Ring-Opening Metathesis Polymerization Kinetics of Cyclooctene with Second Generation Grubbs' Catalyst

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A kinetic study of the ring-opening metathesis polymerization (ROMP) of cis-cyclooctene using the ruthenium initiator benzylidene [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]-dichloro-(tricyclohexylphosphine) (second generation Grubbs' catalyst) was carried out by ^{1}H-NMR. The dependence on the reaction rate with the temperature and the influence of the addition of a chain transfer agent were evaluated. Some kinetic constants are also reported for this system.

Keywords: Cyclooctene, Grubbs' catalysts, kinetics, NMR, ring-opening metathesis polymerization (ROMP)

1 Introduction

Ring-opening metathesis polymerization (ROMP) has expanded as a very useful tool in polymer synthesis for some years now (1). It enables the formation of varied and complex macromolecular architectures including functionalized polymers for a range of applications and copolymers (2).

Key to this success has been the development of suitable initiators (the so-called 'catalysts') leading to well-defined, stable and active systems (3–5). Ruthenium-based initiators have played an essential role in ROMP progress and among them, first and second generation Grubbs' catalysts became very popular owing to their outstanding stability, group tolerance and high metathesis activity as well as being commercially available (6). Not only were they used in polymer synthesis but in organic reactions where they proved to be very useful as well. A 'third generation' complex was also introduced and is now preferred for some applications (7,8). The progress goes on, with new members being added to this family of ruthenium initiators aimed at improving their efficiency and performance (9,10).

Different monomers have been polymerized through this reaction, although most of the work made on ROMP is devoted to norbornene derivatives due to the high strain and reactivity of this bicyclic olefin. The less strained 1,5-cyclooctadiene has been extensively used as a model to compare the activity of metathesis initiators and kinetic constants are available in the literature (11–13). However, there is little information on kinetics of cis-cyclooctene which is a candidate for the synthesis of active materials such as shape memory polymers (14), supports for photoactive compounds (15), that can act as sensors or actuators and for the preparation of functionalized derivatives of polyethylene and interesting copolymers of ethylene through ROMP followed by hydrogenation of the unsaturated polymers (16–18). In this paper ROMP of cis-cyclooctene with the 'second generation Grubbs catalyst' is reported from the point of view of kinetics measurement.

2 Experimental

2.1 Reagents

The monomer, cis-cyclooctene (95%), the initiator, $RuCl_2(PCy_3)(1,3\text{-}Mes_2\text{-}imidazolin\text{-}2\text{-}yliden)(CHC_6H_5)$ (Mes = 2,4,6-trimethylphenyl, Cy = cyclohexyl) ('second generation Grubbs' catalyst') and 1,4-diacetoxy-2-butene (95%) were purchased from Aldrich and used as received. Deuterated solvents (dichloromethane and toluene) with a deuteration degree higher than 99.50% as well as tetramethylsilane (TMS) were obtained from Euriso-top (France).

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2.2 General Procedure

In a typical experiment, the monomer (0.24 mmol, 200 eq.) and the internal standard TMS (8.0 μl) were dissolved in 650 μl of the solvent (either CD_2Cl_2 or $C_6D_5CD_3$) and introduced into a NMR tube via syringe. In the experiments with 1,4-diacetoxy-2-butene it was added (0.0472 mmol, 40 eq) diluted in 50 μl of CD_2Cl_2. The NMR tube was then covered with a standard tube cap and placed in the NMR spectrometer. The tube was left to equilibrate at the desired temperature and all parameters were adjusted. A solution of the initiator (2 mg in 0.4 ml of solvent) was prepared prior to the reaction, weighing the initiator into a vial inside a glove-box under nitrogen atmosphere. All the other manipulations were carried out in ambient atmosphere. The required amount of initiator's solution was taken and transferred to the tube via syringe. The tube was shaken to get the content mixed and introduced in the spectrometer again. A time sequence was immediately started with a time delay depending on the experiment duration.

