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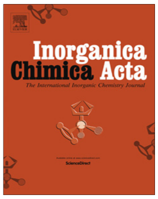

Research paper

Synthesis and structural characterization of poly(dicyclopentadiene) gels obtained with a novel ditungsten versus conventional W and Ru mononuclear catalysts

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ABSTRACT

Poly(dicyclopentadiene) (**PDCPD**) gels were prepared *via* ring opening metathesis polymerization (ROMP) of dicyclopentadiene (**DCPD**), which is known to provide highly crosslinked insoluble polymers. Two catalytic systems were employed, both based on W compounds. The first one was based on the ditungsten complex $Na[W_2(\mu\text{-}Cl)_3 Cl_4(THF)_2]\cdot(THF)_3$ ($\{W\overset{3}{-}W\}^{6+}$, $a'^2e'^4$) and the second one on commercially available WCl_6. Both catalysts require activation by small amounts of phenylacetylene (**PA**). Dry-gels were characterized with TGA, FTIR-ATR, FT-Raman and solid-state NMR, and were compared with **PDCPD** aerogels synthesized using the well-established first and second generation Ru-based Grubbs' catalysts (**Ru-I** and **Ru-II**). Emphasis is given on the determination of the *cis*/*trans* ratio of the polymeric chain. Data confirmed that Ru-based catalysts favor the *trans*-configuration, while W-based catalysts favor the *cis*-configuration, in accord with the stereoselectivity that has been observed with those catalytic systems in other ROMP reactions of substrates that yield soluble polymers. 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 toluene. High-*cis* **PDCPD** gels obtained from the ditungsten catalytic system increased their volume by more than 100 times, while gels obtained with the other catalytic systems swelled to a much lesser extent (WCl_6/**PA**, **Ru-II**), or did not swell at all (**Ru-I**). It is evident that swelling strongly depends on the configuration of the polymeric chain and increases together with the content of the *cis* configuration. Therefore, the ditungsten catalytic system shows unique advantages in terms of stereochemistry and properties of **PDCPD** gels over the mononuclear W- and Ru-based catalytic systems.

1. Introduction

Metathesis reactions induce mild cleavage/formation and redistribution of carbon–carbon multiple bonds, and therefore allow synthesis of complex functional molecules in one-pot. Among those reactions, ring opening metathesis polymerization (ROMP) of cycloolefins (Scheme 1) [1–3], yields unsaturated polymeric materials, and is an important and versatile tool in polymer chemistry. The properties of those materials depend on the stereochemistry of the polymeric chain, which is directly related to the stereoselectivity of the reaction; nevertheless, tuning the conformation of the polymers has been a long-standing problem [4,5]. Therefore, the choice of the ROMP catalyst is important, and one fact to recon with is that high activity and selectivity need to be considered in light of functional group tolerance.

A wide range of catalytic systems have been explored, including uni-, bi- and multicomponent catalytic systems based mainly on mononuclear transition metal complexes along the periodic table [6,7]. In any case, the active catalytic species for metathesis polymerization reactions is a metallocarbene, which is either generated *in situ*, or has been previously synthesized and isolated, such as the well-defined Katz ($[(OC)_5W=C(Ph)R]$; R = OMe, Ph) [8–10], Schrock (Mo- and W-based) [11] and Grubbs (Ru-based) [12] alkylidenes and their numerous variations. For many of the catalytic systems in which metallocarbenes are formed *in situ* the exact nature of the active species remains unknown. Apart from homogeneous systems, immobilized (on polymeric or inorganic supports) and recyclable catalysts have also been developed [13,14].

Bimetallic complexes with metal–metal bonds have been scarcely employed [15,16], although they provide more precise control over stereoselectivity, because both metal centers can be involved in the reaction. We have already reported that ditungsten

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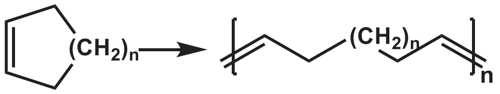


Scheme 1. Ring Opening Metathesis Polymerization (ROMP) of cycloolefins.

complexes $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**W₂**, $\{W\overset{3}{-}W\}^{6+}$, $a'^2e'^4$) and $(Ph_4P)_2[W_2(\mu\text{-}Br)_3Br_6]$ (**W₂(Br)**, $\{W\overset{2.5}{-}W\}^{7+}$, a'^2e^3), are highly efficient and stereoselective room temperature homogeneous and/or heterogeneous initiators for metathesis polymerization of alkynes [17,18] as well as ROMP of norbornene (**NBE**) and some of its derivatives [18,19]. **W₂** acts as a unicomponent initiator in most cases; addition of small amounts of phenylacetylene (**PA**) generates a more reactive system (**W₂**/**PA**), which is also more tolerant to coordinating side groups [20]. Both catalytic systems provide high-*cis* polymers (e.g., 86% *cis* for polynorbornene (**PNBE**)). Their *cis*-specificity is comparable to that observed with low-valent metallocarbenes (Katz) [8,9] and high-valent stereoselective designer catalysts (Schrock [21], Basset [22]). **W₂(Br)** functions in the presence of $AgBF_4$; **W₂(Br)**/$AgBF_4$ is equally effective with respect to yields, but shows lower selectivity [18].

