

Synthesis and Properties of high-*cis* Polydicyclopentadiene Gels

Grigorios Raptopoulos, Despoina Chriti, Georgios Anyfantis,
Patrina Paraskevopoulou

Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian
University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

grigorisrap@chem.uoa.gr

Ring Opening Metathesis Polymerization (ROMP) yields polymeric materials with unique mechanical, optical, electrical and chemical properties. ROMP can be catalyzed by a broad range of metal-based catalytic systems, with forerunners being those of ruthenium, molybdenum and tungsten.¹ Bimetallic complexes with metal-metal bonds have been scarcely employed,^{2,3} although they provide more precise control over the stereoselectivity, since both metal centers can be involved in the reaction. Among those, Na[W₂(μ-Cl)₃Cl₄(THF)₂](THF)₃ (W₂) turns out as an efficient yet inexpensive initiator for ROMP of a range of cycloolefins.^{4,5} In this study, we implement W₂ and commercially available WCl₆ for the synthesis of poly(dicyclopentadiene) (PDCPD) gels via ROMP of dicyclopentadiene (DCPD). Both catalysts require activation by small amounts of phenylacetylene.⁶ Dry-gels were compared with PDCPD aerogels synthesized using the well-established first and second generation Ru-based Grubbs' catalysts.⁷ Data revealed that Ru-based catalysts favor the *trans*-, while W-based catalysts favor the *cis*-configuration. Most importantly, it is also shown that the configuration of the polymeric chain plays a key role in the swelling behavior of those PDCPD dry-gels in various organic solvents.

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 685648. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use, which may be made of the information contained therein.