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DEPARTMENT OF CHEMISTRY

GRADUATE THESIS

**Study of the chemical reactivity of W complexes in ROMP of
urethane-norbornene star-shaped monomers**

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ABSTRACT

This thesis focuses on the synthesis and characterization of polymers based on urethane-norbornene star-shaped monomers, through ring opening metathesis polymerization (ROMP), using W-complexes as catalysts. ROMP is an exceptionally useful reaction for the synthesis of polymers with industrially relevant properties. A wide range of ROMP catalytic systems (homogenous and heterogenous, uni- or multi-component) based on mononuclear complexes of transition elements has been developed. Binuclear complexes, though, have been scarcely employed, and that only recently.

The Inorganic Chemistry Laboratory of the National and Kapodistrian University of Athens, has discovered that the $\text{Na}[\text{W}_2(\mu\text{-Cl})_3\text{Cl}_4(\text{THF})_2]\cdot 3\text{THF}$ (W_2) cluster, bearing a triple metal-metal bond, is a very active and selective pre-catalyst for the ROMP of a large number of cycloolefins. WCl_6 is also a very well-known and industrial ROMP pre-catalyst.

In particular, the scope of this thesis is to discuss the activity of the above complexes in the ROMP reaction of two new star-shaped urethane-norbornene monomers with an aromatic/rigid (TIPM/Desmodur RE) or an aliphatic/flexible (Desmodur N3300) tri-isocyanate core and three norbornene groups at the ends of each of the three branches of the star-shaped monomer. Three catalytic systems were used: W_2/PA , WCl_6 and WCl_6/PA (PA: phenylacetylene)

The yields obtained were low to moderate. The products of the reactions with catalytic system W_2/PA were soluble in deuterated acetone and were studied with ^1H NMR spectroscopy. Although it appears that a reaction has taken place on the double bond of the norbornene group, the product is not a ROMP product, since the characteristic peaks of the polynorbornene double bonds are missing.

The products of the reactions with the catalytic systems WCl_6 or WCl_6/PA were insoluble or partly soluble, which prevented their study with ^1H NMR spectroscopy. The yield was not affected by the presence of PA as co-catalyst.

In all cases, no ROMP products were obtained and the yields were not satisfactory. A possible explanation is that the monomers have groups bearing N and O atoms, which can coordinate to tungsten, and thus reduce the catalytic activity of the complex.

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