	6/7 + 5/6


Catalyst activity
(kg PE/g cat.h)
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0,2
0,3
0,4
0,5
0,0
0,5
1,0
1,5
2,0
wt.% Zr/SMAO

Figure 1.

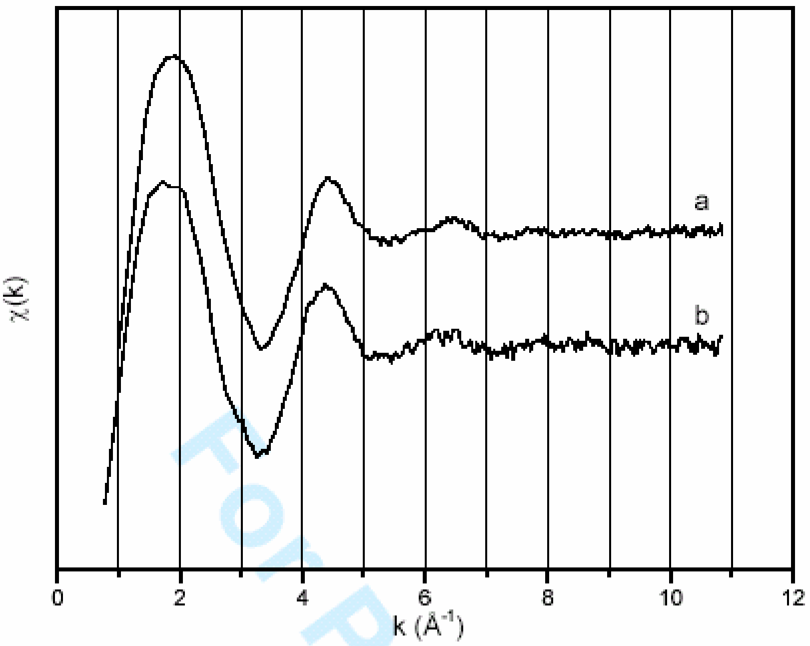
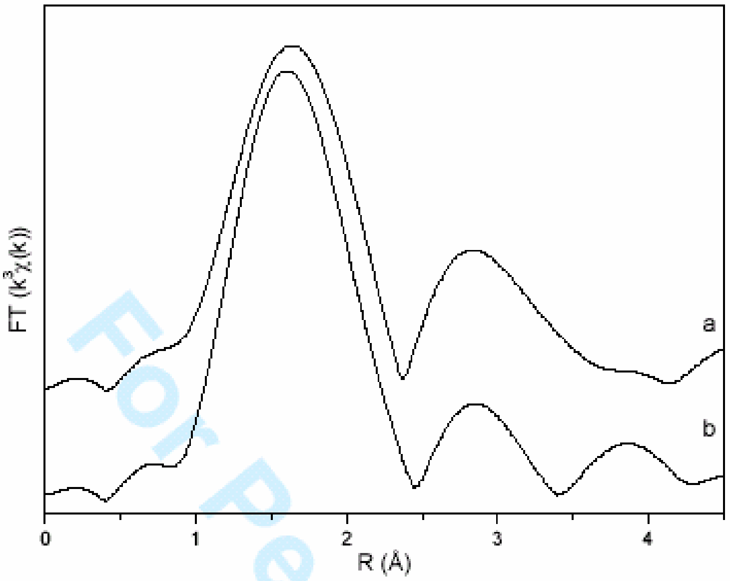


Figure 2



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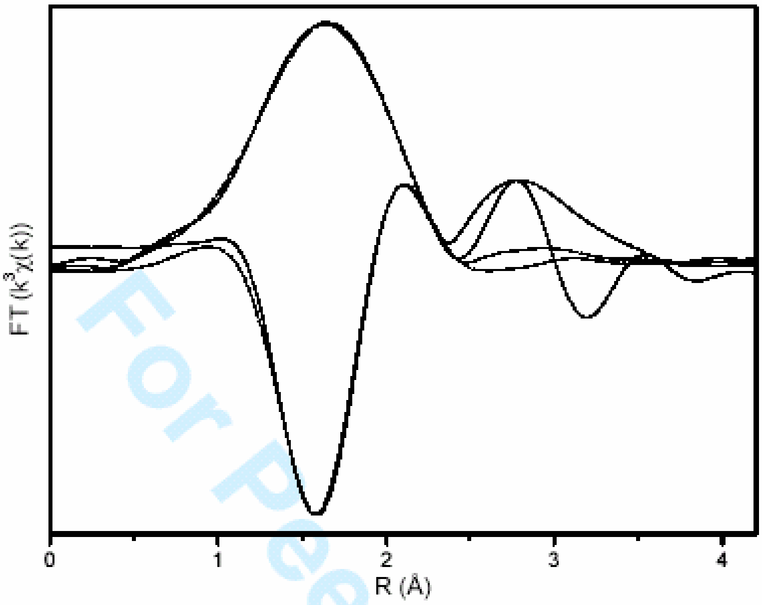
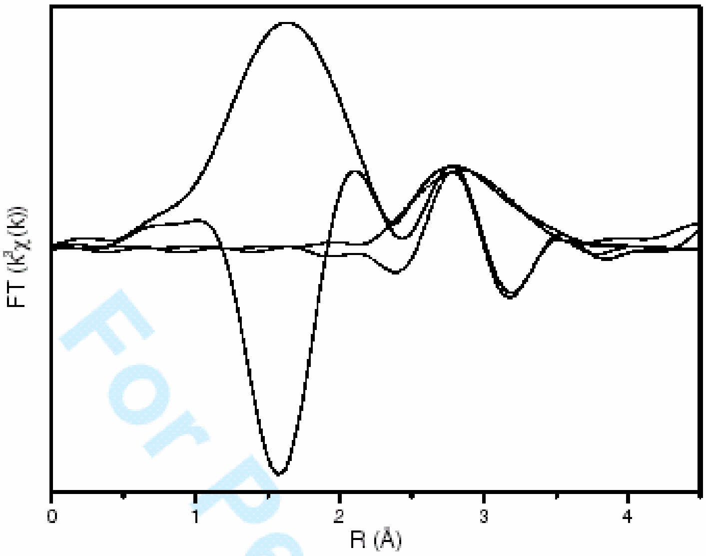


