

Supplementary information

A Ruthenium Catalyst Yielding Crosslinked Polyethylene

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Experimental Procedure

General Considerations

All manipulations were done under inert atmosphere using standard Schlenck and cannula techniques. Dry, oxygen-free solvents were obtained using a Solvent Purification System from MBraun. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Varian Inova 600MHz spectrometer at ambient temperature. NMR spectra are reported relative to external 85% H_3PO_4 (^{31}P) or TMS (^1H , ^{13}C). RuCl_3 and $[\text{RuCl}_2(\text{DMSO})_4]$ were bought from Strem Chemicals inc. and used without further purification. $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuCl}_2(\text{COD})]_n$ and 2-(diphenylphosphanyl)benzenesulfonic acid were synthesized according to published procedures.^[1-3]

All solid state-NMR spectra were obtained at room temperature on a Varian Inova spectrometer operating at 599.94 MHz for ^1H and 150.872 MHz for ^{13}C . A 4 mm magic-angle spinning double-resonance probe was used and samples were spun at 12 kHz. All spectra were recorded at room temperature using radio-frequency fields of 75 kHz on ^{13}C (for cross-polarization or direct excitation) and 87 kHz on ^1H (for cross-polarization and decoupling). The cross-polarization contact time was 1 ms and the acquisition time was 10 ms during which TPPM decoupling was applied. Recycle delays were 30 s and 15 s for direct-pulse or cross-polarization spectra respectively. All spectra were externally referenced with respect to TMS by setting the high frequency peak of adamantane to 38.56 ppm.

MALDI-MS analyses were performed using a Waters Micromass LR M@LDI TOF mass spectrometer. Data were collected in positive reflection mode. Matrix (anthracene) and analyte solutions were prepared in CH_2Cl_2 at concentrations of 10 and 1 mg/mL, respectively.

The molecular weight distributions were determined by gel permeation chromatography (GPC) using a Viscotek HT GPC equipped with triple detection operating at 160 °C. The eluent was 1,2,4-trichlorobenzene, and separation was performed on three PolymerLabs Mixed B(-LS) columns. The dn/dc of pure linear polyethylene was found to be 0.106 mL/g at this temperature.

Differential scanning calorimetry measurements (DSC) of solid samples were performed on a DSC823e (TOPEM modulation) equipped with an FRS5 sample cell, a sample robot, a Julabo FT400 intracooler and an HRS7 sensor from Mettler Toledo. Samples were heated from -60 °C to 150 °C at a rate of 5 °C/minute and data were analyzed with STAR software. All reported values are for the second heating cycle.

