Spectrochimica Acta Part A 77 (2010) 170–174

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# FT Raman—A valuable tool for surveying kinetics in RCM of functionalized dienes

Fu Ding[a,b], Baoyi Yu[a], Stijn Monsaert[a], Ya-guang Sun[b], Enjun Gao[b], Ileana Dragutan[c], Valerian Dragutan[c], Francis Verpoort[a,*]

[a] Organometallics and Catalysis, Department of Inorganic and Physical Chemistry, Ghent University, Ghent 9000, Belgium
[b] Laboratory of Coordination Chemistry, Shenyang Institute of Chemical Technology, Shenyang 100142, China
[c] Institute of Organic Chemistry of the Romanian Academy, Bucharest, Romania

ARTICLE INFO

*Article history:*
Received 25 December 2009
Received in revised form 11 April 2010
Accepted 12 May 2010

*Keywords:*
FT Raman
Ring-closing metathesis
$^{1}$H NMR
Kinetics
Functionalized dienes

ABSTRACT

In this article the suitability of FT Raman spectroscopy for monitoring kinetics of ring-closing metathesis promoted by the Grubbs' 1st generation precatalyst was demonstrated for the first time. Reactions at room temperature and under low catalyst loadings were carried out on a series of representative diene substrates. The time evolution of the characteristic Raman stretching vibrations unequivocally described the reaction progress allowing for precise calculation of the substrate conversion and of the yield in the expected cyclic product, based on the corresponding peak heights. The responsive Raman technique demonstrated clean RCM pathways for diethyl diallylmalonate and diallyl ether whereas a minor olefinic side-product was detected in the case of diallyl phthalate. The study provides essential underpinnings for future utilization of Raman spectroscopy, concurrently with NMR or supplementing it, for the evaluation of RCM reactions.



## 1. Introduction

Olefin (alkene) metathesis is today a well-recognized pathway for formation of new carbon–carbon bonds. As eloquently illustrated in excellent books [1–4] and general reviews [5–8], this reaction enjoys wide application in organic synthesis and materials science.

Among metathesis-based strategies, ring-closing metathesis (RCM) was the first to act as engine towards success, particularly as preferred key-step in unparalleled short syntheses of natural products or of their mimics, of intricate frameworks with targeted stereochemistry, of pharmaceuticals or amphiphilic molecules prone to self-assemble, etc., all promoting olefin metathesis to the forefront of synthetic protocols [9–13]. RCM is the procedure of choice for macrocyclization, frequently encountered in the total synthesis of drugs and natural products, and essential also for developing derivatives that modulate biological activity or pharmacokinetic properties [14]. Not surprisingly, at present, RCM (and ARCM) and cross metathesis attract more and more the attention of metathesis researchers due to their versatility in combining a host of substrates to produce long desired multifunctional compounds, scientifically and economically valuable [15].

Due to the recent impact and great utility of RCM in organic synthesis, the kinetics, mechanism and structure of the reaction products of this type of alkene metathesis have been thoroughly investigated by a variety of physical techniques, frequently used in combination, such as gas-chromatography, $^{1}$H NMR, $^{13}$C NMR, ESR, FT-IR, MALDI-TOF MS, Raman spectroscopy, etc. [16–21].

Of analytical methods, Fourier transform Raman spectroscopy is both non-destructive and suitable for remote analysis (even while the sample is placed inside containers), with no need for special sample preparation. The technique enables fast and accurate measurements on a broad range of samples, be it solids or water-containing specimens. Advanced Raman instruments also allow *in situ* observation at different depths inside materials. It should be kept in mind that for the successful recording of FT Raman spectra of small samples a compromise between large lateral resolution and a large signal/noise ratio has to be found.

Due to the flexibility of the method and improvement of the Fourier transform Raman instrumentation, this non-invasive technique has enormous potential for a widespread range of applications (agrochemical industry, control of pesticide formulations, biodiagnosis, in pharmaceutical production, measurement of APIs in real drug formulations and inside packaging) where high sensitivity needs to be combined with good discrimination between molecular targets [22]. Simplicity and speed make Raman spectroscopy a viable technique for the industrial user. Real time FT Raman spectroscopy also finds utilizations in on-line process monitoring, e.g. in routine quality work within factory environments.