Figure 4a



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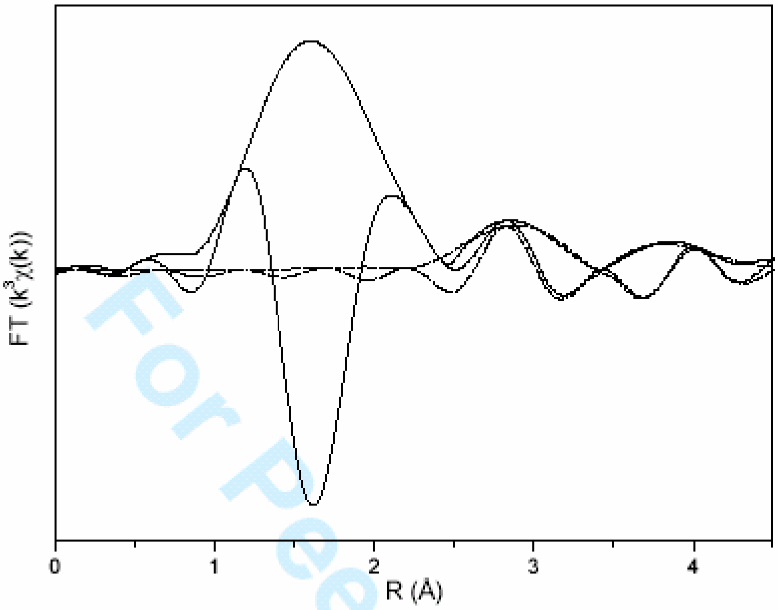
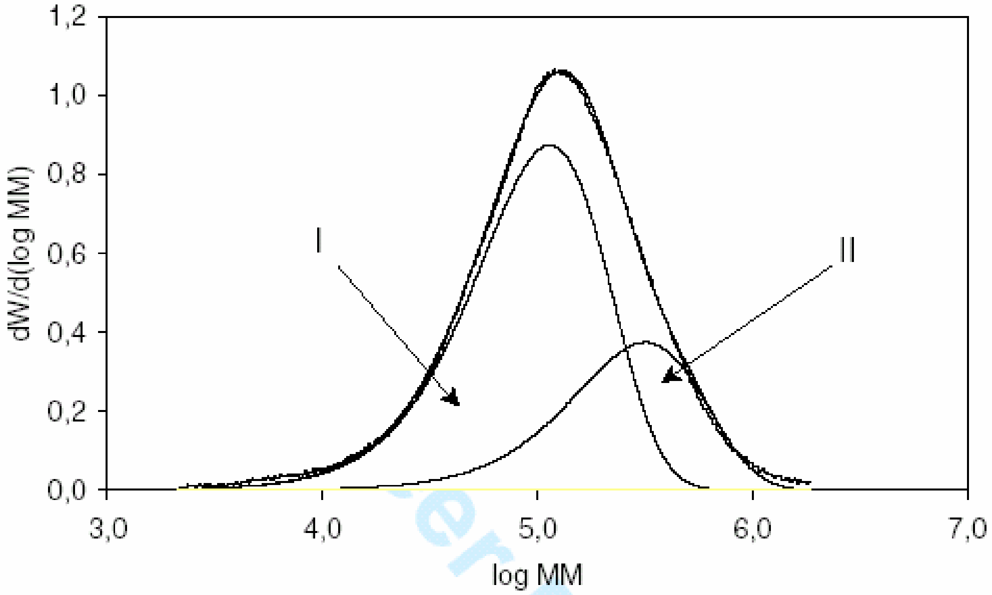


