

First FT-Raman and ^1H NMR comparative investigations in ring opening metathesis polymerization

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ABSTRACT

Kinetics of ring-opening metathesis polymerization (ROMP) of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, promoted by the Grubbs' 1st generation precatalyst, has been effectively monitored by FT-Raman and NMR spectroscopy. Both techniques evidenced similar monomer conversions to be attained under the same reaction conditions. The present FT-Raman study provided information on the polymer steric configuration, the Raman bands at 1670 and 1677 cm^{-1} being specifically assigned to stretching vibrations of double bonds from the *cis*- and *trans*-polymer, respectively. The *trans/cis* ratio observed by FT-Raman parallels the corresponding result from ^1H NMR. For the first time, a comparison was made on application of these complementary methods on the same ROMP reaction, evidencing their assets and disadvantages and reliability of FT-Raman.

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1. Introduction

Transition metal catalyzed C–C bond formation falls into the area of most important reactions applied in organic and polymer synthesis. Within this category olefin metathesis (mainly as ring-closing metathesis, cross-metathesis and ring-opening metathesis polymerization (ROMP)), has won a leading position owing to its success in yielding various natural products, specialty polymers, pharmaceuticals and otherwise hard-to-get organic compounds [1–13].

ROMP involving cyclic alkenes is particularly favoured in the case of strained substrates. It is the reaction of choice to access diversely functionalized polymers in high demand due to their unique characteristics. Materials ranging in properties from soft rubber to hard and tough thermoplastics and highly cross-linked thermosets can be prepared by this chemistry [14,15]. The burgeoning area of ROMP-based “designer materials” needs to always find an efficient solution for reconciling the high reaction rates in ROMP with the precise control over polymer chain lengths.

Because of its importance, ROMP kinetics and mechanism, as well as characterization of the reaction products, have been thoroughly examined and/or continuously monitored by a variety

of physical techniques at the forefront of modern research, frequently used in combination, such as gas-chromatography, ^1H NMR, ^{13}C NMR, ESR, FT-IR, MALDI-TOF MS, molecular mass analysis (gel permeation chromatography, light scattering, osmometry, viscometry), etc. [16–22].

Of all these analytical methods, Fourier transform Raman spectroscopy can be easily applied to real world samples, therefore with no need for special sample preparation. Through coupling of the FT-Raman spectrometer by optical fibre bundles, remote examination of samples (located at a certain distance from the spectrometer) becomes possible. It should be kept in mind, however, that for 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.

Raman has obvious advantages over the IR absorption spectroscopy, a technique which along with Raman accomplishes the full vibrational characterization of a molecule [23–26]. The scattering FT-Raman is usually less complicated, and the interpretation of data is more straightforward, yet the Raman signal is frequently weaker than in FT-IR. If we now compare Raman with the NMR spectroscopy, some of Raman's valuable features have to be highlighted: no solvent and no special analysis tubes are needed, a smaller amount of substrate is necessary, no viscosity changes can influence accurateness of kinetics measurements, as is the case with bulk polymerizations monitored by NMR.

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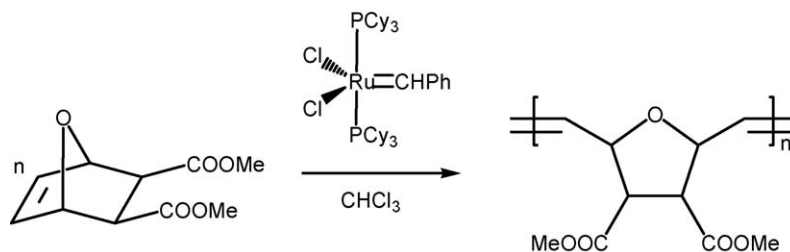


Fig. 1. ROMP of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene using Grubbs' 1st generation catalyst.

Investigation of catalytic reactions by Raman spectroscopy is widely used [27]. As Raman spectroscopy has high sensitivity to nonpolar species (C=C) which make-up polymer chains, this method has long been employed for characterization of various polymers or to follow polymerization kinetics [28–33]. Discrimination between *cis* and *trans* C=C vibrations is also possible. However, following ROMP by FT-Raman can be successfully performed only if there are characteristic $\nu_{\text{C}=\text{C}}$ bands in the monomer and polymer whose intensities change during polymerization [34]. In spite of these assets, there are to date only few reports on ROMP based on such deserving analytical tools (e.g. ROMP of norbornene by in-line fibre-optic NIR-FT-Raman [32], real-time mid-IR monitoring of ROMP of 1,5-cyclooctadiene by fibre-optic FT-IR [35,36]).

