Macromol. Symp. **2010**, 296, 11–20 DOI: 10.1002/masy.201051003

Novel Supports for Ethylene Polymerisation Based on Polystyrene Polymers

Joana Tudella,[1,2,3] *M. Rosário Ribeiro,*[*1] *Henri Cramail,*[2,3] *Alain Deffieux*[*2,3]

Summary: The industrial use of metallocene/methylaluminoxane catalytic systems and late transition metal catalysts requires the use of supports to directly get polyethylene (PE) with spherical morphology. The presence of residues of the inorganic support gives rise to PE contamination problems, therefore less contaminating organic supports may present an interesting alternative. In this work, linear hydroxypolystyrene (PS-OH) and polystyrene-*block*-isoprene copolymer (PS-b-PI) were tested as supports for ethylene polymerisation. The ability of these polymers when dissolved in a selective solvent to form micelles or aggregates, was investigated by light scattering techniques. Next, their capacity to act as MAO or TMA-activated supports towards MeDIP(2,6-iPrPh$_2$FeCl$_2$) catalyst was analysed by carrying ethylene polymerisation tests and PE morphology studies. The PS-b-PI copolymer, used as organic support in heptane, enabled the obtention of PE with well defined spherical morphology.

Keywords: ethylene polymerisation; hydroxypolystyrene; micelles; polymeric supports; polystyrene-*block*-polyisoprene

Introduction

Various routes have been investigated to support metallocenes onto organic particles and a special interest has been focused on polystyrene-bound polymerisation precatalysts. This derives from the idea that the catalytic species reside within a mobile hydrocarbon-rich matrix providing a polymerisation microenvironment that more closely resembles to a homogeneous solution polymerisation.[1] Moreover, polystyrene supports are very versatile materials in terms of the incorporation of functional groups, enabling the development of various routes to anchor metallocene and/or postmetallocene systems. Therefore, polystyrene-based polymers are among the most popular organic polymeric supports.

One of the simplest ways of supporting metallocenes on organic particles is their encapsulation into polystyrene-co-divinylbenzene beads. The metallocene can be introduced in the gel-type particles by a simple swelling-shrinking process carried out in the presence of the solvent. The polyethylene growth on this supported catalytic system replicates the polystyrene-co-divinylbenzene particles, but a large amount of MAO is required for efficient metallocene activation.[2] A different approach involves the in-situ synthesis of polystyrene-bound catalysts. This can be achieved by i) post modification of a preformed PS support, ii) copolymerisation of styrene with a vinyl functionalised ancillary ligand or using metallocenes containing polymerisable functions.[3–5]

---

[1] Instituto de Ciência e Engenharia de Materiais e Superfícies - ICEMS, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
Fax : +351 21 8419198, E-mail: rosario@ist.utl.pt

[2] CNRS, Laboratoire de Chimie des Polymères Organiques, 16 avenue Pey Berland, Pessac Cedex, F33607, France
Fax : +33 5 40008487, E-mail: deffieux@enscpb.fr

[3] Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, ENSCPB, Pessac Cedex, F33607, France

However, all these synthesis require long and complex preparation procedures.

Klapper and co-workers[6–10] have developed a new stategy that consists in the immobilisation of active methylaluminoxane/metallocene complexes, through non covalent bonding with nucleophilic groups of the support. In this way polystyrene supports containing methoxy groups[6] or polyethylene oxide (PEO)[7] functionalities have been used for the synthesis of polyethylene particles with a high bulk density. Further developments of this concept,[8,9] lead to the synthesis of polystyrene nanoparticles functionalised with nucleophilic chains on their surfaces. PPO functionalised PS nanoparticles (60–100 nm) were also prepared by mini emulsion polymerisation of styrene, divinylbenzene and PPO functionalised styrene. The catalytic system $Me_2Si(_2MeBenzInd)_2ZrCl_2/MAO$ supported on these nanoparticles was found adequate for ethylene polymerisation and resulted in improved PE morphologies and high activities. Varying the concentration of PPO chains at the surface of the nanoparticles, the Al/Zr ratio and Zr concentration, the polymerisation activities and the characteristics of the PE could be tuned.[9,10]

Star-shaped polymers, also called microgels, are especially attractive due to their three-dimensional shape and branched structure. Bouilhac *et al.* [11] synthesized star-shaped polystyrene by the ATRP technique (arm first) using bromo-terminated PEO initiators and divinylbenzene as the core linker. Star-like polystyrenes consisting of a microgel core and carrying PS arms with a few number of ethylene oxide units end-capped by methoxy or hydroxy functions were obtained. These supports were used to anchor aluminic activators (TMA, TIBA, MAO) and then tested in the presence of MeDIP(2,6-iPrPh)$_2$FeCl$_2$ catalyst for ethylene polymerisation – Figure 1.

