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Polymerizability of Cycloalkenes in "Living" Ring-Opening Metathesis Polymerization Initiated by Schrock Complexes: 3. Effect of monomer structure

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Summary: The kinetics of the "living" and "controlled" ring-opening metathesis homo- and copolymerization of several cycloalkenes initiated by Mo-based Schrock complexes were investigated in the context of a general study devoted to the relation between the monomer structure on its reactivity. First, the polymerizability of these monomers was measured as a function of both their ring strain and their bulkiness. In a second part, the intrinsic reactivity of both the monomers and the corresponding active centers was evaluated from the determination of the rate constants of homopropagation and the various reactivity ratios. The steric hindrance created by the monomer substituents has only a small effect on the intrinsic reactivity of the cycloalkene. The latter mainly depends on the ring strain exactly as does the polymerizability. Steric crowding around the acyclic double bonds of the polymer chain is another factor affecting the reactivity of the active propagating centers; the latter is indeed found to depend on the capability of these acyclic double bonds to compete with the double bond of the cyclic monomer for the complexation to the transition metal.

Introduction

In the context of a general study devoted to structural and experimental parameters that determine the polymerizability of cycloalkenes in Ring-Opening Metathesis Polymerization (ROMP), the influence of "external" parameters (solvent, ligands, transition metal) has been previously reported [1, 2]. The present paper deals with the relation between the monomer structure ("internal" parameter) and its reactivity as well as that of the corresponding propagating centers.

Studies reporting the influence of the monomer substituents on the rate of polymerization showed that the polymerizability decreases with the electron-withdrawing character of the substituents [3, 4]. Concerning the influence of the cycloalkene ring strain, the discussion is still open. Indeed, Ivin and coll. [5, 6] claimed that the rate of polymerization is a function of the ring strain of the monomer whereas

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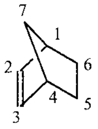
McCarthy and coll. [7] proposed that the observed behavior could be attributed to the relative reactivity of the corresponding active centers and to the steric hindrance created around the active terminal monomeric unit. These two different interpretations of experimental data incited us to carry out the present study, in order to asses the relative effects of the ring-strain of the cycle and the steric hindrance of substituents.

"Living" and "controlled" polymerization systems were chosen for this study since such processes allow an easier measurement of the monomer polymerizability. To this end, the Schrock complex $Mo(=CHC(CH_3)_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (with NAr=$Ph^{(iPr)_2}$) was used to initiate the ROMP of strained bicycloalkenes such as norbornene (1) and two of its homologues [2 and 3], in cyclohexane at 25 °C. Tricyclo[2.3.0]hept-2-ene (2) is a monomer with a similar steric hindrance but a higher ring strain than 1 and tetracyclo[6.2.1.1$^{3.6}$.0$^{2.7}$]dodec-4-ene (3) differs from 1 only by its higher steric hindrance due to norbornanylene moiety.



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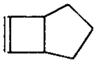

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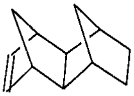

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The polymerizability depends on the intrinsic reactivity of both the monomer and the corresponding active species involved in the process. To determine these two reactivities separately the method consisted in evaluating the kinetic parameters of both homopolymerizations and copolymerizations of the above monomers.

Experimental part

Materials

The catalyst $Mo(=CHC(CH_3)_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (with Ar = $Ph^{(iPr)_2}$) was synthesized according to a previouly published procedure [8, 9].

Monomers 1 and 3 are commercially available. Monomer 2 was synthesized according to reference [10] by rearrangement of 1,3-cycloheptadiene under photochemical activation. It was purified by distillation in a spinning band column. Cyclohexane, toluene-d_8 and undecane (internal standard) were distilled over CaH_2, dried over sodium and finally degassed. Monomers were distilled and dried over sodium and degassed several times just before use.

(Co)polymerizations

The determination of the monomer conversion as a function of time was performed as previously described [11].