Today Raman-based spectroscopic methods have evolved to the stage where they can be used as quantitative analytical techniques. Along this line, the present research examines, for the first time,

* Corresponding author. Tel.: +32 9 264 4436; fax: +32 9 264 4983.
*E-mail address:* francis.verpoort@ugent.be (F. Verpoort).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2010.05.001

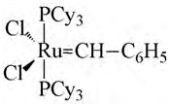



**Fig. 1.** Grubbs' 1st generation catalyst (Cy = cyclohexyl).

the capabilities of FT Raman in monitoring RCM reactions of diene substrates which have been selected so as to yield functionalized cyclic olefins of different sizes and ring strains. In all experiments ring closure is promoted by the well-defined initiator known as the Grubbs 1st generation catalyst (Fig. 1), under low catalyst loadings.

Whereas Raman spectroscopy and in-line fibre-optic NIR-FT Raman spectroscopy have been previously applied to studies on a different type of metathesis reactions, i.e. ring-opening metathesis (ROMP of norbornene, dicyclopentadiene, and *exo*,*exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene) [23–25], to the best of our knowledge there is to date no report on a Raman-based investigation of the metathesis of olefins by ring-closing. A further goal of the paper is to compare the kinetic data arising from Raman spectroscopy with existing information collected by other spectroscopic methods, particularly by NMR. Most importantly, we aim to assess the suitability of Raman spectroscopy as a tool for quantitative observation also of ring-closing metathesis, a reaction forming a cycle and not opening one as happens in ring-opening metathesis (ROM) or ring-opening metathesis polymerization (ROMP).

## 2. Materials and methods

### 2.1. Spectroscopic conditions

A Bruker FT spectrometer Equinox 55S with Raman module FRA 106, a hybrid FT-IR/FT Raman spectrometer, fitted with a germanium high sensitivity detector D418-T (cooled by nitrogen at 77 K) was used. During the monitoring of RCM, the excitation laser wavelength of 1064 nm was produced by an air cooled diode pumped neodyniumyttrium aluminium garnet laser (Nd:YAG). The spectral coverage extends from 100 to 4000 $cm^{-1}$, with a spectral resolution of 4 $cm^{-1}$, number of scans (50), laser power (200 mW). Spectra were recorded at 6 min intervals during a total time of 60 min. Data transfer, collection and processing were fully automated using a Bruker OPUS$^{TM}$ software.

### 2.2. Choice of the solvent

Raman spectroscopy can use cheap solvents. In addition experimental wavenumbers in Raman spectra are independent of the solvent (which is not the case in NMR spectroscopy). However, in RCM some limiting conditions are imposed on the solvent which must not deactivate the catalyst (traces of moisture or oxygen should be avoided because of the sensitivity of the catalyst) [3]. A further restriction comes from the fact that in Raman spectra no interference from the solvent with the C=C stretching vibration ($\nu_{C=C}$) of the substrate and the product should occur (no solvent peaks in the range 1500–1800 $cm^{-1}$ are admissible). Dichloromethane was chosen as the ideal solvent for this Raman study of RCM reactions.

### 2.3. Calibration curves

Crucial to precise measurements by Raman is to first construct a calibration curve for determining the relationship that exists between the intensity of the Raman signal and the concentration of the substrate. Calibration curves were built up for each of the three substrates examined in this RCM study. The same methodology as

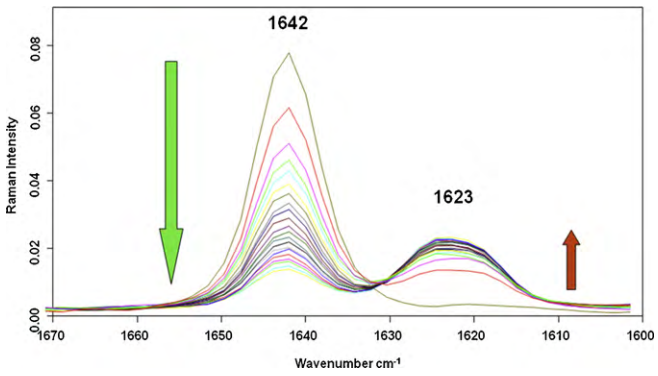



**Fig. 2.** FT Raman spectra for RCM of diethyl diallylmalonate (DEDAM) (2.5 M in $CH_2Cl_2$), promoted by the Grubbs I catalyst (0.4 mol%), recorded at variable time (0–60 min) in a closed vessel.

previously applied for Raman evaluation of ROMP of norbornene has been followed [23]. To minimize variations in intensity of the excitation laser line we used, as necessary, a reference band from the spectrum which remains constant during the RCM reaction, in our case the 704 $cm^{-1}$ band pertaining to the methylene chloride used as the solvent.

