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Qualitative FT-Raman investigation of the ring opening metathesis polymerization of dicyclopentadiene

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Abstract

This study describes the qualitative analysis of the polymerization reaction of DCPD (DiCycloPentaDiene) and its reaction products. The polymerization was carried out using $WCl_6/Si(allyl)_4$ (**1**), first generation Grubbs' (**2**) and second generation Grubbs' (**3**) catalysts. When system **1** was used as a catalyst, solution concentration determined whether soluble or insoluble polymer was obtained. When Grubbs' catalysts were employed, insoluble polymer was formed in all cases. The ring opening metathesis polymerization (ROMP)-reaction and the resulting polymers were monitored in situ via FT-Raman-spectroscopy. Using FT-Raman-spectroscopy, the stereospecific nature of the forming polymer can be determined during the polymerization reaction. The obtained spectra illustrate that the linear polymer has a prevailing *cis* double bond configuration, while the polymer formed using the 1^e generation Grubbs catalyst has a predominant *trans* double bond configuration. The second generation Grubbs catalyst exhibits a poor stereoselectivity. These results are in accordance to literature data where the stereospecific nature of these polymers where determined using NMR-spectroscopy.

Keywords: ROMP; DCPD; Raman; Metathesis; Ruthenium

1. Introduction

Over the past few decades, since the introduction of Fourier transformation (FT) and due to the progress made in the areas of interferometer, detector, laser and computer technology, FT-Raman spectroscopy has proven to be a worthy analytical technique which can be employed for both qualitative as quantitative analysis [1,2]. It is non-destructive and non-invasive, samples can be analysed in glass vessels, fibre optic probes can be used for in situ reaction monitoring and remote detection [3], water can be used as a solvent in contrast to FT-IR, solids can be analysed without further sample preparation and low-frequency measurements are feasible. Thanks to its advantages over other techniques, FT-Raman spectroscopy has been applied extensively for the characterisation of polymers and the monitoring of organic, catalytic and polymeric reactions [4]. FT-Raman spectroscopy and FT-IR however should not be seen as alternative but rather as complementary techniques. Vibrations which cause a change in dipole moment are IR active whereas non-polar symmetric molecular vibrations cause a significant change in the electron polarizability and are most intense in the Raman spectrum.

These characteristics make Raman spectroscopy a very attractive technique for the monitoring of polymerization reactions involving cyclic olefins. In this study FT-Raman spectroscopy has been explored for the monitoring of the ring opening metathesis polymerization (ROMP) of DCPD. The resulting thermoset has great industrial and commercial potential thanks to its excellent mechanical properties and its high corrosion resistance [5]. Previously Barnes et al. studied the cure of DCPD via Raman spectroscopy [6]. However, it has come to our attention that the interpretation of the Raman spectra is not fully accurate. In this study we will describe the characterisation of cross-linked and linear PDCPD by means of FT-Raman spectroscopy and doing so prove the correct interpretation of the resulting Raman spectra.

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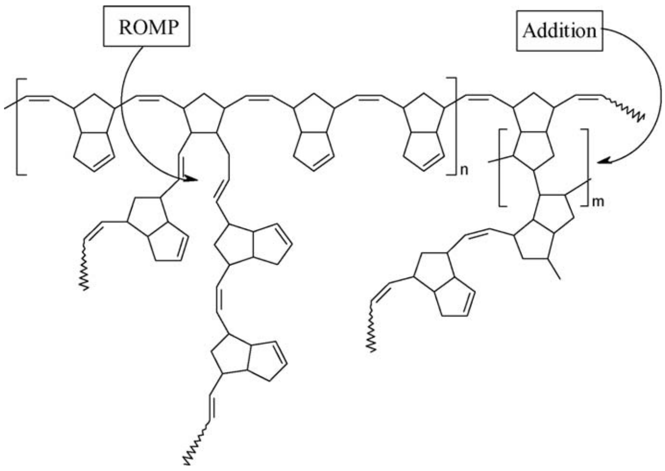


Fig. 1. Cross-linked polydicyclopentadiene.

