Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Site count: is a high-pressure quenched-flow reactor suitable for kinetic studies of molecular catalysts in ethylene polymerization?

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Temperatures profiles

One important question concerns the evolution of the temperature in the reactor. The equation below was used to prove that the adiabatic temperature rise is lower than 1°C (ΔT = 0.1-0.5°C), even in case of monomer consumption higher than 10%.

$$\Delta T = (Q \cdot Mw)/(C_p \cdot \rho \cdot V) \tag{2}$$

Where

Cp is given by eq. $Cp= C_1+C_2T +C_3T^2$ whit C_1 = 140140 C_2=-152.3 C_3=0.695 for toluene

ρ is the toluene density = 0.87 $g \cdot ml^{-1}$;

V is the volume which was passed through the Teflon tube;

Mw is the molar mass of toluene = 92.14 $g \cdot mol^{-1}$;

The released heat, Q, is given by the product between ΔH of polymerization and the mol of monomer consumed. The value of ΔH of polymerization is 25 $kcal \cdot mol^{-1}$.

A series of tests were carried out where we measured the temperature in tubular reactor in order to evaluate the difference temperature between inlet and outlet of the reaction tube. The ΔT during the ethylene polymerization with the catalyst system **I**/MAO was measured using two K thermocouples. The first thermocouple was positioned in point **3** (see Fig. 1 in the paper), replacing the T-mixer with a cross-mixer; the second one was placed in point **5** at the end of tubular reactor. The temperature profiles in Fig. S1 are relative to runs 4 and 5 carried out using tubular reactor of 2 m and run 1 carried out using tubular reactor of 0.5 m which corresponds to residence times of 0.51, 0.7 and 0.09 s respectively, and ethylene consumption up to 6%.

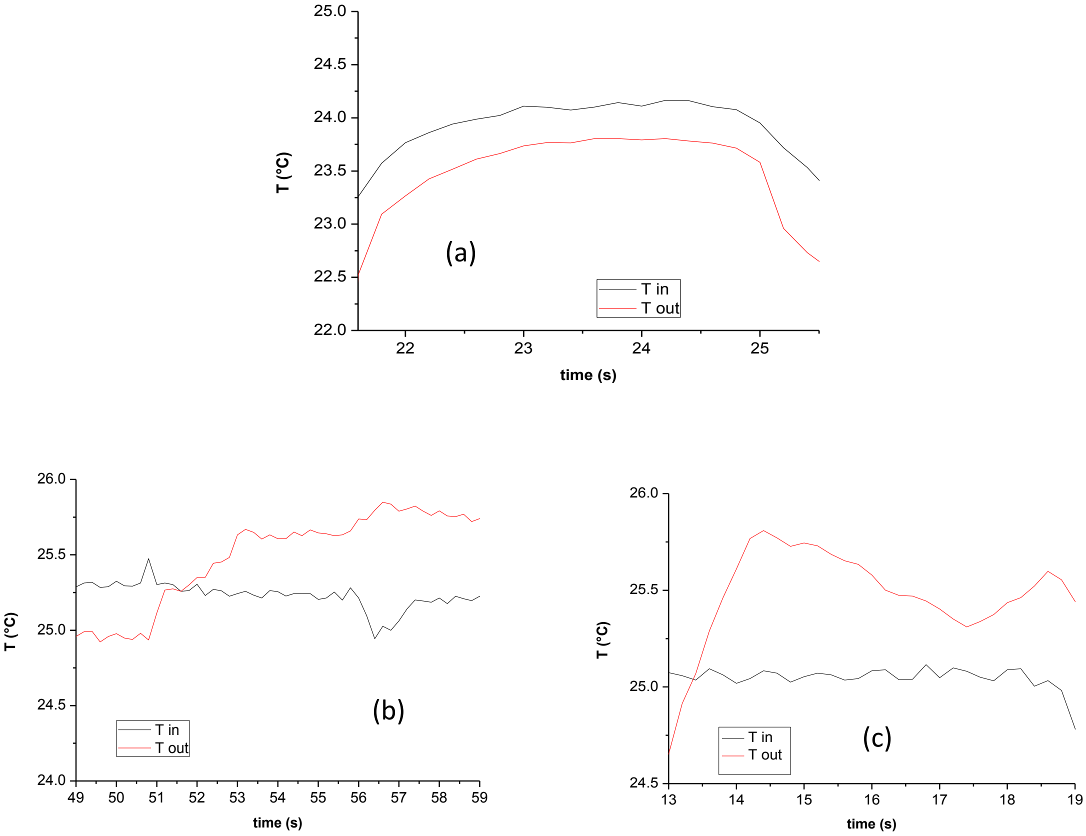

Fig. S1. Temperature profiles of (a) run 1, (b) run 4, (c) run 5

For tests at short reaction times, the ΔT measured was lower than 0.5°C, furthermore for reactions carried out at long reaction time we observed a maximum of 1°C, which means that even for long reaction time the heat release during the polymerization is negligible.