Five standard solutions with different substrate concentrations were prepared for each substrate (e.g. for diallyl ether: 0, 0.4991, 0.9845, 1.5026, 1.9894, 2.5281 and 3.0027 mol/L) and measured five times each by in-line Raman. Measurement conditions for constructing the calibration curve were 50 scans, laser power 200 mW, room temperature and 4 $cm^{-1}$ resolution, with the substrate peaks appearing at 1642, 1647 and 1649 $cm^{-1}$ for DEDAM (Fig. 2), DAE (Fig. 3) and diallyl phthalate (Fig. 5), respectively, and the reference peak ($CH_2Cl_2$) at 704 $cm^{-1}$. For each measurement the height of the substrate peak was corrected by that of the reference (solvent). For every standard solution the average of the corrected peak height (resulting from five successive measurements) was considered. Eventually a calibration curve was obtained in which the relative intensity, $y$ (i.e. intensity of the substrate peak/intensity of the reference peak) was plotted as a function of the substrate concentration, $x$ [23]. In the investigated domain of concentrations a linear relationship was found, e.g. for diallyl ether: $y = 0.1431x - 0.0324$ ($R^2 = 0.9957$). Based on the calibration curve, the degree of substrate conversion could be calculated from the known initial substrate concentration and the transient substrate concentration (above the detection limit), as determined by Raman at a time $t$.

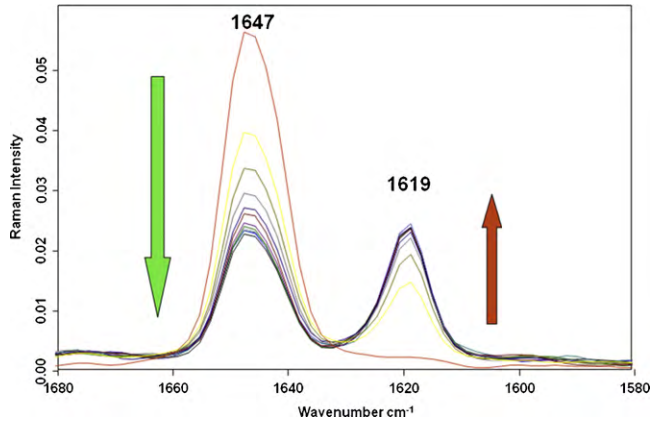



**Fig. 3.** FT Raman spectra for RCM of diallyl ether (DAE) (2.5 M in $CH_2Cl_2$), promoted by the Grubbs I catalyst (0.4 mol%), recorded at variable time (0–60 min.).

### 2.4. Monitoring of ring-closing metathesis by FT Raman

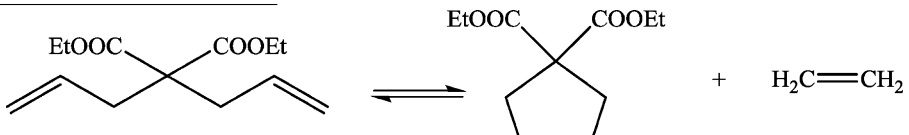
The ring-closing metathesis reaction was carried out in a glass vessel (7 ml) equipped with a magnetic stirring bar. The diene substrate was dissolved in 1 ml $CH_2Cl_2$ under magnetic stirring and the FT Raman spectrum was recorded to obtain the intensity of its C=C stretching vibration at time $t = 0$. Next, the catalyst was added to the substrate solution, the vial containing the reaction mixture placed in the sample compartment of the FT Raman spectrometer, and evolution of the RCM was monitored under the same measurement conditions as employed for the calibration curves (50 scans; laser power, 200 mW; resolution, 4 $cm^{-1}$; room temperature). Conversions were determined from the ratio between the height of the substrate peak (e.g. 1642 $cm^{-1}$, Fig. 2), relative to the height of the reference peak (704 $cm^{-1}$), at a time $t$ and at the time zero ($t = 0$, i.e. in the initial substrate solution). The area under the peak varies linearly with the peak height if resolution is considerably better than the band half-width, which is the case here (Figs. 2, 3 and 5). A small error in placing the background greatly affects the area integral, but less so the peak height, so use of peak heights rather than peak areas is more reliable [23].