2. The polymerization of DCPD

Polydicyclopentadiene (Fig. 1) is a cross-linked polymer formed by a highly exothermic ring opening metathesis polymerization reaction of the tricyclic monomer DCPD in the presence of a metal carbene. The former, which is colourless and has a camphor-like odour, consists of two unsaturated bonds at which the metathesis reaction can take place. The latter is a metathesis catalyst which initiates the ROMP reaction taking course via a metallacyclobutane ring. This mechanism introduced by Herisson and Chauvin in 1970 is depicted in Fig. 2 [7]. Since the development of well-defined metal alkylidene complexes the metathesis reaction has known a boost in popularity by researchers all over the world. Thanks to its ease of handling and excellent applicability the Grubbs' ruthenium carbene catalysts **2** and **3** have attracted much interest and have played a key role in our study.

As a result of the ring strain the ring-opening of the norbornene ring is thermodynamically favoured. In this case linear PDCPD would be formed. However, in the presence of most metathesis catalysts such as the Grubbs' catalysts a cross-linked polymer is produced mainly as a result of thermo olefinic addition caused by the highly exothermic ROMP reaction of the norbornene ring [8]. A second possibility resulting in a cross-linked polymer is the ROMP of the cyclopentene ring. In order to synthesis linear PDCPD a different catalyst is needed such as WCl_6 and WCl_4O in combination with cocatalysts $Si(allyl)_4$ and $SiMe_2(allyl)_2$ [9]. In addition, because of both the sensitivity of these catalytic systems and the very narrow concentration range in which the production of linear DCPD is feasible, it is furthermore required to carry out the reaction under well-defined conditions.

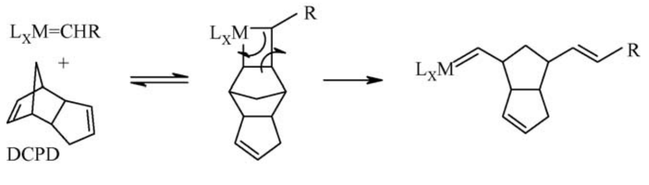
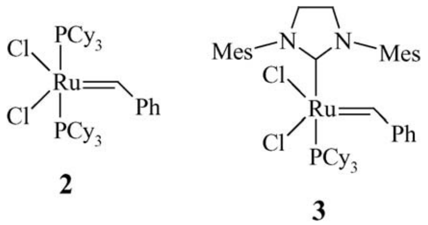


Fig. 2. Mechanism of ROMP.



2 **3**

Fig. 3. Grubbs' catalysts.

3. Experimental

3.1. Raman spectroscopy

The employed spectroscope, the Equinox 55S with Raman module FRA 106 from Bruker, is a hybrid FT-IR/FT-Raman spectrometer fitted with a cooled (77 K) germanium high sensitivity detector D418-T. The data transfer, collection, and processing was automated using the Bruker OPUS^{TM} software. The spectra recorded during each polymerization reaction ranged from 0 to 3500 cm^{-1}. Everything below 50 cm^{-1}, including Rayleigh scattering was filtered away. The laser wavelength used throughout this study was the 1064 nm line of an air cooled diode pumped neodymium yttrium aluminium garnet laser (Nd:YAG) (Fig. 3).

3.2. Calibration curve

To insure reliable quantitative measurements a calibration curve was set up. In this study the solvent was used as an internal standard. The relationship between the Raman intensity and the concentration of the analyte can be given by the following equation (Fig. 4):

$$I_{rel} = JC$$

where I_{rel} is the relative intensity, J the molar intensity, and C is the concentration of the monomer. I_{rel} can be defined as: [(peak intensity of the monomer/peak intensity of the standard)/concentration of the standard].

Standard solutions of DCPD solved in CH_2Cl_2 with varying concentrations were prepared. Each solution was measured five times. The following measurement conditions were applied: 500 scans, 300 mW, 0–3500 cm^{-1}, monomer peak intensity at 1573 cm^{-1}, reference peak intensity at 704 cm^{-1}, room temperature and atmospheric pressure.

