Experimental Report

Proposal: **5-22-707** **Council:** 10/2011

Title: MAO-ROBOTS at work II. - Intermediate structures and chain growth during propagation

This proposal is resubmission of: 5-22-704

Researh Area: Chemistry

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Samples: d-toluene, C7D8
methylaluminoxane, (AlOCH3)n
1-octene

Instrument	Req. Days	All. Days	From	To
D22	3	3	29/06/2012	01/07/2012
			30/10/2012	31/10/2012

Abstract:

Methylaluminoxane (MAO) is a key activator for a large section of the industrial production of polyolefins (POs), which are ubiquitous as commodity polymers. Of an annual world volume of 20 MT linear low density polyethylene (LLDPE), approximately 10% is produced via processes that are based on MAO. Despite many efforts, little is known either about the details of MAO's molecular structure or about the quantitative relationship between the MAO structure and its activating efficiency in the PO production process. In general, MAO is used in huge excess, up to 1000:1, rather like a black-box component.

Structural analysis by means of real time neutron scattering techniques to resolve details of the microscopic structure is the key to understand basic principles of MAO-activated catalyst systems. We therefore propose a comprehensive and systematic investigation of industrial relevant state-of-the-art MAO solutions by time-resolved SANS experiments to unravel the formation of the active catalyst/activator complex and intermediate structures formed during the initial period of the PO polymerisation process.

Structure of MAO in toluene solutions by SANS

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Methylaluminoxanes (MAO) [1] is a key activator widely used in the industrial production of polyolefins (POs). Little is known on details of MAO's molecular structure and the quantitative relationship between the MAO structure and its activating efficiency in the PO production process. Currently, MAO is used in a huge excess over the catalyst, (a typical Al:catalyst ratio is 10^3-10^4 :1), and the price of the production and handling of MAO prevents its broader industrial application.

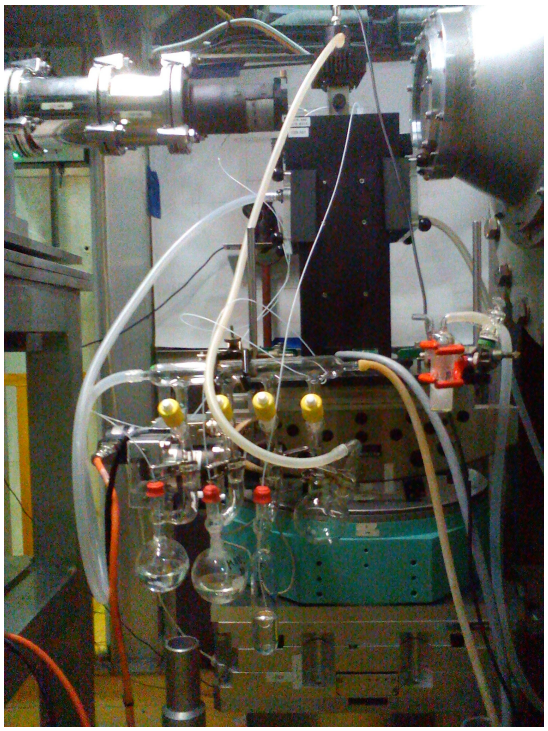

Fig. 1: To feed the 4-syringes stopped-flow with pre-catalyst, activator, monomer and solvent under strictly anaerobic conditions a sophisticated glassware setup was installed at sample position

There are hydrolitic and nonhydrolitic processes to produce MAO. In a hydrolitic process MAO is produced via the reaction of water with trimethylaluminium (TMA). Resulting MAO solutions always contain TMA (several percent by weight). An approximate stoichiometric formula of MAO is $Al(CH_3)_{1.5}O_{0.75}$. Using various experimental and theoretical methods hydrolitic MAO was shown to form cage- or drum-like structures of low (~ 1100 g/mol) molecular weight (see e.g. a theoretical study [2]). No one succeeded to crystallize MAO but several crystal cage-like structures of tret-butyl aluminoxanes were published [3], and this indirectly supports an existence of cage-like MAO structures.

A small angle neutron scattering (SANS) experiment was performed on ILL spectrometer D22. Spectra were recorded with neutron wavelength of 4.5 Å, $\delta\lambda/\lambda$ =10%, aperture diameter 10 mm, and at two sample-detector distances (1.2 m and 8 m, with collimation lengths at 2.8 m and 8 m, respectively), rendering Q region of 0.015 $Å^{-1}$ <Q<0.85 $Å^{-1}$.

