

Research Article

Synthesis of Disentangled Ultra-High Molecular Weight Polyethylene: Influence of Reaction Medium on Material Properties

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The polymerization of ethylene to Ultra-High Molecular Weight Polyethylene (UHMWPE) in certain reaction conditions allows synthesis of nascent powders with a considerably lower amount of entanglements: the material obtained is of great interest from both academic and industrial viewpoints. From an academic point of view, it is interesting to follow the evolution of the metastable melt state with the progressive entanglements formation. Industrially, it is valuable to have a solvent-free processing route for the production of high modulus, high strength tapes. Since the polymer synthesis is performed in the presence of a solvent, it is interesting to investigate the influence that the reaction medium can have on the catalyst activity, resultant molecular characteristics, and polymer morphology at the macroscopic as well as microscopic level. In this paper, we present the effect that two typical polymerization solvents, toluene and heptane, and mixtures of them, have on the catalytic performance and on the polymer properties. The observations are that an unexpected increase of catalyst activity, accompanied by a significant improvement in mechanical properties, is found when using a carefully chosen mixture of solvents. A tentative explanation is given on the basis of the presented results.

1. Introduction

The extremely high melt viscosity of UHMWPE makes conventional processing techniques, including screw extrusion and injection moulding, difficult to accomplish. The most commonly used processing methods are compression moulding or ram extrusion and in both cases the properties of the final products are influenced by a number of processing variables such as sintering time, temperature, and pressure [1].

Thanks to an excellent set of properties such as good resistance to wear, corrosion, and environmental stress-cracking, high impact strength even at very low temperatures, low coefficient of friction, and, last but not least, biocompatibility, UHMWPE has found many applications in different areas, from food processing industries to waste water treatment and from climbing and naval ropes to artificial joints in orthopedics [2].

However, in spite of its good performance in short-term applications, it has been reported that wear, creep, and fatigue fracture are usually observed in long-term applications that can lead to serious consequences: for example, debris generated at articulating surfaces of UHMWPE prostheses is transported to the hard and soft tissues surrounding the joint, causing chronic inflammatory reactions and bone desorption [3]. For this reason, continuous efforts are made to understand the structure-property relationship of this material. It is generally recognized [4] that a major role in the debris formation is played by fusion defects in the material. Complete fusion is difficult to achieve for UHMWPE, due to the presence of entanglements between the very long macromolecular chains [5]: the topological constraints caused by these entanglements limit the solid state deformation of this polymer to moderate draw ratios and its viscosity in the melt is considerably high because it follows the relationship $\eta_0 \propto M^{3.4}$ (where M for UHMWPE is higher than 1×10^6 g/mol)

[1]. This means that, for polymer melts, an increase in average molar mass by a factor of 10 corresponds to an increase in zero shear viscosity by a factor of 1000, making processability of high molar mass polymer a challenge.

Though it is possible to reduce the amount of entanglements via crystallization from dilute solutions (requiring more than 90% weight of solvent) this method is rather cumbersome and provides regular stacking of crystals which tends to reentangle prior to melt [6]. The regular stacking of crystals on melting facilitates the immediate restoration of the entangled state.

Rastogi et al. have recently reported [7–9] that, by carefully controlling the polymerization conditions, it is possible to significantly reduce the amount of entanglements in the UHMWPE and such disentangled crystals can be mechanically deformed below the melting point, providing fibers/tapes having the oriented extended chain crystals.

In commercial processes, the polymer is mostly synthesized using Ziegler-Natta heterogeneous catalyst systems, where the active sites are in close proximity to each other: due to the relatively high polymerization temperatures (60–100°C), the rate of crystallization for the growing chains is slow when compared to rate of polymerization and this facilitates the formation of entanglements. By decreasing the temperature, it is possible to increase the rate of crystallization compared to polymerization; moreover, by using an homogeneous catalytic system at low concentration of catalyst (dilute solutions) and monomer (low monomer pressure), it is possible to have chains growing far from each other and crystallizing independently, leading to a less entangled polymer.

This simple concept allows synthesis of disentangled polymer directly from polymerization, with no need for further treatments with large quantities of solvents, and the material thus obtained can be easily drawn and even compression-moulded at temperatures below its melting temperature. The catalyst used in this work for the synthesis of “disentangled UHMWPE” is a *bis*-(phenoxyimine) titanium complex (Figure 1), activated by methylaluminoxane (MAO): this catalytic system was reported in 2001 by Fujita [10, 11] and coworkers as being able to polymerize ethylene in a living fashion at room temperature, with high yields. Molecular weights as high as 0.4×10^6 g/mol in as little as 1 min reaction time were reported in very mild conditions (25°C, 1 atm pressure of ethylene).

