

New Architecture of Supported Metallocene Catalysts for Alkene Polymerization

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ABSTRACT: We report the synthesis of a supported-metallocene catalyst that exhibits the same activity than the homogeneous catalyst for the polymerization of ethylene. The key of this new catalytic system is a hybrid organic-inorganic polymer obtained by the co-condensation of an organotrialkoxysilane (OTAS, 40 moles %) with tetraethoxysilane (TEOS, 60 moles %). The particular organic group of OTAS enabled to avoid gelation when the hydrolytic condensation was performed with a thermal cycle attaining 150 °C. The resulting product (SFS, soluble functionalized-silica) was a glass at room temperature, soluble in several organic solvents such as THF and toluene. ^{29}Si NMR spectrum of SFS showed that OTAS units were fully condensed (T_3 species) while TEOS units were mainly present as tri- (Q_3) and tetra-condensed (Q_4) units. SFS was grafted on activated silica by reaction of free silanol groups and a metallocene ($(n\text{BuCp})_2\text{ZrCl}_2$) was covalently bonded to the SFS-modified support. The polymerization of ethylene was carried out in toluene in the presence of methylaluminoxane (MAO). The activity of the supported catalyst was similar to the one of the metallocene catalyst in solution. The simplest explanation accounting for this fact is that most of the metallocene was grafted to SFS species issuing from the surface of the support, by reaction with their free silanol groups. This improves the accessibility of the monomer to the reaction sites. Specific interactions of the metallocene species with neighboring organic branches of SFS might also affect the catalytic activity.

Keywords: ethylene polymerization; supported-metallocene catalyst; catalyst activity; soluble functionalized-silica

INTRODUCTION

The immobilization of metallocene on a silica support is a convenient approach for the use of this new generation of catalysts for the industrial polymerization of olefins.¹ However, a decrease in the activity of a supported metallocene is usually found when compared to the activity of the same catalyst in solution because of several factors such as different types of adsorbed species, lower accessibility of the monomer to the catalyst site, deactivation reactions between neighboring metallocene sites, etc.^{2,3} But, on the other hand there is an increase in the average molar mass of the polyolefin because the support hinders chain transfer by β -elimination reactions.⁴

Different ways to improve the activity of supported metallocene catalysts were reported, such as the introduction of spacers between the silica surface and the metallocene or the partial depletion of adsorption sites located on the silica surface by previous reaction with a small monoalkoxysilane.² Spacing of metallocene species decreases the occurrence of bimolecular deactivation reactions between two neighboring catalytic sites. The organic groups covalently bonded to the Si atom may also play a role on the increase in the catalytic activity.^{4,5} When a polyhedral oligomeric silsesquioxane (POSS) functionalized with the bulky organic groups shown in Figure 1 was adsorbed on a silica support, a significant increase in the catalytic activity was observed.⁴ Formation of Zr-O-C bonds between the metallocene and the secondary hydroxyls of the organic group was proved by X-ray photoelectron spectroscopy (XPS) and FTIR photoacoustic and Raman spectroscopies.^{4,6} Reaction of the metallocene with residual silanol groups and interaction with ether and tertiary amine groups, was also observed.⁶ However, when the contact between POSS and metallocene was performed in solution, a decrease in the catalytic activity was found.⁴ The conclusion was that it

was necessary to space the bulky organic groups by the previous adsorption of POSS on the silica support to avoid crowding of organic groups around the metallocene active site.

A possible way to dilute the concentration of organic branches is to go back to the synthesis of this particular POSS. The hydrolytic condensation of two co-monomers: the trimethoxy silane bonded to the organic group (Figure 1) and an appropriate amount of tetraethoxysilane (TEOS), gives place to silica functionalized by the organic branches. It was found that limiting the amount of TEOS to a 65 % mole fraction, the resulting product was a glass at room temperature that could be dissolved in several organic solvents.⁷ The aim of this paper is to show the influence of a soluble functionalized-silica (SFS) synthesized with 60 % moles of TEOS, on the catalytic activity of a typical metallocene/methylaluminoxane (MAO) for ethylene polymerization. The reaction was carried out in two different ways: in solution, in which case the SFS acted as a soluble silica support for metallocene, and in the presence of a heterogeneous catalysts consisting of a silica support previously modified by adsorption of SFS followed by metallocene fixation. The effect of SFS on the overall catalytic activity and on the average molar mass of the polyethylene synthesized by both procedures will be discussed.