Fineman-Ross and Kelen-Tüdos methods were used to evaluate the reactivity ratios. The direct determination of the copolymer composition using ^{1}H NMR of the copolymer was not applicable to our system since the signals of the various monomeric units coincide in the spectrum. The initial monomer concentration ratios ($X=[\mathbf{1}]_0/[M]_0$) were obtained from weighing.

Characterization of polymers and active centers

The techniques used to measure molar masses, molar masses distributions (MMD) and to characterize the structure of the propagating species were described in previous papers [1, 2].

Calculations to obtain the lowest energy level of propagating centers were obtained by using the Hyperchem® software.

Results and discussion

Homopolymerizations

Data on the "living" ROMP of norbornene (1) were given in a previous papers [2]. The "living" character of the polymerization of 2 and 3 when initiated in cyclohexane by $Mo(=CHC(CH_3)_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (with $Ar=Ph^{(iPr)_2}$) was first checked. Assuming (as checked later) that the corresponding processes show a first-order kinetics in monomer, the linear variations of $\ln([M]_0/[M])$ *versus* time and $\overline{M}_{n,exp}$ *versus* conversion respectively indicate the absence of termination and transfer reactions [12, 13] (Fig. 1 and 2).

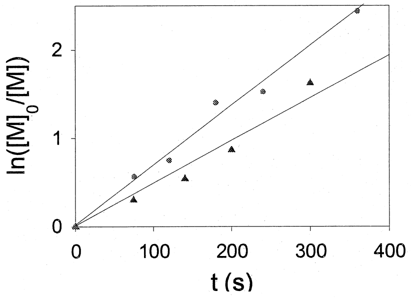


Figure 1: Plots of $\log_e([M]_0/[M])$ *versus* time for polymerizations performed in cyclohexane at 25 °C:

● ⇨ M = 2
$M]_0 = 5.2\ 10^{-2}$mol/L, $[I]_0 = 1.1\ 10^{-4}$mol/L.
▲ ⇨ M = 3
$[M]_0 = 6.1\ 10^{-2}$mol/L, $[I]_0 = 1.5\ 10^{-3}$mol/L

Average molar masses and MMD of the corresponding polymers are reported in Table 1 which shows that a satisfactory control could be achieved for the studied systems.

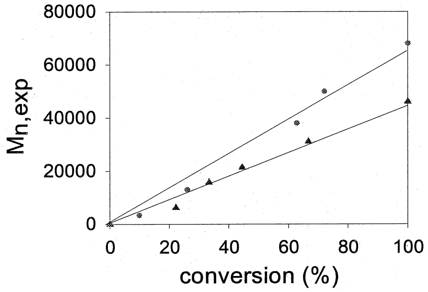


Figure 2: Plots of $\overline{M}_{n,exp}$ *versus* conversion for polymerizations performed in cyclohexane at 25°C:
● ⇨ M = 2
$[M]_0 = 1.3\ 10^{-1}$mol/L, $[I]_0 = 1.4\ 10^{-4}$mol/L
▲ ⇨ M = 3
$[M]_0 = 1.1\ 10^{-1}$mol/L, $[I]_0 = 1.6\ 10^{-4}$mol/L

Therefore, the initial rate of polymerization of monomers 1, 2 and 3 can be expressed by:

$$(R_p)_0 = -(d[M]/dt)_0 = k_p[I]_0^{\alpha}\,[M]_0^{\beta}$$

$[I]_0$ and $[M]_0$ being the initial concentrations in initiator and monomer, respectively. Kinetic orders with respect to initiator (α) and monomer (β) were established by plotting $\ln((R_p)_0/[M]_0)$ *versus* $\ln([I]_0)$ and $\log_e((R_p)_0/[I]_0)$ *versus* $\ln([M]_0)$ respectively for polymerizations of 2 and 3 performed with different initiator and monomer concentrations (Figures 3 and 4).