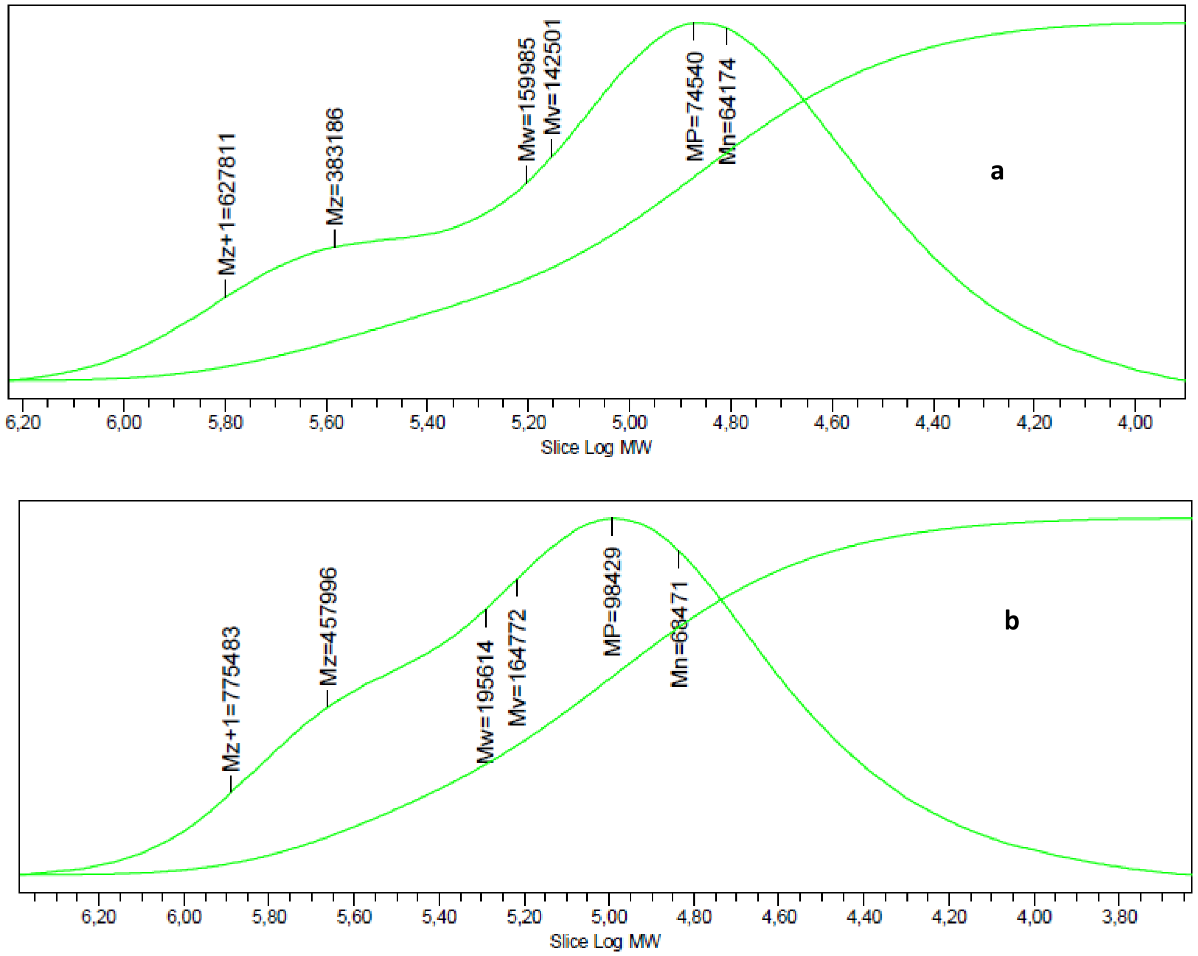

Fig. S2. SEC profiles of polymers obtained with catalyst **II**/MAO/*t*Bu_2-PhOH (runs 7 (a) and 8 (b))