Figure 4c

Figure 5a



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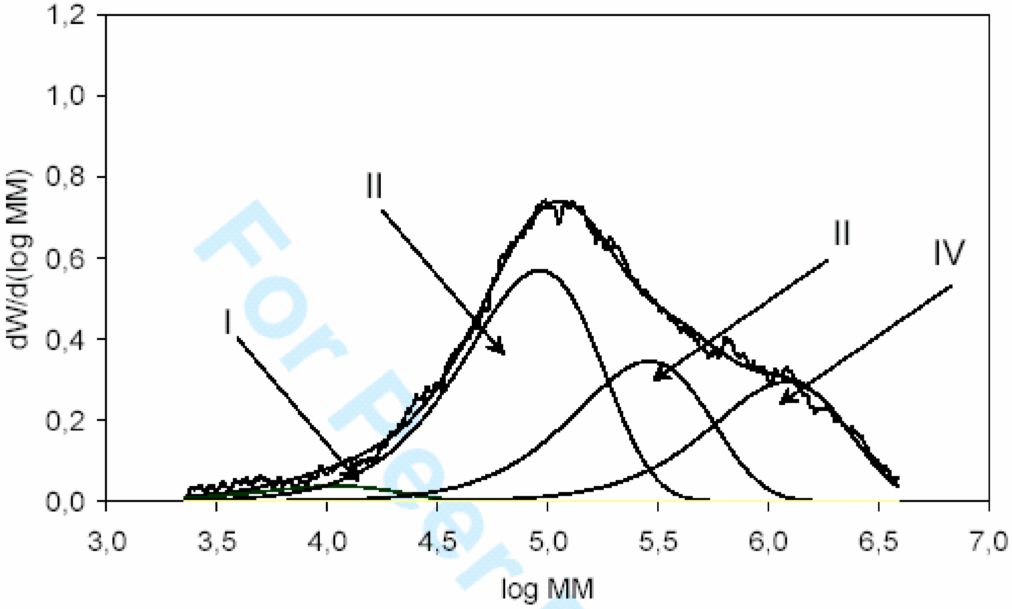
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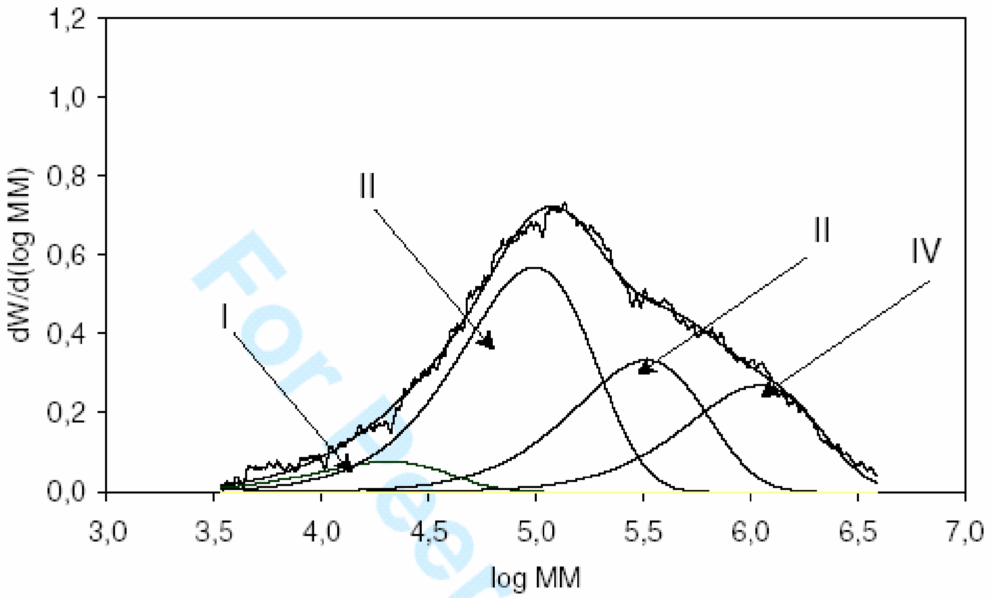
0,6
0,4
0,2
0,0
dW/d(log MM)
3,0
3,5
4,0
4,5
5,0
5,5
6,0
6,5
7,0
log MM
I
II
II
IV

Figure 5c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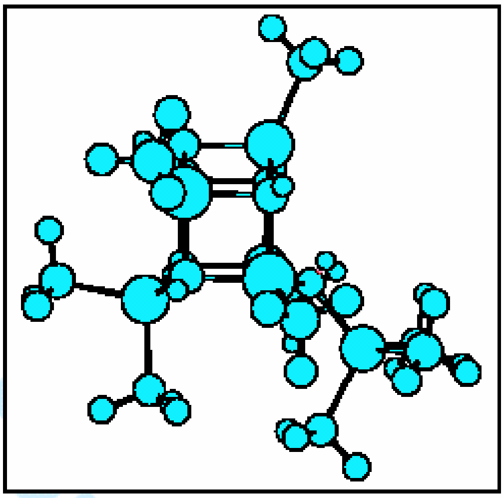
log MM



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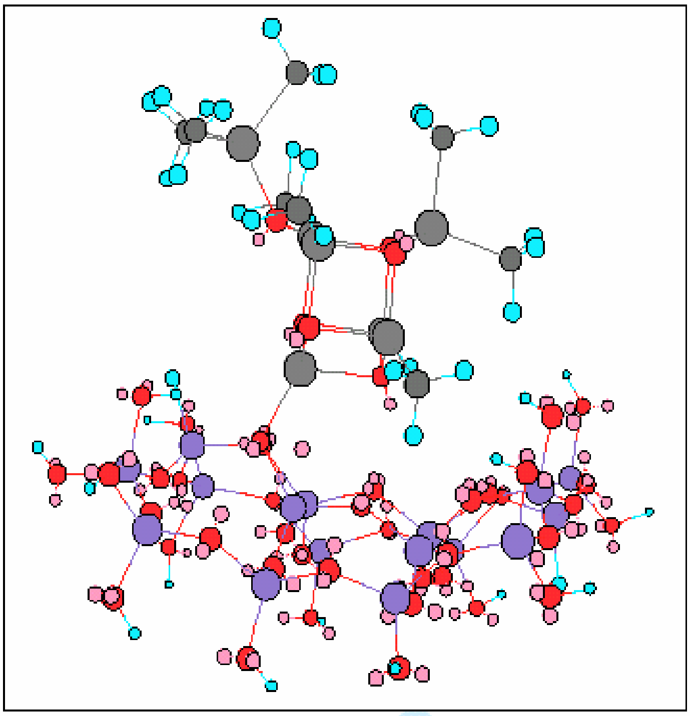