## 3. Results and discussion

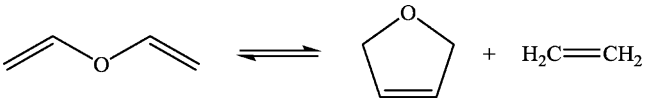
Research in our group has a long standing focus in both RCM reactions [26] and in Raman spectroscopy [23–25]. So far RCM has largely been followed by NMR, with kinetics frequently determined through measurements effected directly in the NMR tube. However, Raman has obvious advantages over NMR spectroscopy: no deuterated solvent and no special analysis tubes are needed, a smaller amount of substrate is necessary, no viscosity changes can influence the accuracy of kinetics experiments. Besides, since FT Raman spectroscopy is effective for molecules whose polarization degree changes by oscillation, the new C=C vibrations appearing as a result of RCM are clearly identifiable when the intensities of the characteristic $\nu_{C=C}$ bands in the substrate and in the product change during the reaction.

### 3.1. RCM of diene substrates in the presence of the Grubbs I catalyst

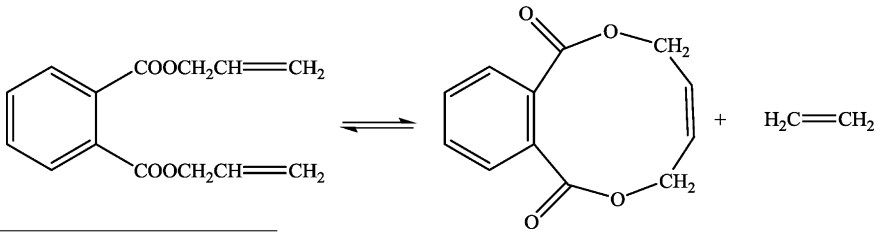
Kinetics of RCM reactions of selected diolefin substrates including diethyl diallylmalonate, diallyl ether and diallyl phthalate (Eqs. (1)–(3), respectively), initiated in all cases by the well-defined Grubbs I catalyst (Fig. 1), have been examined by means of FT Raman spectroscopy. Substrate conversions *vs.* time have been calculated from peak heights in spectra recorded at precise time intervals. Most relevant data are illustrated in Figs. 2–6.




(1)




(2)




(3)

#### 3.1.1. RCM of diethyl diallylmalonate

We first focused on ring-closing of diethyl diallylmalonate (DEDAM) (Eq. (1)), the most studied substrate, in particular by $^1H$ and $^{13}C$ NMR spectroscopy. The Raman-inferred evolution in time of DEDAM conversion to the expected RCM product, 3,3-carbethoxy-1-cyclopentene, is presented in Fig. 2. Curves in Fig. 2 correspond to Raman spectra collected at distinct time intervals extending over 1 h of reaction surveillance.

The 1st generation Grubbs catalyst is a fast-initiating promoter of RCM of this active substrate (see Section 3.2). While the reaction (run in a closed vessel) is progressing, the peak at 1642 $cm^{-1}$ (stretching vibration of C=C double bonds pertaining to the allylic groups of the diolefin substrate) is decreasing. A concomitant appearance of a new band at 1623 $cm^{-1}$ is attributed to vibrations of the endocyclic double bond incorporated in the five-membered carbocyclic product which is being generated in RCM (Fig. 2). The rapid increase in height of band at 1623 $cm^{-1}$ corresponds to a growing conversion, as calculated from the Raman spectra *vs.* time. Under our low catalyst loading (0.4 mol%), conversion reaches 77% after 1 h at 16 °C, a result paralleling that (ca. 84% conversion; the green plot in Fig. 6) earlier reported from $^1H$ NMR measurements in $CDCl_3$ (with the same catalyst, yet at a slightly elevated temperature (20 °C) and at a higher catalyst/substrate ratio (0.5 mol%)) [27]. The absence of additional Raman vibrations, other than the legitimate 1642 and 1624 $cm^{-1}$, is a clear indication that under our experimental setting RCM of diethyl diallylmalonate is a clean process, not accompanied by side-reactions, in agreement with the wealth of literature data based on NMR reported for Grubbs I and later introduced ruthenium catalysts.