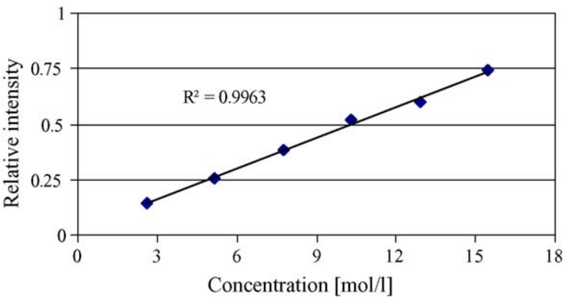


Fig. 4. Calibration curve.

3.3. Monitoring of the polymerization reaction via FT-Raman spectroscopy

First of all the choice of an adequate solvent is essential. In regards to the absence of spectral interference and chemical interactions, dichloromethane was found to be an impeccable solvent. Dichloromethane has no peaks in the spectral range of 1500–1800 cm^{-1} preventing peak interference with $\nu_{\text{C=C}}$ of the monomer and polymer. Furthermore, this solvent has an intense peak at a wavelength of 704 cm^{-1}. The latter can be referred to as the reference peak as neither DCPD nor PDCPD have peaks at this wavelength.

The ideal reaction time was found to be in the range of 4–5 h. However, one should keep in mind that after this elapse of time the conversion is not always quantitative as the formation of polymer can decelerate further polymerization. In addition the ratio of monomer/catalyst should be tuned dependent on the reactivity of the catalyst. An excessive amount of catalyst results in a highly exothermic polymerization reaction causing the monomer to vaporize (DCPD has a b.p. of 170 °C). In this aspect an acceptable ratio for catalyst **2** is 33 000 equiv. of monomer whereas for catalyst **3**, which is far more reactive, 200 000 equiv. of DCPD is reasonable.

The polymerization reactions are performed in small glass vessels of 7 ml containing a screw top to assure autogenous pressure. The Raman measurements are performed by placing these phials in the sample compartment of the Raman spectroscope.

For the polymerization of DCPD with catalyst **2**, 3.75 g of DCPD was diluted in 2.20 ml of dichloromethane whereas for the polymerization of DCPD with catalyst **3**, 2 g of DCPD was diluted in 1 ml of dichloromethane. After weighing and dissolving the catalyst under inert atmosphere the requested amount of catalyst solution was added to the DCPD-containing vessel.

3.4. Synthesis of linear PDCPD

As mentioned before, the synthesis of linear PDCPD requests a different catalytic system and well-defined reaction conditions. In our study catalyst WCl_6 in combination with cocatalyst Si(allyl)_4 were used [9]. The following concentrations were applied: 1.12 mmol/l WCl_6, 1.12 mmol/l Si(allyl)_4 and 1.67 mmol/l *endo*-DCPD. A catalyst/monomer ratio of 1/1491 and a W/Si ratio of 1/1 were applied. The reaction was performed in 25 ml of dry and degassed toluene during 4 h at 0 °C under an argon atmosphere. The monomer was dried prior to the reaction. Once the polymerization reaction has taken course the reaction is terminated by precipitating the polymer in a methanol solution containing 2% NaOH. The polymer is washed until all catalyst is removed. The polymer can subsequently be redissolved in toluene emphasising the linear character of the polymer.

4. Results and discussion

The FT-Raman spectrum of pure DCPD is given in Fig. 5. The two signals at 1573 and 1617 cm^{-1} can be ascribed to the stretching vibrations of the norbornene and the cyclopentene C=C-bonds, respectively. The $\nu_{\text{C=C}}$ of the norbornene ring in DCPD is lower than the $\nu_{\text{C=C}}$ of the cyclopentene ring due to the higher ring strain.