Synthesis

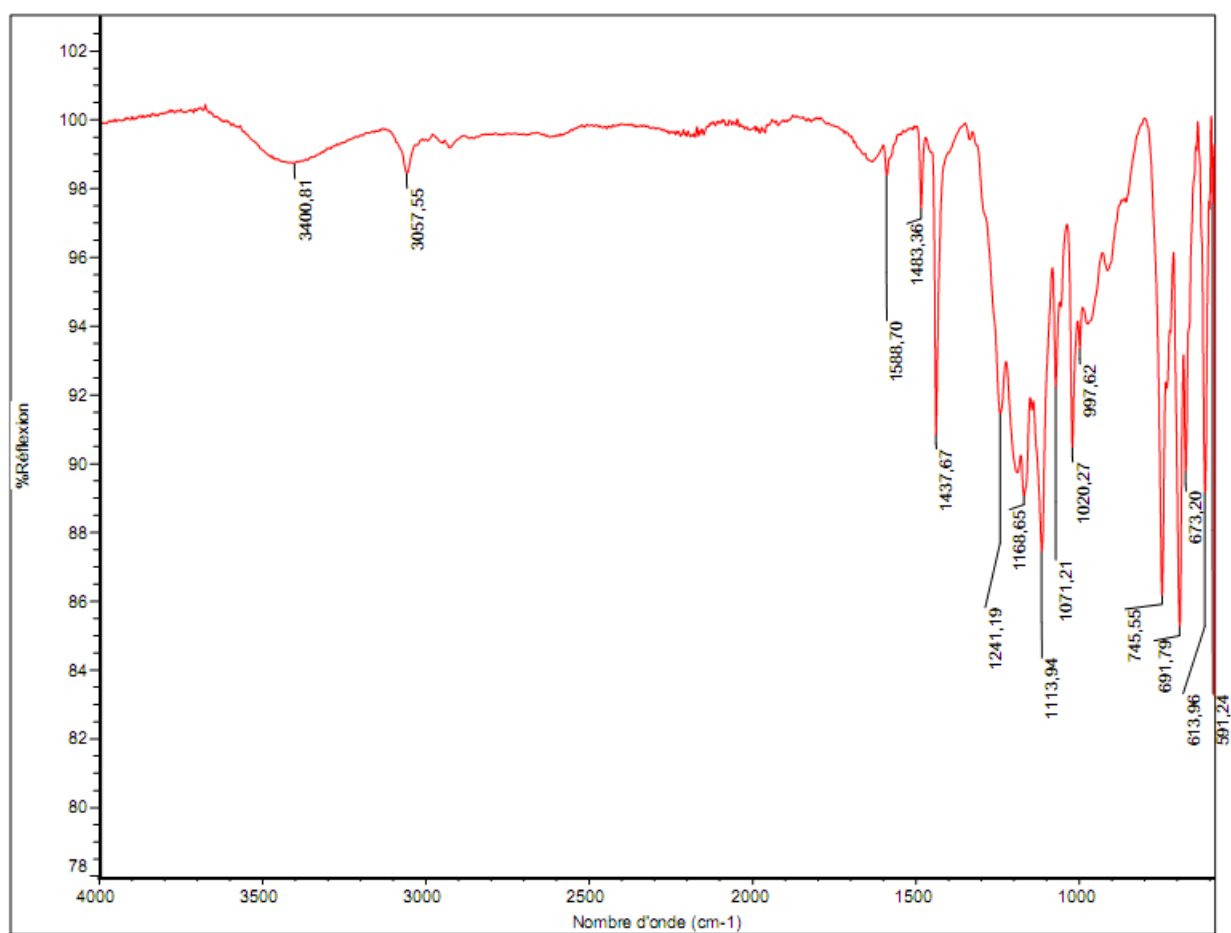
Synthesis of 1: Inside a drybox, 0.240 g of [RuCl₂(PPh₃)₃] (0.250 mmol) and 0.175 g of 2-(diphenylphosphanyl)benzenesulfonic acid (0.510 mmol) were weighed in a Schlenk flask, which was connected to a Schlenk line under a nitrogen atmosphere. Dry dichloromethane, DCM (10 ml) was added and the reaction mixture was stirred for 2 h at room temperature. Diethyl ether was then added to form an orange precipitate, which was filtered and washed three times with cold diethyl ether and dried *in vacuo*, yielding 170 mg of an orange powder (0.217 mmol) (87 %). ¹H NMR (Acetone-d₆): δ: 8.16 (s, 1H, C(SO₃)-CH-) 7.60-7.12 (m, 13H, H_{ortho+meta+para} Ph, H⁴-ArSO₃, H⁵-ArSO₃). ¹³C NMR (CDCl₃): δ: 151.8, 134.47, 133.9, 133.5, 133.0, 132.9, 129.8, 129.6, 129.3, 128.6. ³¹P NMR (Acetone-d₆): δ 28.3 (s). Anal Calcd : C, 55.2; H, 3.6. Found : C, 55.3; H, 4.2. Exact mass (MALDI TOF MS) : 784.00 calcd, 784.02 found