All the measurements were ^{1}H-NMR recorded on a Bruker 500 spectrometer. The polymerization was followed by integration of the olefinic signal at 5.62 ppm taking the TMS singlet for reference.

3 Results and Discussion

3.1 Influence of the Temperature

Effective polymerization of cis-cyclooctene in CD_2Cl_2 was observed by ^{1}H-NMR through the disappearance of the monomer's olefinic signal at 5.62 ppm and the appearance of a new signal at 5.38 ppm corresponding to the olefinic resonance of the polymer. A representative example of the process is shown in Figure 1. The polymerization reaction was performed at three different temperatures 0, 10
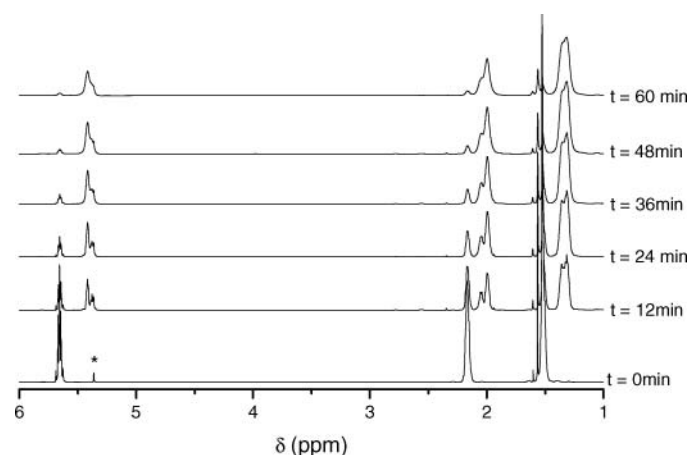

Fig. 2. Monomer conversion vs. time for the ROMP of cis-cyclooctene in CD_2Cl_2 at different temperatures.

Fig. 1. Series of ^{1}H-NMR spectra at different reaction times during the ROMP of cis-cyclooctene at 10°C in CD_2Cl_2 (*corresponds to the solvent peak).
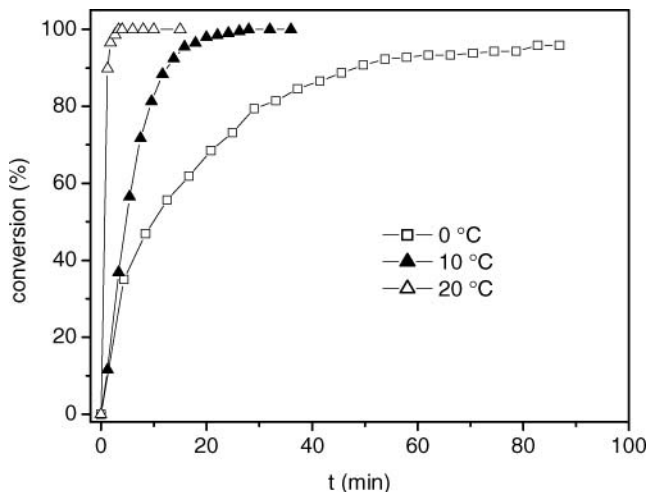
and 20°C. This set of experiments shows a dramatic effect of temperature on the reaction rate. The experiment at 20°C proved to be very fast and complete conversion of the monomer was reached in just 4 min, while after reducing the temperature to 10°C the same conversion level needed around 24 min. Almost complete consumption of monomer was observed in every case, except for the experiment run at the lowest temperature where less than 5% of the monomer remained unreacted after 90 min from the start (Fig. 2). A reason for this lower conversion is that precipitation of the polymer happened at 0°C as seen after the NMR tube was recovered. Part of the polymer precipitated at 10°C as well, whereas at 20°C, the solution was completely clear.