Table 1: Molecular characteristics of poly(1), poly(2) and poly(3) obtained from polymerizations performed in cyclohexane at 25 °C.

monomer	$\overline{M}_{n,th}$ (g.mol^{-1})	$\overline{M}_{n,exp}$ (g.mol^{-1})	I_p $^{d)}$
1	8 200	7 000 $^{c)}$	1.20
	24 800	26 000 $^{b)}$	1.10
	30 000	33 000 $^{b)}$	1.24
2	28 900	29 000 $^{b)}$	1.15
	30 000	33 000 $^{b)}$	1.17
	6 800	6 500 $^{a)}$	1.20
3	49 000	51 000 $^{b)}$	1.08
	2 900	2 700 $^{a)}$	1.08
	3 900	3 500 $^{a)}$	1.12

a) Number-average molecular weight measured by NMR ^{1}H
b) Number-average molecular weight measured by SEC in THF equipped with a light scattering detector
c) Number-average molecular weight measured by tonometry
d) Polydispersity index given by SEC using a polystyrene calibration curve ($I = \overline{M}_w/\overline{M}_n$)

The slopes of the corresponding variations indicate a first-order kinetics both in monomer and in initiator (the same behavior was observed for polymerizations of 1 in similar conditions [2]).

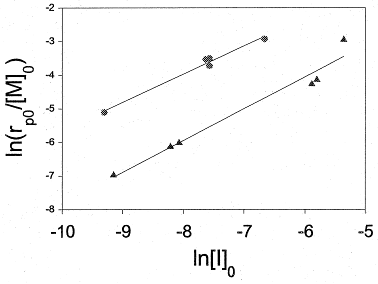


Figure 3: Determination of the kinetic order in initiator: ● : 2, ▲ : 3.

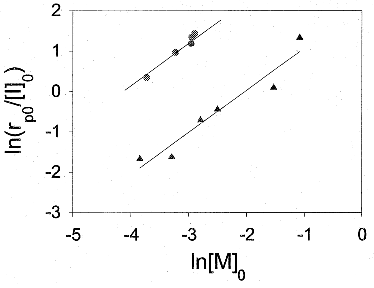
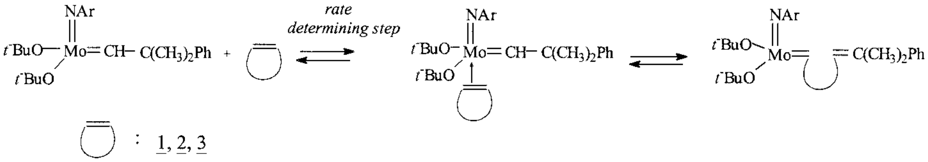


Figure 4: Determination of the kinetic order in monomer: ● : 2, ▲ : 3.

The first-order dependence in initiator was interpreted by the existence of only one type of propagating species in the reaction medium. Moreover, the first order dependence in monomer indicates that the monomer complexation onto the vacant site of the transition metal [2] is the rate-determining step of the polymerization (Scheme 1).



Scheme 1: reaction scheme of the polymerization of 1, 2 and 3, initiated by Mo(=CHC(CH$_3$)$_2$Ph)(NAr)(O-t-Bu)$_2$ in cyclohexane.

The polymerizability of the three monomers is given by the slope of $\ln([M]_0/[M])$ *versus* time which is proportional to the rate constant of polymerization ($\ln([M]_0/[M]) = k_p[I]_0t$). According to the values of k_p obtained for monomers 1 and 3 (Table 2) which appear very close and considering that 1 and 3 exhibit rather similar ring strains but a strong difference in their steric hindrance it can be concluded that the latter factor has no crucial effect on their polymerizability. It can therefore be suggested that the substitution of carbons 5 and 6 of norbornene by a bicycle does not strongly modify the access to the olefinic double bond and therefore its ability to complex the transition metal. On the other hand, monomers 1 and 2 possess a similar steric hindrance around the double bond but a strongly different ring strain (96 kJ/mol for 1 [14] and 155 kJ/mol for 2 [15]), the higher value of k_p determined for 2 compared to that of 1 can therefore be attributed to the higher ring-strain of 2.

