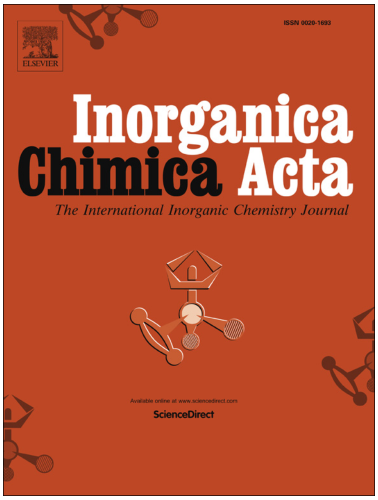


Research paper

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

Grigorios Raptopoulos, George C. Anyfantis, Despoina Chriti, Patrina Paraskevopoulou

PII: S0020-1693(16)30512-6
DOI: http://dx.doi.org/10.1016/j.ica.2016.09.008
Reference: ICA 17253

To appear in: *Inorganica Chimica Acta*

Received Date: 25 July 2016
Revised Date: 6 September 2016
Accepted Date: 7 September 2016

Please cite this article as: G. Raptopoulos, G.C. Anyfantis, D. Chriti, P. Paraskevopoulou, Synthesis and structural characterization of poly(dicyclopentadiene) gels obtained with a novel ditungsten versus conventional W and Ru mononuclear catalysts, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.09.008

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

Grigorios Raptopoulos, George C. Anyfantis, Despoina Chriti, Patrina Paraskevopoulou*
Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 15771, Greece.
* Correspondance: paraskevopoulou@chem.uoa.gr (P.P.); Tel.: +30-210-727-4381; Fax: +30-210-727-4782

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 $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ ($\{W\overset{3}{—}W\}^{6+}$, $a'^2e'^4$) 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.

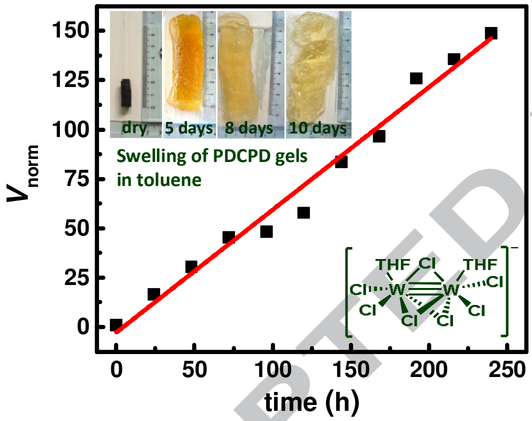
Keywords: ditungsten; metal-metal bonds; metathesis; ROMP; dicyclopentadiene; gel swelling

Highlights

- Synthesis of high-*cis* poly(dicyclopentadiene) gels using a ditungsten complex.
- FTIR-ATR, FT-Raman, solid state ^{13}C NMR and thermogravimetric analysis of dry-gels.
- Comparison of dry-gels with those from mononuclear W and Ru catalytic systems.
- High-*cis* gels increased their volume by more than 100 times in toluene.
- Gels swell more as the *cis* content increases.

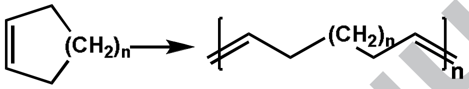
Graphical abstract

Poly(dicyclopentadiene) (**PDCPD**) gels prepared *via* ROMP of dicyclopentadiene (**DCPD**) using the ditungsten complex Na[$W_2(\mu\text{-}Cl)_3Cl_4(THF)_2$]·$(THF)_3$ were high-*cis* and swelled in toluene by more than 100 times, while gels prepared using mononuclear W- and Ru-based catalytic systems swelled to a much lesser extent, or did not swell at all.



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.



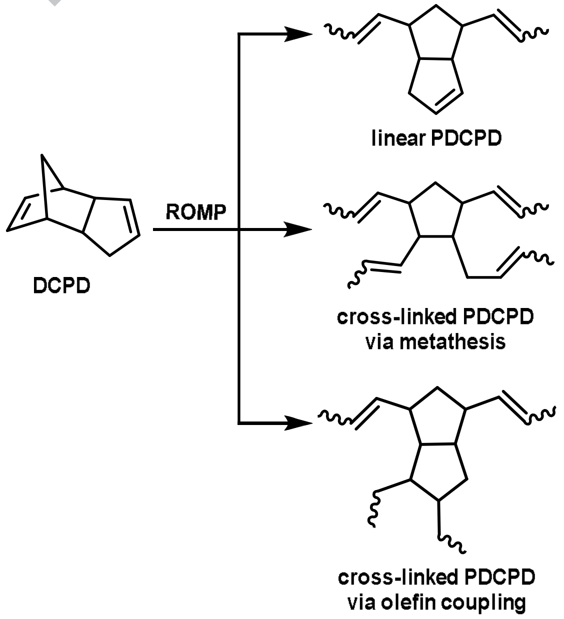
Scheme 1. Ring Opening Metathesis Polymerization (ROMP) of cycloolefins.

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].