In the general framework of a systematic study on the influence that reaction conditions have on polymer properties, papers reporting on the influence of cocatalyst amount, reaction time, and reaction temperature have been previously published [12–14].

In the present article we wish to report a new insight arising from the use of different solvent and solvent mixtures in the polymerization reaction.

2. Experimental Section

2.1. General Considerations. All manipulations were performed under nitrogen or argon atmosphere using standard

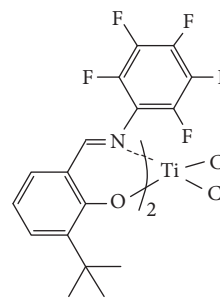


FIGURE 1: Bis-[N-(3-tert-butylsalicydene)-2,3,4,5,6-pentafluoroanilate]TiCl₂ catalyst used in this study.

high-vacuum Schlenk techniques or in a glovebox. Solvents (anhydrous toluene and anhydrous heptane) were purchased from Aldrich, further dried on 4 Å Molecular Sieves, and degassed by a dry nitrogen stream. Ethylene (grade 3.0) purchased from BOC, MAO solution (10% wt in toluene) purchased from Aldrich, and precatalyst **1** purchased from MCat were used as received. For the polymerization and polymer characterization we followed the methods previously described in [13].

2.2. Polymerizations

2.2.1. 1l Vessel. The polymerization was performed in a jacketed Pyrex glass reactor equipped with a magnetic stirrer, a temperature probe, a gas inlet/outlet, and a rubber septum for catalyst injection. The oven-dried reactor was purged from air with three vacuum-nitrogen (moisture- and oxygen-free) cycles and cooled to room temperature under nitrogen flux.

2.2.2. 10l Vessel. The large scale tests were performed in a wall-mounted, jacketed Pyrex reactor equipped with a double plane propeller blade mechanical stirrer, a temperature probe, a gas inlet/outlet, and a rubber septum for catalyst injection. The reactor was kept overnight at 125°C, and then the temperature was brought to room temperature while the vessel was purged with three cycles of vacuum/nitrogen.

The solvent upload in the reactor and the polymerization were performed in the same way for both types of vessels: the desired amount of dried solvent(s) was transferred under inert gas into the vessel and further degassed with nitrogen stream. The temperature was set to the desired value by means of a thermostat and when the right value was reached, the stream of gas was switched from nitrogen to ethylene.

After stirring for 30 min, methylaluminoxane (MAO) was added, followed by a solution of the catalyst in toluene + MAO to start the polymerization. The reaction was carried on for the required time under vigorous stirring and constant feed of ethylene, controlled by means of a Buchi pressflow gas controller bpc 6002, and then quenched by addition of acidified methanol (CH₃OH/HCl 95/5 v/v). The polymer was filtered out, washed with additional methanol, and oven dried under vacuum at 40°C for one night.

2.3. Polymer Characterization

2.3.1. DSC. Differential scanning calorimetry was performed using standard TA Instruments Q2000. Samples of 1.0–1.5 mg mass were weighed with a Mettler-Toledo XS3DU precision balance and crimped in Tzero Aluminum pans of known mass. An identical empty pan was used as a reference. A heating rate of $10^{\circ}\text{C min}^{-1}$ was used for heating/cooling/heating cycle. Nitrogen was purged at a rate of 50 ml min^{-1} . DSC was calibrated using indium.

2.3.2. SEM. Scanning Electron Microscopy investigations on morphologies of nascent reactor powders were carried out with a high resolution FEG SEM (Carl Zeiss Leo 1530 VP) operated at 5 kV. As-polymerized particles were carefully deposited on SEM stubs and the samples were coated with gold by a sputtering technique.

2.3.3. Rheology. Disks of 12 mm diameter were sampled by punching sintered sheets of $\phi = 35\text{ mm}$ obtained by compression moulding the nascent powder at 125°C . Such nonstandard size was used to avoid excessive torque to the rheometer transducers imposed by the rubber-like melt state of the UHMWPE. Samples were loaded at 110°C and heated rapidly to 130°C ($\approx 30^{\circ}\text{C min}^{-1}$), normal force was applied (up to $\approx 0.4\text{ N}$), and autonormal force function was activated to avoid slippage between plates and specimen.