Nevertheless, the polymerizability of a given monomer depends on both its intrinsic reactivity and that of the corresponding active centers. As these two parameters cannot be evaluated from the sole homopropagation rate constants, this study was completed by performing copolymerizations between 1, 2 and 3 using the same reaction conditions.

Table 2: Values of k_p of polymerizations of 1, 2 and 3 initiated by Mo(=CHC(CH_3)$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (with NAr=Ph$^{(iPr)_2}$), in cyclohexane.

monomer	$[I]_0$ (10^{-4} mol/L)	$[M]_0$ (10^{-2} mol/L)	$(R_p)_0$ (10^{-3} mol/L.s)	k_p (L/(mol s)	Average value of k_p (L/(mol s)
1	0.55	2.99	0.018	10.9	9.2 (± 1.5)
	1.40	3.10	0.037	8.6	
	34.90	30.71	9.53	8.9	
	4.60	7.27	0.29	8.8	
2	4.87	5.22	1.63	64	58 (± 5)
	5.16	5.21	1.69	63	
	8.86	6.20	2.91	53	
	5.16	5.43	1.62	58	
3	3.12	8.17	0.21	8.3	8.3 (± 1.1)
	2.71	6.11	0.15	9.3	
	1.06	2.13	0.19	8.6	
	5.83	3.80	0.38	7.2	

Copolymerizations

From copolymerization experiments discontinued at low monomer conversion and involving 1 and 2 as well as 1 and 3, experimental data were treated by using Fineman-Ross [16] and Kelen-Tüdos [17] methods (Figures 5 and 6). The corresponding values of reactivity ratios r_{ij} are reported in Table 3. They does not depend on the method used for the treatment of data. The values of $r_{1,2}$ and $r_{2,1}$ are in agreement with the observation made by Grubbs and coll. in a previous study [15] : $r_{1,2} < 1$ and $r_{2,1} >> 1$. Reactivity ratios and homopropagation rate constants were then used to determine the cross-addition rate constants.

To compare the reactivity of the various monomers and their respective active species, norbornene and its corresponding active center $\sim\sim\sim$1* were chosen as references. The different values of the rate constants of cross-addition k_{1j} indicate that the intrinsic reactivity of the monomer depends mainly on its ring strain and not on the size of its

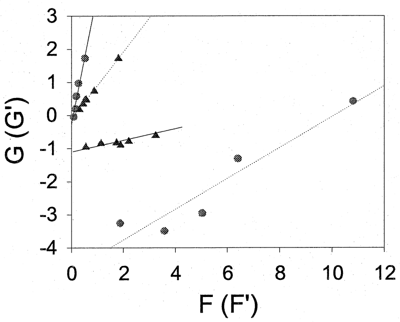


Figure 5: Determination of the reactivity ratios by the Fineman-Ross method: copolymerization of 1 with 2 (•) and copolymerization of 1 with 3 (▲).

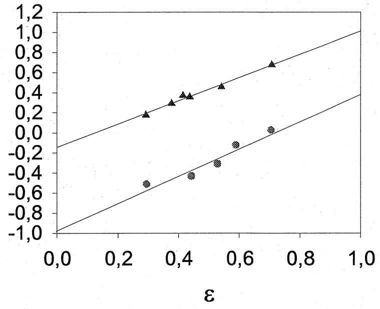
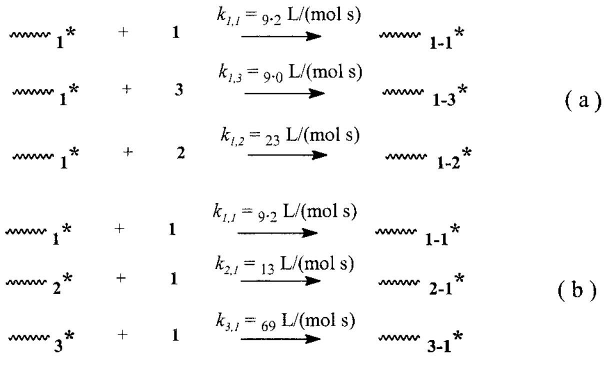


Figure 6: Determination of the reactivity ratios by the Kelen-Tüdos method: copolymerization of 1 with 2 (•) and copolymerization of 1 with 3 (▲).