EXPERIMENTAL

Synthesis of SFS

Tetraethoxysilane (TEOS, Aldrich, 98 % purity) was dissolved in tetrahydrofuran (THF), in a concentration of 0.67 g/ml. A diluted formic acid solution was added to **obtain** the following molar ratios: $\text{HCOOH/Si} = 0.1$, $\text{H}_2\text{O/Si} = 3$. The hydrolytic condensation was advanced at 50 °C for 4 h. On the other hand, the trimethoxysilane

with the organic group shown in Figure 1, was synthesized by reaction of stoichiometric amounts of *N*-(β -aminoethyl)- γ -aminopropyl trimethoxysilane (Aldrich, 97 % purity) with a stoichiometric amount of phenyl glycidyl ether (Aldrich, 99 % purity) at 50 °C for 24 h.^{8,9} The resulting silane was dissolved in THF in a concentration of about 0.5 g/ml and a diluted solution of formic acid was added to obtain the following molar ratios: HCOOH/Si = 0.1, H₂O/Si = 3. The pre-hydrolyzed solution of TEOS was added to the solution of trimethoxysilane giving a molar fraction of TEOS equal to 0.6 (moles of TEOS divided by the sum of moles of TEOS and moles of the trimethoxysilane). Temperature was kept at 50 °C for 24 h, and then increased in steps: 1 h at 75 °C, 3 h at 100 °C, 3 h at 120 °C and 1 h at 150 °C. Volatiles were eliminated during this thermal cycle leading to a glassy material at room temperature. SFS was dried at 60 °C for 2 h under vacuum (10^{-3} bar), before its use.

Characterization of SFS

The glass transition temperature (onset of the change in the specific heat), was determined using differential scanning calorimetry (DSC Pyris 1, Perkin-Elmer). Dynamic runs were performed at 10 °C/min under nitrogen flow.

Solid-state ²⁹Si and ¹³C cross polarization magic angle spin nuclear magnetic resonance (CP/MAS NMR) measurements were performed on a Chemagnetics CMX-300 (Varian, USA). Samples were transferred to zirconia rotors. Measurements were performed at room temperature at 59.5 MHz (²⁹Si) and 75.3 MHz (¹³C), with a speed rotation of 4000 Hz at a magic angle of (54° 44'). The interval between pulses varied between 2 and 5 s. For ²⁹Si. NMR, 25,000 scans were employed with a contact time of 3 ms and a recycle time of 2 to 5 s.

Elemental analysis was performed using a Perkin Elmer M-CHNSO/2400 analyzer. Reported results are the average of three samples.

Size exclusion chromatography (SEC) of solutions of SFS in THF was performed in a Knauer K-501 device using a set of Phenomenex 5 μ -columns: 50A, 100A and M2, and a refractive index detector (Knauer K-2301). THF was used as a carrier at 1 ml/min.

Small-angle X-ray scattering (SAXS) experiments were carried out using synchrotron radiation at LNLS (Campinas, Brasil) with a wavelength $\lambda = 0.1488$ nm. The beam was directed to a silicon monochromator and collimated by a set of slits defining a pin-hole geometry. Samples were prepared by filling a 5 mm diameter cavity made in a 1 mm thickness mylar film sealed with two 0.05 mm mica windows. A solid-stated CCD detector (MAR 160) was used to collect two-dimensional (2D) images with 1048×1048 pixels. The angular range of the scattering vector ($q = 4\pi \sin \theta / \lambda$) was $0.02 \text{ nm}^{-1} \leq q \leq 0.49 \text{ nm}^{-1}$. Data were corrected by parasitic scattering and sample attenuation, and normalized by beam intensity and sample thickness.

Synthesis and Characterization of Supported Catalysts

Silica (surface area $470 \text{ m}^2/\text{g}$; pore volume $0.43 \text{ cm}^3/\text{g}$; pore diameter 32 \AA) was synthesized through acid precipitation of a sodium silicate solution. The product was dried, heated at $550 \text{ }^\circ\text{C}$ for 2 h, and milled. Then, it was activated by heating at $130 \text{ }^\circ\text{C}$ for 8 h under vacuum (10^{-3} bar).