3.2 Effect of the Addition of CTA

Under the conditions used in the NMR experiments ($[M]_0 = 0.3$ M, $[M]_0/[I]_0 = 200$) ROMP of cis-cyclooctene proceeds satisfactorily while moving to the lab scale experiments (19), gelation occurs within minutes and insoluble polymers are formed. A well-known solution to this problem is the use of a chain transfer agent (CTA) which enables good control over molecular weight (20, 21). The use of a symmetric low molecular weight olefin, 1,4-diacetoxy-2-butene, enabled us to obtain soluble polymers from which molecular weights were measured by GPC (22). In order to study the influence of this CTA in the reaction rate, several experiments were also conducted in the NMR spectrometer at 0, 10 and 20°C, using a monomer to CTA ratio of 5.

Figure 3 shows the conversion curves in CD_2Cl_2 at 0 and 20°C. As can be seen, the use of CTA makes the reaction slower compared to that of the monomer alone. Moreover, a period of induction can be observed when the CTA is added to the reaction mixture meaning that the process
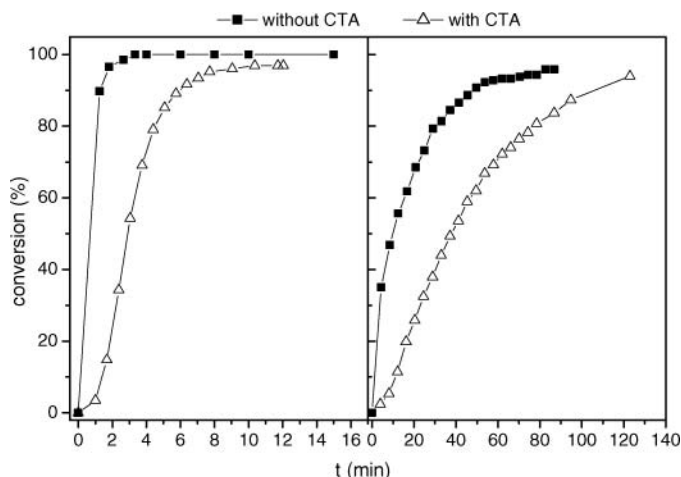
Fig. 3. Effect of the addition of CTA on the ROMP rate in CD_2Cl_2 at 20°C (left) and 0°C (right).

is slowed down from the very start and after which the polymerization continues at a faster rate.

In addition, the variation of the monomer to CTA ratio at a given temperature also influences the rate of polymerization. As long as the amount of CTA is increased, the reaction is slowed down, as seen in Figure 4 for experiments run at 20°C. Using a lower amount of CTA than in the previous experiments ($[M]_0/[CTA]_0 = 25$) the reaction is faster and conversion of monomer to polymer reaches 100%. The lowest polymerization rate is observed for an equimolar mixture of monomer and CTA. In this case, the polymerization is partially inhibited at the beginning of the experiment due to the competence between the two olefinic substrates. As a consequence, the conversion of monomer is low at prolonged reaction times, being around 20% after 180 min from the addition of the initiator. This would
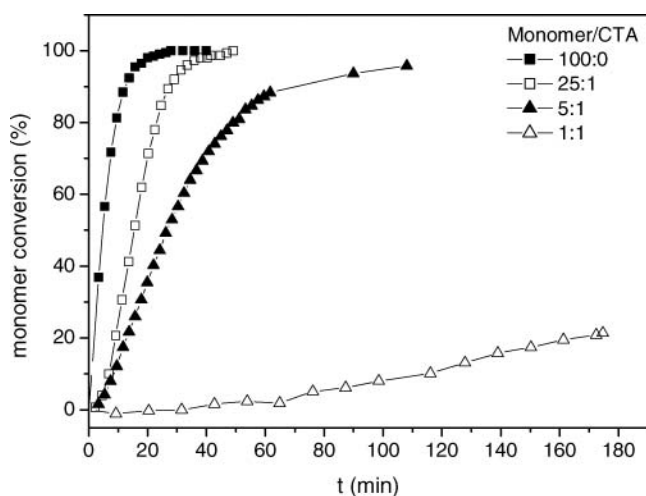

Fig. 4. Monomer conversion vs. time for the ROMP at 20°C of cis-cyclooctene using 1,4-diacetoxi-2-butene as a CTA at different monomer to CTA ratios.

mean that during the first instants of the reaction the initiator prefers to react with the CTA rather than with the monomer.

