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Communication

N-Heterocyclic carbenes (NHC) in olefin metathesis: influence of the NHC-ligands on polymer tacticity

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Abstract

Various well-defined ruthenium alkylidene complexes bearing *N*-heterocyclic carbene ligands were used for the ring-opening metathesis polymerization of 7-methylnorbornene and 7-methylnorbornadiene. The influence of the ligands on the tacticity of the resulting polymers was examined and compared with polymers obtained using the Grubbs' catalyst. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The olefin metathesis reaction is a central topic of industrial, as well as academic research due to its great synthetic usefulness [1,2]. Probably the most thoroughly investigated olefin metathesis reaction is the ring-opening metathesis polymerization (ROMP) [3,4]. The discovery of the ruthenium alkylidene complex **1** by Grubbs et al. [5], combining high catalytic activity and remarkable tolerance towards polar functional groups, was a breakthrough and has triggered extensive research activities in this field [4] (Fig. 1).

The substitution of phosphine ligands by *N*-heterocyclic carbenes (NHC) [6] represents a remarkable improvement with respect to the catalytic activity [7–9]. However, it is well known that the final physical properties of any given polymer depend strongly not only on its molecular weight and polydispersity, but also on the microstructure of the polymer, e.g. especially tacticity (Scheme 1).

Herein, we report a comparative study on the influence of the NHC-ligands of the catalysts **2**–**4** on the tacticity of poly(7-methylnorbornene) [poly(7-MeNBE)] and poly(7-methylnorbornadiene) [poly(7-MeNBD)].

2. Results and discussion

Tacticity arises in ROMP polymers formed from norbornene and its derivatives as a result of the relative orientation of the cyclopentyl rings which form the main polymer chain (Scheme 1), and its determination and mechanistic significance has been the subject of numerous studies in recent years [1]. Most of the ground work has been carried out using classical

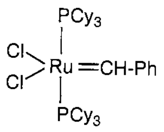

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Fig. 1. Grubbs' catalyst.

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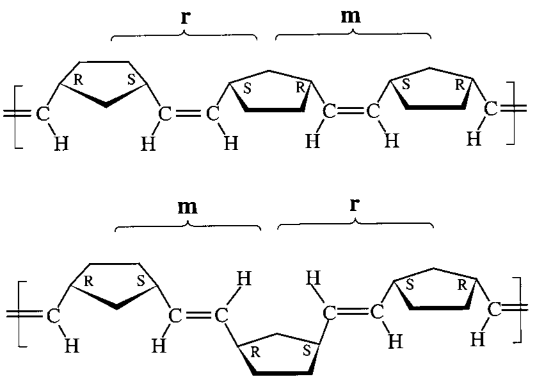
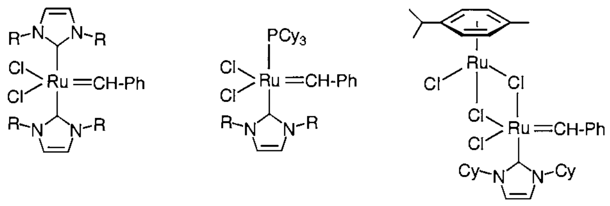


Scheme 1.



2a: R = Cyclohexyl
2b: R = *R*-NaphEt
2c: R = *R*-CyEt
3a: R = Cyclohexyl
3b: R = *R*-PhEt
4