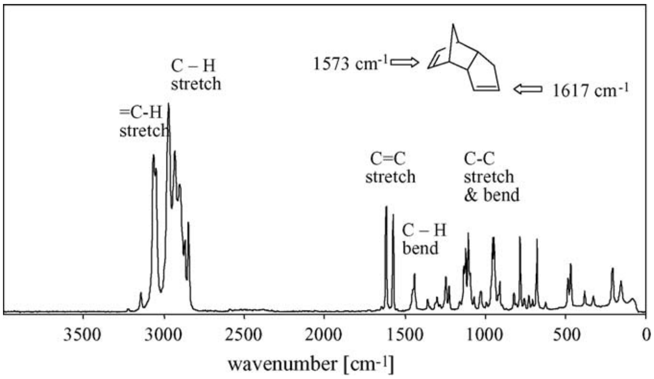


Fig. 5. FT-Raman spectrum of DCPD.

4.1. The ROMP of DCPD with catalyst 2: interpretation of the Raman spectra

Fig. 6 illustrates the Raman spectra of the polymerization reaction of DCPD with catalyst **2** at different time intervals. Only the spectral range of interest is depicted. The most noticeable characteristics here are the decrease of the peak intensity at 1573 cm^{-1} assigned to the $\nu_{\text{C=C}}$ stretching vibration of the double bond in the norbornene ring and the increase of the band intensity at 1665 cm^{-1} assigned to the $\nu_{\text{C=C}}$ stretching vibration of the aliphatic double bonds in the polymer backbone. Less perceptible is the asymmetric outline of the band at 1665 cm^{-1}. Previously this tailing was ascribed to the local electronic environment of the double bonds on cross-linking of the polymer chains [6], however we believe it is a result of the stereospecific nature of the aliphatic disubstituted double bonds in the polymer backbone. NMR-studies conducted by Rooney et al. have revealed the stereospecific nature of PDCPD obtained with catalyst **2**. Herein the disubsituted aliphatic double bond had a 87% *trans*-configuration and a 13% *cis* configuration [10]. Although it is impossible to precisely determine the *trans*/*cis* ratio of the resulting polymer on the basis of these Raman spectra one can

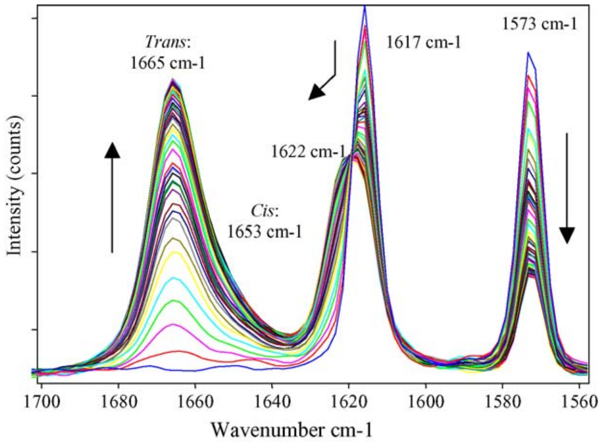


Fig. 6. Raman spectra taken at different points in time of the polymerization of DCPD with catalyst **2**.

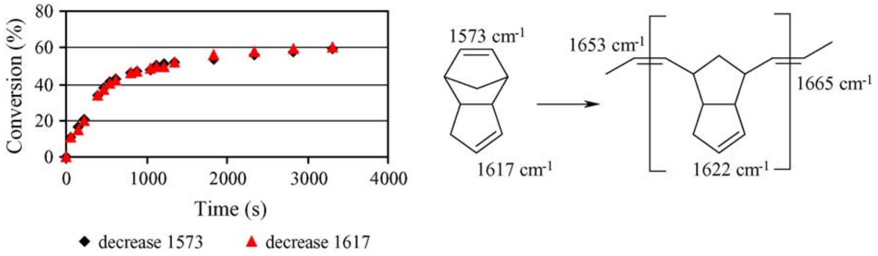


Fig. 7. Conversion plots of the norbornene (1573 cm^{-1}) and the cyclopentene (1617 cm^{-1}) bands.

comprehend the correlation. Furthermore, results revealed by our study on the ROMP of DCPD with catalyst **3** will confirm these assumptions.

