Syn/Anti Rotamer Interconversion as the Rate-determining Initiation Step in Ring-opening Metathesis Polymerisations using Well-defined Molybdenum Alkylidene Complexes

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The kinetics of initiation of metathesis polymerisation of methyl-substituted norbornenes initiated by complexes of the type [Mo(=CHR^1)(=NC$_6$H$_3$Pr$^i_2$-2,6)(OR^2)$_2$] [R^1 = Bu^t, CMe$_2$Ph; OR^2 = OCMe$_3$, OCMe(CF$_3$)$_2$] reveal a zero-order dependence on monomer concentration in some cases; *syn* → *anti* alkylidene conversion of the initiator is proposed as the rate-limiting step.

Four-coordinate molybdenum alkylidene complexes of the type [Mo(=CHR^1)(=NC$_6$H$_3$Pr$^i_2$-2,6)(OR^2)$_2$] [R^1 = Bu^t, CMe$_2$Ph; OR^2 = OCMe$_3$, OCMe(CF$_3$)$_2$] have been shown to offer an unprecedented level of control over the ring-opening metathesis polymerisation (ROMP) of a variety of functionalised cyclic monomers.[1–4] These developments have been accompanied by significant advances in our understanding of the intricacies surrounding the mechanism of operation of these four-coordinate initiators.[2–7] For relatively unhindered norbornenes and norbornadienes where the polymerisation is fast, the disappearance of the initiator is expected to follow a first-order dependence on monomer concentration. However, in recent studies on the polymerisation of the methyl-substituted derivatives **1–3**, we have observed either a zero-order dependence on monomer concentration or a tendency towards zero order as the monomer concentration is raised. Here, we report some results on these systems and offer an explanation in terms of rate-determining *syn* → *anti* alkylidene rotamer interconversion,[5,6] followed by rapid reaction of the monomer with the *anti*-rotamer.

The polymerisations of **1–3** were followed by 400 MHz ^{1}H NMR spectroscopy (Table 1). *Anti*-7-methylnorbornene **1** is very much more reactive than its *syn* isomer **2**. Starting from a 1 : 1 mixture of **1** and **2**, the reaction of **1** could be followed by using the less reactive *tert*-butoxide initiators **4** or **4′** (R^1 = CMe$_3$ **4** or CMe$_2$Ph **4′**, OR^2 = OCMe$_3$) and working at low temperature. The reaction yields the propagating alkylidene species **5** in which the end-group R^1 is attached to a *trans* double bond (Table 1).

In the reaction of a mixture of **1** and **2** with the much more

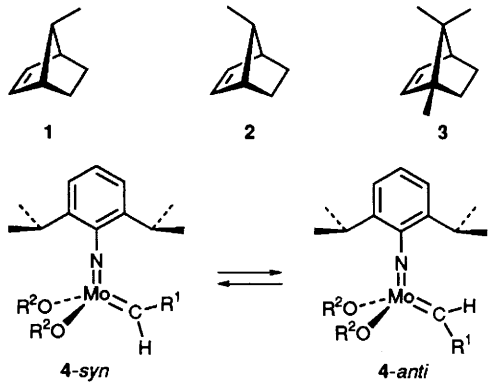
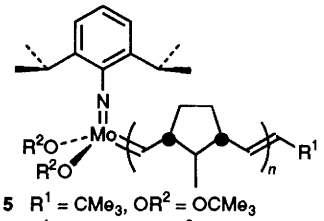


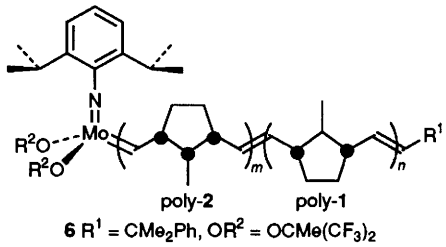
Table 1 Some initiation reactions of molybdenum alkylidene complexes with norbornene derivatives which are zero order or tend to zero order with respect to monomer (M)