#### 3.1.2. RCM of diallyl ether

On changing now to a different substrate, the diallyl ether, where the two allyl substituents are connected by a heteroatom (O) instead of the C atom from the above diethyl diallyl malonate, we applied the FT Raman spectroscopy to kinetically follow RCM leading to a five-membered oxocyclic product (Eq. (2), Fig. 3). Again the expected decrease of the peak (1647 $cm^{-1}$) corresponding to stretching vibrations of C=C double bonds in diallyl ether is noticeable and is accompanied by an augmenting new signal at 1619 $cm^{-1}$ assigned to the endocyclic double bond in the product. The reaction is initially fast, with ca. 30% conversion being attained within the first 2 min but then slows down (after 10 min, 50% conversion)

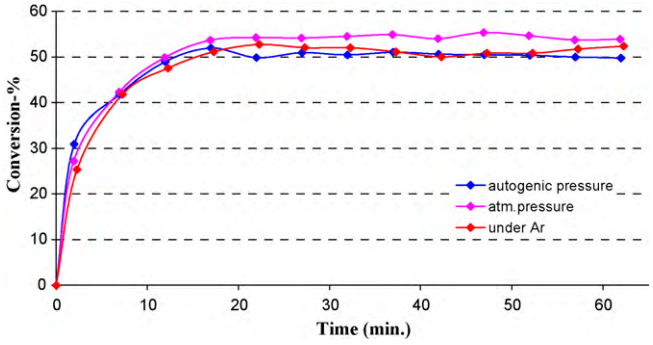



**Fig. 4.** Conversion plots for RCM reactions of diallyl ether (2.5 M in $CH_2Cl_2$), promoted by the Grubbs I catalyst (0.4 mol%), conducted under Ar, in air (open vessel) or autogenic pressure (closed vessel).

leveling subsequently to a plateau (Figs. 3 and 4). Moreover, Raman spectra evidence a third, minor peak slowly increasing in time at 1680 $cm^{-1}$ (unidentified olefinic side-product). As compared with diethyl diallyl malonate, this behaviour is indicative of a less reactive substrate, allowing for side-reactions to also intervene along with the ring-closing process. A plausible rationalization of the reaction level after the 50% conversion is a competing complexation of the ether oxygen atom from the substrate to the ruthenium core of the Grubbs I catalyst, generally considered to be very sensitive to functionalities and therefore having limited applications in such cases. Blocking some of the catalyst as a metathesis inactive species (vibrating in Raman outside the recorded domain of the spectrum) may prevent RCM to progress with complete conversion to the desired product, especially under low catalyst loading as is our case. Indeed, RCM of dienes containing ether functionalities is not a frequently encountered reaction in the metathesis body of knowledge, high RCM yields been reported only for higher catalyst concentrations (2–5 mol%)[28] or in template-directed RCM where oxygen atoms are coordinated by metal cations [29]. A further support for the formation of a complex between the catalyst and the substrate comes from results depicted in Fig. 4 which unquestionably evidence that the plateau occurs at ca. 50% conversion irrespective of the experimental conditions under which RCM was conducted (under Ar, in an open vessel or in a closed vessel (autogenic pressure)), conditions that normally influence both the reaction equilibrium and the integrity of the catalyst.

### 3.1.3. RCM of diallyl phthalate

Interesting results have also been collected from the Raman-monitored RCM of diallyl phthalate, in the presence of the same Grubbs I catalyst (Fig. 5). While the previous two substrates, diethyl

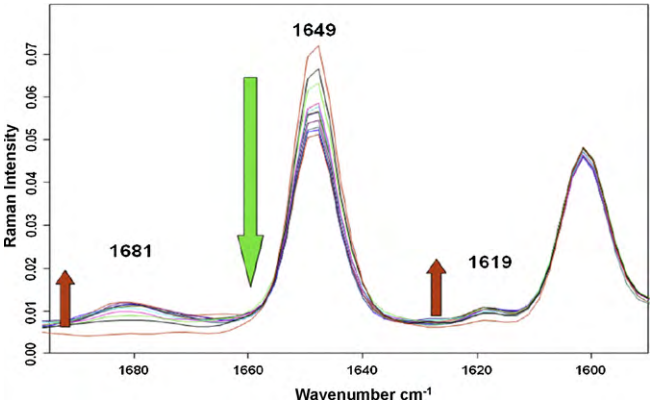



**Fig. 5.** FT Raman spectra for RCM of diallyl phthalate (2.5 M in $CH_2Cl_2$), promoted by the Grubbs I catalyst (0.4 mol%), recorded at variable time (0–60 min.).