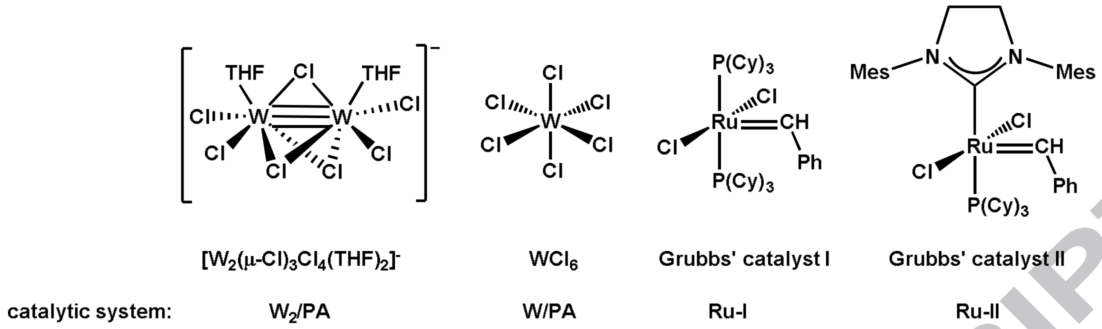
Bimetallic complexes with metal-metal bonds have been scarcely employed [15,16], although they provide more precise control over stereoselectivity, because both metal centers can be involved in the reaction. We have already reported that ditungsten complexes $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**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]). **W_2(Br)** functions in the presence of $AgBF_4$; **W_2(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 [18–22,23–25], 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 (**W_2/PA**) is based on ditungsten compound **W_2** 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.



Scheme 2. ROMP of **DCPD**.



Scheme 3. Schematic representation of all metal compounds employed in this study.

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. **W_2** [41] and **W_2(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. 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).

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 ^{o}C in a 60 mL/min flow of N_2 at a heating rate of 10 ^{o}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. 300mW 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. 5,000–8,000 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 **W_2/PA***

PA (225 μL, 209 mg, 2.05 mmol) was added to a solution of **W_2** (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). All solutions gelled within 18 h. The resulting wet-gels were aged in their molds for 6 h at room temperature. Subsequently, wet-gels were transferred into toluene and were washed 4× 8 h per wash cycle, using 4× the volume of the gels. It is noted that during processing wet-gels swell in toluene. That was accounted for by adjusting the volume of the wash solutions to be always 4× the volume of the wet-gel. Next, pore-filling toluene was exchanged with pentane (4 washes, 8 h per wash cycle, 4× the volume of the gel per cycle), and wet-gels were air-dried in the oven at 50 °C. It is noted that wet-gels deswelled in pentane almost to their original volume. The resulting gels are referred to as **W_2-PDCPD** (where **W_2** stands for the catalytic system **W_2/PA**).

*2.2.1. Catalytic system **WCl_6/PA***

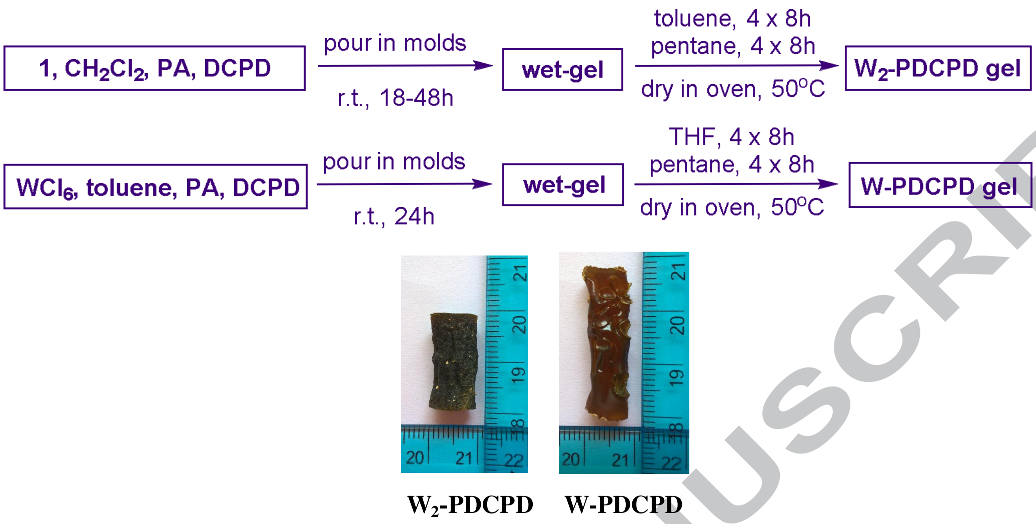
PA (50 μL, 46.5 mg, 0.455 mmol) was added to a solution of WCl_6 (160.0 mg, 0.403 mmol) in toluene (15.0 mL), followed by **DCPD** (5.0 mL, 4.89 mg, 37.0 mmol). The mixture was stirred vigorously at room temperature for 1 min and was poured into molds (Wheaton polypropylene OmniVials, 1.1 cm in diameter). All solutions gelled within 5 min. The resulting wet-gels were aged in their molds for 15 min at room temperature. Subsequently, wet-gels were transferred into THF and were washed 4×, 8 h per wash cycle, using 4× the volume of the gels. Next, pore-filling THF was exchanged with acetonitrile (4 washes, 8 h per wash cycle, 4× the volume of the gel per cycle) and pentane (4 washes, 8 h per wash cycle, 4× the volume of the gel per cycle). No change in the volume of the gels was observed during wash cycles. The wet-gels were air-dried in the oven at 50 ^{o}C. The resulting gels are referred to as **W-PDCPD** (where **W** stands for the catalytic system **W/PA**).

3. Results and Discussion

*3.1. Synthesis of **PDCPD** Gels*

The synthesis of **W_2-PDCPD** and **W-PDCPD** wet-gels was carried out at room temperature, as shown in Table S1 and Scheme 4. The process was analogous to the one previously reported for the **Ru-I-PDCPD** and **Ru-II-PDCPD** aerogels [38]. The weight percent of **DCPD** was the same for all samples (20% w/w). Attempts to work with lower concentration sols (e.g., 10 or 5% **DCPD**) gave gels (within 24 to 48 h), which were not very sturdy, and could not be handled easily during post-gelation solvent exchange. This behavior is attributed to a higher amount of linear **PDCPD**, which is soluble in common organic solvents, and therefore is dissolved away in toluene during post-gelation washes as confirmed with ^{1}H NMR (Figure S1). Formation of linear **PDCPD** in low **DCPD** concentrations has been observed and reported previously by both our laboratory and others [23,37,42]. Using various molar ratios of the catalytic system **W_2(Br)**/$AgBF_4$ in CH_2Cl_2 under similar reaction conditions we observed no gelation even after long reaction times (>48 h), even though we have previously shown that the ROMP of **DCPD** proceeds almost quantitatively [18].