A dynamic Oscillatory Amplitude (OA) sweep test at a fixed frequency of 10 rad s^{-1} was performed to determine the Linear Viscoelastic Regime (LVE), where the rheological response of the material is independent of the amplitude of the deformation applied during the test.

Dynamic Oscillatory Time sweep tests (OT or modulus build-up) were performed to follow the entanglement formation at a fixed frequency of 10 rad s^{-1} and the strain obtained by OA test (usually in the region of $\approx 0.1\text{--}0.5\%$). Once the modulus build-up had reached a plateau value, Oscillatory Frequency (OF) sweeps were performed at angular frequencies ω between 100 and 0.001 rad/s to determine M_w and MWD as described elsewhere [12].

3. Results and Discussion

In Table 1 the results are listed of ethylene polymerizations performed with the catalytic system I/MAO in various conditions. Three sets of experiments have been performed, with the aim to explore the influence of reaction conditions on the activity of the catalytic system and on the molecular weight, molecular weight distribution, and macro/microscale morphology of the polymer produced. In the first set (PE1–5) we have tested different concentrations of catalyst, in the second set (PE6–12) we have performed reactions with different solvents and mixtures of them, and in the third set (PE 13–15) we have explored the influence of upscaling the process from a 1 l to a 10 l reactor.

All reactions are run at $T = 10^{\circ}\text{C}$ and $\text{Al/Ti} = 1200$ conditions that, according to previous studies, were found to be the best ones to get disentangled polymer in a controlled fashion with this particular catalytic system [15].

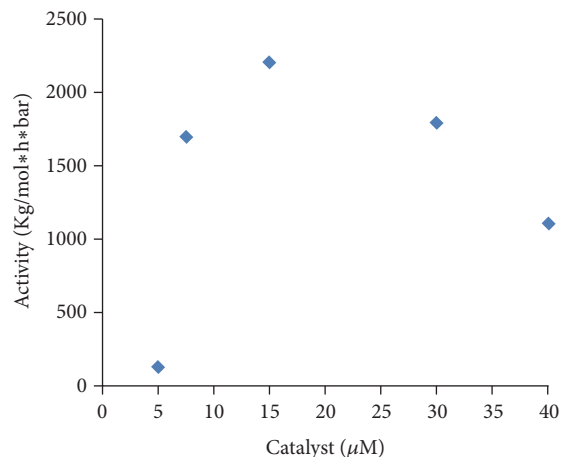


FIGURE 2: Catalyst activity versus catalyst concentration for polymerizations run in toluene.

When considering the dependence of activity on the catalyst concentration, from samples PE 1–5 it is evident that there is a distinct trend for the reactions run in toluene, with a maximum of activity centered around $15\text{ }\mu\text{M}$ (Figure 2).

Our hypothesis to justify this result is that the very high activity of this catalytic system makes the amount of ethylene present in solution at monomer partial pressure of $\sim 1\text{ bar}$ too low to comply with the fast consumption when the catalyst concentration is higher than $20\text{ }\mu\text{M}$, thus leading to a process limited by the ethylene uptake rate. For catalyst concentration lower than $10\text{ }\mu\text{M}$, when keeping constant the ratio catalyst/cocatalyst, the activity is lower probably because the MAO amount is not high enough to scavenge the impurities present in the system and properly activate the catalyst. We then chose to use $15\text{ }\mu\text{M}$ as the catalyst concentration for the following experiments.

Forlini et al. [16] reported in 1997 a study on the influence of increasing dichloromethane (DCM) content in a toluene/DCM mixture. Their findings showed gradual increase of catalyst activity with increasing DCM content. The cause of the increase in the catalyst activity was attributed to the larger dielectric constant of DCM that enhances the ionic dissociation of the catalyst/cocatalyst ionic couple. We decided to perform a similar set of experiments (PE6–12), using toluene/heptane mixtures, with the aim to achieve a finer control of the polymerization rate. In order to keep a fine control over the ethylene feed, a Gas Control Unit in combination with a PC was used, allowing us to follow the instant ethylene consumption of the system.

The results were quite surprising: contrary to our expectations, the catalytic activity of the system I/MAO was not gradually increasing with increasing toluene content, but it showed a maximum value instead, centered around a toluene/heptane ratio of 70/30 (Figure 3).