Figure 7

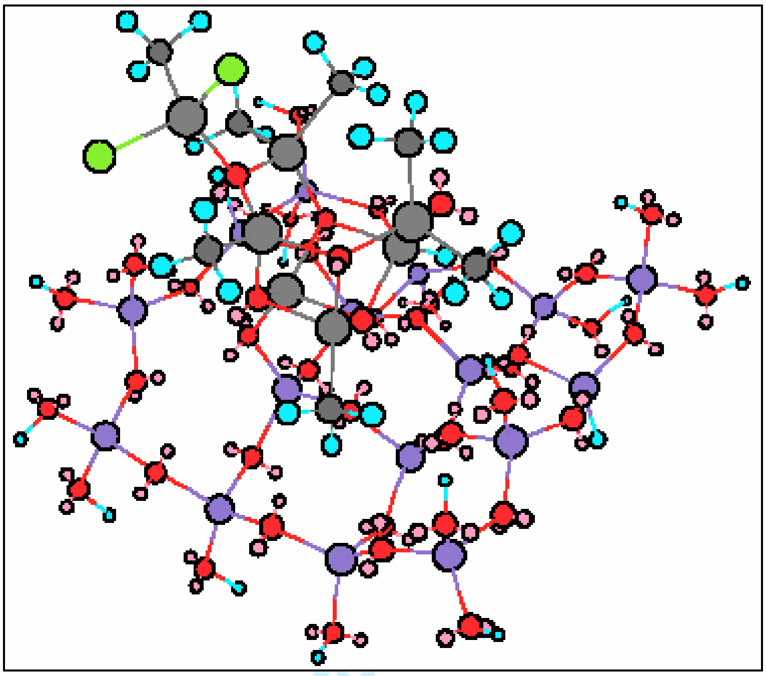
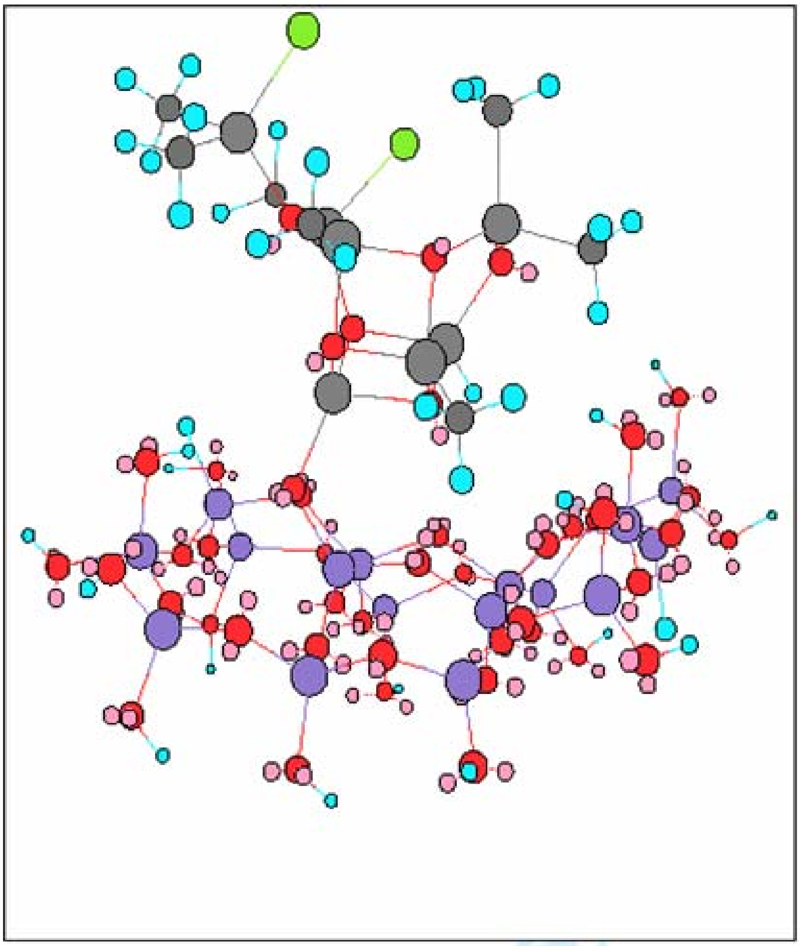