After aging, **PDCPD** wet-gels were removed from their molds and were washed with toluene or THF and acetonitrile (4×), then pentane (4×) and were air-dried at 50 ^{o}C. The reactions were quantitative (yields >98%). It is noted that gels were not aged for a long time, in order to prevent isomerization of *cis* double bonds. During washing with toluene, **W_2-PDCPD** wet-gels exhibited significant swelling as a function of time (Figure 1). This behavior is discussed further in Section 3.5. As soon as wet-gels were transferred to pentane, they deswelled rapidly without any noticeable deformation (Figure 1). Insoluble **PDCPD** dry-gels were characterized using spectroscopic techniques (FTIR-ATR, FT-Raman and ^{13}C CPMAS) and thermogravimetric analysis (TGA). All those techniques provided complementary information on the structure of the polymer and the configuration of the polymeric chain.



Scheme 4. Synthesis of **W_2-PDCPD** and **W-PDCPD** gels.

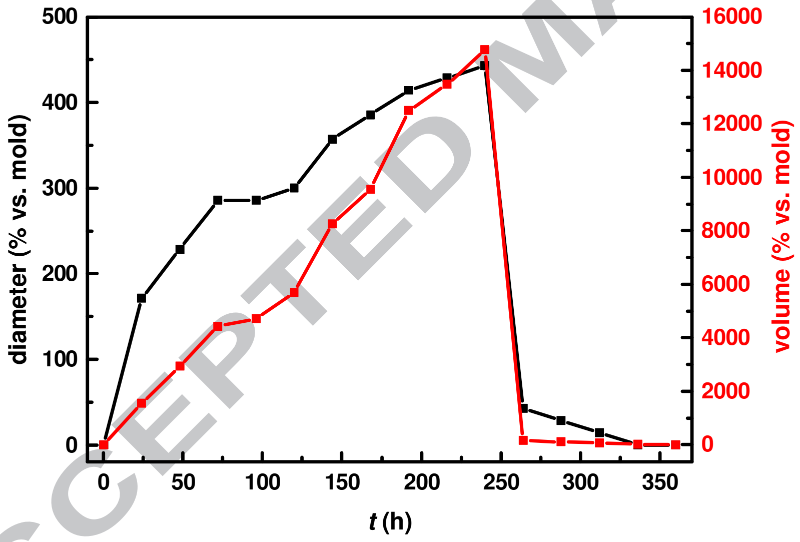


Figure 1. Swelling data for **W_2-PDCPD** wet-gels in toluene and de-swelling in pentane.

3.2. Vibrational Spectroscopy

Since *cis* and *trans* carbon-carbon double bonds provide distinct bands, vibrational spectroscopy is a useful tool for studying unsaturated systems. Characteristic bands of FTIR-ATR spectra of all **PDCPD** gels are shown in Figure 2. Assignments were made based on literature reports [23,38]. Bands at 1660 and 1650 cm^{-1} were assigned to stretching vibrations of *trans* and *cis* C=C bonds, respectively, and bands at 972 and 752 cm^{-1} to deformation vibrations of C–H bonds on *trans* and *cis* double bonds, respectively. An estimation of the *cis/trans* ratio is possible from the relative absorbance values of the latter bands to the absorbance at 1450 cm^{-1}, which is assigned to deformation vibration of $-CH_2-$ groups of the polymeric chain [34]. From those values (Tables 1 and S2) it is clear that Ru catalysts favor formation of *trans* polymeric chains, while W-based catalytic systems show the opposite trend (although marginally in the case **W/PA**). The most extreme cases are **Ru-I**, for which bands related to *cis* configuration are almost invisible and the *cis/trans* ratio is very low, and **W$_2$/PA**, for which bands related to *trans* C=C bonds are very weak and the *cis/trans* ratio is high. Bands at 1620 and 708 cm^{-1}, which are due to vibrations of the unreacted pendant cyclopentene ring, were present in all spectra showing that cyclopentene rings did not get involved in crosslinking quantitatively.

Those findings were further supported by FT-Raman spectroscopy (Figure 3), which is a very sensitive technique for non-polar groups, such as carbon-carbon double bonds. Raman bands at 1650 and 1664 cm^{-1} were assigned to stretching vibrations of the *cis* and *trans* double bonds of the polymeric chain [28]. Although it is not possible to calculate accurately the *cis/trans* ratio along the polymeric chain, it is obvious that **Ru-I** yielded high-*trans* **PDCPD**, while **W$_2$/PA** provided high-*cis* **PDCPD** dry-gels; the remaining two catalytic systems gave mixtures of *cis* and *trans* double bonds, with the *trans* configuration prevailing when **Ru-II** is used, and the *cis* configuration when **W/PA** is employed. The Raman band at 1620 cm^{-1} is assigned to the stretching vibration of the double bond on the pendant cyclopentene ring, and is present in all four spectra, confirming that not all cyclopentene rings were involved in crosslinking.