In the present research we propose to monitor kinetics of ROMP of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (*exo*-ONDAME), initiated by the well-defined Grubbs' 1st generation catalyst (Fig. 1). The main goal is to assess, for the first time, the merits of FT-Raman and ^1H NMR in providing complementary information on the chemistry of the ROMP catalytic process. To the best of our knowledge there is no previous report on such a comparative kinetic study.

2. Experimental

2.1. Materials

Exo,exo-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (*exo*-ONDAME) was prepared according to literature (yield: 41%) [37].

Grubbs' 1st generation catalyst is commercially available (Strem Chemicals, Inc.) and was used as received.

2.2. 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 ROMP, the excitation laser wavelength of 1064 nm was produced by an air cooled diode pumped neodymium–yttrium 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 (100), laser power (350 mW). Spectra were recorded at 3 min intervals. Data transfer, collection and processing were fully automated using a Bruker OPUSTM software.

^1H NMR spectra were recorded using a Varian 300 MHz spectrometer. Chemical shifts are reported in ppm vs. TMS, in the range 0–10.

2.3. Choice of the solvent

In this ROMP study limiting conditions on the solvent are imposed. The solvent must not deactivate the catalyst and in

Raman spectra no interference from the solvent with the $\nu_{\text{C}=\text{C}}$ band of the monomer and/of the polymer should occur (no solvent peaks in the range 1500–1800 cm^{-1} are admissible). No traces of moisture or oxygen are acceptable because of the sensitivity of the catalyst [1]. Furthermore, a suitable solubility of the monomer and polymer have to be assured for a homogeneous polymerization reaction. Chloroform was chosen as the ideal solvent in Raman, and deuterated chloroform in ^1H NMR measurements, respectively.

2.4. Calibration curve

To determine the relationship between the intensity of the Raman signal and the concentration of the monomer we had to first construct a calibration curve. The same methodology as previously applied for Raman evaluation of ROMP of norbornene has been followed [32]. To minimize variations in intensity of the excitation laser line we used, as necessary, a reference band from the spectrum (668 cm^{-1}) which remains constant during the ROMP reaction.

Five standard solutions with different monomer concentrations (0, 0.493, 0.972, 1.298, and 2.001 mol/l) were prepared and measured five times each by in-line Raman. Measurement conditions for building the calibration curve were the same as those listed above for monitoring ROMP of *exo,exo*-ONDAME (50 scans, laser power: 200 mW, room temperature, 4 cm^{-1} resolution), with the monomer peak appearing at 1573 cm^{-1} and the reference peak (CHCl_3) at 668 cm^{-1} .

For each measurement the height of the monomer 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 monomer peak/intensity of the reference peak) was plotted as a function of the monomer concentration, x [32]. In the investigated domain of concentrations a linear relationship was found, $y = 0.044x - 0.0004$ ($R^2 = 0.9998$).

Based on this calibration curve, the degree of monomer conversion could be calculated from the known initial monomer concentration and the transient monomer concentration (above the detection limit), as determined by Raman at a time t .

3. Results and discussion

3.1. Monitoring of polymerization by FT-Raman

The ROMP reaction was carried out in a glass vessel (7 ml) equipped with a magnetic stirring bar. The monomer, *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, was solved in 1 ml CHCl_3 under magnetic stirring and the FT-Raman spectrum was recorded to obtain the intensity of its $\nu_{\text{C}=\text{C}}$ band at time $t = 0$. Next, the catalyst was added to the monomer solution, the vial containing the reaction mixture placed in the sample compartment of the FT-Raman spectrometer, and evolution of polymerization (Table 1) was monitored under the following measurement

Table 1

Reaction conditions for ROMP of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, used in experiments monitored by FT-Raman and ^1H NMR.