At first, we tried to measure using our stopped flow apparatus specially prepared for maintaining anaerobic conditions, see Figure 1. Unfortunately, flow cell broke repeatedly due to blocking of flow lines, and we switched to using standard Hellma cells and filling them with samples freshly prepared in the glove box. Dilution series (1%, 0.75%, 0.5 % and 0.25 %) were measured for two MAO solutions (both contained ≈10% MAO by weight, but were synthesized in a different way) at 11°C, 20°C, and 40°C. In addition, two MAO 1% solutions (prepared from different stock solutions) were measured after addition of a catalyst $(n\text{-}BuCp)_2ZrCl_2$ to Al:Cat ratio of ≈ 100, and then after addition of n-hexene monomer (catalyst:hexene ratio was ≈3). All MAO solutions were prepared either in d:h=90:10- or d:h=97:3 toluene mixtures.

In Figure 2 temperature dependence is shown for two MAO solutions (0.75% by weight). Interestingly, the temperature dependence is rather weak and may be, at least partially, explained by a decrease of solution density with increasing temperature.

In Figure 3 concentration dependence is shown for two series of MAO solutions measured at 20°C. As we already saw before, there are slightly attractive solute-solute interactions that lead to an increase in scattering intensity at low Q.

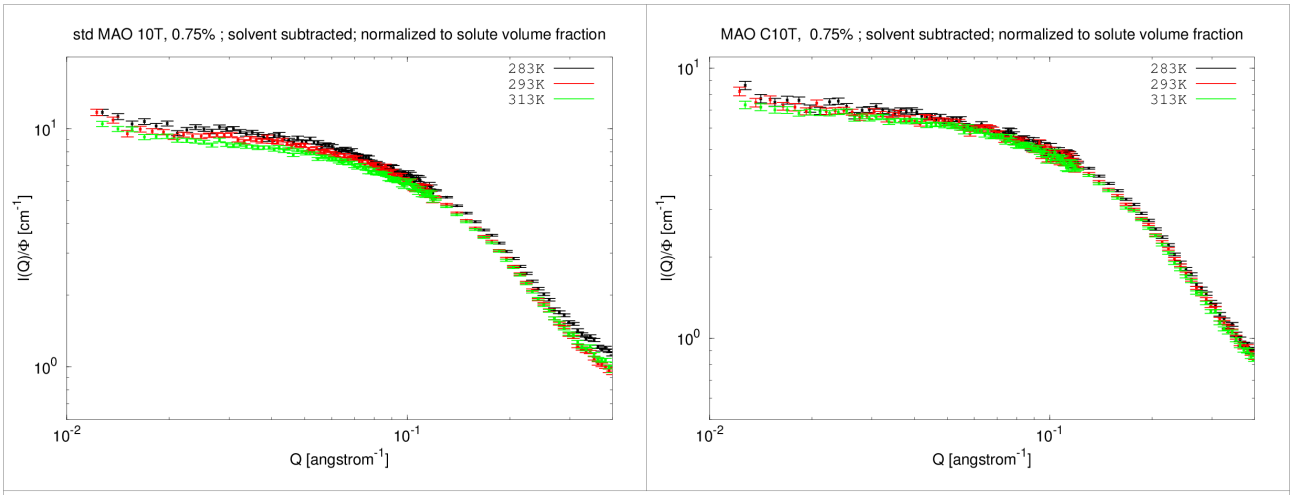

Fig. 2: Temperature dependence for two MAO solutions in d:h=90:10-toluene, 0.75% MAO by weight.