3.3 Effect of the Change of Solvent

Moving from dichloromethane to toluene a similar trend is observed when cis-cyclooctene is polymerized directly and in the presence of the same CTA. The polymerization rate increases with increasing temperature from 0 to 20°C and, comparing two experiments at the same temperature, the reaction with CTA is slower. Once again, the addition of this olefin alters the curve of monomer conversion approaching to that of a sigmoid for all the temperatures employed.

From the experiments performed with ciclooctene in these two media, it is found that the reaction is faster in toluene ($\varepsilon = 2.38$) than in dichloromethane ($\varepsilon = 8.9$). Apart from some studies regarding the initiation process of the 1st and 2nd generation Grubbs' catalysts (11), there is little information about the influence of the solvent in the propagation rate. Sutthasupa et al. (23) showed that polymerization rate does not clearly depend on the dielectric constant of the medium in the ROMP of amino acid-functionalized norbornenes performed in solvents of different polarity. In fact, it proceeds faster in benzene-d_6 ($\varepsilon = 2.28$) than in chloroform ($\varepsilon = 4.81$) and a similar behaviour was reported by Demel et al. while studying the ROMP kinetics of a diester functionalized norbornene derivative (24).

Although trying to explain the differences in the propagation rate only from the point of view of polarity proves to be difficult, they could be interpreted in terms of the Transition state theory that would predict a higher stabilization of the transition state in a less polar solvent and, consequently, an increase in the propagation rate.

3.4 Determination of Kinetic Constants

Considering the propagation step of the ROMP of cyclooctene represented by Scheme 1, the propagation rate can be expressed as follows:

$$v = k_P[\text{monomer}][\text{active centers}]$$

where k_P is the corresponding kinetic constant and the so called 'active centers' are those species bearing a ruthenium moiety which give rise to a growing polymer chain.

From the experimental data, the variation of monomer conversion can be adjusted to first-order kinetics' plots. As there is a linear relationship up to high conversion, a constant concentration of active centers can be assumed and a pseudo-constant, the observed rate constant (k_{obs}), defined. Thus, $k_{obs} = k_P$ [active centers]. When 1,4-diacetoxy-2-butene is used, the values of monomer conversion can be adjusted to first-order kinetics after the induction period.

The values of k_{obs} obtained are shown in Tables 1 and 2 for the experiments performed in dichloromethane and toluene, respectively. As expected, the propagation
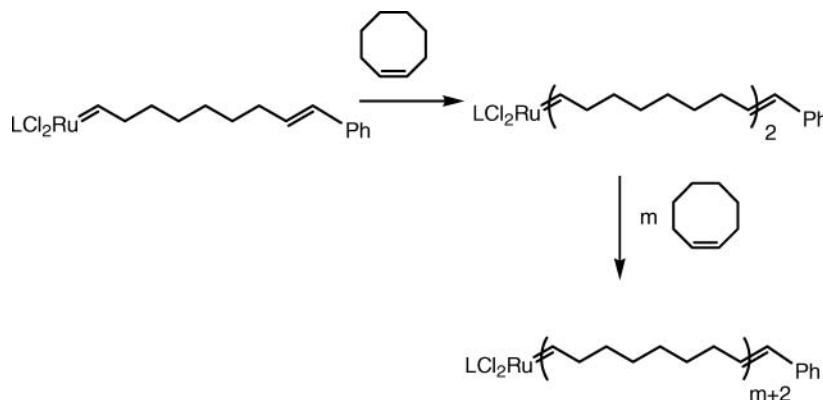
Sch. 1. Propagation of the ROMP of cyclooctene.