Figure 8



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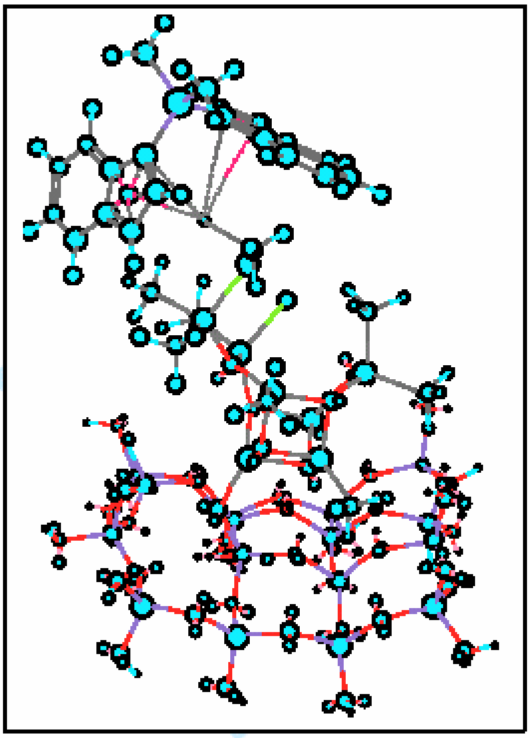
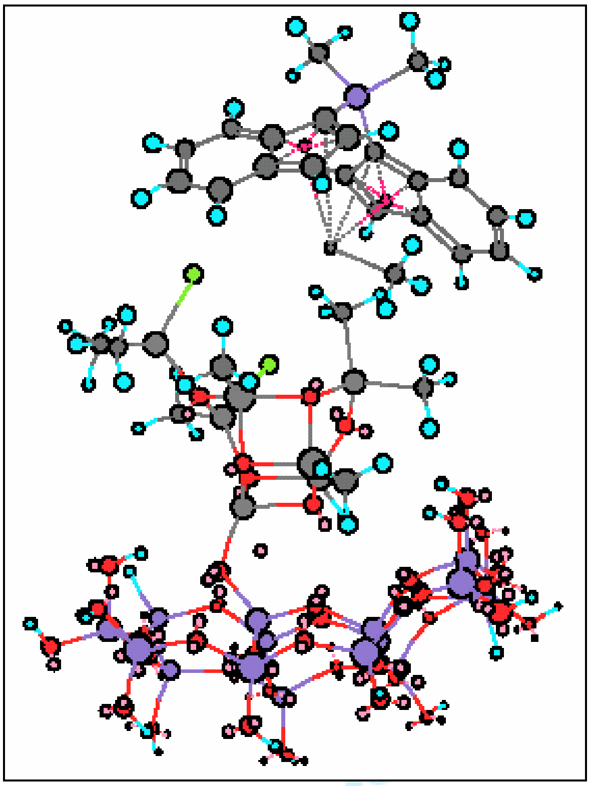


Figure 10



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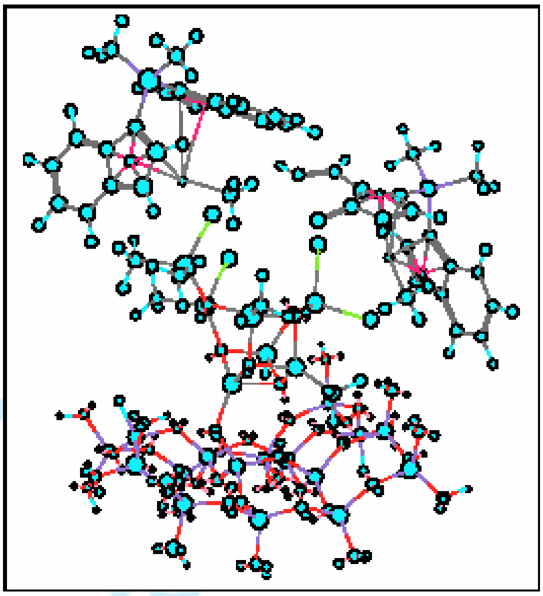

Figure 12

6. CONCLUSÕES:

6.1. A suportação in-situ dos catalisadores $Me_2Si(Ind)_2ZrCl_2$ e $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ sobre SMAO gerou sistemas catalíticos ativos para a polimerização de propeno na presença de alquilalumínios simples tais como TEA, TIBA e IPRA. A atividade catalítica obtida, contudo, foi baixa.

6.2. As reações de polimerização via suportação in-situ foram realizadas com relação Zr/Al (catalisador/SMAO) de 0,2 %, valor 10 vezes inferior ao nível de saturação do suporte com o catalisador $Me_2Si(Ind)_2ZrCl_2$, o qual foi determinado através da isoterma de adsorção como sendo de 2,0 %. Ou seja, na relação Zr/Al_{SMAO} empregada é possível imobilizar todo catalisador dosado sobre o suporte. Os polímeros obtidos via suportação in-situ apresentaram morfologia controlada e semelhante a do polímero obtido via suportação ex-situ, replicando a forma do suporte, e propriedades diferenciadas das obtidas no polímero obtido em condição de polimerização homogênea. Estes resultados indicam que de fato a polimerização ocorreu sobre o suporte, ou seja, houve imobilização do catalisador sobre o SMAO.

6.3. Na ausência de um alquilalumínio externo como TEA, TIBA ou IPRA, ou seja, na presença apenas de SMAO, não houve polimerização de propeno com o catalisador $Me_2Si(Ind)_2ZrCl_2$, indicando que a reação não ocorre por lixiviação do MAO presente no suporte para a solução.

6.4. A natureza e a quantidade de alquilalumínio empregado influenciaram a atividade do sistema catalítico $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$ e as propriedades do polímero obtido, o que demonstra que o alquilalumínio desempenha função relevante na polimerização e não atua apenas como eliminador de impurezas do meio reacional.

6.5. A massa molar dos polipropilenos produzidos com os catalisadores $Me_2Si(Ind)_2ZrCl_2$ e $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ suportados in-situ sobre SMAO aumentou, em função do tipo de alquilalumínio empregado, na ordem TEA < IPRA, TIBA. Provavelmente, na presença de cocatalisadores mais volumosos houve redução da ocorrência de reações de terminação de cadeia.

6.6. Os polipropilenos produzidos com o sistema catalítico $Me_2Si(Ind)_2ZrCl_2$/SMAO/AlR_3 suportado in-situ apresentaram menor temperatura de fusão e de cristalização, menor cristalinidade e maior massa molar do que os polímeros obtidos via polimerização homogênea.