Synthesis of 2: 0.250 g of **1** was dissolved in dichloromethane and 0.10 mL of water was added. The reaction mixture was stirred for 30 minutes and the solvent was removed *in vacuo*. ¹H NMR (Acetone-d₆): δ: 8.2 (s), 7.6-7.1 (m). ¹³C NMR (CDCl₃): δ: 151.75, 134.47, 133.85, 133.50, 133.05, 132.90, 129.78, 129.60, 129.30, 128.62. ¹³C NMR (Acetone-d₆): 151.9, 134.5, 133.0, 132.8, 129.8, 129.3, 128.7, 128.5. ³¹P NMR (Acetone-d₆): δ 28.3 (s). Anal Calcd : C, 52.7; H, 3.9. Found : C, 52.6; H, 4.3. Exact mass (MALDI TOF MS) : 784.00 calcd (**2** – 2 H₂O), 784.02 found

Crystallization of **2**

A small amount of **1** was solubilized in acetone and water was added. After evaporation, suitable crystals of **2** for X-ray crystal structure determination were obtained.

IR Spectra of **2**



Polymerizations

Polymerizations were carried out in a stainless steel reactor (100 mL, Parr). Catalyst, comonomer, MAO or AlEt₃ and toluene (50 mL) were added to a Schlenk flask in a nitrogen-filled glove box. Solid MAO was obtained by removing toluene and AlMe₃ under vacuum at 50 °C overnight from a commercial solution (10 wt.-%, Aldrich). The reactor, which was first dried and kept under nitrogen, was loaded with the toluene solution by cannula transfer from the Schlenk flask under nitrogen. The reactor was then sealed, pressurized with ethene, stirred and heated. The polymerizations were performed at constant pressure. At the end of the reaction, the reactor was cooled down to room temperature and slowly depressurized. Precipitation of the polymer was performed according to a standard procedure used for UHMWPE^[4]: the reaction mixture was poured into a solution containing ethanol (200 mL), HCl (37 %, 100 mL) and water (700 mL) and stirred overnight. The resulting polymer was filtered off and washed successively with water and EtOH and dried at 60 °C. The dried polymers were then washed by Soxhlet extraction overnight, using MeOH containing 10% HCl.

In order to assess whether the purification procedure successfully removed alumina from the polymer, Al content was titrated Inductive Coupled Plasma (ICP):

Aluminum titration of an isolated polymer (run 1): 128 ppm (0.0128%).

Aluminum titration of polymer which has not been precipitated in ethanol/HCl/water and not extracted in a Soxlet apparatus, but simply dried after reaction: 9500 ppm (0.95%).

Swelling experiments

The degree of swelling in xylene and molecular weight between crosslinks was determined according to published procedure.^[5] In order to remove any uncrosslinked material, the polymer (200mg) was stirred for 3 days in boiling *p*-xylene containing 0.01% of di-*tert*-butyl-*p*-cresol as antioxidant. The gel was transferred to fresh *p*-xylene and allowed to equilibrate at 120 °C for 3 hours. The gel was then picked with a hook, transferred quickly to a stoppered bottle, and weighed (w_s). The sample was then extracted in chloroform for 12 hours to remove *p*-xylene, dried under vacuum at 50 °C, and weighed (w).

The degree of swelling is given by:^[6]

$$\text{degree of swelling} = 1 + \left[\frac{w_s - w}{w} \frac{\rho}{\rho_0} \right]$$