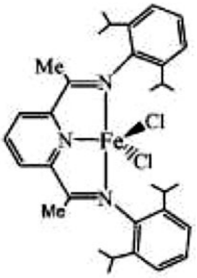


Figure 1.
Structure of the MeDIP(2,6-iPrPh$_2$FeCl$_2$) catalyst.

In most cases good activities and polyethylene beads of spherical morphology were obtained. However, a preliminary treatment of the ATRP-derived PS stars was necessary to displace the remaining bromo end groups, which were proved harmful for an efficient catalysis of ethylene polymerisation. To avoid the use of MAO, the same authors subsequently synthesized polystyrene functionalised microgels containing benzoic acid or benzophenone functionalities at the end of the chain.[12] Trimethylaluminum added over these functionalised supports allowed the generation of non-hydrolytic MAO at the surface. At the end, addition of the iron catalyst on the activator-support complex, enabled the preparation of PE beads with a spherical morphology and high bulk density. Supporting the iron catalyst also narrowed the PE molar mass distribution and suppressed the PE oligomer fraction, which forms under homogeneous conditions in the presence of TMA. Although organic supports described so far are effective for ethylene polymerisation and yield polyethylene beads, their synthesis requires sophisticated techniques, which limit their potential for an industrial development.

More recently, Cramail and coll. reported the use of micelle-type structures as organic supports.[13,14] The latter can be obtained from end-capped functional polymers or block copolymers, which self-assemble spontaneously in a selective solvent. The authors have explored the self-assembly in toluene of benzoic acid end-functionalised polystyrene into micelle-like structures, in which trimethylaluminium is trapped, and this way generated encapsulated methylaluminoxane-like species. These nano-micellar structures were subsequently used to support the bis(imino)pyridinyl iron catalyst for ethylene polymerisation. High catalytic activities were obtained and polyethylenes with unimodal molar mass distribution showed a controlled morphology.[13] Following a similar strategy, spherical micellar objects formed by the self-assembly of polystyrene-*b*-poly(4-vinylbenzoic acid) block copolymers in toluene, were also used as supports of iron-based complexes for the production of PE beads.[14]

In this work, polymers and copolymers obtained from more common and simpler synthesis procedures have been investigated as supports. Linear hydroxy-terminated polystyrene (PS-OH) and polystyrene-*block*-isoprene copolymers (PS-*b*-PI) are tested for the production of micelle-type organic supports for ethylene polymerisation. The behaviour of these polymers in toluene and heptane, their ability to form aggregates, their subsquent use to anchor TMA or MAO and to activate MeDIP(2,6-iPrPh)$_2$FeCl$_2$ for the production of polyethylene with controlled morphology are discussed.

Experimental Part

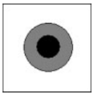
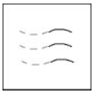
Reagents

PS, PS-OH and PS-*b*-PI were synthesised following anionic polymerisation procedures. Briefly, PS was prepared in toluene at 20 °C using butyl lithium as initiator and methanol as terminating agent. $M_n = 7240$ g/mol, $M_w/M_n = 1.04$. PS-OH was prepared in a similar way by adding a small amount of ethylene oxide at the end of the styrene polymerisation. $M_n = 4860$ g/mol, $M_w/M_n = 1.04$.

PS-*b*-PI block copolymers were obtained by sequential anionic polymerisation of styrene and isoprene. $M_n = 37000$ g/mol., $M_w/M_n = 1.20$. (weight composition PS 37%; PI 63%)

The iron catalyst [MeDIP(2,6-iPrPh$_{2\text{-}}$FeCl$_2$)] was synthesised according to literature.[15] Trimethylaluminium (2M solution in heptane) and Methylaluminoxane (10% w/v in toluene) were purchased from Aldrich and were used without further treatment. Heptane and toluene were purified and dried over polystyryl lithium seeds according to standard procedures.

