



# Metathesis co-polymerization as a means of comparing the reactivity of ruthenium initiators in conventional solvents and ionic liquids

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## ABSTRACT

Ring opened metathesis polymerization was carried out on a number of cyclic olefins using  $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}[\text{CH}(\text{Ph})]$  and  $[(\eta^6\text{-}p\text{-cymene})(\text{PCy}_3)\text{RuCl}(=\text{C}=\text{C}=\text{CPh}_2)]\text{OTf}$  in dichloromethane and a range of ionic liquids. Microstructural parameters were determined from the  $^{13}\text{C}$  NMR spectra recorded of the polymers. The findings indicate that an increase in activity of both catalysts can occur in certain ionic liquids systems. It was also observed that the activity of  $[(\eta^6\text{-}p\text{-cymene})(\text{PCy}_3)\text{RuCl}(=\text{C}=\text{C}=\text{CPh}_2)]\text{OTf}$  increases upon addition of an excess of phenol.

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## 1. Introduction

Ionic liquids are currently receiving much attention as an environmentally acceptable alternative to conventional solvents and there has been much interest in carrying out metal catalysed reactions in these solvent systems [1]. To date a number of groups have successfully carried out alkene metathesis reactions and polymerizations catalysed by complexes 1 [2,3], 2 [4,5] and 3 [2,3,6,7] (Fig. 1) in ionic liquids and there is some speculation that catalysts 2 and 3 may be more reactive in these solvents.

The mechanism of ring opening metathesis polymerization involves two steps, an initiation step in which the active catalyst is first formed, and the propagation step in which the polymer is formed. A generalised scheme for the initiation and propagation steps of Grubbs type catalysts is shown in Scheme 1. It is known that the higher reactivity of catalyst 3 arises from the greater activity of the propagating species it forms [8]. The current study sets out to directly probe if the reactivity of the propagating species formed from Catalysts 1 and 2 are altered in unusual solvent systems. In addition the relative reactivity of catalyst 2 compared to catalyst 1, and the ability of phenol to act as a ROMP promoter towards catalyst 2 are also investigated.

One means of investigating the reactivity of a propagating species in a ROMP reaction is to use two monomers of differing reactivity and then investigate the microstructure of the co-polymer

formed [9]. The extent to which the less active monomer is incorporated into the polymer gives a relative indication of the catalyst's reactivity. In order for this type of study to be carried out the experimental conditions must be carefully controlled. The co-polymer must be made at yields of less than 10% in order that the composition and microstructure of the co-polymer can be considered a true reflection of the nature of the initial polymer produced. When using well-defined initiators the polymer is living and as such all the monomers will, at some point, be polymerized. Then the overall composition of the co-polymer will be the same as the amount of monomers in the feedstock and no information about the progress of the co-polymerization can be obtained.

In this paper we investigate, using  $^{13}\text{C}$  NMR spectroscopy, the microstructure of polymers and co-polymers formed using catalysts 1 and 2 in conventional solvents and in ionic liquids. The information that can be derived from this type of analysis is well established and is outlined as follows.

The microstructure of co-polymers formed may be studied by analysing the olefinic region of their  $^{13}\text{C}$  NMR spectra. The integrals of the peaks are taken as a direct representation of the relative abundance of that particular carbon atom in the polymer chain. Although it is unusual to quantify the integrals of the peaks in a  $^{13}\text{C}$  NMR spectrum this has proven to be a reasonable approximation under the conditions used here and is an established practise for ROM polymers [9]. It is possible to work out the following parameters (where  $M_1$  denotes one monomer and  $M_2$  denotes the other):

- $a$ : integral of the peaks in the olefinic region due to  $M_1M_2$ .
- $b$ : integral of the peaks in the olefinic region due to  $cis\ M_1M_1$ .

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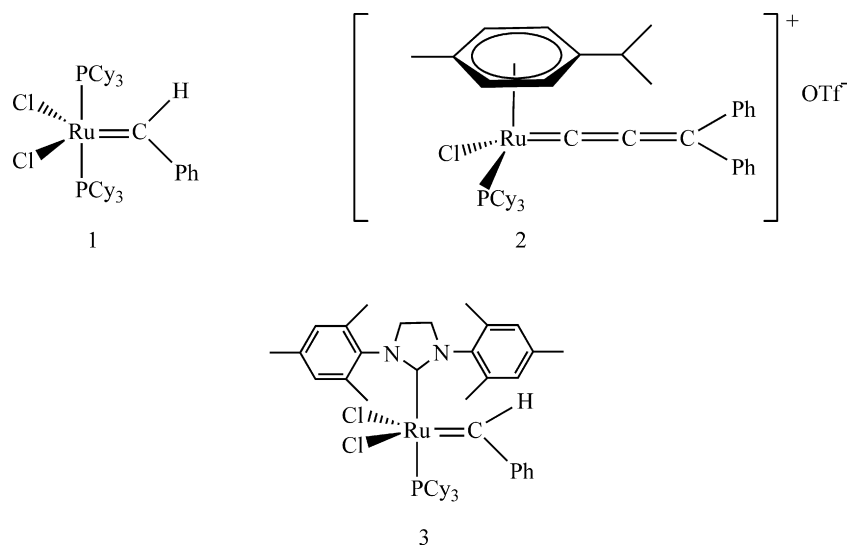


Fig. 1. Ring opening metathesis ruthenium catalysts.