System	Mo complex (I)[a]		Monomer	Solvent, T/°C	[M]$_0$/[I]$_0$	k_1/10^{-5} s^{-1}	Observations: Kinetics	Observations: End group
I	**4**, R^1 = CMe$_3$ OR^2 = OCMe$_3$		**1**	CD$_2$Cl$_2$ 13	19	350	First-order decay of **4** maintained over 4 half-lives while [**1**] fell by factor of 4.5	–CH=C*H*CMe$_3$, δ 5.41, ^3J = 15.6 Hz[b]
II	**4′**, R^1 = CMe$_2$Ph OR^2 = OCMe$_3$		**1**	CD$_2$Cl$_2$ −45	11	26	First-order decay of **4′** maintained over 1.7 half-lives[c] while [**1**] fell by factor of 2.3	–CH=C*H*CMe$_2$Ph, δ 5.57, ^3J = 15.4 Hz[b]
III	**5″**, R^1 = CMe$_2$Ph OR^2 = OCMe(CF$_3$)$_2$		**2**	CD$_2$Cl$_2$ 20	22	46	First-order decay of **5″** maintained over 2.5 half-lives while [**2**] fell by factor of 40	
IV	**5″**		**2**	C$_6$D$_6$ 20	23	28	First-order decay of **5″** maintained over 3.5 half-lives while [**2**] fell by factor of 4.7	
V	**4″**, R^1 = CMe$_2$Ph OR^2 = OCMe(CF$_3$)$_2$	10^2[I]$_0$ 1.9	**3**	CD$_2$Cl$_2$ 20	5.2	1.02	First-order decay of **4″** maintained over 4 half-lives while [**3**] remained almost constant in each experiment	–CH=C*H*CMe$_2$Ph, δ 5.58, ^3J = 15.6 Hz[b]
		2.85			14	2.84		
		2.6			23[d]	3.51		
		2.85			34	4.12		
		—			∞	6.1[e]		

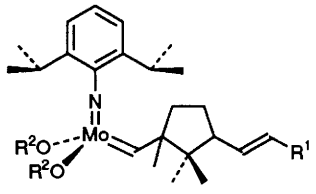
[a] Reaction mixtures of monomers **1–3** and initiator (I) for study at room temperature were made up in CD$_2$Cl$_2$ or C$_6$D$_6$ and transferred to 5 mm NMR tubes in the dry box, as described elsewhere.[7] For reactions at lower temperatures the initiator solution was first prepared in an NMR tube closed with a serum cap, and cooled to −80 °C. The monomer was then injected into the top of the tube and the mixing performed at low temperature. In all cases the reaction was followed by 400 MHz ^{1}H NMR using the olefinic proton peaks to monitor **1–3** and the alkylidene proton peaks to monitor **4**. [I] in the range 2–3 × 10^{-2} mol dm^{-3}. [b] Characteristic of *trans* C=C. [c] After this the concentration of **4′** fell less rapidly, corresponding to a tendency for the order with respect to monomer to become greater than zero. [d] This experiment was performed with the (−) enantiomer; the others with (±) monomer. The four points, when plotted as $1/k_1$ *vs.* $1/[M]_0$, fall on a single straight line. [e] Extrapolated to $1/[M]_0 = 0$.