The activated silica was dispersed in a solution of SFS in toluene, using a ratio of 0.5 wt % SFS/activated silica. Toluene was previously purified by refluxing over metallic sodium with benzophenone as indicator. The contact was performed stirring for 30 min at room temperature. The solvent was removed by vacuum, and then a solution

of the metallocene, (*n*BuCp)₂ZrCl₂ (Boulder), in purified toluene with a ratio of 0.5 wt % Zr/activated silica was added and stirred for 30 min at room temperature. The slurry was then filtered through a fritted disk. The resulting solid was washed 14 times with 2 ml toluene aliquots and dried under vacuum for 4 h. A supported catalyst without SFS was also prepared starting the procedure with the dispersion of the activated silica in the metallocene solution. The Zr loadings in supported catalysts were determined by Rutherford backscattering spectrometry as described in a previous paper.⁴ A fraction of 90 % of the added Zr was effectively incorporated to the neat activated silica. The fraction increased to 98 % when SFS was previously adsorbed on the activated silica.

Ethylene Polymerization

Ethylene was deoxygenated and dried before use employing BTS columns (BASF) and activated molecular sieves (13 Å). The polymerization was performed at 2 bar in a 1-liter glass reactor (Parr). The homogeneous polymerization in the absence of SFS was carried out by addition of purified toluene and methylaluminoxane (MAO, Witco) to the reactor. After purging with ethylene, a solution of metallocene in purified toluene was added. The amounts of metallocene and MAO were adjusted to 3×10^{-6} moles Zr and a molar ratio Al/Zr = 1420. The final volume of the solution was 240 ml. The polymerization was carried out at 60 °C for 30 min with a stirring velocity of 1000 rpm.

The heterogeneous polymerization in the absence of SFS was performed adding the metallocene supported on the activated silica to the MAO solution, and purging the reactor with ethylene. The amounts of metallocene and MAO, and the total volume were the same as in the homogeneous case.

The effect of SFS was analyzed by adding it in three different ways:

- (a) Pre-contact of SFS and metallocene. The pre-contact was performed at 60 °C for 15 min in a toluene solution, employing a ratio of 0.5 wt % Zr/SFS. The reactor was filled with toluene and the MAO solution, and purged with ethylene. Then, the SFS-metallocene solution was added keeping the same molar ratios as in the polymerization without SFS.
- (b) In situ addition of SFS. A solution of SFS in toluene was added to the MAO solution, the reactor was purged with ethylene and the metallocene added as a toluene solution.
- (c) The same procedure of the heterogeneous polymerization was followed using the supported catalyst containing SFS.

In every case the reaction was stopped after 30 min by the addition of a solution of HCl in ethanol (5 vol %). The polymer was recovered by filtration, washed with ethanol, dried overnight at room temperature and weighed. The catalyst activity was expressed as the mass of polyethylene produced per unit time per mol of Zr and per unit pressure ($\text{kg mol}^{-1} \text{bar}^{-1} \text{h}^{-1}$).

Polyethylene Characterization

The molar mass distributions were determined by size exclusion chromatography (SEC) using a Waters Alliance 2000 device, equipped with three Styragel HT type columns (HT3, HT5 and HT6). The solvent was 1,2,4-trichlorobenzene at a flow rate of 1 ml/min and the operation was carried out at 135 °C. Calibration was performed with polystyrene standards.

Melting points (T_m) and crystallinities (X_c) were determined by differential scanning calorimetry using a Perkin Elmer DSC7 device, at a rate of 10 °C/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of SFS

Of the two co-monomers used for the synthesis of SFS, TEOS exhibits the slowest hydrolysis and condensation rates because of the faster hydrolysis of methoxy with respect to ethoxy groups,¹⁰ and the fact that the hydrolysis and condensation rates of organotrialkoxysilanes are significantly faster than those of tetraalkoxysilanes.^{11,12} Therefore, SFS was synthesized in two steps: first TEOS was pre-hydrolyzed and then the organotrialkoxysilane was added and the reaction was carried out to high conversions (expected at the high final temperature employed in the synthesis). The final product exhibited a glass transition temperature of 29 °C (onset value determined by DSC), and could be stored as a glass at room temperature. It was soluble in several solvents including THF (used for characterization purposes), and toluene (used for the synthesis of polyethylene).