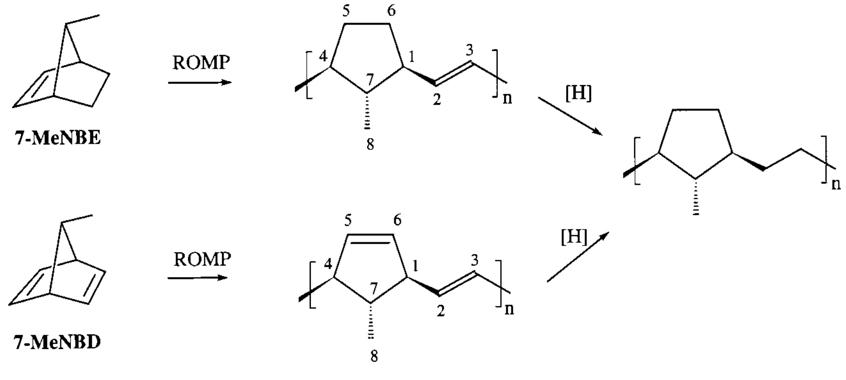
Fig. 2. Ruthenium alkylidene complexes bearing *N*-heterocyclic carbenes; CyEt = CH(Cy)Me; NaphEt = CH(Naphthyl)Me; PhEt = CH(Ph)Me.

metathesis catalysts where the active catalytic species is formed in situ by a reaction between a transition metal salt and a cocatalyst, which may in some cases be the monomer molecule itself. In contrast to the present catalysts, these are poorly defined and there is little opportunity to vary their structure systematically; nevertheless they have been used successfully for the polymerization of a number of key monomers [10] and a wide range of polymer microstructures have been identified providing a firm basis for studying the behavior of better defined catalysts such as those currently under consideration.

With regard to tacticity determination, the most important of these monomers are the 7-methyl derivatives of norbornene [11] and norbornadiene [12] (Scheme 2). Certain signals in the ^{13}C-NMR spectra of the polymers formed show fine structures assignable to the tacticity of dyad units embracing both *cis* and *trans* double bonds, an important feature because almost invariably, for all polymers, these units have different tacticities associated with them. In addition the polymers are easily hydrogenated and so tacticity assignments may be checked further and compared directly (Scheme 2) as the main line splitting in the spectra of the hydrogenated materials is due only to *m* (*iso*tactic) and *r* (*syndio*tactic) effects.

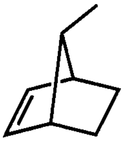
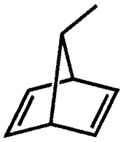
The analysis is also facilitated by the fact that only the *anti* isomer reacts in the case of the monoene [11] (an equimolar mixture of *syn* and *anti* isomers) and that reaction is exclusively at the *anti* face in the diene [12]. This is in contrast to the fact that the formation of *cis* and *trans* units is rather unselective (Table 1), which implies that the propagating species are highly reactive in spite of the bulk of the permanent ligands. The regioselectivity must therefore have its origins in the relative energetics of forming *syn* and *anti* metallacycles for the *cis* and *trans* units. The interaction of the *syn* methyl group with the *exo* face of the diene or monoene is therefore an important adverse feature which is also evident in the polymerization of the 7-^{t}butyl ether of norbornadiene using the Grubbs' catalyst, where only *anti* attack is observed. Though the use of certain other catalysts gives polymers with comparable proportions of *syn* and *anti* units [13] attributable to the lone pair of electrons on the proximate oxygen atom promoting *syn* attack in spite of steric hindrance.

We have made a number of observations with respect to tacticity from our analysis of the ^{13}C-NMR spectra of the polymers. For example, the *cis* and *trans* junctions in polymers formed from 7-MeNBE (a typical example of a ^{13}C-NMR spectrum is shown in Figs. 2 and 3) have a different tactic bias. i.e. *cis* junctions are predominantly isotactic and *trans* predominantly syndio-



Scheme 2.