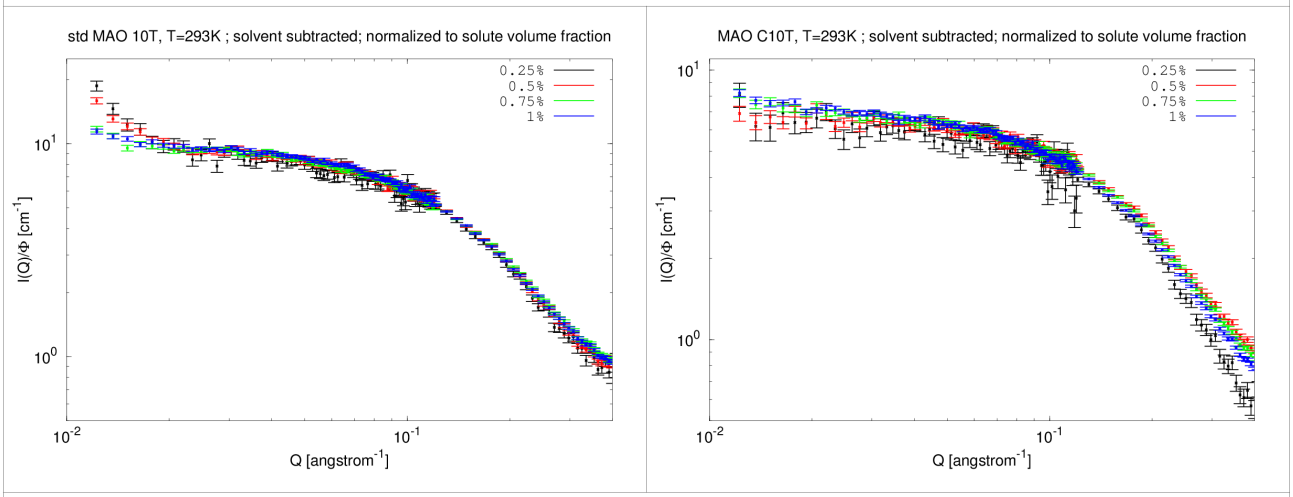

Fig. 3: Concentration dependence for two series of MAO solutions, at 20°C.

In Figure 4 scattering curves for MAO+catalyst, and MAO+catalyst+hexene are shown. We hoped to observe a polymerization of n-hexene, but apparently the polymerization reaction is too slow. Interestingly, the increase in scattering intensity towards low Q (due to aggregates in MAO solution) seems to disappear (or reduce) upon hexene addition, for both solutions.

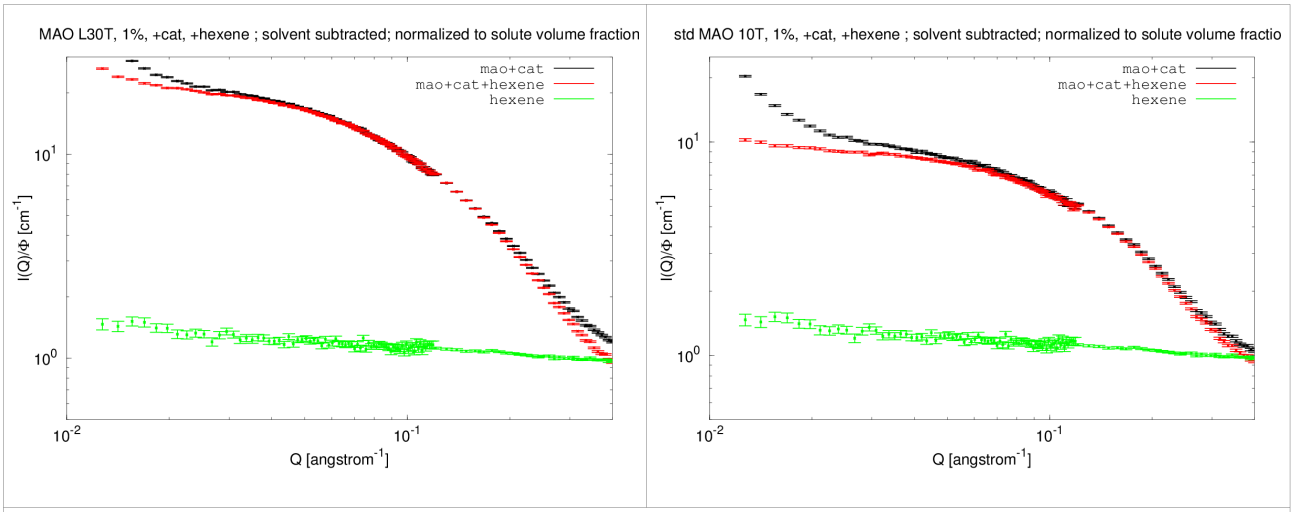

Fig. 4 Scattering curves before and after addition of n-hexene for two different MAO 1% solutions. For comparison, a scattering curve for a 1% solution of n-hexene in d:h=97:3-toluene is shown.

In conclusion, we still have one D22-day left (on 30.10.2012) and we plan to measure MAO solutions in d8-toluene, where, thanks to a low hydrogen content, we will be able to measure solutions in the MAO concentration range from 0.5 to 30% by weight. In the first part of D22 experiment we tried but could not use our stopped flow device and continued to use standard SANS cells coupled with an on-site sample preparation in the glove box. We observed, for the 1st time, a temperature dependence of SANS spectra for dilute MAO solutions and tried to observe a formation of MAO-catalyst-hexene adduct in samples with low catalyst : hexene and MAO : catalyst ratios.

References

[1] H. Sinn et al., *Angew. Chemie Int. Ed. Engl.,* **19,** 390, 1980.

[2] Linnolahti et al., *Angew. Chemie Int. Ed.*, **47**, 9279, 2008.

[3] M. R. Mason et al., *J. Am. Chem. Soc.* **115**, 4971, 1993.