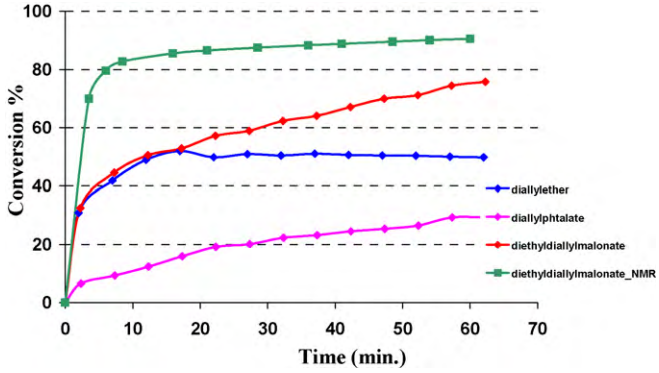



**Fig. 6.** Conversion plots for RCM reactions of diethyl diallylmalonate, diallyl ether and diallyl phthalate (2.5 M in $CH_2Cl_2$), promoted by the Grubbs I catalyst (0.4 mol%) and conducted under autogenic pressure (closed vessel), as determined by Raman spectroscopy and $^1H$ NMR (green plot [27]).

diallylmalonate and diallyl ether, gave rise by RCM to 5-membered cyclic products, diallyl phthalate may only ring-close to a 10-membered oxocyclic product having a different ring strain and stereoconfiguration. Therefore, *a priori* the reaction must proceed distinctly with respect to both kinetics and thermodynamics. In truth, FT Raman spectra *vs.* time (Fig. 5), indicate the expected slower decrease in height of the stretching vibration at 1649 $cm^{-1}$ (allylic C=C from the starting material) and the simultaneous growth of the band at 1681 $cm^{-1}$, attributed to the endocyclic C=C of the 10-membered ring product. The product arises at a comparatively reduced rate (ca. 30% yield after 60 min) (Fig. 6). Fortunately, the remarkable sensitivity and discriminatory power of the Raman spectroscopic technique allows detection of a minor side-product (1619 $cm^{-1}$, Fig. 5) emerging along with the targeted benzoannelated compound during RCM of this sluggish diene substrate. More importantly, based on the exquisite resolution of the band specific to the starting material, a quantitative evaluation of the Raman spectrum is still possible—a condition rarely fulfilled by NMR spectra of mixed olefinic products.

### 3.2. Dependence of conversion in RCM on the diene substrate

Results obtained in our FT Raman investigation of RCM of diethyl diallylmalonate, diallyl ether and diallyl phthalate using the Grubbs 1st generation catalyst undoubtedly indicate that, under identical reaction conditions, the evolution of conversion in time essentially depends on the nature of the diene substrate. Of the three investigated substrates, DEDAM proved to be the most active, reaching a conversion of 77% after 60 min and 90% after 100 min (not shown), even under the unusually low catalyst loading we choose to employ in our experiments for the sake of accuracy. In this series, diallyl phthalate is the least active diene, giving in RCM a 30% conversion within the same reaction time (Fig. 6). This behavioural discrepancy arises from the unlike ring-strain associated with the ring-closure process (5-membered rings for the first two substrates and a 10-membered ring for diallyl phthalate), and also from differences in steric hindrance of the conformations that the cyclic compounds may adopt. Whereas a *cis* configuration of the endocyclic double bond is present in all three RCM products, in the 10-membered heterocycle the double bond is forced out of the plane of the adjacent conjugated moiety (phenyl ring and COO groups).

## 4. Conclusions

For the first time, the present research gives convincing evidence on the utility and assets of FT Raman spectroscopy in accurately monitoring kinetics of RCM reactions promoted by the 1st genera-

tion Grubbs catalyst. Advantage was taken of a set of functionalized diene substrates (diethyl diallylmalonate, diallylether and diallyl phthalate) chosen so as to have distinct tendenties for RCM. Even under low catalyst loading (0.4 mol%) and the otherwise very mild conditions employed, the evolution in time of the characteristic Raman vibrations could unequivocally reveal the reaction progress allowing for a precise calculation of the substrate conversion, at every reaction time, from the corresponding peak height. The sensitivity of the Raman technique gave proof of clean RCM pathways for diethyl diallylmalonate and diallyl ether whereas a minor olefinic side-product was detected in the case of diallyl phthalate. Results from this Raman investigation on RCM of diethyl diallylmalonate compare well with data acquired earlier in our group by $^{1}$H NMR. Overall, this study highlights the potentiality of Raman spectroscopy as a worthy research tool for the extremely dynamic domain of metathesis chemistry.