Table 1
Polymerization of 7-methylnorbornene and 7-methylnorbornadiene using a variety of well-defined Ru-based catalysts

Catalyst	Monomer			
				
	σ_{c} [a]	Tacticity [b]	σ_{c} [a]	Tacticity [b]
2a	0.34	*Iso/cis* *Syndio/trans*	0.48	*Syndio/cis* Atactic/*trans*
2b [c]	0.55	*Iso/cis* *Syndio/trans*	–	–
2c [c]	0.56	*Iso/cis* *Syndio/trans*	0.70	[d]
3a	0.44	*Iso/cis* *Syndio/trans*	–	–
3b [c]	0.44 [e]	*Iso/cis* *Syndio/trans*	0.53	*Syndio/cis* Atactic/*trans*
3b [c]	0.50 [f]	*Iso/cis* *Syndio/trans*	–	–
4	0.44	*Iso/cis* *Syndio/trans*	–	–
1	0.2	*Iso/cis* *Iso/trans*	0.29	*Syndio/cis* *Syndio/trans*

[a] The fraction of *cis* double bonds.

[b] This only implies tacticity bias.

[c] Substituents on the ring nitrogen atoms are chiral.

[d] Insufficient polymer for tacticity analysis.

[e] Reaction carried out at room temperature.

[f] Reaction carried out initially at −20°C and then at room temperature.

tactic; this is maintained using both the bis(NHC) complexes and the mixed phosphane/NHC complexes. The presence of a chiral environment at the metal center has no significant effect on tacticity.

However, when the analogous tricyclohexylphosphine Grubbs' compound is used, the *trans* junctions are now isotactic without any significant change in the tacticity of the *cis* junctions. For comparison, the olefinic region of the spectrum of this polymer is shown in the inset of Fig. 3. Catalyst dependent variations in tacticity are encountered frequently when using classical systems [1], but to our knowledge this is only the second example of a metathesis polymerization where a single ligand substitution in a well-defined initiator has produced such an effect [14].

Recent studies have shown that, for a given catalyst, tacticity may also be highly dependent on the type of monomer [15] and a comparison of the tacticity of poly(7-MeNBE) and poly(7-MeNBD) (Table 1), shows that this is also the case here. The ^{13}C-NMR spectra of two polymers of 7-MeNBD, formed using the same catalysts as for 7-MeNBE (Table 1), shows that there are now more syndiotactic *cis* junctions and fewer syndiotactic *trans* junctions so that the polymers are now essentially syndiotactic *cis* and atactic *trans*. The spectrum of one of these polymers is shown in Fig. 4(a) and the spectrum of an atactic polymer made using WCl_6/Me_4Sn is also shown (Fig. 4(b)), to illustrate how tacticity effects the complex C^7 signal; this latter polymer has a similar *cis* content but the *cis* junctions are now atactic. Similar changes in tacticity from monene to diene monomer are also observed when the Grubbs' catalyst is used (Table 1).