constant increases when the temperature is raised and the value of k_{obs} is higher for toluene at each temperature. The values obtained for these constants are considerably higher than those published for other ruthenium initiators and monomers (24–27). In the experiments with CTA, the constant is smaller as a consequence of a slower propagation rate. Having in mind that the presence of CTA will not modify the nature of the active centers, a reduction on its concentration must be admitted. In any case, the loss of active centers should take place during the first instance of reaction, otherwise, the kinetic order would not be preserved. It is difficult to compare with other published results since a change of any of the components (monomer, initiator or CTA) would alter the value of k_{obs}. Even so, in a kinetic study by Buchmeiser et al. (27) in which cyclooctene was polymerized with a ruthenium complex derived from the second generation Grubbs' catalysts

Table 1. Observed propagation constants under different conditions for the ROMP of cis-cyclooctene in CD_2Cl_2 (M = monomer, I = initiator, CTA = chain transfer agent) [M] = 0.3 M

Entry	[M]/[I]	T (°C)	[M]/[CTA]	k_{obs} (min^{-1})
1	200	0	—	0.043
2		10	—	0.201
3		20	—	1.56
4		0	5	0.024
5		10	1	—[a]
6		10	5	0.040
7		10	25	0.133
8		20	5	0.525
9	40	20	—	—[b]
10	1000	20	—	0.627
11	500	10	—	0.230
12	1000	10	—	0.155
13	2000	10	—	0.065
14	3000	10	—	0.046

[a]Conversion of monomer is around 20% after 3 h reaction time.
[b]The monomer is totally consumed in less than a minute.

Table 2. Observed propagation constants under different conditions for the ROMP of cis-cyclooctene in $C_6D_5CD_3$ (M = monomer, I = initiator, CTA = chain transfer agent) [M] = 0.3 M

Entry	[M]/[I]	T (°C)	[M]/[CTA]	k_{obs} (min^{-1})
1	200	0	—	0.086
2		10	—	0.431
3		20	—	1.87
4		0	5	0.011
5		10	5	0.071
6		20	5	0.379
7	500	10	—	0.338
8	1000		—	0.212
9	2000		—	0.098
10	3000		—	0.071

(RuCl$_2$ (1,3-dimesitylimidazolin-2-ylidene) (CHC$_6$H$_5$) (Py)$_2$), different amounts of pyridine were added to control the speed of the reaction. Values of k_P ranging from 0.11 to 0.56 min^{-1} were determined in dichloromethane which are near to our reported values.

Furthermore, considering an Arrhenius-like behavior, an estimated value of the activation energy can be calculated from entries 1 to 3 of both Table 1 and 2 resulting in values of 119 kJ·mol^{-1} in dichloromethane and 117 kJ·mol^{-1} in toluene-d$_8$.

In order to establish the concentration of active centers and as a result the propagation constant of the process, information is needed regarding the initiation step. However, this initiator is known to provide very low initiation efficiency (19, 24) and direct measurement of the initiation constants was not accomplished, since there was no observable change in the intensity of the initiator's carbene peak (centerd at 19.02 ppm in dichloromethane and at 19.57 ppm in toluene) during the duration of the experiment and no propagation species were found to change. Another set of experiments were conducted using a higher initiator concentration and a lower ratio of monomer to initiator in

order to evaluate the relative ratio of propagation to initiation (k_P/k_i) according to the method used by Conrad et al. (25). In this case, the reaction was too fast even at 10°C and no better results were obtained.

4 Conclusions

The ROMP of cis-cyclooctene initiated by the second generation Grubbs' catalysts is very fast at ambient temperature. At 20°C in dichloromethane, total conversion of the monomer into polymer is observed within a few minutes and the reaction proceeds even faster in toluene. The addition of a low molecular weight chain transfer agent is an effective method to reduce the rate of polymerization at a given temperature. However, by adding this substance the kinetic pattern is altered and an induction period appears at the beginning of the process. Rate constants proportional to the actual propagation rate constants of the process (k_{obs}) have been determined for all the experiments performed and show high values compared with other monomer/initiator systems.

Acknowledgments

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