6.7. A taticidade dos polímeros produzidos com $Me_2Si(Ind)_2ZrCl_2$ não foi alterada em função do sistema catalítico empregado, ou seja, homogêneo ou heterogêneo. Foram obtidos polipropilenos com isotaticidade entre 93 e 94 %, demonstrando que a estereosseletividade do catalisador não foi influenciada pela suportação sobre SMAO.

6.8. A deconvolução das curvas de GPC dos polipropilenos indicou a presença de dois tipos de sítios ativos para o sistema catalítico $Me_2Si(Ind)_2ZrCl_2$/MAO (homogêneo) e de três tipos de sítios ativos no sistema catalítico $Me_2Si(Ind)_2ZrCl_2$/SMAO/AlR_3 (heterogêneo in-situ). A única exceção ocorreu nas polimerizações realizadas na presença de TEA com razão molar $Al_{TEA}/Zr \geq 500$ mol/mol, onde o melhor ajuste foi obtido com somente dois picos, indicando a presença de dois tipos de sítios ativos. Este resultado pode indicar que em maiores concentrações o TEA cause a desativação seletiva de um dos tipos de sítios ativos. O inverso da massa molar numérica média ($1/M_n$) do polímero formado em cada tipo de sítio ativo aumentou com o aumento da concentração de alquilalumínio até $Al_{alquilalumínio}/Zr$ igual a 250 mol/mol, resultado esperado em função da correlação existente entre $1/M_n$ e a razão entre as constantes de transferência de cadeia e a constante de propagação de cadeia. Entretanto, para valores acima de 250 mol/mol a correlação acima não foi válida.

6.9. Os polipropilenos produzidos com $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO/$AlR_3$ suportado in-situ apresentaram, como era esperado devido à presença do grupo metila na posição 2 do anel de cinco membros do grupo indenila, maior massa molar e maior temperatura de fusão que os obtidos com $Me_2Si(Ind)_2ZrCl_2$/SMAO/AlR_3. Nos dois sistemas o efeito do aumento da concentração do alquilalumínio sobre a massa molar foi o mesmo: o aumento da concentração de TEA causou diminuição da massa molar, enquanto com TIBA e IPRA houve aumento. A curva de DSC dos polímeros produzidos com o catalisador $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ suportado in-situ, apresentou um pico de menor temperatura de fusão inexistente no polímero obtido em condições de polimerização homogêneas e nos polímeros obtidos com $Me_2Si(Ind)_2ZrCl_2$ tanto em condição homogênea quanto heterogênea de polimerização. Este pico de menor temperatura de fusão provavelmente esteja associado à ocorrência de estereoirregularidades (porções atáticas e/ou sindiotáticas) e/ou regioirregularidades (inserções 1,3 e/ou 2,1 de propeno) ao longo da cadeia.

6.10. O comportamento obtido com o sistema catalítico $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$ na polimerização de propeno foi distinto do verificado com eteno. Em função do tipo e da concentração de alquilalumínio empregados, foram obtidos diferentes efeitos sobre a atividade catalítica e sobre as propriedades dos polímeros produzidos.

6.11. Com base nos resultados das deconvoluções das curvas de GPC dos polímeros obtidos com o catalisador $Me_2Si(Ind)_2ZrCl_2$ e de cálculos teóricos, foram propostas as estruturas dos diferentes tipos de sítios ativos para polimerização de propeno e de eteno presentes nos sistemas catalíticos $Me_2Si(Ind)_2ZrCl_2/MAO$ (homogêneo) e $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$.

6.12. O aumento da razão Zr/SMAO no catalisador $Me_2Si(Ind)_2ZrCl_2$ suportado ex-situ levou à redução da atividade até o teor de 0,8 % Zr/SMAO. A partir desta razão a atividade manteve-se constante. A maior atividade foi obtida na menor razão avaliada, 0,1 % Zr/SMAO. Na análise de EXAFS do catalisador contendo 0,3 % Zr/SMAO duas camadas de Al foram detectadas, sendo uma a 3,43 Å e outra a 4,12 Å. No catalisador preparado com 0,8 % Zr/SMAO, somente uma camada de Al a 3,40 Å foi observada ao redor do átomo de Zr. A maior distância média Zr-Al (3,78 Å) do sistema catalítico $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$ contendo 0,3 % Zr/SMAO pode favorecer a obtenção de um par iônico $[SiO\text{-}Al(Me)O]^-$ $[R_2ZrMe]^+$ mais fraco. Esta interação mais fraca do par iônico facilitaria a dissociação durante a etapa de coordenação da olefina e a propagação da reação de polimerização, tornando, portanto, o catalisador contendo 0,3 % Zr/SMAO mais ativo.

7. CONSIDERAÇÕES FINAIS:

Neste capítulo são apresentados resultados práticos que foram obtidos após a publicação dos artigos apresentados no corpo da Tese e que são relevantes para o melhor entendimento dos resultados obtidos. Além disto, também são apresentadas considerações sobre possíveis avaliações que poderiam ser realizadas como continuação do trabalho realizado.