	<i>exo</i> -ONDAME monomer (M)	
	^1H NMR spectroscopic method	Raman spectroscopic method
Temperature ($^{\circ}\text{C}$)	17	17
Solvent	CDCl_3	CHCl_3
[M] (mol/l)	2.08	2.092
Catalyst initiator (I)	Grubbs' 1st gen.	Grubbs' 1st gen.
[M]/[I] ₀	105	104

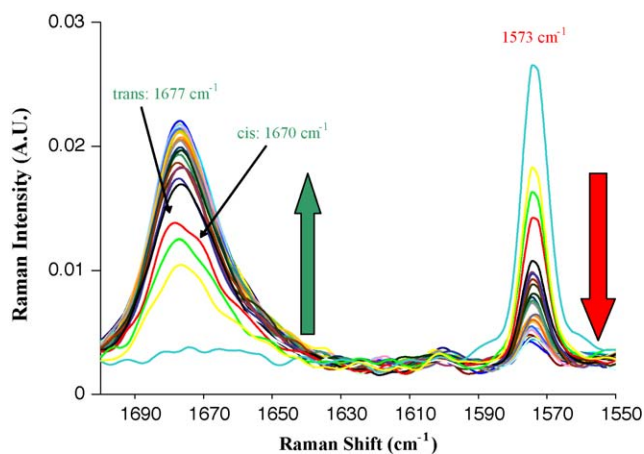


Fig. 2. FT-Raman spectra ($1550\text{--}1700\text{ cm}^{-1}$). Spectra were collected at 3 min intervals.

conditions: 50 scans; laser power, 200 mW; resolution, 4 cm^{-1} ; temperature, $17\text{ }^{\circ}\text{C}$ (Fig. 2).

Conversions have been determined from the ratio between the height of the monomer peak (1573 cm^{-1}), relative to the height of the reference peak, at a time t and at the time zero ($t = 0$, i.e. in the initial monomer solution). The reference peak (668 cm^{-1}) is used for spectral intensity normalization and in this study is that of the solvent. 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 (Fig. 2). 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 [32].

3.2. Monitoring of polymerization by ^1H NMR

Due to the good solubility of *exo*-ONDAME in chloroform it was possible to monitor the progress of our ROMP reaction also by ^1H NMR (in deuterated chloroform).

The catalyst, and next the monomer, were weighed in the tube before starting the reaction by adding the solvent. The tube was swirled to ensure complete mixing of its contents, then placed in the NMR spectrometer in order to monitor the polymerization process (at 17 or $19\text{ }^{\circ}\text{C}$) by taking spectra of the reaction mixture at constant time intervals. Fifteen spectra were recorded at 2 min intervals (Fig. 4), that is during the most rapid phase of ROMP (the reaction is essentially complete after 24 h) [38].

To enable a fair comparison between the two sets of data, from the Raman and the NMR spectroscopy, the same reaction conditions (Table 1) have been applied in both cases.

In kinetic measurements performed by Raman spectroscopy, we focussed primarily on the stretching vibrations of double bonds which, owing to their significant polarizability, exhibit strong

signals in FT-Raman spectra. The intense bands at 1573 and 1677 cm^{-1} , clearly evidenced in our FT-Raman spectra taken during polymerization of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene where both the monomer and its polymer are present (Fig. 2), have been, respectively, assigned to $\nu_{\text{C}=\text{C}}$ vibrations in the monomer and the polymer. The lower value of the $\nu_{\text{C}=\text{C}}$ in the monomer may be rationalized by the considerable strain of the bicyclic oxanorbornene ring system, while the higher $\nu_{\text{C}=\text{C}}$ observed for the polymer results from release of this ring strain during ring-opening polymerization yielding the sterically more favourable structure of the polymer [39].

As the reaction proceeds, the concentration of the polymer increases at the expense of the monomer concentration and this development is reflected in Raman spectra by the evolution of intensity of the respective $\nu_{\text{C}=\text{C}}$ vibrations: the 1573 cm^{-1} continuously diminishes while the 1677 cm^{-1} band increases. Therefore, measuring the intensity of the 1573 cm^{-1} band, it is possible to calculate the monomer concentration $[\text{M}]_t$ at any time during the reaction, and thereupon build the evolution of the monomer conversion as a function of time. The curve is characterized by a fast conversion in the beginning of the reaction (the first 20 min.). Then conversion slows down as should be anticipated from the kinetic characteristic behaviour of the Grubbs' 1st generation catalyst [1], known to exhibit fast initiation and slower propagation (Fig. 3).

Conclusive results in NMR, that compare well with literature data [38] (Table 2), were obtained by following polymerization of *exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, when carried out directly in the NMR-tube. Spectra consist of monomer and polymer signals (sharp for the monomer and somewhat broadened for the polymer), along with the distinctive signal due to the carbene proton (from the initiating and propagating ruthenium species) which appears considerably downfield from the organic proton region of interest and therefore was omitted from Fig. 4.