Table 1.
Solubility characteristics and organization in heptane and/or in toluene of PS-OH and PS-*b*-PI copolymers in absence and in presence of MAO or TMA.

Polymer	Heptane	Toluene
PS-OH	Insoluble	Formation of micelles with -OH groups in the core and PS in the shell. Mean Size: Varying with concentration
PS-OH + MAO	Insoluble	Formation of micelles/aggregates with -OH groups and MAO in the core and PS in the shell. Mean Size: 1000–1200 nm
PS-*b*-PI	Formation of micelles; PI block: soluble PS block: not soluble (PS Core; PI Shell) Mean Size: 250 nm 	No Micelles; PI block: soluble PS block: soluble Single PS-b-PI Chains. 
PS-*b*-PI + MAO	Formation of micelles/aggregates with PI groups and MAO in the shell and PS in the core. Mean Size: 3900 nm	Completely soluble. No Micelles
PS-*b*-PI + TMA	Formation of micelles/aggregates with PI groups and TMA in the shell and PS in the core. Mean Size: 770 nm	Completely soluble. No Micelles.

Light Scattering Studies of Polymer Solutions in Toluene and Heptane

10 ml of purified and dried toluene or heptane preliminarily filtered through a 0.22 μm PTFE membrane was added to a desired polymer amount placed in a glass tube fitted with a measuring cell previously degassed under vacuum. The solution was then left under stirring for 24 h at 25 °C for complete dissolution before light scattering measurements. A similar protocol was applied for experiments in presence of TMA, MAO and the iron complex, which were added under nitrogen on the polymer solution. The light scattering measurements were carried out in a Malvern Zetasizer (3000 HSA) apparatus. The measuring angle was 90 ° and the samples were kept in a glass cell at constant temperature during measurements. The data were fitted using the regularisation algorithm (CONTIN).

Table 2.
Ethylene polymerisation activities using the iron complex in the presence of PSOH/MAO systems, at several PSOH/MAO ratios.

Co-Catalyst system	C_{PSOH} (g/l)	PSOH/ MAO (w/w)	Mean Activity [KgPE (molFe*h*bar)]
Com. MAO	—	—	3960
PSOH / MAO	0.019	0.05	3660
PSOH / MAO	0.037	0.10	2620
PSOH / MAO	0.074	0.20	2720
PSOH /MAO	0.111	0.30	1780

[a] Polymerisation conditions: Al/Fe = 400; V(toluene) = 50 ml; Catalyst: MeDIP(2,6- iPrPh)$_2$FeCl$_2$; n(Fe) = 0.8^*10^{-6} mol; T = 30°C; t = 1h; $P_{ethylene} = 1$ bar; C(MAO) = 0.37 g/l.

Polymerisation Tests

Polymerisations were performed in a Schlenk apparatus. The organic support was first dispersed in the solvent, then MAO or TMA and the iron catalyst were successively added in this order. In some experiments, the schlenk was fitted with a light scattering cell, thus allowing measurements of the aggregation state of the catalytic system, just prior polymerisation. Polymerisation reaction was triggered by adding ethylene in the following conditions: $[Fe] = 1.6^*10^{-5}$ M; $P_{ethylene} = 1$ bar, T = 30 °C; reaction time = 1 h. The amount of MAO or TMA with respect to iron catalyst was varied from 400 to 2 000 according to the experimental conditions, see Tables 2 and 3. The weight ratio between the polymer support and MAO or TMA was also varied to find the optimized reaction conditions. The corresponding values are indicated in Tables 2 and 3.

Characterisation of Polyethylene Morphology

They were observed under scanning electron microscopy (SEM) performed using a JEOL JSM 2500 apparatus.

Table 3.
Polymerisation activities obtained upon immobilisation of MAO or TMA and iron complex over the PS-b-PI block copolymer, in heptane.

Co-catalyst System	$C_{PS-b-PI}$ (g/l)	PS-b-PI/ (TMA or MAO) (w/w)	Al/Fe	Polymerisation Activity KgPE/(molFe*h*bar)	Mean size of aggregates [a] (nm)
MAO	0	0	400	360	–
MAO	0	0	1000	310	–
PS-b-PI / MAO	0.07	0.08	1000	380	10700
PS-b-PI / MAO	0.35	0.2	2000	1000	3900
TMA	0	0	2000	1680	–
PS-b-PI / TMA	0.06	0.005	1000	70	3100
PS-b-PI / TMA	0.02	0.010	2000	390	4400
PS-b-PI / TMA	0.05	0.026	2000	980	770
PS-b-PI / TMA	0.10	0.050	2000	1460	1600

n(Fe) = 0.8^*10^{-6} mol; V(heptane) = 50 ml; T = 30°C, $P_{et} = 1$ bar; t = 1h.