7.1. Conforme apresentado na Tabela 1 do Artigo 2 (*Macromol Chem. Phys.*, **2004**, *205*, 1525-1529), os polipropilenos produzidos com o sistema catalítico suportado in-situ $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$/SMAO apresentaram duas temperaturas de fusão nas endotermas de DSC, sendo que o pico de menor temperatura de fusão foi atribuído à ocorrência de regioirregularidades durante o crescimento da cadeia. Ou seja, devido a inserções de propeno do tipo 1,3 e/ou 2,1. Posteriormente, amostras de polipropileno produzidas com $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ em condição homogênea e via suportação in-situ, na presença de IPRA com relação molar Al_{IPRA}/Zr igual a 100, foram analisadas por ^{13}C-NMR e os resultados obtidos são apresentados a seguir. As análises foram realizadas no equipamento Varian INOVA-300 (7,1 T de campo magnético), na concentração de aproximadamente 20% em solução de ODCB/TCE-d2 (ortodiclorobenzeno com capilar de tetracloroetano deuterado) à temperatura de 120^{o}C em tubos de 10 mm. As condições experimentais qualitativas utilizadas foram freqüência: 75,4 MHz, janela espectral: 16,5 kHz, tempo de aquisição: 1,8 s, pulso: 15 μs (90°), intervalo entre pulsos:10 s, núcleo desacoplado: ^1H e número de transientes: > 1000.

taticidade	polimerização homogênea		polimerização in-situ - IPRA	
	díades (%)	pêntades (%)	díades (%)	pêntades (%)
mm	94,5		89,9	
mmmm		87,3		80,1
mmmr + rmmr		7,2		9,8
mr	4,0		7,5	
mmrr + mmrm		3,5		4,2
rmrr + rmrm		0,5		3,3
rr	1,5		2,6	
rrrr		0,1		0,4
rrrm + mrrm		1,4		2,2

Os resultados obtidos demonstram que o polipropileno produzido com o catalisador suportado in-situ apresenta 89,9% de isotaticidade, com maior quantidade de díades sindiotáticas (7,5%)

e atáticas (2,6%), enquanto no polímero obtido em condições homogêneas e que não apresenta o pico de menor temperatura de fusão, a isotaticidade foi de 94,5%, mesma isotaticidade obtida no polipropileno produzido com o catalisador $Me_2Si(Ind)_2ZrCl_2$ tanto em condição homogênea quanto via suportação in-situ. Portanto, mesmo sendo possível a ocorrência de regioirregularidades (inserções 1,3 e/ou 2,1 de propeno), o pico de menor temperatura de fusão verificado nos polipropilenos produzidos com catalisador $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ suportado in-situ SMAO provavelmente seja devido à ocorrência de estereoirregularidades (porções atáticas e sindiotáticas). Possivelmente, o polímero de menor isotaticidade obtido com o sistema catalítico $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2/SMAO/AlR_3$ seja, de fato, composto de duas frações com distintas isotaticidade ou cristalinidade. Ou seja, parte do polímero formado apresentaria isotaticidade semelhante a do polímero produzido em condição homogênea, próxima a 94%, e parte do polímero apresentaria isotaticidade menor do que 89%, de modo que o resultado médio obtido foi de 89,9%. O fracionamento do polímero em função da cristalinidade por PREP ou CRYSTAF e a análise por ^{13}C-NMR das frações obtidas permitiria avaliar as frações de diferente isotaticidade formada.

7.2. Nas condições de polimerização empregadas, a atividade dos sistemas catalíticos suportados in-situ na polimerização de propeno foi muito inferior à obtida em condições homogêneas. Com base nos resultados descritos no Artigo 2 (*Macromol Chem. Phys.*, **2004**, *205*, 1525-1529), verifica-se que para maximizar a atividade catalítica poderia ser avaliado o uso de IPRA em relações Al_{IPRA}/Zr abaixo de 100 mol/mol. Outra possibilidade seria o emprego de menor relação Zr/SMAO, pois todas as polimerizações foram feitas com 0,2% Zr/SMAO (Al_{SMAO}/Zr = 500 mol/mol) e, conforme Artigo 5 (submetido ao *J. Polym. Sci. Part A: Polym. Chem.*, **2006**), foi constatado que quanto menor a relação Zr/SMAO maior a atividade catalítica obtida. Nos dois casos, entretanto, deve ser determinado qual o valor ótimo para cada variável.

Embora o emprego de maior temperatura de polimerização favoreça o aumento da atividade catalítica, todas as polimerizações foram realizadas a 60^oC porque o trabalho experimental foi iniciado com o catalisador $Me_2Si(Ind)_2ZrCl_2$ que, nesta condição, produz polímero de massa molar muito baixa e o aumento da temperatura de polimerização faria com que a massa molar diminuísse ainda mais. Para comparação, na tabela a seguir são apresentados valores de massa molar de polímeros comerciais produzidos com catalisadores Ziegler-Natta e metalocênico.

resina	catalisador	MFR (230/2,16)[(a)] (g/10 min)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
A[(b)]	Ziegler-Natta	20	54	231	4,3
B[(b)]	Ziegler-Natta	42	54	190	3,5
C[(b)]	metaloceno	72	55	148	2,7
homogênea[(c)]	$Me_2Si(Ind)_2ZrCl_2$	nd	16	34	2,1
in-situ - TIBA[(d)]	$Me_2Si(Ind)_2ZrCl_2$	nd	34	69	2,1
in-situ - IPRA[(e)]	$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$	nd	155	247	1,6

nd: Não determinado.

(a) Taxa de fluidez determinada a 230ºC e 2,16 kg. Propriedade inversamente proporcional à viscosidade da resina.

(b) Resina comercial indicada para produção de utensílios de uso geral pelo processo de injeção.

(c) Conforme Tabela 1 do Artigo 2.

(d) Conforme Tabela 1 do Artigo 3 - relação molar $Al_{TIBA}/Zr = 1000$. Polímero de maior massa molar produzido com o catalisador $Me_2Si(Ind)_2ZrCl_2$ suportado in-situ.