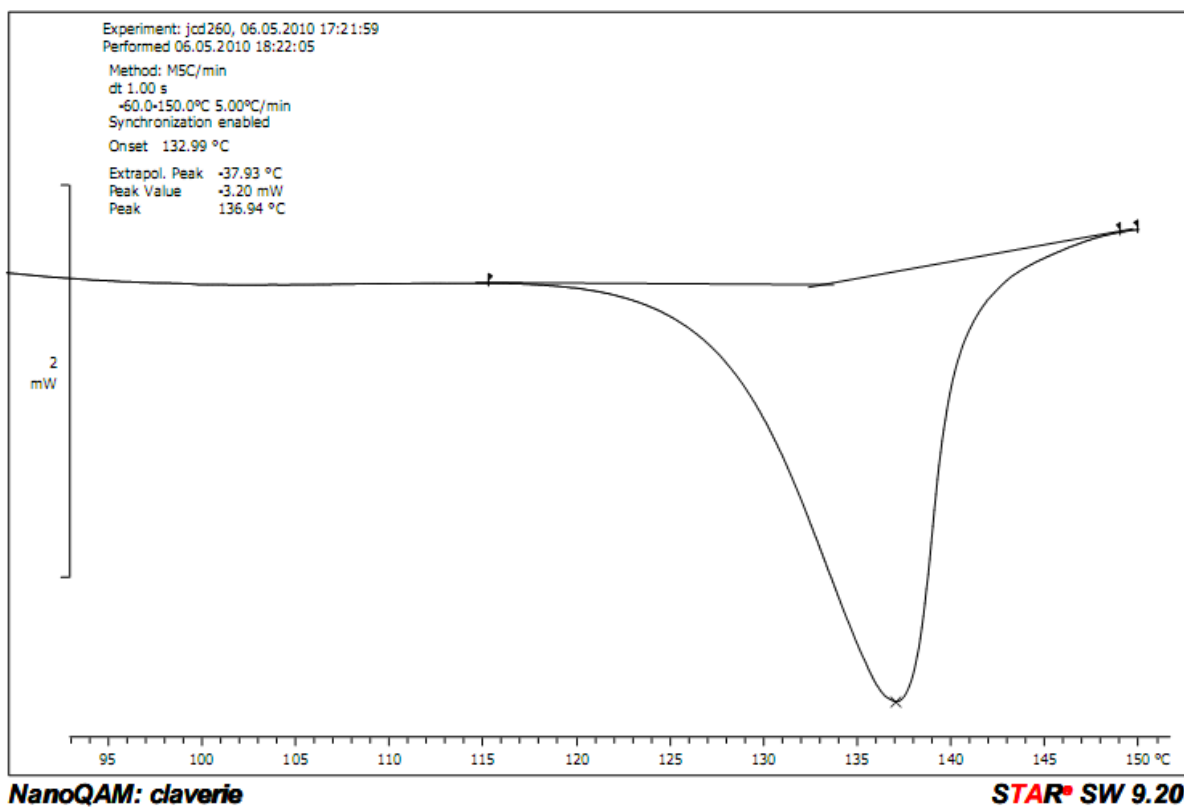
where ρ and ρ_0 are respectively the density of solvent and polymer

The number of monomer units between two reticulation points is given by:^[6]