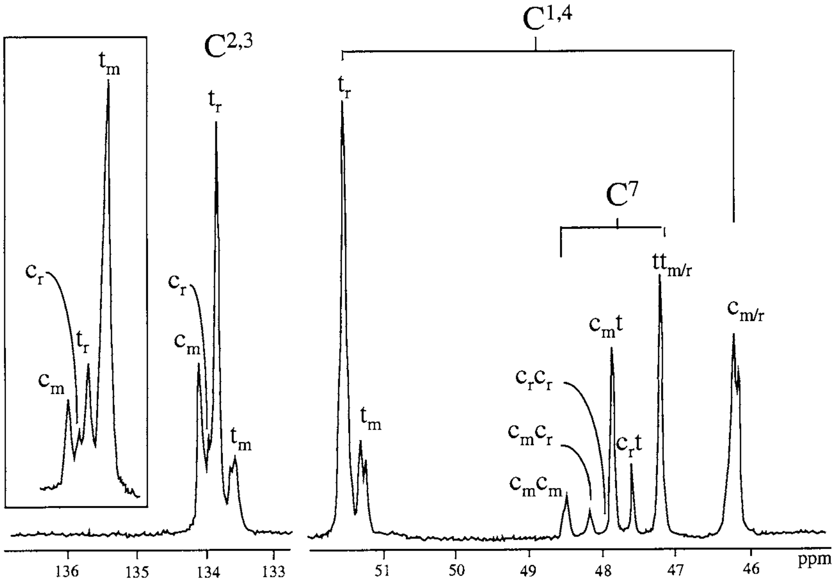


Fig. 3. C^7, $C^{1,4}$ and $C^{2,3}$ signals in the ^{13}C-NMR spectrum of poly(7-methylnorbornene) prepared using **2a** as the catalyst, showing a syndiotactic (*r*) bias on the *trans* junctions and an isotactic (*m*) bias on the *cis* junctions; inset, the $C^{2,3}$ region of the same polymer prepared using **1** as catalyst.

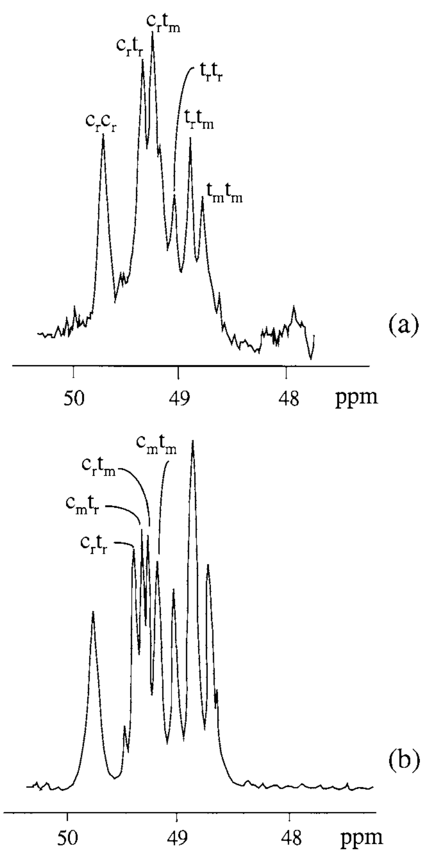
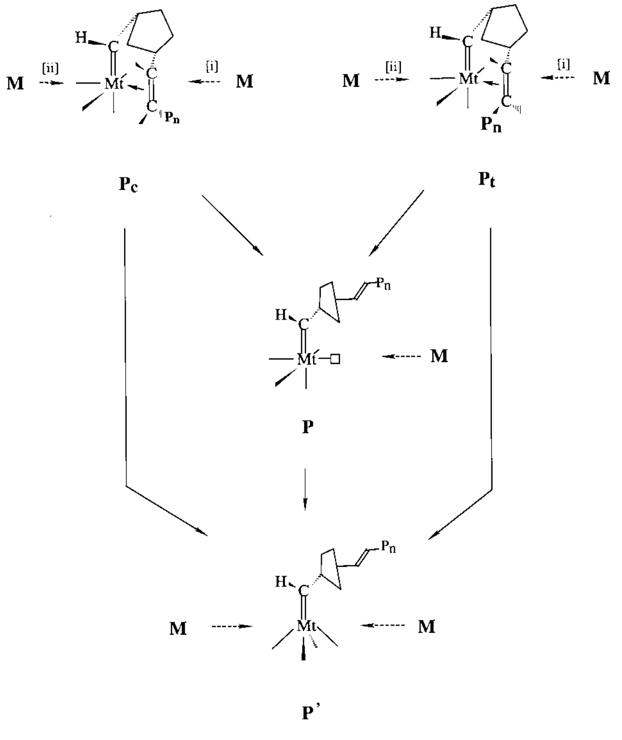


Fig. 4. C^7 region of the ^{13}C-NMR spectra of poly(7-MeNBD); (a) prepared using **2a** as catalyst showing a syndiotactic (*r*) bias on the *cis* junctions and atactic *trans* junctions; and (b) an atactic polymer prepared using a WCl_6/Me_4Sn catalyst.