Table 3: reactivity ratios derived from the copolymerizations of 1 with 2 and 1 with 3 initiated by Mo(=CHC$(CH_3)_2$Ph)(NAr)(O-*t*-Bu$)_2$ (with NAr=Ph$^{(iPr)_2}$), in cyclohexane

monomers	reactivity ratio	Fineman-Ross method	Kelen-Tüdos method
1, **2**	$r_{1,2}$ (=$k_{1,1}/k_{1,2}$)	0.38	0.40
	$r_{2,1}$ (=$k_{2,2}/k_{2,1}$)	4.36	4.40
1, **3**	$r_{1,3}$ (=$k_{1,1}/k_{1,3}$)	1.02	1.01
	$r_{3,1}$ (=$k_{3,3}/k_{3,1}$)	0.12	0.12

subtituents (Scheme 2a) thus corroborating the results obtained for the homopropagation. The structure of the propagating species strongly determines their reactivity (scheme 2b) since ~~~3* is more reactive than the two other types of active centers.



Scheme 2: kinetic scheme of the copolymerization of 1 with 2 or 3.

From the structure of the three types of actives species represented in their lowest energy level (Figure 7) it can be seen that the last monomeric unit inserted in the chain does not affect the steric hindrance around the metalla-alkylidenic double bond. The geometry of the monomer complexed to the transition metal atom is therefore similar whatever the propagating species considered. Consequently, the strong differences observed in the values of k_{i1} could not be accounted for by the steric hindrance around the last monomer unit.

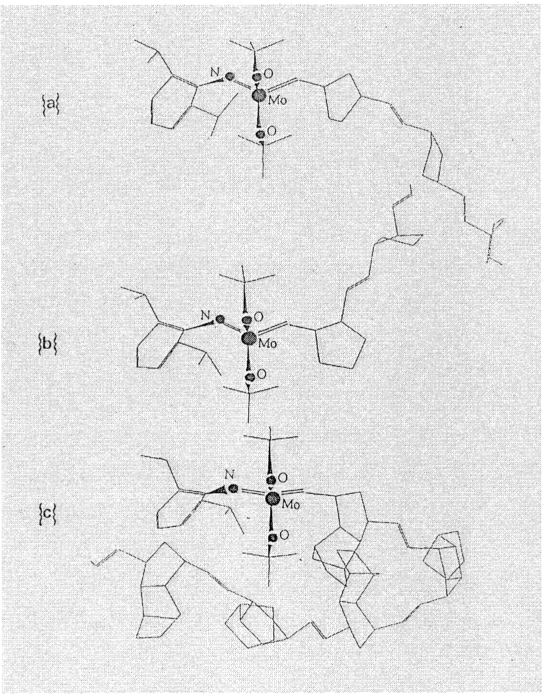


Figure 7: conformational structure of the 3 types of propagating species : $\sim\sim\underline{1}^{*}$ (a), $\sim\sim\underline{2}^{*}$ (b), $\sim\sim\underline{3}^{*}$ (c).

Another possible explanation could be the variation of the electron density on the transition metal atom. Indeed, Bazan and coll. [18] reported that the coordination of monomer molecules which is also the rate-determining step is made easier when the transition metal becomes more electro-positive, inducing in turn an enhancement of the reactivity of the metalla-alkylidenic species. An increase of the electro-positive character of the transition metal atom should be mirrored in a change of the H_α chemical shift. To confirm this hypothesis the ^1H chemical shift due to the metalla-alkylidenic protons ($\delta_{H\alpha}$ appears as a doublet) of the three types of species was measured and the results are given in Table 4. Electron density on the transition metal decreases as follow : ~~~**1*** > ~~~**2*** > ~~~**3***. The easier coordination of monomer to more negative metal atom is responsible for an the increase of the reactivity of the corresponding propagating species.