Figure 2 shows a ²⁹Si NMR spectrum of SFS. The organotrialkoxysilane was almost fully condensed as revealed by the presence of a significant peak assigned to R-Si(-O-)₃ (T₃) fragments. A very high conversion in the condensation of TEOS units was also attained as shown by the predominant presence of peaks assigned to HO-Si(-O-)₃ (Q₃) fragments and Si(-O-)₄ (Q₄) fragments. In spite of the high condensation degree there still remains a fraction of Si-OH groups in Q₃ fragments that constitute primary anchoring groups for the metallocene.

Elemental analysis of SFS gave the following results: 53.54 % C, 6.01 % H, and 3.75 % N. Theoretical values calculated assuming complete condensation of both monomers are: 53.61 % C, 5.91 % H and 4.04 % N, in very good agreement with experimental results.

The SEC chromatogram of SFS shows a main band corresponding to a bimodal distribution of reaction products together with a small fraction of low-molar mass species (small peaks present at high elution volumes) (Figure 3). As the signal mainly arises from the concentration of the organic branches of SFS, the SEC chromatogram gives their distribution in species of different sizes. Of both peaks of the main band, the one located at higher elution volumes lies in the same position than the one of the products of the self-condensation of the organotrialkoxysilane (OTAS). Therefore, this peak can be associated to the presence of T_8 , T_9 , and T_{10} (polyhedral oligomeric silsesquioxanes, POSS), that are the main species present in this reaction product.⁹ The other peak of the main band is associated to species resulting from the co-condensation of TEOS with OTAS.

A significant result is the fact that the addition of 40 % moles of OTAS to the initial formulation enabled to avoid gelation (observed when condensing TEOS alone under the same experimental conditions). But an unexpected result was the presence of polyhedra arising from OTAS self-condensation occurring in the presence of pre-hydrolyzed TEOS. This evidences the existence of strong interactions among functional groups of the organic branches leading to associations of hydrolyzed OTAS species that finally led to the formation of the observed polyhedra. Therefore, the SFS should be regarded as a blend of co-condensation products of both co-monomers and polyhedral oligomeric silsesquioxanes obtained by the self-condensation of OTAS.

Small angle X-ray scattering can reveal the contrast of electronic densities between organic and inorganic phases and can give evidence of a phase separation in the hybrid material. The SFS might exhibit a nanostructuration of inorganic clusters arising from the self-condensation of TEOS (inorganic-rich phase) and the organic branches supplied by OTAS. As the mass fraction of the inorganic part of SFS is

significantly lower than the mass fraction of organic material, the picture of SFS in the solid state may be depicted as inorganic clusters dispersed in an organic phase. Due to their higher electron density, the inorganic clusters should act as scattering centers of X-ray radiation. The broad scattering peak with a maximum at $q_{\max} = 0.26 \text{ nm}^{-1}$, present in Figure 4, is associated with a characteristic length $2\pi/q_{\max} = 24 \text{ nm}$. This is the average length separating the inorganic clusters present in SFS in the solid state.

Ethylene Polymerization and Polyethylene Characterization

Table 1 shows the activity of the different catalytic systems and some characteristics of the resulting polyethylenes. Both systems devoid of SFS can be first compared. Supporting the metallocene on silica produces the well-known decrease of activity and a significant increase in the average molar mass. The supporting procedure did not change the single-site nature of the catalyst, as it is shown by the fact that the polydispersity did not vary significantly.

A pre-contact of metallocene with SFS generates a catalyst that resembles the behavior of metallocene supported on activated silica. There is a significant decrease in the catalytic activity and an increase in the average molar mass of the resulting polyethylene. During the pre-contact period most of the metallocene should be grafted to the SFS by reaction with the free silanol groups (a large excess of SFS with respect to metallocene was used). Therefore, the reaction product effectively acts as a supported catalyst. The decrease in activity is explained by the strong interactions with the organic branches of SFS present in large concentration in solution. Some crowding of organic branches around catalyst sites may be expected. A polymerization carried out in the presence of SFS in solution but in the absence of a pre-contact period (in situ system),

resembled the homogeneous case with a slight decrease in the observed activity (notice that the concentration of SFS was much lower than that used in the pre-contact system).