[a] The mean size of the aggregates formed in polymerisation conditions, for PS-b-PI in heptane upon addition of MAO and the iron catalyst, were measured by in-situ light scattering prior to polymerisation start.

Results and Discussion

Light Scattering Studies

Hydroxy-Polystyrene (PS-OH) in Toluene Solution

A first set of measurements was performed to investigate the formation (or not) of PS- (M_n= 7240 g/mol.) and PS-OH-based (PS-OH, M_n = 4 860 g/mol.) micelles/aggregates in toluene medium. As expected, since toluene is a good solvent for PS, no peak corresponding to the formation of PS aggregates is observed with PS chains bearing an H terminal, indicating the only presence of isolated chains. A different situation is observed with PS bearing a CH_2-CH_2-OH terminus, Figure 2a. Although at low PS-OH concentrations (< 10 g/l), the formation of aggregates/micelles is not observed, they clearly form at higher PS-OH concentrations (20, 50, 100 g/l). These results confirm the possibility of PS-OH to self-assemble in toluene likely through hydrogen bonding between the OH termini, forming the core, while PS chains constitute the soluble corona, see Scheme b Figure 2.

The ability of PS-OH to remain in the form of agregates or micelles in presence of MAO was then investigated. Light scattering results are shown in Figure 3 a, before and after addition of MAO to a 10 g/l solution of PS-OH. Although initially the PS-OH chains do not form detectable aggregates in toluene at 10 g/l, addition of MAO to their solution leads to the formation of unimodal aggregates with a diameter ranging from about 1 000 to 1 200 nm, which remain present down to PS-OH concentrations of 3 to 5 g/l. Once formed, these aggregates remain quite stable and do not change significantly in size and concentration over the examined 24h period. It is worthy to note that commercial MAO alone in toluene also forms aggregates with narrow dispersity centered around 750 nm diameter at high concentration. We assume that in PSOH/MAO systems, MAO molecules (that contain some TMA as side product) are forming the core of the aggregates, whereas the PS-OH attached by their hydroxyl end to MAO or TMA molecules form the peripherical shell, as illustrated Scheme b, Figure 3.

PS-b-PI Block Copolymers in Heptane

A large number of research groups have investigated the formation of micellar systems based on PS-*b*-PI block copolymers with linear,[16–18] branched,[19,20] and cyclic architectures.[21,22] Besides many other factors, they observed that the size and shape of the micelles depend on the composition of the PS-*b*-PI chains and on the total molar mass of PS + PI blocks. For linear PS-*b*-PI copolymers in heptane, spherical and quite stable micelles with an average size of 50–60 nm generally form.[21]. Since heptane is a bad solvent

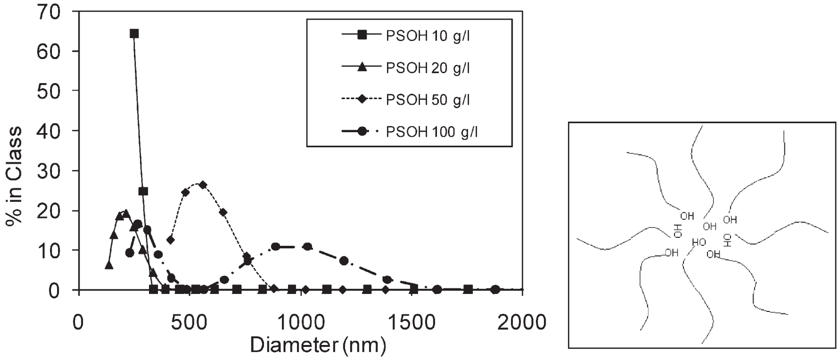


Figure 2.

a) PSOH populations observed in toluene by light scattering at different polymer concentrations and b) proposed structure for the aggregates.