## Acknowledgements

ID, VD and FV thank FWO-Flanders for financial support during elaboration of this work. FV and FD are indebted to Ghent University for financial support.

## References

[1] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, London, 1997.
[2] V. Dragutan, A.T. Balaban, M. Dimonie, Olefin Metathesis and Ring-opening Metathesis Polymerization of Cycloolefins, John Wiley, Chichester, UK, 1985.
[3] R.H. Grubbs (Ed.), Handbook of Metathesis, vols. I–III, Wiley–VCH, Weinheim, 2003.
[4] (a) Y. Imamoglu, V. Dragutan (Eds.), Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials, Springer, Dordrecht, The Netherlands, 2007;
(b) V. Dragutan, A. Demonceau, I. Dragutan, E.Sh. Finkelshtein (Eds.), Green Metathesis Chemistry: Great Challenges in Synthesis, Catalysis and Nanotechnology, Springer, Dordrecht, The Netherlands, 2010.
[5] (a) R.R. Schrock, R.H. Grubbs, A. Furstner (Eds.), Special Issue: Olefin Metathesis, Adv. Synth. Catal., 349, 2007, pp. 1–265;
(b) R.R. Schrock, Chem. Rev. 109 (2009) 3211–3226.
[6] (a) A.H. Hoveyda, A.R. Zhugralin, Nature 450 (2007) 243–251;
(b) P.H. Deshmukh, S. Blechert, Dalton Trans. (2007) 2479–2491.
[7] (a) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S.P. Nolan, Angew. Chem. Int. Ed. 46 (2007) 6786–6801;
(b) R. Drozdzak, N. Ledoux, B. Allaert, I. Dragutan, V. Dragutan, F. Verpoort, Cent. Eur. J. Chem. 3 (2005) 404–416.
[8] (a) V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, Coord. Chem. Rev. 251 (2007) 765–794;
(b) F. Ding, Y. Sun, S. Monsaert, R. Drozdzak, I. Dragutan, V. Dragutan, F. Verpoort, Curr. Org. Synth. 5 (2008) 291–304;
(c) S. Monsaert, R. Drozdzak, F. Verpoort, Chim. Oggi/Chem. Today 26 (2008) 93–96;
(d) A.M. Lozano, A. Bajek, S. Monsaert, R. Drozdzak, F. Verpoort, Chim. Oggi/Chem. Today 27 (3) (2009) 20–23 (Suppl. "Focus on Metathesis");
(e) F. Verpoort, I. Dragutan, V. Dragutan, Olefin Metathesis, http://www.scitopics.com/Olefin_Metathesis.html;
(f) M.R. Buchmeiser, Chem. Rev. 109 (2009) 303–321.
[9] K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4490–4527.
[10] F. Amblard, S.P. Nolan, L.A. Agrofoglio, Tetrahedron 61 (2005) 7067–7080.
[11] V. Dragutan, I. Dragutan, J. Organomet. Chem. 691 (2006) 5129–5147.
[12] P. Compain, Adv. Synth. Catal. 349 (2007) 1829–1846.
[13] W.A.L. van Otterlo, C.B. de Koning, Chem. Rev. 109 (2009) 3743–3782.
[14] A. Gradillas, J. Pérez-Castells, Angew. Chem. Int. Ed. 45 (2006) 6086–6101.
[15] (a) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier, P.H. Dixneuf, Green Chem. 11 (2009) 152–155;
(b) M.A.R. Meier, Macromol. Chem. Phys. 210 (2009) 1073–1079;
(c) B. De Clercq, F. Lefebvre, F. Verpoort, New J. Chem. 26 (2002) 1201–1208;
(d) T. Opstal, K. Couchez, F. Verpoort, Adv. Synth. Catal. 345 (2003) 393–401.