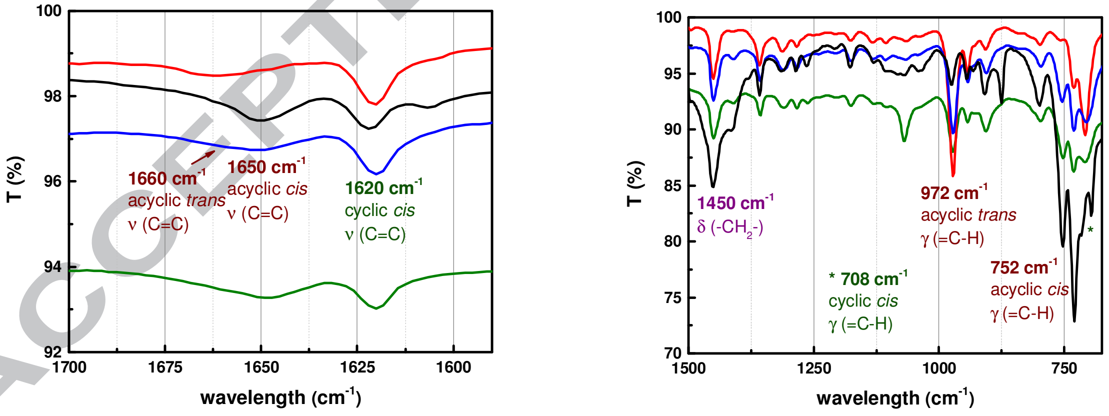


Figure 2. FTIR-ATR spectra (left: 1700-1590 cm^{-1}; right: 1500-600 cm^{-1}) of **PDCPD** dry-gels obtained from the ROMP of **DCPD** by the following catalytic systems: **W$_2$/PA** (black line), **W/PA** (green line), **Ru-II** (blue line) and **Ru-I** (red line).

Table 1

IR characterization of **W2-PDCPD**, **W-PDCPD**, **Ru-I-PDCPD** and **Ru-II-PDCPD**.

Catalytic system	**A_{752} / A_{972} / A_{1450}**
W_2/PA	1.40 / 0.38 / 1
W/PA	1.18 / 1.12 / 1
Ru-II	1.01 /1.41 / 1
Ru-I	0.36 / 2.71 / 1

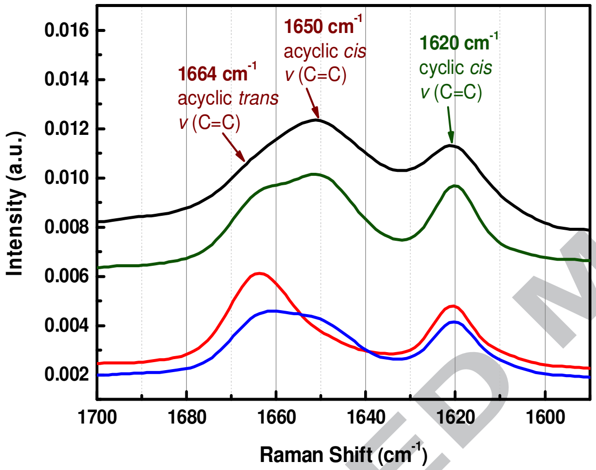


Figure 3. FT-Raman spectra (1700-1580 cm^{-1}) of **PDCPD** dry-gels obtained from the ROMP of **DCPD** by the following catalytic systems: **W_2/PA** (black line), **W/PA** (green line), **Ru-II** (blue line) and **Ru-I** (red line).

3.3. NMR spectroscopy

Further characterization of **PDCPD** dry-gels was carried out with solid-state ^{13}C CPMAS and HC LG-HETCOR, 1 and 2 D experiments, respectively. The peak at 129 ppm in the ^{13}C NMR spectrum (Figure 4), was assigned to the olefinic carbons, and peaks in the 26–60 ppm region to aliphatic carbons. The HC LG-HETCOR experiment made assignment of the aliphatic carbons possible, as shown on Figure 5. That assignment is in accord with the APT spectrum of **DCPD** in $CDCl_3$ [38], which discriminates –CH– from –CH_2– groups. The key identifier of the *cis* versus the *trans* configuration was the chemical shift of carbons C5 and C7, which were different in the two configurations. The peak at 40 ppm, assigned to *cis*-polymeric chains [38], predominates for **PDCPD** obtained from the W-based catalytic systems, while the peak at 44 ppm, assigned to *trans*-polymeric chains, predominates for **PDCPD** obtained from the Ru-based catalytic systems, as has been previously reported [38]. The two peaks are overlapping; therefore the exact determination of the *cis*/*trans* ratio was not feasible; however the stereoselectivity of each catalytic system is rather straightforward.

^{13}C CPMAS spectra also provide information on the mechanism of the ROMP of **DCPD**. Scheme 3Scheme 2 shows all possible products of **PDCPD** polymerization *via* ROMP. Polymers obtained may be linear or crosslinked. Crosslinked polymers are formed by reactions taking place on the double bond of the cyclopentene ring. Those can be either metathetic or olefin coupling reactions and have been well-studied for **PDCPD** [37]. The ratio of olefinic/aliphatic carbons depends on the mechanism of crosslinking and is equal to 2/3 (metathetic) and 1/4 (olefin coupling). Therefore, the olefin coupling contribution can be calculated *via* equation (1) that takes the ratio of the integrated areas of the corresponding ^{13}C CPMAS peaks as input [39]. Thus, $C_{olefinic}$ refers to the total sp^2 carbons, $C_{aliphatic}$ to sp^3 carbons and x is the fraction of polymer double bonds that participate in crosslinking *via* olefin coupling. Integration of **PDCPD** spectra provided the ratios shown in Table S3. The results show that crosslinking *via* olefin coupling ranges from 21 to 33 %, with W-based catalytic systems showing the highest values. It should be noted that the x values calculated for **PDCPD** dry-gels obtained from W-based systems may be a bit higher, depending on the **PPA** content of the polymeric chain. Those values are given in parentheses (Table S3). However, we believe that the value of x is much closer to the value calculated from eq. 1, because most of linear **PPA** is removed during washes of the wet-gels. In addition, the NMR spectra show symmetrical peaks at 129 ppm and not any peaks apart from the ones expected for **PDCPD**. In any case, the difference in x values for the four catalytic systems is not considered significant.