As to uncovering the cross-linking mechanism on the basis of these results it would be rather rash to draw conclusions. Previously the reduction in intensity of the band at 1617 cm^{-1} has been related to the opening of the cyclopentene ring preceding cross-linking of the polymer chains [6]. Furthermore, the shoulder at 1622 cm^{-1} has been thought to be consistent with the stretching of the vinylic C=C double bonds in the *trans*-conformation formed during the cross-linking process [6]. Though these assumptions seem acceptable we believe they are misinterpreted. The Raman band at 1617 cm^{-1} can indeed be ascribed to the stretching vibration of the cyclopentene ring. However, it is our opinion that the reduction in intensity of this band is in fact a result of the opening op the norbornene ring and not of the cyclopentene ring itself. As the norbornene ring opens it will cause a change in ring tension stabilising the cyclopentene ring and resulting in a shift of the stretching vibration to a higher wavenumber, namely 1622 cm^{-1}. To prove this hypothesis we performed a quantitative comparison between the decrease in peak intensity at 1617 cm^{-1} and the decrease in peak intensity at 1573 cm^{-1}. These results are given in Fig. 7.

According to the results given in Fig. 7 it is obvious that both conversion plots initially have the same course. Hereby can be concluded that, the decrease and the shift of the band which can be ascribed to the stretching vibration of the double bond in the cyclopentene moiety, is clearly a result of the ring opening of norbornene. These conclusions are further confirmed by analyzing the Raman spectrum of linear PDCPD (see further). Additionally one should keep in mind that the amount of cross-linking is not deducible on the basis of these spectra. The resulting disubstituted aliphatic double bond upon cross-linking via ROMP is most likely unobservable as the resulting band will be parent in the same spectral range as the *trans* and *cis* isomers of the polymer backbone.

4.2. *The ROMP of endo-DCPD with catalyst **3**: interpretation of the Raman spectra*

In Fig. 8 the Raman spectra are given of the polymerization reaction of DCPD with catalyst **3** at different points in time. Once more only the spectral range of interest is depicted.

The main difference which can be observed when comparing these spectra with those depicted in Fig. 6 is the *trans*/*cis* ratio. While the first generation Grubbs' catalyst **2** polymerizes DCPD with a high *trans*-selectivity the second generation Grubbs' catalyst **3** is not diastereoselective. To our knowledge no NMR-studies have yet been performed to determine the *trans*/*cis* ratio of PDCPD obtained with catalyst **3**. However, available data on the polymerization of different monomers such as cyclooctadiene, cyclopentene, and 2-methylcyclopentene with catalysts **2** and **3** confirm the low selectivity of the second generation Grubbs' catalyst in comparison with the first generation Grubbs' catalyst [11]. Further NMR-investigations on the selectivity of these catalysts are currently being performed.

4.3. *Raman study of linear PDCPD*

The Raman spectrum of pure solid linear PDCPD is given in Fig. 9.

The most striking features of this spectrum are the bands at 1654 and 1622 cm^{-1}. The former being consistent with the stretching vibration of the aliphatic *cis*-conformed double bond of the polymer backbone, the latter can be ascribed to the stretching vibration of the cyclopentene double bond. The stereoselectivity of the obtained pure linear PDCPD was also determined by ^1H NMR spectroscopy. The peaks at $\delta = 5.35$ and 5.55 ppm in the concerned ^1H NMR ($CDCl_3$) spectrum can be ascribed to the *cis*- and *trans*-conformed double bond, respectively. When the stereoselectivity was determined by means