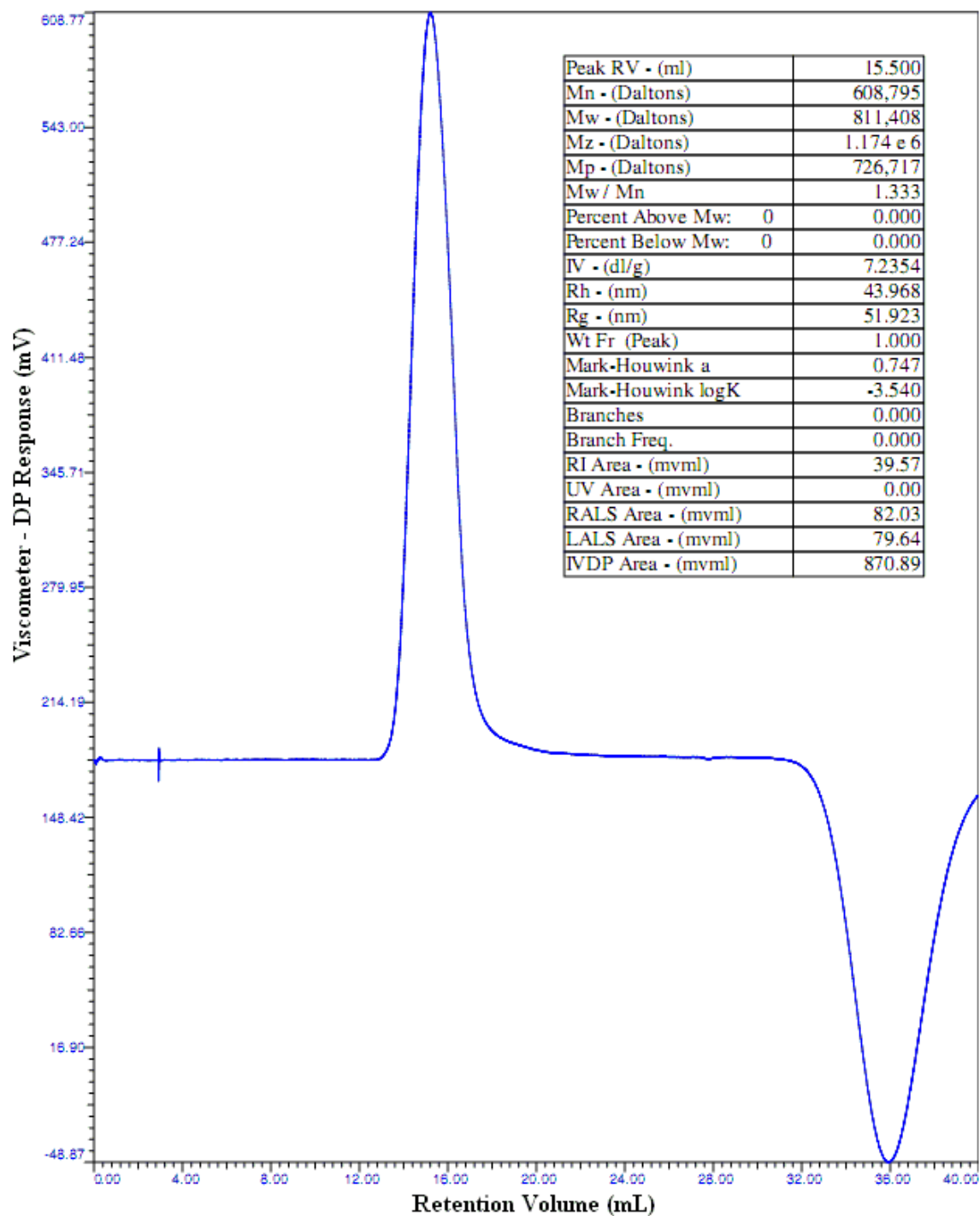
$$L_{ret} = \frac{\frac{\phi_p}{2} - \phi_p^{1/3}}{\ln \phi_s + \phi_p + \chi \phi_p^2}$$

where ϕ_p and ϕ_s are respectively the volume fractions of the polymer and the solvent in the swollen gel and χ is the Flory Huggins parameter (0.71 in p-xylene at 120°C).