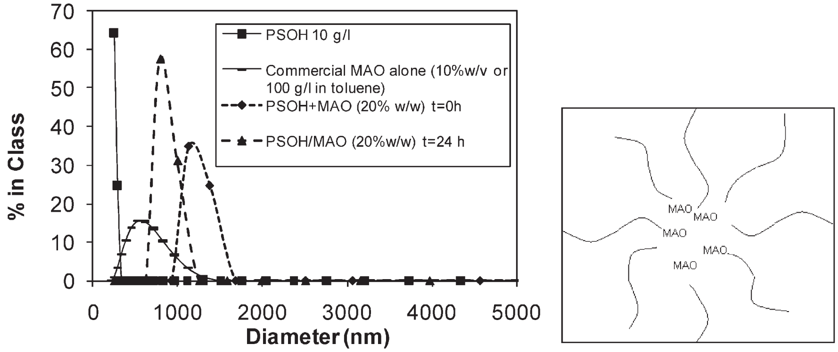


Figure 3.
a) Typical size and distribution of populations of PSOH, PSOH + MAO and MAO alone in toluene as observed Light Scattering; b) simplified representation of aggregates formed in PSOH + MAO systems.

for PS and a good solvent for PI, these micelles consist of a PI "corona" and a PS "core".

As expected from these previous data, the linear PS-*b*-PI block copolymer used in this work ($DP_{PS} = 239$ and $DP_{PI} = 280$) also forms well defined micelles in heptane, see Figure 4. The size distribution of these micelles was found to only show a slight dependence on the polymer concentration, with a mean size value varying between 200 and 250 nm. Once formed, the micelles are stable and do not change significantly with time.

The effect of TMA, MAO and iron catalyst addition on the PS-*b*-PI self-assembly was further investigated. After adding successively the iron catalyst ($[Fe] = 1.6^{*}10^{-5}$ M), and MAO ($[MAO] = 0.032$ M) to the PS-*b*-PI dispersed in heptane, very large and disperse objects with a diameter of approximately 3–4 microns are formed, see Figure 5. When TMA is used in place of MAO, the increase of aggregate size is less important, and two populations are observed centred respectively at about 300 and 1300 nm.

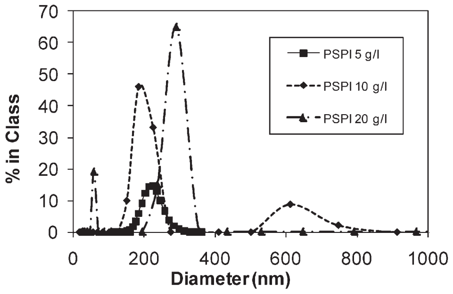


Figure 4.
Size and distribution of PS-*b*-PI micelles in heptane as a function of the PS-*b*-PI concentration, as observed by Light Scattering ($DP_{PS} = 239$, $DP_{PI} = 280$).

The self-assembly behavior of PS-OH and PS-*b*-PI block copolymers in toluene and in heptane in absence and in presence of MAO or TMA are resumed in Table 1.

Polymerisation Tests and Morphology of the Synthesized PE

PS-OH aggregates as catalyst support, in toluene
Activities towards ethylene polymerisation of the iron complex activated by the PS-OH/MAO systems, at different PS-OH/

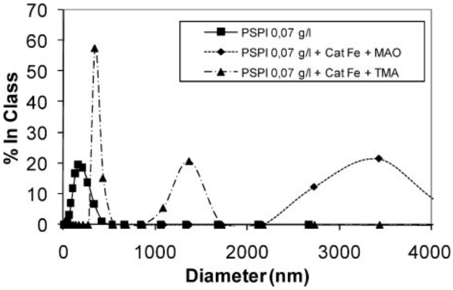


Figure 5.
Evolution of the PS-*b*-PI aggregates in heptane, as observed by light scattering upon successive addition of the iron catalyst and MAO or TMA. n (Cat. Fe) = $0.8^{*}10^{-6}$ mol; n(Al/Fe) = 2000; $V_{(heptane)}$ = 50 ml; $[Fe] = 1.6^{*}10^{-5}$ M; [MAO] = [TMA] = 0.032 M.

MAO ratio are indicated in Table 2. Replacing commercial MAO alone by these systems, lead to a slight decrease of the ethylene polymerisation activities, which is not very important for the lower PS-OH ratio but increases with the relative amount of PS-OH introduced. At a PS-OH/MAO ratio of 0.30, the activity is decreased by a factor of about 2. This activity loss may be due to reaction between PS-OH chains and MAO active sites, leaving less free MAO in the polymerisation media to activate the iron catalyst.