$$\mathbf{(2-\mathit{x}) / (3+\mathit{x}) = [C_{olefinic} / C_{aliphatic}]_{experimental}} \qquad (1)$$

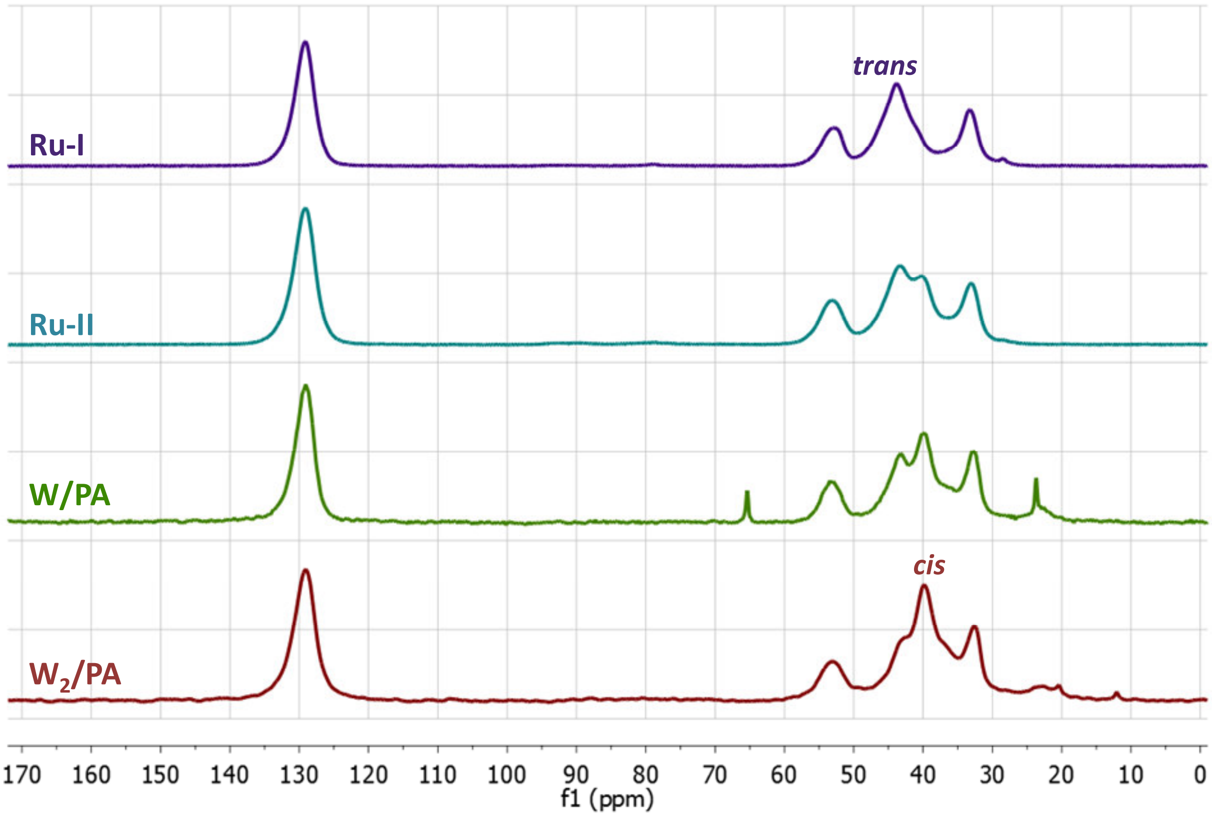


Figure 4. ^{13}C CPMAS spectra of **PDCPD** dry-gels and aerogels obtained from four different catalytic systems, as indicated. Spectra of **Ru-I-PDCPD** and **Ru-II-PDCPD** aerogels were taken from ref. [38].

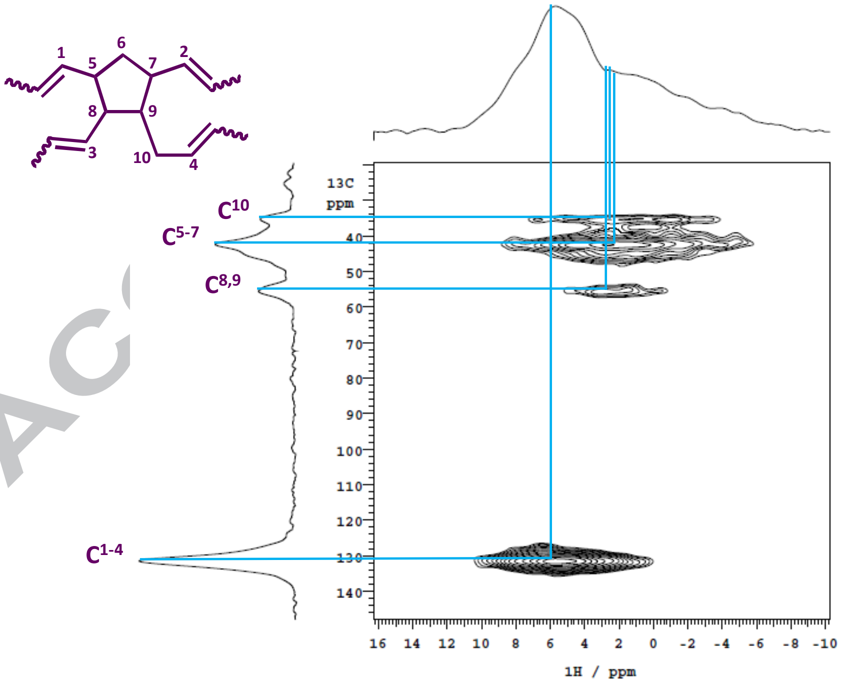


Figure 5. HC LG-HETCOR NMR spectrum of **W$_2$-PDCPD** gel.