5 $R^1 = CMe_3$, $OR^2 = OCMe_3$
5″ $R^1 = CMe_2Ph$, $OR^2 = OCMe(CF_3)_2$



poly-2 poly-1
6 $R^1 = CMe_2Ph$, $OR^2 = OCMe(CF_3)_2$



7 $R^1 = CMe_2Ph$, $OR^2 = OCMe(CF_3)_2$

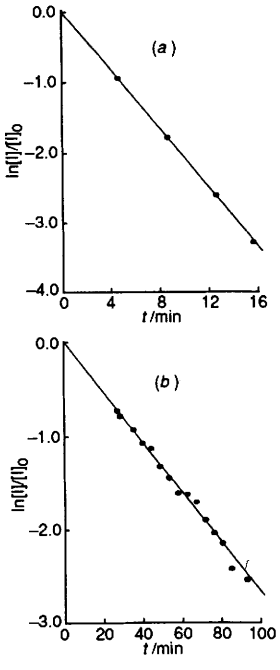


Fig. 1 First-order decay of I (**4**) in system I(*a*) and III(*b*) (see Table 1). The time-scales have been chosen such that $\ln[I]/[I]_0 = 0$ at $t = 0$. [M] decreased by a factor of 4.5 in the time range 4–15 min for system I and by a factor of 40 in the time range 27–92 min for system III.

reactive hexafluoro-*tert*-butoxide initiator **4″** [$R^1 = CMe_2Ph$, $OR^2 = OCMe(CF_3)_2$], the reaction of **1** at room temperature was so fast that it had reacted completely before the first spectrum was obtained (*ca.* 6 min); the subsequent disappearance of **5″** by reaction with **2** to yield **6** could then be followed.

The reaction of **4″** with 1,7,7-trimethylnorbornene **3** is *very* slow. It initially produces **7** and eventually an all-*trans*, all-head–tail polymer which is isotactic when made from (−)-monomer and atactic when made from (±)-monomer. Details will be published elsewhere.[7]

The kinetic results are summarised in Table 1, and, as examples, the first-order plots for the decay of initiating species **4** and **5″** in systems I and III are shown in Fig. 1. For systems I–IV the first-order decay of the initiating complex is maintained while the monomer concentration decreases by a substantial factor, showing that the initiation reaction is zero-order with respect to monomer within the limits indicated. The extent of decrease of monomer concentration varies markedly with the system, being dependent on the rate of the subsequent propagation reaction compared with the rate of initiation. Propagation is very fast for system III, but extremely slow for system V. However, for system V, experiments at different initial monomer concentrations show clearly that the order of the initiation rection with respect to monomer tends to zero as the monomer concentration is increased.

The zero order in this limiting case and in the other systems is accounted for if the rate-controlling step is the conversion of the predominant but inactive *syn* rotamer of **4** into the *anti*-rotamer,[5,6] which then immediately reacts with monomer. In agreement with the observations of Oskam and Schrock,[6] reaction of the *anti*-rotamer of **4** leads exclusively to the formation of a *trans* double bond in the initiation reaction, while for system V the limiting value of $k_1 = 6.1 \times 10^{-5}\ s^{-1}$ at high [M] agrees well with their directly determined value for the rate of conversion of the *syn*-rotamer to the *anti*-rotamer in toluene as solvent ($7 \times 10^{-5}\ s^{-1}$).[6]

For systems III and IV, we were not able to identify the *cis*/*trans* nature of the double bond corresponding to the initiation reaction of **5″** with **2**, and the rate constants k_1 for the systems I–IV cannot be compared directly with any known rate constants. However, they are of the same order of magnitude as would be expected by extrapolation from Schrock's data for related systems. Although the rate of exchange of *syn* and *anti* rotamers is much faster for the complexes with the *tert*-butoxide ligands than for those with the hexafluoro-*tert*-butoxide ligands,[5,6] nevertheless the reaction of monomer **1** is still fast enough in systems I and II for the reaction to be zero-order with respect to monomer. Under the conditions used for system II, this is true only at the beginning of the rection; see footnote *b* of Table 1.

In summary, we have observed, for the first time, a zero-order dependence on monomer concentration of the initiation rection in the polymerisations of substituted norbornenes initiated by Schrock-type molybdenum alkylidenes. This observation is consistent with the earlier hypothesis[5] that reaction proceeds *via* the more reactive *anti* alkylidene rotamer. The agreement between the rate of *syn* → *anti* interconversion determined by Oskam and Schrock for the isolated four-coordinate complexes and that derived from our measurements of initiation rates is remarkable and provides strong evidence in support of the mechanistic hypothesis.

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