Early microstructural studies on ROMP polymers led to a theory which postulated the existence of kinetically different propagating metallacarbenes because it was necessary to explain both the blocky distribution of *cis* and *trans* double bonds (found with many high *cis* content polymers) and the different tacticities frequently associated with each type of double bond [1]. This theory provides a rationale for the present observations. On the assumption that the monomer always reacts at the *exo* face, the central tenet of the theory is that the outcome of a given propagation event is influenced by the previous propagation event. Whether the last formed double bond is *cis* or *trans* and whether it is still in the coordination sphere of the metal as the latter encounters the next monomer, is of primary importance to the theory. Two basic propagating species, P_{c} and P_{t}, are then postulated (Scheme 3). P_{c} and P_{t} may relax to P, and directly or sequentially to the symmetrical P' before propagation. P_{c}, P_{t} and P are chiral by virtue of their octahedral geometry, with the plane of the alkylidene moiety at right angles to the line of approach of the monomer, i.e. the horizontal axis ([i] in Scheme 3). If rotation about the Mt=C bond is slow compared with the rate of propagation, the chiral identity of the propagating species is maintained between propagation steps and the formation of *cis* syndiotactic junctions and *trans* isotactic junctions, which was observed with a number of catalysts, is therefore rationalized [1].

However with other catalysts *cis* junctions were syndiotactic but *trans* junctions were atactic, so it was reasoned that in these cases P_{t}, less accessible to incoming monomer than P_{c} by virtue of the coordinated *trans* double bond, was not a chain carrier. Relaxation of P_{t} to the less crowded P and thus to the symmetrical P', where monomer attack from both prochiral faces of the alkylidene moiety is equally probable (Scheme 3), gave rise to atactic *trans* junctions in the same chain as the syndiotactic *cis* junctions formed using P_{c}. Propagation by P_{c}, P_{t} etc. also accounted for the observed blocky distribution of *cis* and *trans* double bonds.

With the present catalysts the same basic rules apply, but it is now necessary to invoke both P_{t} as a chain carrier, and attack at P_{c} and P_{t} from the side remote from the last formed double bond ([ii] in Scheme 3) in order to explain the observed isotactic *cis* and syndiotactic *trans* junctions. It is also possible that the direction of attack may change for one chain carrier but not for the other with the result that both *cis* and *trans* junctions can have either an isotactic or a syndiotactic bias. This is seen now with poly(7-MeNBD) and poly(7-MeNBE) (Table 1), where the tacticity of the *cis* junctions remains the same, but the tacticity of the *trans* junctions is reversed as one changes from the



Scheme 3.

NHC to the phosphane-type catalyst. Although this five to sixfold coordination and the reverse may apply to the Ru initiators currently under consideration, we are in general postulating $n \rightarrow n+1$ fold coordination in the Tolman cycle where the $(n+1)$ fold species has a chiral metal center.

Another major distinction between the phosphane and NHC-type catalysts is that the *cis* contents, σ_c (Table 1), are much closer to 0.5 for all polymers formed from the latter type of catalyst, including some samples of poly(5,5-dimethylnorbornene) which we have prepared also. We attribute this decreasing *cis*/*trans* selectivity to the higher reactivity of the NHC-based catalysts [7].

3. Experimental

All reactions were performed under nitrogen using standard Schlenk techniques. Nitrogen was purified by passage through columns of BASF R3-11 catalyst and molecular sieves. ^{1}H-NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ at 298 K.

Solvents and monomers were distilled, dried and degassed according to common methods before use. Common reagents were reagent grade and were used without further purification. 7-Methylnorbornene [11] and 7-methylnorbornadiene [12] were synthesized according to literature methods.

Complexes **2**–**4** have been prepared according to the methods published recently in high yields by ligand-exchange from the related triphenylphosphine and tricyclohexylphosphine substituted ruthenium compounds [7,8].

Polymerization reactions were carried out in a small amount of CH_2Cl_2 at room temperature, if not otherwise noted ([monomer]/[catalyst] approx. 100).

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