3.4. Thermal Analysis

Thermogravimetric analysis (TGA) of **W_2-PDCPD** under N_2 showed a small weight loss up to almost 450 ^{o}C, which can be divided into two stages (Figure 6, inset). The first stage (7% weight loss), from 100 to 400 ^{o}C, corresponds to evaporation and decomposition of unreacted monomers and small polymer chains. Similar behavior has been observed in other polymeric materials [43]. For **W-PDCPD** the weight loss up to 400 ^{o}C is higher (14%) and this stage can be clearly divided into two steps; one from 100-200 ^{o}C (3% weight loss) and another one from 200-400 ^{o}C (11% weight loss). For **Ru-I-PDCPD** and **Ru-II-PDCPD** the weight loss was very small (3%) during the first stage (up to 400 ^{o}C). The second stage, starting after 400 ^{o}C, was similar for all dry-gels: all samples showed a sharp weight loss, indicating rapid degradation of the polymeric backbones. It is obvious from these results that the thermal stability practically did not change, and did not seem to depend on the configuration of the polymeric chain.

Differential thermogravimetry (DTG) of **W_2-PDCPD** showed a single decomposition peak at 470 ^{o}C (Figure 6), indicating a high degree of crosslinking [26] and a rather simple decomposition mechanism, involving mainly degradation reactions along the polymeric backbone. For the other three gels the decomposition peaks were bimodal (460 ^{o}C and 470 ^{o}C; Figure 6), indicating a more complex mechanism of thermal decomposition. For example, isomerization of *cis* to *trans* chains during thermal decomposition is a process that cannot be excluded. This type of reaction has been observed during the thermal decomposition of 1,4-polyisoprene and 1,4-polybutadiene, starting at 300 and 200 ^{o}C, respectively [44].

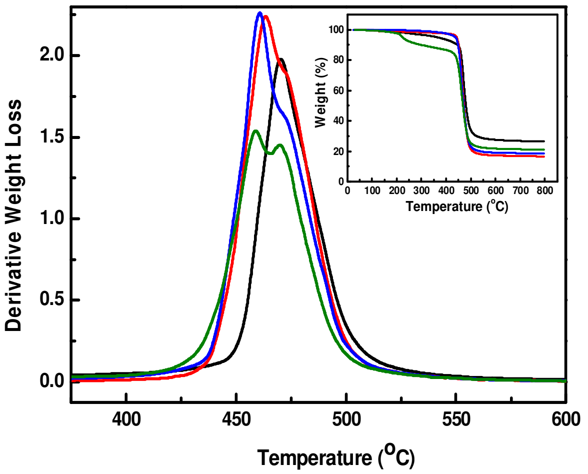


Figure 6. Derivative weight loss with temperature (°C) and weight loss (%/°C) with temperature (°C; inset) for **PDCPD** dry-gels obtained from the polymerization of **DCPD** by the following catalytic systems: **W_2/PA** (black line), **W/PA** (green line), **Ru-I** (red line) and **Ru-II** (blue line).

3.5. Swelling Studies

As mentioned above (section 3.1), **W_2-PDCPD** wet-gels swelled in a number of solvents, with toluene being the most extreme case. That property was further studied with **W_2-PDCPD** dry-gels placed in toluene at room temperature. Those gels showed a linear increase (Figure 7, inset) of their volume by up to 150 times in 10 days, without loss of their integrity (Figures 7 and 8). Placing the swollen gels in pentane caused rapid shrinkage down to almost to the original volume of the dry-gels. When gels shrunk in pentane, were re-dried and reused, they swelled up to the same volume, with the same rate, for at least three consecutive times. Similar behavior was observed in many other organic solvents (e.g., THF, chlorinated solvents, etc.), although with slower rates and to a different extent. Detailed studies on the extent and mechanism of swelling of **W_2-PDCPD** gels are underway. Gels prepared using **W/PA** and **Ru-II** swelled significantly less, whereas **Ru-I-PDCPD** did not swell at all (Figure 7). A similar trend was observed in the other organic solvents studied. The relationship between the *cis* content of the polymeric chain and the extent of swelling is evident: gels swell more as the *cis* content increases.

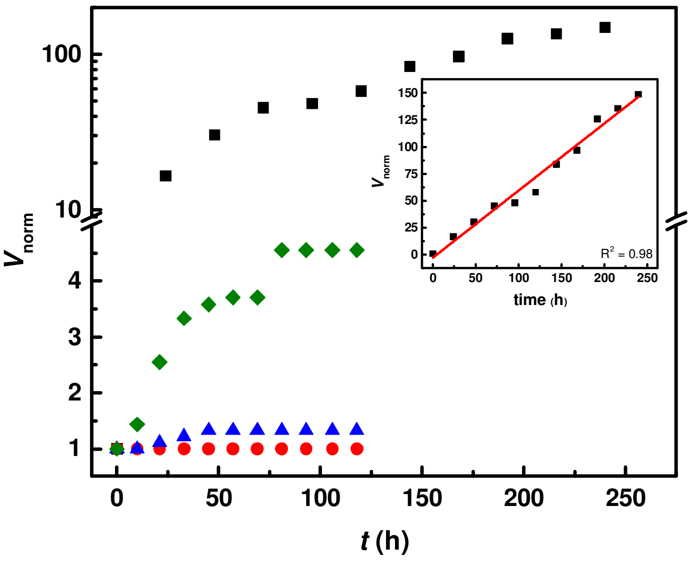


Figure 7. Swelling of **PDCPD** wet-gels in toluene as a function of the catalytic system: **W_2/PA** (black squares), **W/PA** (green diamonds), **Ru-II** (blue triangles) and **Ru-I** (red dots). Inset: Swelling of a **W2-PDCPD** wet-gel in toluene with time.