Table 4 ^{1}H NMR chemical shift of the metalla-alkylidenic proton ($\delta_{H\alpha}$) of the three active species.

Active Center In presence of	~~~**1***	~~~**2***	~~~**3***
-	11.48 ; 11.52	11.68 ; 11.72	11.78 ; 11.82
Poly(**1**)	-	-	11.55 ; 11.59
Poly(**3**)	11.49 ; 11.53	-	-

On the other hand, McCarthy and coll. [7] showed that the apparent reactivity of propagating species could be modified owing to the competition between the acyclic double bonds of the polymer chains and the monomer for coordination to the transition metal atom. In order to check whether of such a phenomenon could explain differences in the reactivity, the H_α chemical shifts (doublet) of ~~~**1*** and of ~~~**3*** were measured in the presence of deactivated poly(**3**) chains (δ_{H1*3}) and in the presence of deactivated poly(**1**) chains (δ_{H3*1}) respectively (Table 4). The values of δ_{H1*3} (11.49 ; 11.59) under these conditions are close to those of ~~~**1*** (11.48 ; 11.53) in absence of deactivated chains. In contrast, the presence of deactivated poly(**1**) chains in the ~~~**3*** solution induces a downfield chemical shift (11.55 ; 11.59).

To account for these results, it can be argued that the coordination of poly(**1**) monomeric units to the transition metal is strong whereas it is weak for poly(**3**) thus favouring the monomer coordination in the latter case. Steric crowding around each monomeric unit of poly(**3**) should be the reason for this difficulty to coordinate the transition metal atom.

References

[1] C. Cazalis, V. Héroguez, M. Fontanille, *Macromol. Chem. Phys.*, 201 (2000) 869.

[2] C. Cazalis, V. Héroguez, M. Fontanille, *Macromol. Chem. Phys.*, 202 (2001) 1513.

[3] G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas, W. M. Davis, *J. Am. Chem. Soc.*, 112 (1990) 8374.

[4] M. G. Perott, B. M. Novak, *Macromolecules,* 29 (1996) 1817.

[5] K. J. Ivin, "*Enc. Polym. Sci. Tech.*", vol.9, Wiley Interscience, New York (1987).

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

[7] P. A. Patton, T. J. McCarthy, *Macromolecules*, 17 (1984) 2940.

[8] R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. B. O'Regan, *J. Am. Chem. Soc.*, 112 (1990) 3875.

[9] R. R. Schrock, *Pure Appl. Chem.*, 66 (1994) 1447.

[10] W. G. Dauben, R. L. Cargill, *Tetrahedron*, 12 (1961) 186

[11] V. Héroguez, M. Fontanille, *J. Polym. Sci., Part A : Polym. Chem*, 32 (1994) 1755.

[12] K. Matyjaszewski, *J. Phys. Org. Chem.*, 8 (1995) 197.

[13] R. P. Quirk, B. Lee, *Polym. Int.*, 27 (1992) 359.

[14] N. L. Allinger, J. T. Sprague, *J. Am. Chem. Soc.*, 94 (1972) 5735.

[15] Z. Wu, A. D. Benedicto, R. H. Grubbs, *Macromolecules*, 26 (1993) 4975.

[16] M. Fineman, S. D. Ross, *J. Polym. Sci.*, 5 (1947) 269.

[17] E. Kelen, F. Tüdos, B. Turcsanyi, *J. Polym. Sci.*, 15 (1977) 3047.

[18] G. C. Bazan, J. H. Oskam, H-N. Cho, L. Y. Park, R. R. Schrock, *J. Am. Chem. Soc.*, 113 (1991) 6899.