[16] M. Bassetti, F. Centola, D. Semeril, C. Bruneau, P.H. Dixneuf, Organometallics 22 (2003) 4459–4466.
[17] M. Rosillo, G. Domingez, L. Casarrubios, U. Amador, J. Perez-Castells, J. Org. Chem. 69 (2004) 2084–2093.
[18] R. Guan, Ch. Zhou, Sh. Feng, D.J. Berg, S.R. Stobart, J. Chin. Chem. Soc. (Taipei, Taiwan) 52 (2005) 113–118.
[19] B.R. Galan, A.J. Giessert, J.B. Keister, S.T. Diver, J. Am. Chem. Soc. 127 (2005) 5762–5763.
[20] C. Ornelas, D. Mery, E. Cloutet, J. Ruiz Aranzaes, D. Astruc, J. Am. Chem. Soc. 130 (2008) 1495–1506.
[21] M.A. Bañares, G. Mestl, Adv. Catal. 52 (2009) 43–128.
[22] (a) T. Vankeirsbilck, A. Vercauteren, W. Baeyens, G. Van der Weken, F. Verpoort, G. Vergote, J.P. Remon, TrAC Trends Anal. Chem. 21 (2002) 869–877;
(b) T.R.M. DeBeer, G.J. Vergote, W.R.G. Baeyns, J.P. Remon, C. Vervaert, F. Verpoort, Eur. J. Pharm. Sci. 23 (2004) 355–362;
(c) S. Cinta Pinzaru, I. Pavel, N. Leopold, W. Kiefer, J. Raman Spectrosc. 35 (2004) 338–346;
(d) G. Zhou, R. Guenard, Z. Ge, in: D.E. Pivonka, J.M. Chalmers, P.R. Griffith (Eds.), Application of Vibrational Spectroscopy in Pharmaceutical Research and Development, John Wiley, Chichester, UK, 2007, pp. 185–211;
(e) S. Armenta, G. Quintas, S. Garrigues, M. de la Guardia, TrAC Trends Anal. Chem. 24 (2005) 772–781;
(f) S.-Y. Lin, M.-J. Li, W.-T. Cheng, Spectroscopy 21 (2007) 1–30;
(g) J.W. Niemantsverdriet, A Wide Spectrum for Analysis: Spectroscopy in Catalysis. An Introduction, VCH, Weinheim, 1993;
(h) M.H. Jamróz, M.E. Jamróz, J.E. Rode, E. Bednarek, J.Cz. Dobrowolski, Vibrational Spectrosc. 50 (2009) 231–244.
[23] B. De Clercq, T. Smellinckx, C. Hugelier, N. Maes, F. Verpoort, Appl. Spectrosc. 55 (2001) 1564–1567.
[24] D. Schaubroeck, S. Brughmans, C. Vercaemst, J. Schaubroeck, F. Verpoort, J. Mol. Catal. A: Chem. 254 (2006) 180–185.
[25] F. Ding, S. Monsaert, R. Drozdzak, I. Dragutan, V. Dragutan, Y. Sun, E. Gao, P. Van Der Voort, F. Verpoort, Vibrational Spectrosc. 51 (2009) 147–151.
[26] (a) B. De Clercq, F. Verpoort, Tetrahedron Lett. 43 (2002) 9101–9104;
(b) N. Ledoux, A. Linden, B. Allaert, H. Vander Mierde, F. Verpoort, Adv. Synth. Catal. 349 (2007) 1692–1700;
(c) T. Opstal, F. Verpoort, J. Mol. Catal. A: Chem. 200 (2003) 49–61;
(d) N. Ledoux, R. Drozdzak, B. Allaert, A. Linden, P. Van Der Voort, F. Verpoort, Dalton Trans. (2007) 5201–5210;
(e) S. Monsaert, E. De Canck, R. Drozdzak, P. Van Der Voort, F. Verpoort, J.C. Martins, P.M.S. Hendrickx, Eur. J. Org. Chem. (2009) 655–665.
[27] S. Monsaert, R. Drozdzak, V. Dragutan, I. Dragutan, F. Verpoort, Eur. J. Inorg. Chem. (2008) 432–440.
[28] (a) B. Schmidt, H. Wildemann, Eur. J. Org. Chem. (2000) 3145–3163;
(b) D.-W. Hahn, D.-M. Byun, J. Tae, Eur. J. Org. Chem. (2005) 63–67;
(c) B. Schmidt, J. Mol. Catal. A: Chem. 254 (2006) 53–57.
[29] H.D. Maynard, R.H. Grubbs, Macromolecules 32 (1999) 6917–6924.