The PE particles obtained in the presence of the PS-OH/MAO system, at ratio 0.2 (w/w), and the iron complex can be compared with PE obtained in homogeneous conditions in Figure 6. Although the concentration of PS-OH used in this polymerisation is significantly lower than the concentration where aggregation is detected by light scattering measurements, a clear improvement of PE morphology, with formation of PE particles is observed in presence of the PS-OH/MAO system.

PS-b-PI Aggregates as Support, in Heptane

Polymerisation tests were conducted in heptane using either MAO or TMA trapped into PS-*b*-PI block copolymer aggregates and the iron complex as catalyst. With this system, *in-situ* light scattering studies were performed directly on the supported catalyst complex, before ethylene polymerisation, to check the formation and size of aggregates/micelles in polymerisation conditions. The mean size of the aggregates as well as the activity values obtained are given in Table 3. It is worthy noting that in absence of the organic support the use of heptane as solvent instead of toluene leads to a significant decrease of polymerisation activity. The latter falls from 3960 to 360 KgPE/(mol-Fe*h*bar)) for the reference experiment with MAO alone. In contrast with the reference experiment with non-supported TMA as activator, activities in toluene and heptane are similar.

Compared to these homogeneous conditions, the polymerisation activities

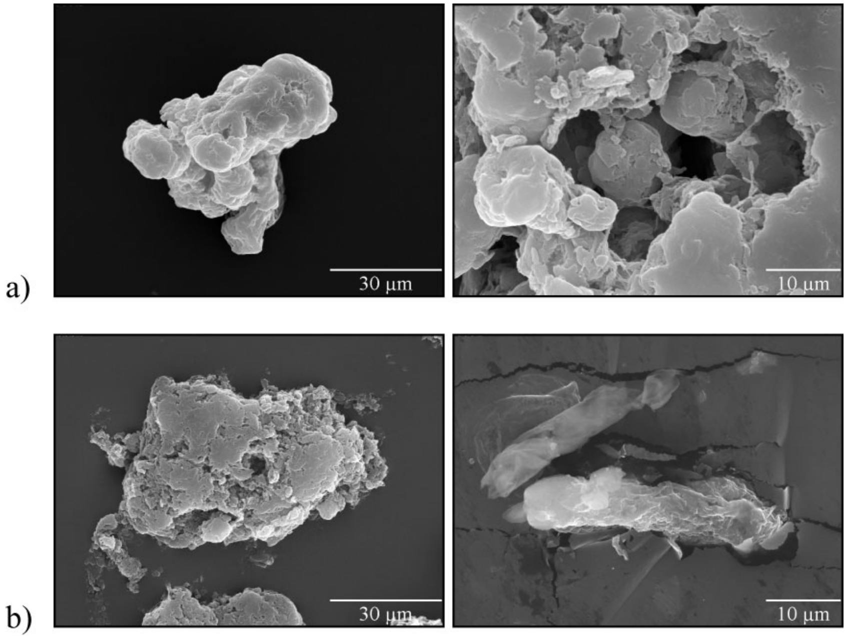


Figure 6.
SEM pictures of: (a) PE particles obtained in the presence of PS-OH/MAO, at ratio 0.2 (w/w), and the iron catalyst and (b) PE obtained with the iron catalyst and MAO alone in homogeneous conditions.

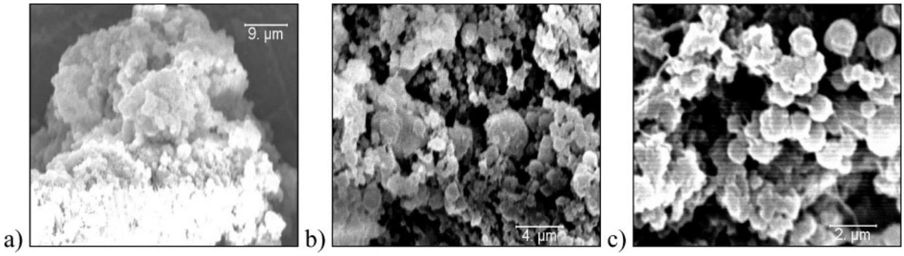


Figure 7.
SEM pictures of PE obtained in heptane media: (a) iron catalyst in homogeneous conditions, TMA/Fe= 2000; (b) PS-b-PI/TMA and iron catalyst, average aggregate size 3100 nm; (c) *idem*, average aggregate size 770 nm.

observed for PS-b-PI/MAO and PS-*b*-PI/TMA supported systems in heptane are quite acceptable, best activities being observed for PS-*b*-PI/TMA support/cocatalyst system. The PS-*b*-PI/TMA ratio seems to influence the polymerisation activity; higher amounts of PS-*b*-PI chains relatively to TMA (i.e. PS-b-PI/TMA ratios) lead to an increase of the activity. However the reason for this behaviour is not completely understood.