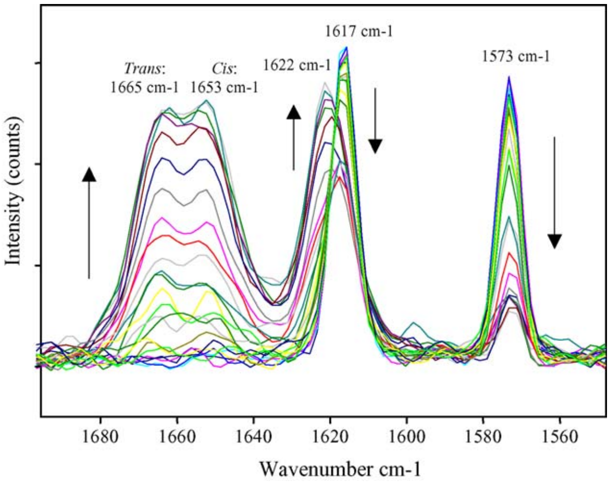


Fig. 8. Raman spectra taken at different points in time of the polymerization of DCPD with catalyst **3**.

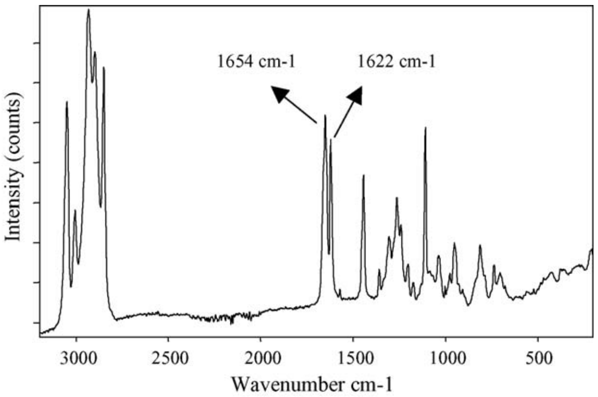


Fig. 9. Raman spectrum of pure solid linear polydicyclopentadiene. This polymer was obtained using catalyst WCl_6 and cocatalyst $Si(allyl)_4$ in a 1/1 ratio and with a catalyst/monomer ratio of 1/1491. Reaction was performed in dry and degassed toluene during 4 h at 0 °C under an argon atmosphere.

of integration a predominant *cis*-selectivity (63%) was found. The high *cis*-selectivity is in agreement with the literature [9].

As no cross-linking has occurred during this reaction it is obvious that the band at $1622\,cm^{-1}$ can and should not be ascribed to the stretching of the *trans*-conformed vinylic double bonds formed during cross-linking. Moreover, the presence of the band at $1622\,cm^{-1}$ confirms our previously postulated theory concerning the ascription of this band in the cross-linked polymer obtained with catalysts **2** and **3**.

4.4. Comparison and discussion of the stereoselectivity of the different applied catalysts

In an attempt to compare the selectivity of the different applied catalytic systems, the spectral range of interest of the Raman spectra of linear and cross-linked PDCPD are given in Fig. 10.

Fig. 10 gives a more detailed image of the *trans*/*cis* selectivity of the obtained linear PDCPD. A shoulder at $1665\,cm^{-1}$ is clearly present and can be ascribed to the stretching vibration of the *trans*-conformed aliphatic double bond in the polymer as was the case with the cross-linked polymer attained with catalysts **2** and **3**.

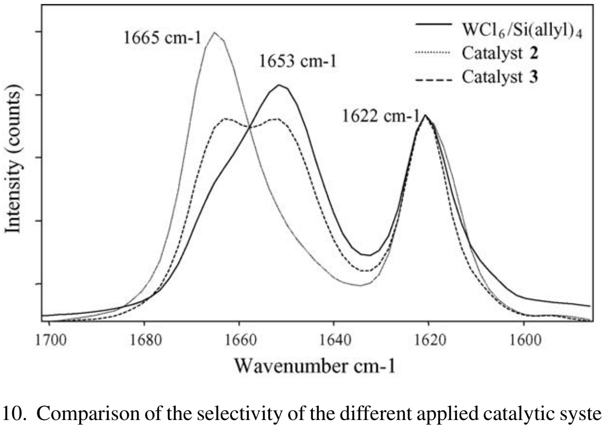


Fig. 10. Comparison of the selectivity of the different applied catalytic systems.

