Polymeric Aerogels via Ring Opening Metathesis Polymerization of Urethane-Norbornene Star Monomers

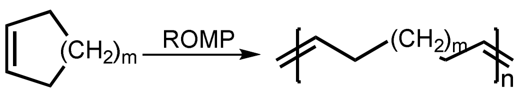
Aspasia Kanellou[*1], Georgios Anyfantis[*2], Despoina Chriti[*1], Grigorios Raptopoulos[*1], Nicholas Leventis[*2], Patrina Paraskevopoulou[*1]

[*1] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

[*2] Department of Materials Science, University of Patras, 26504 Rio, Patras, Greece

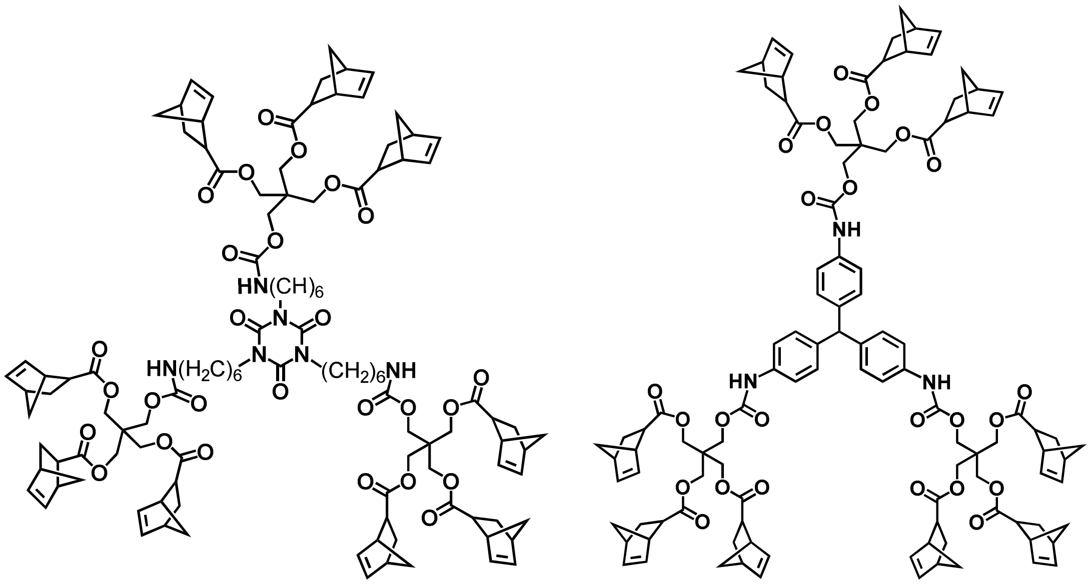
aspakan@chem.uoa.gr

The ring opening metathesis polymerization (ROMP) reaction (Scheme 1) yields polymeric materials with unique mechanical, optical, electrical and chemical properties, and has been adopted recently for the synthesis of robust organic aerogels.[1] ROMP can be catalyzed by a broad range of metal-based catalytic systems, with forerunners being those of ruthenium, molybdenum and tungsten.[2] Bimetallic complexes with metal-metal bonds have been scarcely employed as catalysts, however, since both metal centers can be involved in the reaction, they may provide more precise control over stereoselectivity. Among those, $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3)$ (**1**) turns out to be an efficient, yet inexpensive initiator for ROMP of a range of cycloolefins,[3] providing high-*cis* polymeric backbones, in contrast to the Ru-based catalysts, e.g., first or second generation Grubbs' catalysts (**GC-I** and **GC-II**), which provide all-*trans* or mixtures of *cis* and *trans* backbone configurations, respectively.



Scheme 1. Ring Opening Metathesis Polymerization (ROMP).

In this study, we implement **GC-I** and **1** for the synthesis of aerogels via ROMP of urethane-norbornene star monomers, **aL-9-star-NBE** and **aR-9-star-NBE**, based on an aliphatic or an aromatic core, respectively (Scheme 2). The morphostructural properties of those aerogels are discussed as a function of the catalyst and their density.



aL-9-star-NBE **aR-9-star-NBE**

Scheme 2. Monomers for the synthesis of polymeric aerogels via Ring Opening Metathesis Polymerization (ROMP).

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