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Catalytic Polymerization of Olefins and Cycloolefins with Transition Metal Complexes

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ABSTRACT

In this thesis we study two types of metal-mediated polymerization reactions: Controlled Radical Polymerization (**CRP**) and Ring Opening Metathesis Polymerization (**ROMP**).

CRP. We studied the catalytic activity of a family of tripodal Co^{II} and Mn^{II} complexes bearing trianionic triphenylamido-amine ligands towards **CRP** of styrene and methyl methacrylate. Co^{II} complexes were more reactive than Mn^{II} complexes, with the steric factor playing an essential role in their reactivity and control over the polymerization. In many cases polymers featured bimodal molecular weight distributions, which indicate that two parallel mechanisms may be in operation.

ROMP. We used the bimetallic compound $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**{W_2}**, $\{W\equiv W\}^{6+}$, $a'^2e'^4$) for the synthesis of new polymeric materials. **{W_2}** is a highly efficient room-temperature initiator for the **ROMP** of norbornene (**NBE**) and some of its derivatives. We synthesized statistical **NBE/NBD** (**NBD**: norbornadiene) copolymers, which combine the properties of linear and crosslinked polymers. The catalytic activity of **{W_2}** can be improved by addition of small amounts of phenylacetylene (**PA**) as co-initiator. Both catalytic systems (**{W_2}** and **{W_2}/PA**) provided polymers with high-*cis* content. We investigated the reactivity of **{W_2}/PA** and we used this system for the synthesis of highly crosslinked poly(dicyclopentadiene) (**PDCPD**) gels via **ROMP** of dicyclopentadiene (**DCPD**); their structure and properties were compared to those of **PDCPD** gels obtained using the commercially available WCl_6 and the well-established 1st and 2nd generation Ru-based Grubbs' catalysts. The configuration of the polymeric chain plays a key role in the swelling behavior of those **PDCPD** dry-gels in organic solvents, which was studied extensively and exploited for the estimation of Hansen Solubility Parameters (HSP) of mostly-*cis* **PDCPD** and for the separation of chlorinated solvents from water. Therefore, it is concluded that **{W_2}/PA** shows unique advantages in terms of stereochemistry, properties and potential applications of **PDCPD** gels over the mononuclear W- and Ru-based catalytic systems.

SUBJECT AREA: Catalysis

KEYWORDS: controlled radical polymerization, ring opening metathesis polymerization, metal-metal bonds, crosslinked polymers, gel swelling

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