The different behavior of the system I/MAO in the different mixtures is even more striking if we compare the profiles of ethylene uptakes (Figure 4).

From the uptake profiles we can retrieve useful information on the catalyst performance. The ethylene uptake for

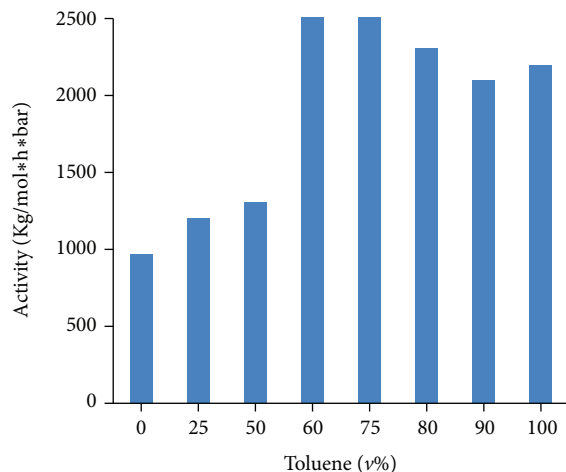


FIGURE 3: Catalyst activity versus volume% of toluene in the reaction medium.

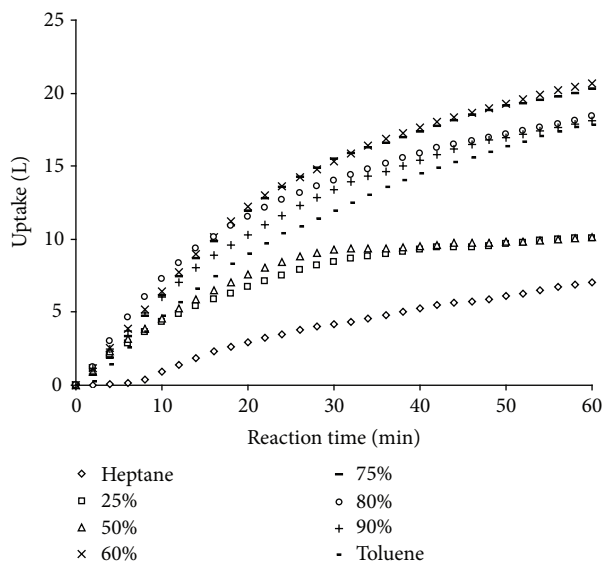


FIGURE 4: Profiles of ethylene uptake in Litres of ethylene versus minutes of reaction during polymerization experiments as registered by the Gas Control Unit.

the polymerization in heptane shows an induction period of several minutes, after which the consumption starts and continues quite linearly for the entire hour. This behavior is not observed in any of the mixtures where toluene is present, thus indicating a strong role of toluene in facilitating the access of ethylene to the catalyst/cocatalyst ion pair. The profiles for solvent mixtures 25/75 and 50/50 T/H are intermediate between the two solvents, while for any mixture containing more than 50% of toluene the uptake profiles show a faster reaction and a higher total consumption, even compared to the pure solvents.

It should be noted that for the samples PE 9 and PE10 the amount of polyethylene formed after 45 min of reaction was so high that efficient stirring of the reaction was hampered: we therefore assume that the activities values in Table 1 for PE 9 and PE10 are underestimated. This is further confirmed by

the fact that the reactions run in a larger vessel with improved stirring, as is the case of the runs PE13 to PE15, all showed higher catalyst activity.

To our knowledge, this result is unprecedented in the literature [17, 18] and a tentative explanation can be given, for this particular catalytic system. For the explanation we take into account the data on molecular weight obtained from rheological experiments, according to the method published elsewhere [12].

In all the analyzed samples it is possible to observe a storage modulus (G') build-up due to the reentanglement process happening in the molten state [19]. The storage modulus in the rubbery plateau region (G_n^0) of a polymer sample at equilibrium is inversely proportional to a quantity, M_e , defined as the mass between entanglements, according to the equation:

$$G_n^0 = \frac{g_n \rho RT}{\langle M_e \rangle}, \quad (1)$$

where g_n is a numerical factor (1 or 4/5 depending upon convention), ρ is the density, R is the gas constant, and T is the absolute temperature [20]. During a "time sweep" experiment, a constant shear is applied to the polymer in the melt state. Commercial UHMWPE shows a value of G' basically constant with time of 2.0 MPa that can be correlated with a value of M_e of about 1300 g/mol. The disentangled UHMWPE shows instead a starting value of G' considerably lower than 2.0 MPa, an indirect proof of the high value of M_e , that is, a low amount of entanglements. The tests are done at 160°C, a temperature at which the material is in the melt state. Interestingly, once in the melt, the value of G' for disentangled UHMWPE increases with time: this indicates that the disentangled state is metastable and the chains reptation in the melt ultimately leads to the thermodynamically stable, fully entangled melt.

