THEORETICAL INVESTIGATION INTO ASPECTS OF THE OLIGOMERIZATION OF LONGER α-OLEFINS WITH CP_2ZRME^+

C Viviers and HCM Vosloo

School for Chemistry and Biochemistry, Potchefstroom University, Private Bag X6001, Potchefstroom, South Africa

ABSTRACT

Polymerisation of olefins with metallocenes have been studied extensively on both theoretical and experimental level1[1]. Computational modelling has yielded substantial insight2[2] into the various proposed mechanisms. The proposed mechanisms for the polymerisation of ethylene have been supported or contradicted by calculations on different levels of theory: ie. on ab intio (HF, DFT and molecular dynamics), semiempirical as well as molecular mechanics level.

A Cossee-like mechanism in which the growing polymer is stabilised by β- or γ-agostic interactions is supported in most studies and hence used in this project.

The advantages of high-level ab initio/DFT calculations of systems containing longer chain olefins are often overshadowed by the high computational cost, while the lack of electronic information from molecular mechanics renders it unsuitable for mechanistic studies. Calculations on semiempirical level suit the purpose of this project very well and comparisons with ab initio work in previous publications suggest that such an approach is feasible3[3].

The insights gained from previous studies will be extended upon and compared with theoretical results obtained for longer α-olefins.

The cationic zirconocene reactants, transitions states and products are optimized on PM3(tm) semiempirical level of theory and the possible impact of steric effects illustrated. Potential energy surfaces along chosen reaction coordinates are presented, compared and elucidated.

1[1] W Kaminsky, *Catal. Today*, 1994, **20**, 257-271; PC Möhring and NJ Coville, *J of Organom. Chem*., **479**,
1– 29, (1994)

2[2] K Thorshaug, JA Stϕvneng, *et al*, *Macromolecules*, **31**, 21, 7149-7165 (1998); PS Subramanian and KJ

Chou, *Trends in Polymer Science*, Vol 3, 10 (1995)

3[3] VL Cruz *et al*, *J. of Polymer Science: Part A: Polymer Chemistry*, **36**, 1157 (1998)