- $c$ : integral of the peaks in the olefinic region due to *trans*  $M_1M_1$ .
- $d$ : integral of the peaks in the olefinic region due to *trans*  $M_2M_2$ .
- $e$ : integral of the peaks in the olefinic region due to *cis*  $M_2M_2$ .
- $f$ : integral of the peaks in the olefinic region due to  $M_2M_1$ .

#### Parameters determined

1.  $f_1$ : mole fraction,  $M_1/M_1 + M_2$ , in the feedstock;  $f_2$ : mole fraction,  $M_2/M_1 + M_2$ , in the feedstock.
2.  $F_1/F_2$ : mole ratio of  $M_1/M_2$  units in the co-polymer:

$$F_1 = \frac{a+b+c}{\sum_{\text{int}}}, \quad F_2 = \frac{d+e+f}{\sum_{\text{int}}} \quad \text{and} \quad 1 - F_1 = F_2$$

#### 3. $\sigma_c$

$$\sigma_c(M_1M_1) = \frac{b}{b+c} \quad \sigma_c(M_2M_2) = \frac{e}{d+e}$$

where  $\sigma_c(M_1M_1)$  gives a measure of the number of  $M_1M_1$  dyads which have *cis* stereochemistry and  $\sigma_c(M_2M_2)$  gives a measure

- of the number of  $M_2M_2$  dyads which have *cis* stereochemistry.
4.  $r_1r_2$ : compositional blockiness parameter

$$r_1r_2 = \frac{(b+c)(d+e)}{af}$$

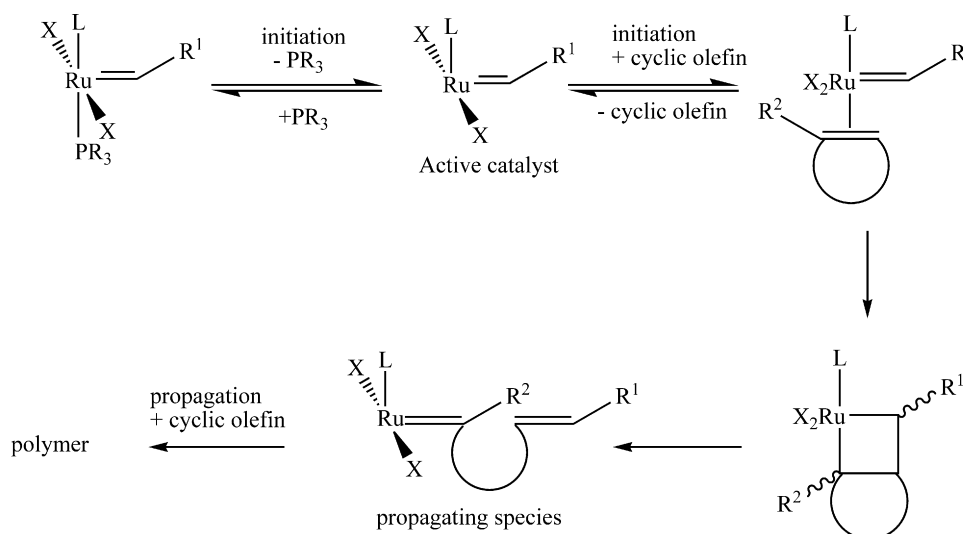
where  $F_1$  gives information about the relative reactivity of  $M_1$  compared to  $M_2$  towards the propagating species.

$r_1r_2 = 1$ , the co-polymer is random,  $r_1r_2 \gg 1$  it is blocky, and alternating when  $r_1r_2 \ll 1$ .

## 2. Experimental

### 2.1. Chemicals

Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (1), ethyl vinyl ether, and phenol were purchased from Aldrich and used as received. Norbornene and cyclopentene were purchased from Aldrich and distilled prior to use. [(*p*-cymene)(PCy<sub>3</sub>)ClRu=C=C=CPh<sub>2</sub>]<sup>+</sup>[OTf]<sup>-</sup> (2) [10], benzonorbornadiene [11], and the ionic liquids [12] were synthesised



Scheme 1. The initiation and propagation steps of a metathesis reaction for a Grubbs-type catalyst.

according to literature procedures. All ionic liquids were dried overnight at 70 °C under vacuum prior to use.

## 2.2. Instrumentation

Broadband proton decoupled  $^{13}\text{C}$  NMR spectra were recorded of the polymers dissolved in  $\text{CDCl}_3$  on a Bruker Avance 300 Spectrometer that operated at 75.5 MHz for  $^{13}\text{C}$ .