Once the plateau has been reached, frequency sweep experiments can be performed on the thermodynamically stable, fully entangled melt to evaluate M_w and PDI of the polymers using the software provided by the instrument.

The different activities observed in the different solvent mixtures can be related to two factors: (1) the different polymerization rate of active sites and (2) the different number of active sites. If changing the solvent has an influence on the polymerization rate of the active sites, but not on their number, the molecular weights of the resulting polymers should increase with increasing activities. Otherwise, if changing the solvent has an influence only on the number of active sites, but not on their polymerization rate, the molecular weight should be roughly constant. Obviously, the real situation will be a combination of the two cases, but the information gathered from the molecular weights can indicate which of the two factors is actually predominant.

The results show that M_n and M_w are increasing with increasing activities, thus suggesting that there is an effect on the polymerization rate of the system once it is used in a mixture of solvents. In all cases the PDI is greater than 1, indicating the loss of a truly living character in the time scale of our experiments.

TABLE I: Results of ethylene polymerization with I/MAO.

Sample	Solvent(s) ^(a)	Catalyst [μM]	Yield [g]	R_p ^(b)	M_n ^(c)	M_w ^(c)	PDI
PE1	Toluene	2.5	0.24	120			
PE2	Toluene	7.5	8.81	1700			
PE3	Toluene	15	23.5	2200	1.7	6.0	3.5
PE4	Toluene	30	39.2	1800			
PE5	Toluene	40	65	1100			
PE6	Heptane	15	12	970	1.4	3.5	2.5
PE7	T/H 25/75	15	15	1200	0.9	3.9	4.3
PE8	T/H 50/50	15	16	1300	1.5	3.0	2
PE9	T/H 60/40	15	30.5	2500			
PE10	T/H 75/25	15	30.2	2500	2.2	7.0	3.2
PE11	T/H 80/20	15	28	2300			
PE12	T/H 90/10	15	26.5	2100	2.3	7.6	3.3
PE13	Heptane	15	131	1300	1	3.1	3.1
PE14	T/H 75/25	15	283	2900	1.8	6.9	3.8
PE15	Toluene	15	255	2600	1.7	6.2	3.6

(a) Toluene/heptane solvent mixtures are expressed as volume%.

(b) Expressed in $[\text{kg}_{\text{PE}}/\text{mol}_{\text{cat}} \cdot \text{h} \cdot \text{bar}]$.

(c) Data from rheological experiments, in 10^6 g mol^{-1} .

Other reaction conditions: time: 1 h; temperature: 10°C , $\text{Al}_{\text{MAO}}/\text{Ti} = 1200$, ethylene: 1.1–1.4 bar; PE1–5, solvent amount: 0.5–0.75 l; PE6–12, solvent amount: 0.75–1.0 l; PE13–15, solvent amount: 6 l.

In order to justify the synergetic effects of the solvent mixture on the polymerization rate, we should consider that, in toluene, thanks to its higher dielectric constant (2.38 at 25°C instead of 1.92 of heptane [21]), the ion pair will be “solvent-separated” and this would lead to a faster rate of polymerization when compared to the contact ion pair present in heptane [17]. On the other side, the solubility of ethylene in heptane is higher than in toluene, so the monomer availability in heptane is higher than in toluene [22].

This means that the rate of reaction will be limited by the ethylene concentration when in pure toluene, and by the opening of the ion pair when in pure heptane: by using a mix of the two solvents it is thus possible to overcome both these limitations, leading to the highest activity when a 75/25 v/v Tol/Hept mixture is used instead of pure solvents.

The second set of experiments (PE13–15) has been performed in a 10 l reactor vessel, in order to check that the influence of solvent mixture is maintained while upscaling the process. The 10 l reactor vessel is equipped with a double plane propeller blade stirrer that allows a better stirring compared to the magnetic stirrer used for the 1 l vessel: in fact, the activity values for all the runs are higher than those obtained in the smaller vessel.