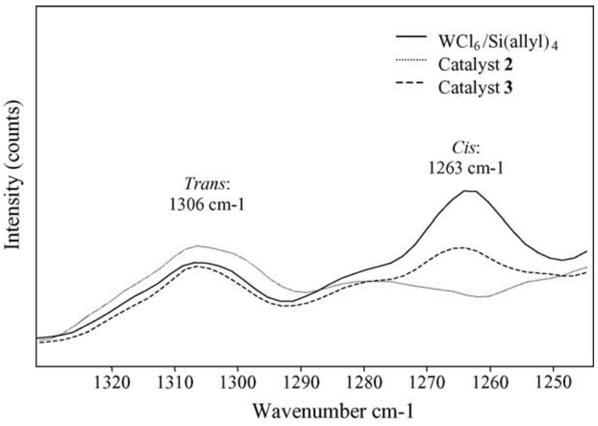


Fig. 11. Selectivity determined by the investigation of the in plane C—H deformation of the =C—H bond.

Qualitatively, the described *trans*/*cis* selectivity can further be elucidated by examining the 'in plane C–H deformations' of the =C–H bonds. According to the literature these can be found in the spectral range of 1251–1270 and $1290–1314\,cm^{-1}$ for the *cis*-dialkyl and for the *trans*-dialkyl, respectively [12]. The Raman bands of linear and cross-linked PDCPD that can be ascribed to the mentioned in plane C–H deformation are given in Fig. 11.

For the *trans*-conformed disubstituted aliphatic double bond a Raman band is found at $1306\,cm^{-1}$ while for the *cis*-conformation one is located at $1263\,cm^{-1}$. In accordance to previously presented results the Raman spectra in Fig. 11 exemplify the high *trans*-selectivity of catalyst **2**, the poor selectivity of catalysts **3**, and the high *cis*-selectivity of the catalyst system $WCl_6/Si(allyl)_4$ for the polymerization of DCPD. Furthermore, these results confirm our interpretation of the presented Raman spectra.

5. Conclusion

We have shown that Raman spectroscopy is a feasible analytical technique for in situ reaction monitoring. Hereby detailed spectra are obtained which can be applied for qualitative analysis. Moreover, we have illustrated that Raman spectroscopy can be applied for the qualitative analysis of cross-linked PDCPD. A differentiation has been made between the *cis*- and *trans*-confirmations present in the resulting polymer obtained with the mentioned catalysts. In this aspect the Raman bands at 1665 and $1653\,cm^{-1}$ have respectively been consigned to the stretching vibrations of the *trans* and *cis* aliphatic double bond in the polymeric backbone of PDCPD. In accordance to previously performed NMR-investigations the first generation Grubbs' catalyst has a moderate *trans*-selectivity (87%) while the second generation Grubbs' catalyst is not stereoselective. The Raman band at $1617\,cm^{-1}$ has been assigned to the stretching vibration of the cyclopentene double bond. The generation of a band at $1622\,cm^{-1}$ in the Raman spectrum has proven to be caused by the loss of ring strain in the cyclopentene ring due to the opening of the norbornene ring.

Furthermore, linear PDCPD was synthesized using a WCl_6/Si(allyl)$_4$ catalytic system and successfully analysed with Raman spectroscopy. The appearance of a band at $1622\,cm^{-1}$ in the Raman spectrum of linear PDCPD confirms that this band can not be ascribed to cross-linking of the polymer but rather to the loss of ring strain in the cyclopentene ring upon opening of the norbornene moiety, as previously stated. Further investigation is being conducted concerning the in situ monitoring of ROMP reactions of different substituted norbornene monomers. NMR-investigations on the selectivity of the applied catalysts are also currently being performed. These NMR-studies will have to determine in which degree the results, which were obtained on the base of Raman spectroscopy, are quantitative.

Acknowledgements

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