Change of spectra in time clearly illustrates progress of polymerization through a decrease in intensity of the monomer signals (at 6.46 ppm (H_a), 5.28 ppm (H_b) and 2.83 ppm (H_c)) and a simultaneous increase of the characteristic signals for the corresponding protons in the growing polymer (at 5.82 (*trans*) and 5.52 (*cis*); 4.95 (*cis*) and 4.59 (*trans*); 2.98) (Table 2, Fig. 4).

Integration of these signals for each spectrum enabled us to establish the monomer conversion at the time t when the spectrum was recorded.

As clearly apparent from Table 2, the solvent employed plays a great influence on the chemical shift at which various protons are

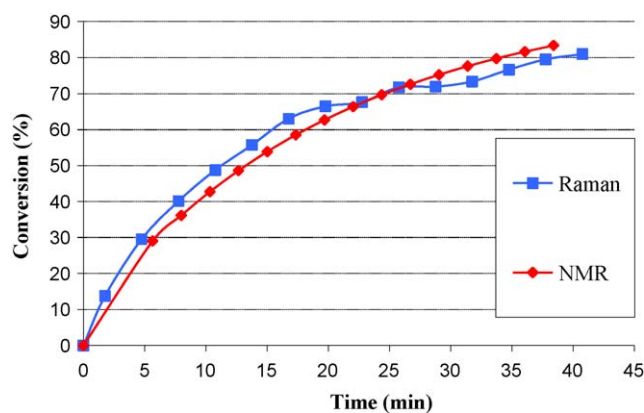
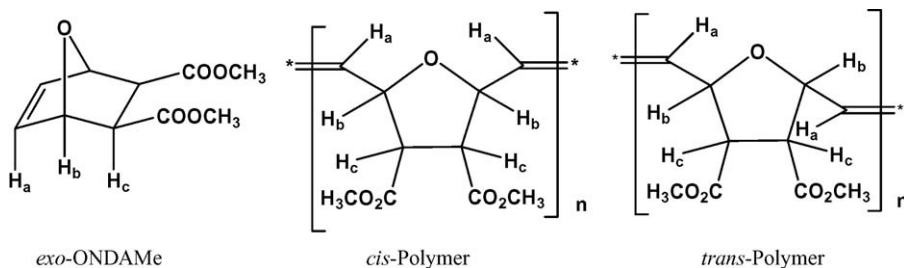
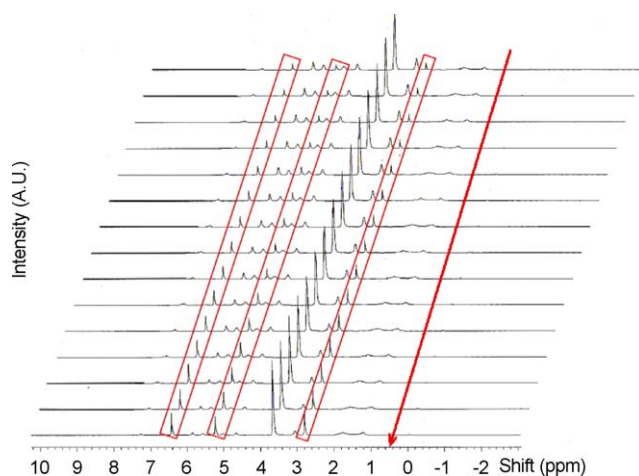


Fig. 3. Comparison of monomer conversions (%; at $17\text{ }^{\circ}\text{C}$) vs. time, as obtained by Raman and NMR spectroscopy.

Table 2Chemical shifts (ppm) of protons from *exo,exo*-ONDAME and its ROMP polymer in CDCl₃ and C₆D₆.