The SEM images of polyethylene obtained in the presence of PS-b-PI/MAO and PS-b-PI/TMA systems are shown in Figure 7 and 8 respectively.

Contrarily to PE obtained from PS-b-PI/MAO, the PE prepared from PS-b-PI/TMA show a clear improvement of their particle-like morphology when compared to homogeneous catalysts (MAO or TMA). Data in Figures 7 and 8 points out to a correlation between the size of the aggregates formed in polymerisation conditions and the morphology of the PE particles: increasing the size of aggregates affect negatively the polymer morphology. In fact the extremely large aggregates (up to 10.7 micron) observed for PS-b-PI in heptane, after addition of MAO and the iron catalyst, lead to very poor morphologies, similar to those characteristic of homogeneous catalysis. On the other hand a defined PE spherical morphology is found for PS-b-PI/TMA (at ratio 0.026 (w/w)), which corresponds to the smallest aggregate size (770 nm) followed by PS-*b*-PI/TMA (at ratio 0.055 (w/w)) corresponding to an intermediate aggregate size (3100 nm). The most favourable mass ratio is obtained at PS-*b*-PI/TMA ratio of 0.026 (w/w), since it combines the best morphology with a quite good activity.

The bulk densities for these PEs were found to be in the range 200 to 260 g/L, these are higher values than the one

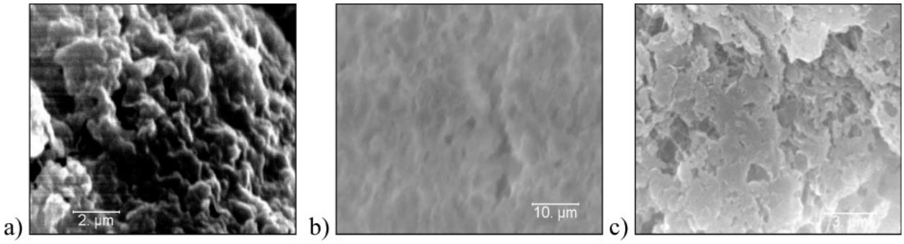


Figure 8.
SEM pictures of PE obtained in heptane media and: (a) iron catalyst in homogeneous conditions, MAO/Fe= 1000; (b) PS-b-PI/MAO and iron catalyst, average aggregate size 10.7 micron; (c) *idem* average aggregate size 3.9 micron.

observed for the PE obtained in homogeneous conditions (150g/L).

DSC analysis of PE samples obtained with these immobilised systems show melting temperatures in the range of 133 to 134 °C, and higher than those obtained in corresponding homogeneous conditions. Accordingly high molar masses may be expected for these supported systems. PE produced by iron catalysts in homogeneous conditions, exhibit molar mass in the range 100 000 to 500 000 g/mol [23].

Conclusion

The presence of the –OH terminus in linear hydroxy-polystyrene yields in toluene the self-assembly of the polymer chains, and the formation of aggregates at PS-OH concentrations above 20 g/l. The addition of MAO over these PS-OH solutions leads to the formation of much larger aggregates, with an average diameter value of about one micron, which are still stable at PSOH concentrations of about 3–5 g/l. Ethylene polymerisations performed in the presence of PS-OH/MAO as supported cocatalyst show activities of the same order of magnitude as for homogeneous MAO polymerisation conditions. Moreover, in contrast to PE obtained in homogeneous conditions (MAO alone as cocatalyst), the presence of some spherical polyethylene particles is observed for high PSOH/MAO ratios.