(e) Conforme Tabela 1 do Artigo 2 - relação molar $Al_{IPRA}/Zr = 500$.

Pode-se constatar nos dados da tabela acima que os polímeros produzidos com o catalisador $Me_2Si(Ind)_2ZrCl_2$ apresentam massa molar muito inferior a das resinas comerciais. Entretanto, com o catalisador $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ a massa molar da resina produzida foi significativamente maior, sendo superior a da resina A, de maior massa molar. Catalisadores metalocênicos com substituintes na posição 2 (anel de 5 carbonos) e na posição 4, 6 ou 7 (anel de 6 carbonos) do anel indenílico permitem a produção de polipropileno com massa molar ainda maior, abrindo, portanto, a possibilidade de temperaturas de polimerização mais altas, favorecendo o aumento da atividade catalítica.

As resinas comerciais A e B são produzidas em processo *bulk*, ou seja, tendo com meio de reação propeno líquido, em temperaturas próximas a 80^{o}C e sob pressão acima de 20 bar. Portanto, a combinação de um catalisador com substituintes nas posições 2 e 4, 6 ou 7 do anel indenílico, temperatura de polimerização > 60^{o}C, pressão de polimerização > 20 bar com o emprego de propeno líquido como meio de reação, uso de IPRA como cocatalisador com relação $Al_{IPRA}/Zr < 100$ mol/mol e teor de zircônio suportado sobre SMAO < 0,2% Zr/SMAO podem levar a produção de polipropileno, utilizando o procedimento de suportação in-situ, com alta atividade e massa molar adequada para o uso comercial.

Deve ser salientado, contudo, que embora seja importante a obtenção de alta atividade catalítica, para que o processo seja economicamente viável, e de alta massa molar, para que a resina apresente boas propriedades mecânicas, é fundamental que o polímero produzido apresente tamanho de partícula adequado, sem formação excessiva de finos (partículas de tamanho de partícula pequeno), para que o catalisador possa ser empregado em escala industrial. Portanto, junto com a otimização das condições de polimerização com o uso da técnica de suportação in-situ, deve ser avaliada a distribuição granulométrica do polímero gerado para verificar a adequação do polímero gerado ao uso em planta industrial.

7.3. No trabalho descrito no Artigo 3 (*J. Appl. Polym. Sci.*, **2005**, *95*, 1050-1055) foi determinado o número de tipos de sítios ativos e no Artigo 4 (*Macromol. Mater. Eng.*, **2006**, *291*, 279-287) foi proposta a estrutura dos sítios durante a polimerização em condição homogênea e via suportação in-situ do catalisador $Me_2Si(Ind)_2ZrCl_2$. Através da deconvolução das curvas de GPC foi verificado que os polímeros produzidos com o catalisador suportado in-situ apresentam 3 tipos de sítios ativos, mas com o uso de TEA com Al_{TEA}/SMAO > 250 mol/mol há apenas 2 tipos de sítios ativos. Para tentar confirmar estes resultados e auxiliar na caracterização dos sítios ativos, sugere-se como trabalho futuro que seja simulada a preparação do catalisador em condições de suportação in-situ, ou seja, misturando o catalisador, o suporte e o alquilalumínio, em condições similares às utilizadas nas polimerizações, variando o teor de alquilalumínio. Após a manutenção do sistema catalítico por 1 h a 60^oC, para simular as condições de polimerização, mas sem a adição do monômero, o catalisador deve ser lavado e seco e as amostras analisadas por XPS (Espectroscopia Fotoeletrônica de Raios-X) para verificar quantas espécies diferentes de zircônio serão obtidas.

7.4. Durante a realização do trabalho experimental, foram realizadas polimerizações com o sistema catalítico $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3/(nBu)_3SnH$, sendo o catalisador suportado in-situ e ex-situ, e constatou-se que com a adição do hidreto de tri-butilestanho - $(nBu)_3SnH$, utilizado como espaçador horizontal, o catalisador foi inativo na polimerização de propeno, sendo ativo apenas para eteno. Estes resultados não foram completamente explorados e poderia ser objeto de trabalho futuro.

7.5. Conforme mencionado na introdução da Tese, existem três rotas principais para a heterogeneização de catalisadores metalocênicos: (1) imobilização inicial do MAO sobre o suporte e posterior adição do catalisador; (2) imobilização inicial do catalisador sobre o suporte e posterior adição do MAO; (3) preparação de um aduto entre o MAO e o catalisador e, depois de determinado tempo de pré-contato, imobilização sobre o suporte. O tempo de pré-contato durante a formação do aduto, na rota (3), apresenta papel importante sobre a reação de polimerização e sobre as propriedades finais do polímero. Assim sendo, o procedimento (3) de imobilização do catalisador poderia ser estudado, avaliando o efeito do tempo de pré-contato tanto do catalisador metalocênico com, neste caso, o suporte SMAO, quanto com o alquilalumínio empregado, bem como poderia ser avaliado o efeito da realização de pré-contato entre os três componentes: catalisador, suporte e alquilalumínio.

7.6. Apesar do principal suporte empregado para imobilização de catalisadores metalocênicos ser a sílica, motivo pelo qual o suporte escolhido nesta Tese foi o SMAO, há a possibilidade da utilização de outros tipos de suportes tais como alumina, zeolita, polímero e sílica modificada, por exemplo, com perfluorfenilborato. Devido à viabilidade da técnica de suportação in-situ com o uso de SMAO, este procedimento também poderia ser avaliado com outros suportes, como parte de um trabalho futuro.