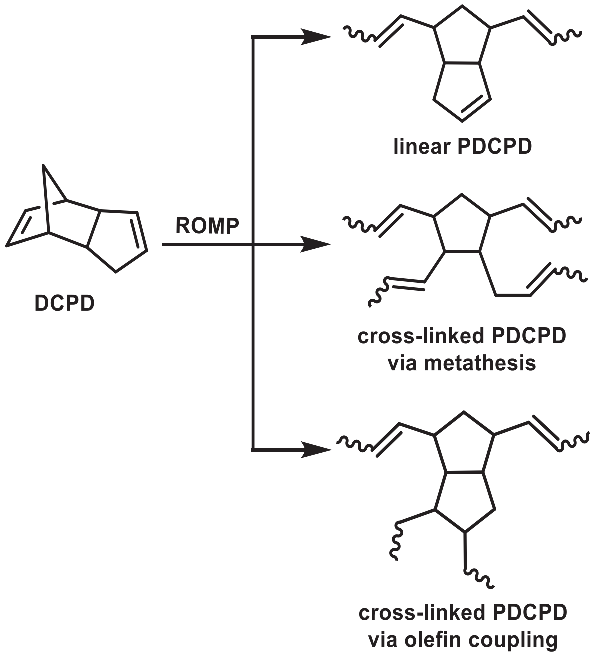
In ROMP-derived polymers, one of the most important features of the polymeric chain is the *cis*/*trans* ratio of the carbon–carbon double bonds. W-based catalytic systems usually favor formation of polymers with higher *cis* content [18–25], while Ru-based catalytic systems show the opposite trend [26–29], with notable exceptions though [30,31].

In this study, we describe the synthesis of polydicyclopentadiene (**PDCPD**) gels obtained from ROMP of dicyclopentadiene (**DCPD**) solutions using two catalytic systems, both based on W-compounds. The first one (**W₂/PA**) is based on ditungsten compound **W₂** and the second one (**W/PA**) on the commercially available WCl_6 complex. ROMP of **DCPD** can be induced by WCl_6 alone [32,33], in the presence of organometallic alkylating reagents [6], oxygen-containing compounds [34], or **PA** [35]. **DCPD** was chosen as an inexpensive and readily available monomer that provides industrial polymers with high mechanical strength [13,26,36]. **PDCPD** is an insoluble polymer, because of extensive crosslinking *via* secondary metathesis or radical coupling reactions on the double bond of the pendant cyclopentene ring (Scheme 2) [37]. The stereochemistry of the **PDCPD** gels from the two W-based catalysts is compared with those of **PDCPD** synthesized using the well-established first and second generation Ru-based Grubbs' catalysts (**Ru-I** and **Ru-II**) [38–40], and we provide an example of how different configurations can affect the properties and applications of those materials. The structures of all metal catalysts involved in this study along with their abbreviations are shown on Scheme 3.

2. Experimental

2.1. Materials and physical measurements

WCl_6 was purchased from Alfa Aesar in sealed ampules. **Ru-I** and **Ru-II** were purchased from Sigma-Aldrich and **DCPD** (>91% *endo*-isomer) was purchased from Acros. **W₂** [41] and **W₂(Br)** [18] were prepared according to literature procedures. **PDCPD** aerogels synthesized using **Ru-I** and **Ru-II** are referred to as **Ru-I-PDCPD** and **Ru-II-PDCPD**, respectively, and were kindly provided by Prof. Nicholas Leventis [38]. **DCPD** and **PA** were dried by stirring with CaH_2 and were distilled under vacuum·THF and toluene were distilled over Na/Ph_2CO and CH_2Cl_2 was distilled over P_4O_{10}. All solvents were distilled under inert atmosphere, and were degassed by three freeze-pump-thaw cycles. All operations were performed under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O_2, $H_2O < 1$ ppm).



Scheme 2. ROMP of **DCPD**.

The thermal stability of the polymers was studied by thermogravimetric analysis (TGA) employing a Q50 TGA model from TA instruments. Samples were placed in platinum crucibles. An empty platinum crucible was used as a reference. Samples were heated from ambient temperatures to 600 °C in a 60 mL/min flow of N_2 at a heating rate of 10 °C/min.

Mid-IR spectra (525–4000 cm^{-1}) were measured on a Fourier-transform instrument (Equinox 55 by Bruker Optics) equipped with a single-reflection diamond ATR accessory (DuraSamplIR II by SensIR Technologies). Contact between the powder samples and the diamond element was ensured by a suitable press. Each spectrum represents the average of 100 scans recorded at an optical resolution of 4 cm^{-1}.

FT-Raman spectra were obtained on a Fourier transform instrument (RFS 100 by Bruker Optics) employing for excitation ca. 300 mW of the Nd:YAG 1064 nm line in a backscattering geometry. The spectra have been measured at a resolution of 4 cm^{-1} and represent averages of ca. 5000–8000 scans.

Solid-state NMR spectra were obtained with a 600 MHz Varian spectrometer (Palo Alto, CA) operating at 150.80 MHz for ^{13}C. For ^{1}H-^{13}C ramped CPMAS (Cross-Polarization Magic Angle Spinning) and HC LG-HETCOR (HETeronuclear CORrelation) spectra the spinning rate used was 5 kHz and the temperature run the experiment was 25 °C.

2.2. Synthesis of *PDCPD* gels

All formulations and molar concentrations are summarized in Table S1. Experimental polymerization procedures are described below.

2.2.1. Catalytic system *W₂/PA*

PA (225 µL, 209 mg, 2.05 mmol) was added to a solution of **W₂** (105.0 mg, 0.105 mmol) in CH_2Cl_2 (15.0 mL), followed by **DCPD** (5.0 mL, 4.89 g, 37.0 mmol). The mixture was stirred vigorously at room temperature for 30 min and was poured into molds (Wheaton polypropylene OmniVials, 1.1 cm in diameter).

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