The increased dimensions of the polymerization vessel and the consequent slower diffusion of ethylene in the reaction medium may be responsible for the slightly larger molecular weight distribution observed, as the monomer concentration may not be homogenous throughout the reactor.

The reaction medium and the concentration of ethylene seem to have a strong influence also on the morphology

of polymer particles: those obtained from pure heptane (PE6 in Figure 5) are smaller and denser, while those obtained from pure toluene (PE3 in Figure 5) are bigger and lighter.

This is in agreement with a study from Hermann and Bohm [23] on the morphology of particles obtained using a very active homogeneous catalyst in toluene: the authors claimed that the observed morphology was a result of aggregation due to Brownian motions and growth controlled by a faster diffusion of ethylene in the outer part of the particle.

When using toluene it is possible to notice a dramatic change in particle morphology just by changing the monomer feeding: finer particles are obtained if the monomer is fed through a gas dispersion tube instead of a straight feeding tube.

This observation can be justified considering that the smaller gas bubbles produced by the dispersion tube will have a higher surface area and this will help the solubility, thus increasing the instantaneous concentration of ethylene. In support of this hypothesis, we did not observe a similar behavior in heptane, where the slower rate of reaction ensures that the monomer concentration is always high enough to produce a smaller morphology without the need for finer gas dispersion.

SEM images confirm on a micro- and nanometer scale that the density of the sample depends on the solvent used: the sample obtained from pure toluene (Figures 6(a) and 6(b)) shows a structure composed of large lamellae loosely stacked on each other, while that obtained from pure heptane (Figures 6(c) and 6(d)) is formed by smaller lamellae packed

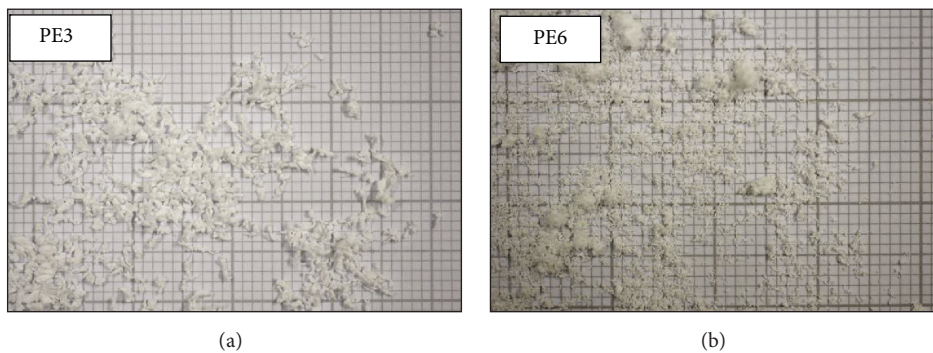


FIGURE 5: Nascent particles of UHMWPE obtained from pure toluene (PE3, a) and pure heptane (PE6, b).