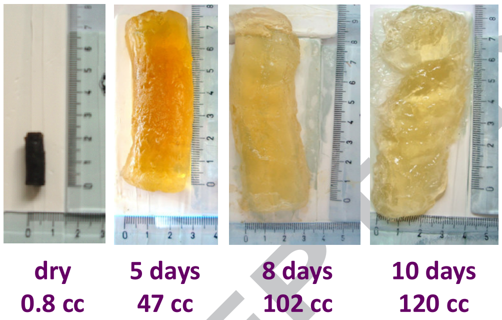


Figure 8. Swelling of a **W_2-DCPD** gel in toluene.

4. Conclusion

Poly(dicyclopentadiene) (**PDCPD**) gels were prepared *via* ROMP of dicyclopentadiene (**DCPD**) using two W-based catalytic systems; the first one was based on the ditungsten complex $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**W_2/PA**), and the second one on the mononuclear WCl_6 complex (**W/PA**). Dry-gels were highly crosslinked, as corroborated by their high thermal stability. Solid-state ^{13}C CPMAS NMR spectroscopy revealed the operation of two mechanisms for crosslinking (one metathetic and one radical), with metathesis being the major pathway (~ 70-80%) in all cases. Most importantly, solid-state ^{13}C NMR along with vibrational spectroscopy (FTIR-ATR and FT-Raman) revealed differences in the *cis/trans* ratio of the double bonds of the polymeric chains. Results were compared also with aerogels **Ru-I-PDCPD** and **Ru-II-PDCPD**, which were synthesized using the first and the second generation Grubbs' catalysts, respectively. Spectroscopic data showed that the configuration of the polymeric chain was predominantly *cis* for W-catalyzed systems and predominantly *trans* for Ru-catalyzed systems. The most extreme cases were **Ru-I-PDCPD**, which consisted of high-*trans* **PDCPD**, and **W_2-PDCPD** dry-gels, which consisted of high-*cis* **PDCPD**. The different *cis* content played a major role in the swelling behavior of the corresponding dry-gels in toluene. In toluene, **W_2-PDCPD** dry-gels swelled and increased their volume by more than 100 times. Such extreme swelling phenomena are rare and may be useful in environmental remediation, shape memory applications, actuators, chemical delivery systems etc. By comparison of **W_2-PDCPD** with **W-PDCPD** dry-gels, as well as with **Ru-II-PDCPD** and **Ru-I-PDCPD** aerogels, it is evident that swelling strongly depends on the configuration of the polymeric chain and increases together with the content of the *cis* configuration. Similar behavior was observed in many other organic solvents (e.g., THF, chlorinated hydrocarbons, etc.), although with slower rates and to a different extent. Therefore, it is concluded that the ditungsten catalytic system considered in this study shows unique advantages in terms of stereochemistry and properties of **PDCPD** gels over the mononuclear W- and Ru-based catalytic systems.

Acknowledgments

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 authors, and the Commission cannot be held responsible for any use, which may be made of the information contained therein. Prof. Nicholas Leventis (Missouri University of Science & Technology, Rolla MO, USA), Prof. Marinos Pitsikalis and Prof. Thomas Mavromoustakos (Department of Chemistry, N.K.U.A., Athens, Greece), Prof. Gregor Mali (National Institute of Chemistry, Ljubljana, Slovenia), Dr. Georgios D. Chryssikos and Dr. Constantinos Tsiantos (National Hellenic Research Foundation, Athens, Greece) are gratefully acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

References

[1] S. Sutthasupa, M. Shiotsuki, F. Sanda, Polym. J. 42 (2010) 905–915.

[2] A. Leitgeb, J. Wappel, C. Slugovc, Polymer 51 (2010) 2927–2946.

[3] K. Nomura, M.M. Abdellatif, Polymer 51 (2010) 1861–1881.

[4] R.R. Schrock, J.-K. Lee, R. O'Dell, J.H. Oskam, Macromolecules 28 (1995) 5933–5940.

[5] R.R. Schrock, Dalton Trans. 40 (2011) 7484–7495.

[6] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, 1997.

[7] V. Dragutan, R. Streck, Catalytic Polymerization of Cycloolefins: Ionic, Ziegler-Natta and Ring-Opening Metathesis Polymerization, Elsevier, 2000.

[8] T.J. Katz, Angew. Chem. 117 (2005) 3070–3079.

[9] T.J. Katz, Angew. Chem. Int. Ed. 44 (2005) 3010–3019.

[10] T.J. Katz, S.J. Lee, J. Am. Chem. Soc. 102 (1980) 422–424.

[11] R.R. Schrock, Angew. Chem. Int. Ed. 45 (2006) 3748–3759.

[12] R.H. Grubbs, Angew. Chem. Int. Ed. 45 (2006) 3760–3765.

[13] M.R. Buchmeiser, Chem. Rev. 109 (2009) 303–321.

[14] H. Balcar, J. Čejka, Coord. Chem. Rev. 257 (2013) 3107–3124.