H	Monomer		Polymer		
	δ (ppm) CDCl ₃	δ^a (ppm) C ₆ D ₆	δ (ppm) CDCl ₃	δ^a (ppm) CDCl ₃	δ^a (ppm) C ₆ D ₆
H _a	6.46	5.64	5.82 (<i>trans</i>), 5.52 (<i>cis</i>)	5.88 (<i>trans</i>), 5.59 (<i>cis</i>)	6.07 (<i>trans</i>), 5.58 (<i>cis</i>)
H _b	5.28	4.97	4.95 (<i>cis</i>), 4.59 (<i>trans</i>)	5.05 (<i>cis</i>), 4.69 (<i>trans</i>)	5.41 (<i>cis</i>), 4.98 (<i>trans</i>)
CH ₃	3.71	3.37	3.60	3.68	3.34
H _c	2.83	2.34	2.98	3.08	3.05

^a Ref. [18].**Fig. 4.** NMR spectra collected during the polymerization of *exo,exo*-ONDAME (at 19 °C; M/catalyst = 105 mol/mol).

found. However, a change of solvent from C₆D₆ to CDCl₃ results in a negligible effect on this reaction (Table 2). Our NMR study on kinetics of ROMP of *exo,exo*-ONDAME (Fig. 4) leads to very similar polymer spectra as earlier reported [38,40,41], indicating that our choice of CDCl₃ as the solvent for NMR does not bear on the ROMP itself. Checking our NMR results against literature is a crucial requirement in view of our intended parallelism and a reliable comparison with results from Raman spectroscopy.

The present FT-Raman study on ROMP of *exo,exo*-5,6-bis(-methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene also allowed relevant information to be obtained on the stereospecific configuration of the polymer. The stretching vibration at 1670 cm⁻¹ was attributed to double bonds from the *cis*-polymer and the band at 1677 cm⁻¹ from the *trans*-polymer, on the basis of previous findings in Raman investigations on ROMP of norbornenes [32,42]. Further rationale for this assignment is that the higher steric interference between the substituents at the double bond in the *cis*-polymer should translate into easier vibrating and hence lower wavenumbers in the Raman spectra, as compared to the *trans*-polymer. Although it is impossible to exactly determine the *trans/cis* ratio in the resulting polymer, because of partial overlapping of the above two bands in the spectra acquired during this ROMP

study, preponderance of the *trans* configuration is obvious. This conclusion perfectly correlates with our NMR data, as fully illustrated by Fig. 4 and Table 2, and is in total agreement with the ample literature information on the preferred formation of the *trans* isomer in ROMP initiated by Grubbs' 1st generation catalyst [1,43].

Comparative kinetics of ROMP of *exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, determined by the two spectroscopic techniques applied in this research, was illustrated in Fig. 3. It can be observed that values for monomer conversions at a given time are close, be it that they result from Raman or NMR data. Small deviations of conversions determined by FT-Raman vs. NMR, visible at the beginning and end of the monitoring period, can be accounted for by differences in stirring of the reaction mixture imposed by the two types of instrumentation. Increasing viscosity with progress of the reaction emphasizes the role of adequate agitation for assuring homogeneity; whereas stirring in our Raman experiment was more vigorous than in the NMR tube, the Raman effect only occurs at the place of the radiation incidence.

The obvious similarity of conversion curves determined by FT-Raman and ¹H NMR (Fig. 3) is irrefutable proof that the much less exploited Raman methodology is a valuable tool for monitoring ROMP kinetics, reliably comparing with kinetics [44,45] from NMR spectroscopy. Useful information from the vast library of existing NMR data on ROMP of a variety of cyclic monomers [14,15,46] could thus be transferred to Raman, in anticipation of new results.

4. Conclusions

Kinetics of ring-opening metathesis polymerization of *exo,exo*-5,6-di(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, in the presence of the Grubbs' 1st generation precatalyst, has been effectively monitored using successively FT-Raman and NMR spectroscopy. Under the same reaction conditions, both techniques evidenced that similar monomer conversions (vs. time) were attained. The FT-Raman study provided relevant information on the stereospecific configuration of the polymer, the Raman bands at 1670 and 1677 cm⁻¹ being specifically assigned to stretching vibrations of double bonds from the *cis*- and *trans*-polymer, respectively. The *trans/cis* ratio observed by FT-Raman parallels the corresponding result from ¹H NMR.

The Raman technique was proved to be a worthy approach for evaluating kinetics of ROMP reactions and an attractive alternative

to the traditional ^1H NMR spectroscopy. For the first time, a comparison was made on application of these complementary methods on the same ROMP reaction, evidencing their assets and disadvantages. Raman spectroscopy can use cheaper solvents, and furthermore experimental wavenumbers in Raman spectra are independent of the solvent which is not the case in NMR spectroscopy, yet solvents not interfering with Raman bands of the polymer and monomer are recommended.

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