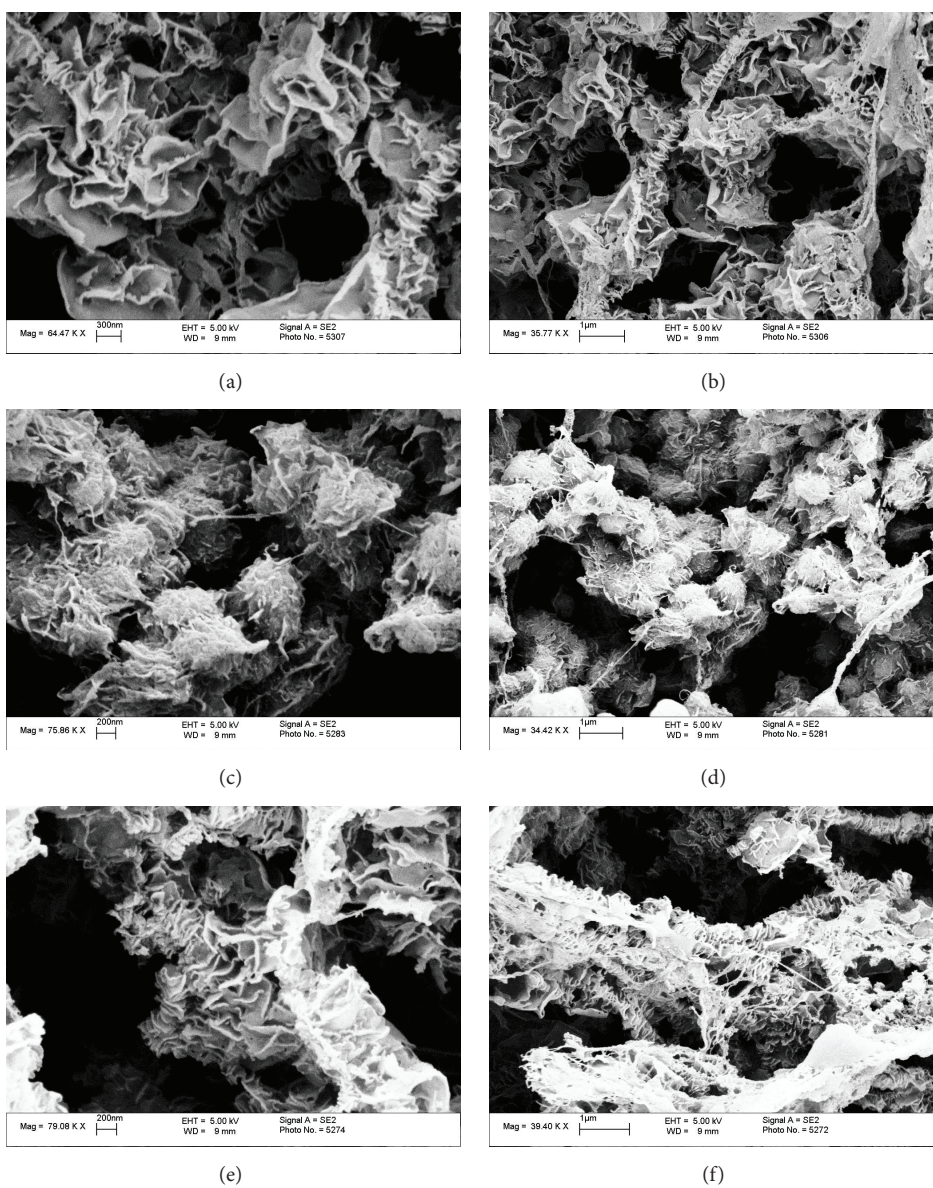


FIGURE 6: SEM images of nascent UHMWPEs obtained from polymerizations run in pure toluene (a, b), pure heptane (c, d), and 50/50 v/v mixture (e, f).

in nearly spherical, dense aggregates. The sample from 50/50 toluene/heptane (Figures 6(e) and 6(f)) has an intermediate character, having lamellae that are bigger than those from heptane but more densely packed.

4. Conclusions

We have reported the polymerization results obtained with system I/MAO at different catalyst concentrations and different solvents (toluene and heptane). When using mixtures of the two solvents, a peculiar behavior of the systems arises, because the observed catalyst activity is higher than those measured in pure solvents. The number of average molar mass dependence on the solvent(s) and solvent mixtures for the same polymerization conditions suggests a strong influence of solvent-catalyst interaction on the catalyst activity. The higher catalytic activity in toluene compared to that in heptane suggests that in toluene the catalyst is more accessible to the monomer thanks to the opening of the MAO-catalyst ion pair. This is a common observation that makes toluene the solvent of choice for polymerization with homogeneous, single-site catalysts. However, the enhanced catalytic activity demands high feed of the monomer at the active sites: this is confirmed by the observation that the catalyst activity decreases when increasing the catalyst concentration over $15\ \mu\text{M}$, possibly due to local starving of the catalyst due to insufficient rate of monomer feed. On the other side, ethylene solubility is known to be higher in heptane, thus the judicious choice of a solvent mixture, toluene/heptane ($\sim 70/30\ \text{v/v T/H}$), can provide saturated pockets of ethylene in heptane for the fast consumption of the monomer to the catalytic sites present in toluene. Our hypothesis is supported by two additional observations: (1) even if using the same reaction time and monomer pressure, higher molecular weights can be achieved when the reaction is run in a solvent mixture; (2) higher yields are obtained when using a larger reaction vessel with more efficient monomer feeding and stirring. This also suggests that the observed difference between the catalyst activity in the solvent mixture and that in pure toluene may decrease with an increase in monomer pressure that can compensate for the fast ethylene consumption.

Moreover, a careful choice of the reaction medium can improve the morphology and density of nascent particles.

We believe that the high activity of this catalytic system, combined with the disentangled state and good particle morphology of the polymer produced, can be appealing for industrial scale production, provided the right set of conditions are chosen.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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