Excellent results were obtained with the supported catalyst containing SFS. The activity was similar than the one of the homogeneous system and a high molar mass of the resulting polyethylene, typical of a heterogeneous reaction, was observed. This can be explained by the increase in the accessibility of the monomer to a reaction site that is not located on the catalyst surface but on a hybrid organic-inorganic structure that is covalently bonded to the support. In this case, crowding of organic branches around the catalytic site is not produced because of the previous covalent bonding of SFS to the silica support. Specific interactions of the grafted metallocene with neighboring groups present in the organic branches,^{4,6} might also have a bearing on the observed values of the catalytic activity.

Melting temperatures and crystalline fractions of polyethylenes are typical values for products arising from these polymerizations.

CONCLUSIONS

A soluble functionalized-silica (SFS) was synthesized using an organotrialkoxysilane and TEOS. The nature of the organic group enabled to avoid gelation for formulations containing up to 60 % moles of TEOS, condensed with a thermal cycle attaining 150 °C. The SFS was a glass at room temperature, soluble in several organic solvents such as THF and toluene. A heterogeneous catalyst was synthesized by grafting SFS on activated silica and covalently bonding a metallocene to the resulting support. The activity of the supported catalyst was similar to the one of the metallocene catalyst in solution. To the best of our knowledge this is the first study reporting that the metallocene activity can be maintained on a supported catalyst. The simplest

explanation accounting for this fact is that most of the metallocene is grafted to the SFS species issuing from the surface of the support, by reaction with their free silanol groups. This improves the accessibility of the monomer to the reaction sites. Specific interactions of the metallocene species with neighboring organic branches of the support might also affect the catalytic activity.

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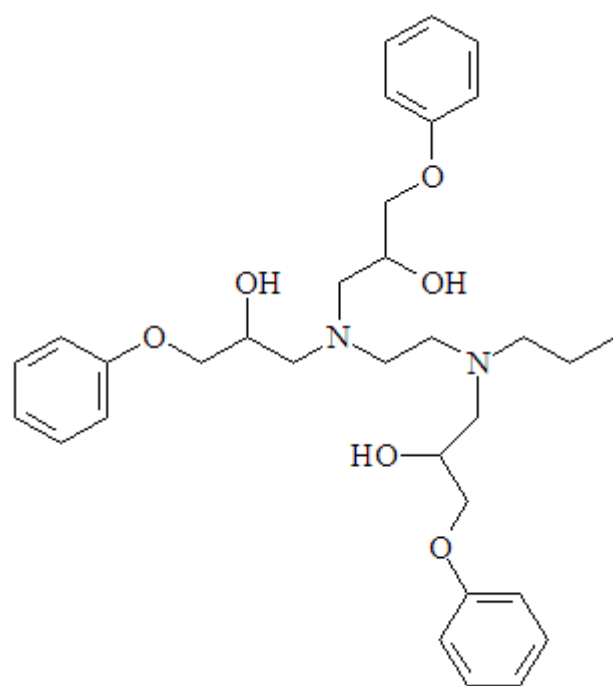