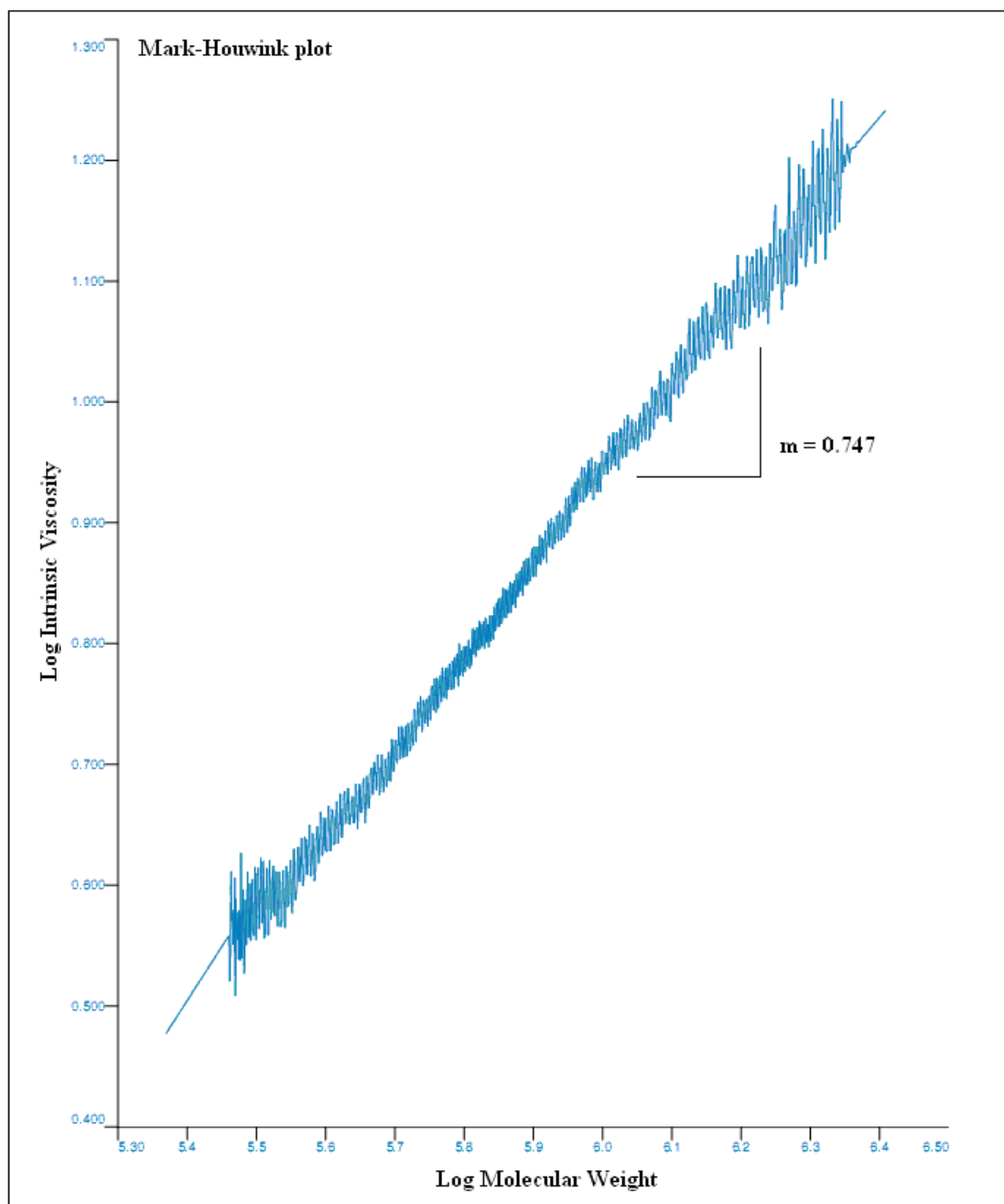
DSC measure for PE prepared in run. 1



GPC Trace for PE prepared in run no. 1



Mark-Houwink Plot for PE prepared in run no. 1



- [1] T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1966**, 28, 945.
- [2] L. Piche, J. C. Daigle, R. Poli, J. P. Claverie, *Eur. J. Inorg. Chem.*, **2010**, 4595.
- [3] M. A. Bennett, G. Wilkinson, *Chem. Ind. (London)* **1959**, 1516.
- [4] a) M. Frediani, D. Semeril, A. Comucci, L. Bettucci, P. Frediani, L. Rosi, D. Matt, L. Toupet, W. Kaminsky, *Macromol. Chem. Phys.* **2007**, 208, 938. b) J. Espinas, U. Darbost, J. Pelletier, E. Jeanneau, C. Duchamp, F. Bayard, O. Boyron, J. P. Broyer, J Thivolle-Cazat, J. M. Basset, M. Taoufik, I. Bonnamour, *Eur. J. Inorg. Chem.*, **2010**, 1349.
- [5] A. De Boer, A.J. Pennings, *J. Polym. Sci.* **1976**, 14, 187.
- [6] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, **1953**.