Polyisoprene-polystyrene (PS-*b*-PI) block copolymers, used as organic supports in heptane, yield very interesting results for ethylene polymerisation. The well-defined micellar PS-*b*-PI systems, with size around 200–250 nm are converted into big aggregates upon addition the iron complex and of TMA or MAO. PE morphology seems to be correlated to the aggregate size. Very large aggregates results in a poor morphology control whereas the best PE particle morphology is observed with the smaller aggregates. Polymerisation activities in heptane, of the order of 1000 KgPE/(molFe*h*bar) are only slightly lower than the ones in homogeneous conditions (around 1600 KgPE/(molFe*h*bar)). Formation of spherical PE may be tentatively attributed to the heterogeneisation of the catalyst system around the micelles/aggregates through electrostactic interaction between the insoluble PS blocks and the cationic active species (formed by the reaction of the cocatalyst with the metal catalyst). The dimensions of the aggregates is crucial for morphology and small size aggregates favour the production of well-defined spherical particles.

Acknowledgements: Joana Tudella is gratefull to Fundação para a Ciência e Tecnologia (Portugal) for the PhD fellowship.

[1] J. Severn, J. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073.
[2] S. Hong, U. Rief, M. Kristen, *Macromol. Rapid Commun.* **2001**, *22*, 1447.
[3] M. Stork, M. Koch, M. Klapper, K. Mullen, H. Gregorius, U. Rief, *Macromol. Rapid Commun.* **1999**, *20*, 210.
[4] B. Peifer, W. Milius, H. G. Alt, *J. Organomet. Chem.* **1998**, *553*, 205.
[5] A. I. Licht, H. G. Alt, *J. Organomet. Chem.* **2003**, *687*, 142.
[6] M. Koch, M. Stork, M. Klapper, K. Mullen, H. Gregorius, *Macromolecules* **2000**, *33*, 7713.
[7] N. Nenov, M. Koch, M. Klapper, K. Mullen, *Polymer Bulletin* **2002**, *47*, 391.
[8] Y.-J. Jang, N. Nenov, M. Klapper, K. Mullen, *Polymer Bulletin* **2003**, *50*, 351.
[9] Y.-J. Jang, N. Nenov, M. Klapper, K. Mullen, *Polymer Bulletin* **2003**, *50*, 343.
[10] M. Koch, A. Faucou, N. Nenov, M. Klapper, K. Mullen, *Macromol. Rapid Commun.* **2001**, *22*, 1455.
[11] C. Bouilhac, E. Cloutet, H. Cramail, A. Deffieux, D. Taton, *Macromol. Rapid Commun* **2005**, *26*, 1619.
[12] C. Bouilhac, E. Cloutet, H. Cramail, A. Deffieux, D. Taton, *Macromol. Chem. Phys.* **2007**, *208*, 1349.
[13] C. Bouilhac, E. Cloutet, D. Taton, A. Deffieux, R. Borsali, H. Cramail, *Macromolecules* **2008**, *41*, n° (20), 7321.
[14] C. Bouilhac, E. Cloutet, D. Taton, A. Deffieux, R. Borsali, H. Cramail, *J. Polym. Sci. - Part A: Polym. Chem.* **2009**, *47*, 197.
[15] B. L. Small, M. Brookhart, A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049.
[16] K. Gupta, R. Krishnamoorti, J. Kornfield, S. Smith, *Macromolecules* **1995**, *28*, 4464.
[17] R. Krishnamoorti, M. Modi, M. Tse, H.-C. Wang, *Macromolecules* **2000**, *33*, 3810.

[18] E. Kesselman, Y. Talmon, J. Bang, S. Abbas, Z. Li, T. Lodge, *Macromolecules* **2005**, *38*, 6779.
[19] P. Tian, D. Uhrig, J. Mays, H. Watanabe, S. Kilbey, *Macromolecules* **2005**, *38*, 2524.
[20] H. Watanabe, Y. Matsumiya, S. Ishida, T. Takigawa, T. Yamamoto, D. Vlassopoulos, J. Roovers, *Macromolecules* **2005**, *38*, 7404.
[21] E. Minatti, P. Viville, R. Borsali, M. Schappacher, A. Deffieux, R. Lazzaroni, *Macromolecules* **2003**, *36*, 4125.
[22] R. Borsali, E. Minnati, J.-L. Putaux, M. Schappacher, A. Deffieux, P. Viville, R. Lazzaroni, T. Narayanan, *Langmuir* **2003**, *19*, 6.
[23] T. Dalet, H. Cramail, A. Deffieux, *Macromol. Symp.* **2006**, *231*, 110.