[15] G. Raptopoulos, A. Grigoropoulos, K. Mertis, P. Paraskevopoulou, M. Pitsikalis, in:, S. G. Pandalai (Ed.), Recent Res. Dev. Polym. Sci., Transworld Research Network, Kerala, India, 2014, pp. 83–106.

[16] T. Szymańska-Buzar, Coord. Chem. Rev. 249 (2005) 2195–2202.

[17] N. Saragas, G. Floros, P. Paraskevopoulou, N. Psaroudakis, S. Koinis, M. Pitsikalis, K. Mertis, J. Mol. Catal. Chem. 303 (2009) 124–131.

[18] D. Chriti, A. Grigoropoulos, G. Raptopoulos, G. Charalambidis, V. Nikolaou, A.G. Coutsolelos, M. Pitsikalis, K. Mertis, P. Paraskevopoulou, Polymers 7 (2015) 2611–2624.

[19] G. Floros, N. Saragas, P. Paraskevopoulou, N. Psaroudakis, S. Koinis, M. Pitsikalis, N. Hadjichristidis, K. Mertis, Polymers 4 (2012) 1657–1673.

[20] N. Saragas, G. Floros, G. Raptopoulos, M. Pitsikalis, P. Paraskevopoulou, K. Mertis, Molecules 20 (2015) 21896–21908.

[21] R.R. Schrock, Chem. Rev. 109 (2009) 3211–3226.

[22] J.-M. Basset, M. Leconte, F. Lefebvre, J.G. Hamilton, J.J. Rooney, Macromol. Chem. Phys. 198 (1997) 3499–3506.

[23] M.J. Abadie, M. Dimonie, C. Couve, V. Dragutan, Eur. Polym. J. 36 (2000) 1213–1219.

[24] E.P. Bokaris, M.M. Kosmas, J. Mol. Catal. Chem. 192 (2003) 263–273.

[25] R.R. Schrock, Acc. Chem. Res. 47 (2014) 2457–2466.

[26] A. Muhlebach, P.A.V.D. Schaaf, A. Hafner, R. Kolly, F. Rime, H.-J. Kimer, in:, E. Khosravi, T. Szymanska-Buzar (Eds.), Ring Open. Metathesis Polym. Relat. Chem., Springer Netherlands, Netherlands, 2002, pp. 23–44.

[27] V. Amir-Ebrahimi, D.A. Corry, J.G. Hamilton, J.M. Thompson, J.J. Rooney, Macromolecules 33 (2000) 717–724.

[28] D. Schaubroeck, S. Brughmans, C. Vercaemst, J. Schaubroeck, F. Verpoort, J. Mol. Catal. Chem. 254 (2006) 180–185.

[29] F. Ding, S. Monsaert, R. Drozdzak, I. Dragutan, V. Dragutan, Y. Sun, E. Gao, P. Van Der Voort, F. Verpoort, Vib. Spectrosc. 51 (2009) 147–151.

[30] L.E. Rosebrugh, V.M. Marx, B.K. Keitz, R.H. Grubbs, J. Am. Chem. Soc. 135 (2013) 10032–10035.

[31] J.G. Hamilton, K.J. Ivin, J.J. Rooney, J. Mol. Catal. 36 (1986) 115–125.

[32] T. Oshika, H. Tabuchi, Bull. Chem. Soc. Jpn. 41 (1968) 211–217.

[33] D.T. Laverty, M.A. McKervey, J.J. Rooney, A. Stewart, J. Chem. Soc. Chem. Commun. (1976) 193–194.

[34] H. Balcar, A. Dosedlová, L. Petrusová, J. Mol. Catal. 77 (1992) 289–295.

[35] J.M. Kamphaus, J.D. Rule, J.S. Moore, N.R. Sottos, S.R. White, J. R. Soc. Interface 5 (2008) 95–103.

[36] C. Slugovc, in:, K. Grela (Ed.), Olefin Metathesis, John Wiley & Sons, Inc., 2014, pp. 329–333.

[37] T.A. Davidson, K.B. Wagener, D.B. Priddy, Macromolecules 29 (1996) 786–788.

[38] A. Bang, D. Mohite, A.M. Saeed, N. Leventis, C. Sotiriou-Leventis, J. Sol-Gel Sci. Technol. 75 (2015) 460–474.

[39] D.P. Mohite, S. Mahadik-Khanolkar, H. Luo, H. Lu, C. Sotiriou-Leventis, N. Leventis, Soft Matter 9 (2013) 1516–1530.

[40] D.P. Mohite, S. Mahadik-Khanolkar, H. Luo, H. Lu, C. Sotiriou-Leventis, N. Leventis, Soft Matter 9 (2013) 1531–1539.

[41] M.H. Chisholm, B.W. Eichhorn, K. Folting, J.C. Huffman, C.D. Ontiveros, W.E. Streib, W.G. Van der Sluys, Inorg. Chem. 26 (1987) 3182–3186.

[42] N. Saragas, Selective Polymerization of Alkynes and Cycloolefins with Bimetallic Complexes of the Transition Metals, N.K.U.A., 2009.

[43] V.P. Carvalho Jr., C.P. Ferraz, B.S. Lima-Neto, Eur. Polym. J. 48 (2012) 341–349.

[44] M.A. Golub, R.J. Gargiulo, J. Polym. Sci. [B] 10 (1972) 41–49.

Highlights

- Synthesis of high-*cis* poly(dicyclopentadiene) gels using a ditungsten complex.
- FTIR-ATR, FT-Raman, solid state ^{13}C NMR and thermogravimetric analysis of dry-gels.
- Comparison of dry-gels with those from mononuclear W and Ru catalytic systems.
- High-*cis* gels increased their volume by more than 100 times in toluene.
- Gels swell more as the *cis* content increases.