Figure 1

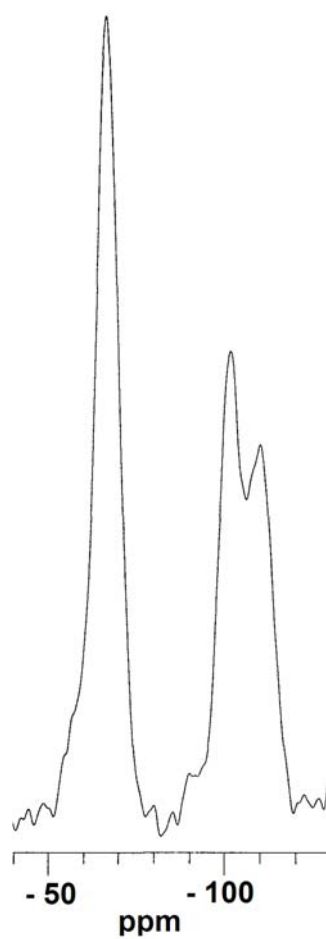


Figure 2

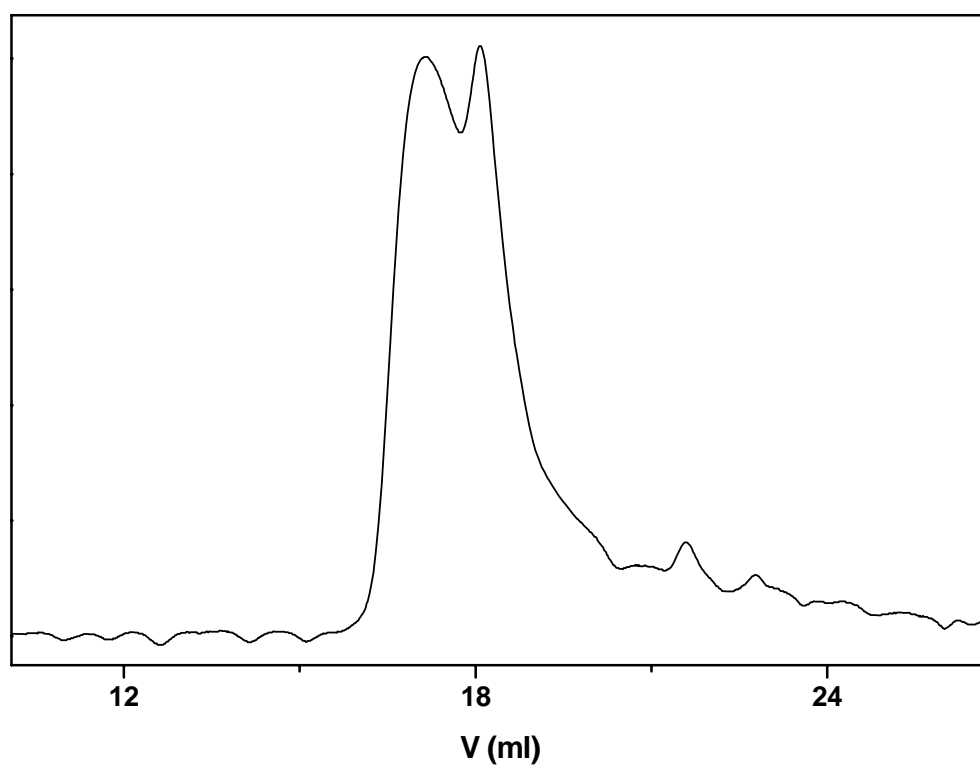


Figure 3

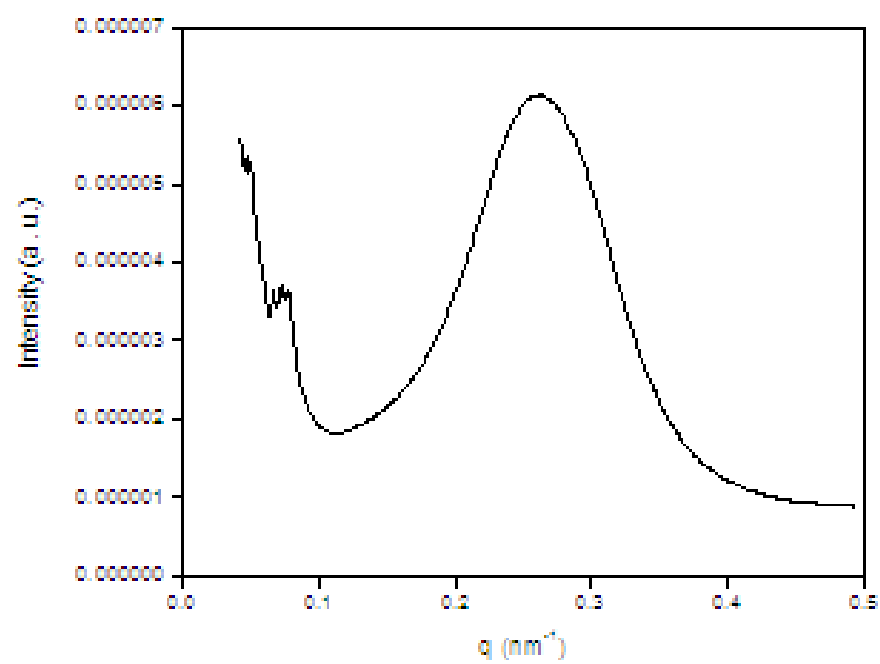


Figure 4