## 2.3. General procedure for ROM polymers formed using catalyst 1 and 2

All polymerization reactions were carried out under nitrogen in dried degassed solvent. In all cases the polymerization was quenched upon addition of ethyl vinyl ether and the polymer was precipitated into methanol, separated and washed with methanol. A number of reaction conditions were used to form the co-polymers. However, as the microstructural parameters of the polymers give information about the relative reactivity of the two monomers involved in the co-polymer it is valid to compare the results from the different reactions.

### 2.3.1. Formation of homopolymers in dichloromethane solvent

The monomer (0.5 g) was dissolved in 9  $\text{cm}^3$  (catalyst 1) or 4  $\text{cm}^3$  (catalyst 2) of dichloromethane. The catalyst (0.003 mmol) was dissolved in 1  $\text{cm}^3$  of dichloromethane and transferred via syringe into the solution of the monomer. The solution was stirred at room temperature for 2 h for norbornene (catalysts 1 and 2) and 20 h for cyclopentene (catalyst 1).

### 2.3.2. Formation of co-polymers in dichloromethane solvent

The reaction conditions (Table 1) used in each case were determined on a 'trial and error' basis to determine the conditions required to ensure that the reaction went in lower than 10% yield. In each case the catalyst was dissolved in 1  $\text{cm}^3$  of dichloromethane and added via syringe to a stirred mixture of the two monomers dissolved in dichloromethane. For the co-polymerization of norbornene and cyclopentene using catalyst 2 and phenol as the promoter the reaction was carried out using the conditions given in Table 1, except that phenol (5.3 mmol) was added to the solution of the catalyst before addition to the monomers.

### 2.3.3. Formation of homopolymers in neat ionic liquids

Catalyst 1 (0.012 mmol) was added to 1  $\text{cm}^3$  of an ionic liquid and was stirred for 1 h at 40 °C to dissolve the catalyst. Norbornene (2 mmol) or cyclopentene (5.3 mmol) were added to the solution and stirred at 40 °C for a further hour. The reaction was quenched and the polymer extracted into chloroform.

### 2.3.4. Formation of co-polymers in neat ionic liquids

Catalyst 1 (0.003 mmol) was added to 1  $\text{cm}^3$  of an ionic liquid and was stirred for 1 h at 40 °C to dissolve the catalyst. Norbornene (1.06 mmol) and cyclopentene (4.24 mmol) were mixed with the ionic liquid. The catalyst solution was added to the mixture of the monomers via syringe. The reaction was quenched immediately and the polymer was extracted into chloroform.

**Table 1**  
The reaction conditions used to form co-polymers in dichloromethane.

Catalyst amount (mmol)	Monomer ratios	Temp	Reaction time	Amount of solvent ( $\text{cm}^3$ )
1 (0.006)	Norbornene:benzonorbornadiene (0.70 mmol:2.80 mmol) (1:4)	r.t.	Instantaneous	10
1 (0.003)	Norbornene:cyclopentene (1.06 mmol:4.24 mmol) (1:4)	0 °C	Instantaneous	10
1 (0.003)	Cyclopentene:benzonorbornadiene (0.70 mmol:0.7 mmol) (1:1)	r.t.	19 h	5
2 (0.003)	Norbornene:cyclopentene (1.06 mmol:4.24 mmol) (1:4)	r.t.	1 h	5

**Table 2**

The  $\sigma_c$  values for homopolymers formed using catalyst 1 using a range of solvent systems.

Solvent	Monomer	$\sigma_c$
DCM	Norbornene	0.15
DCM	Cyclopentene	0.14
DCM	Benzonorbornadiene	Not determined as <i>cis</i> and or <i>trans</i> signals overlap with other signals in the $^{13}\text{C}$ NMR
BMIMBF <sub>4</sub> /toluene	Norbornene	0.20
BMIMPF <sub>6</sub> /toluene	Norbornene	0.14
BMIMOTf/toluene	Norbornene	0.15
BMIMBF <sub>4</sub>	Norbornene	0.34
BMIMPF <sub>6</sub>	Norbornene	0.21
BMIMOTf	Norbornene	0.33
BMIMBF <sub>4</sub>	Cyclopentene	0.19
BMIMPF <sub>6</sub>	Cyclopentene	0.19
BMIMOTf	Cyclopentene	0.20

**Table 3**

The  $\sigma_c$  values for polynorbornene formed using catalyst 2 using a range of solvent systems.

Solvent	$\sigma_c$
DCM	0.14
BMIMBF <sub>4</sub> /toluene	0.15
BMIMPF <sub>6</sub> /toluene	0.10
BMIMOTf/toluene	0.29

### 2.3.5. Formation of polynorbornene in biphasic toluene/ionic liquids

Catalyst 1 (0.012 mmol) or 2 (0.0048 mmol) was added to the ionic liquid (1  $\text{cm}^3$ ) held at 40 °C and stirred until it had dissolved. Toluene was added to the ionic liquid (1  $\text{cm}^3$  for catalyst 1 and 4  $\text{cm}^3$  for catalyst 2) and the norbornene (2 mmol) was added to the reaction mixture and stirred for 1 h at 40 °C. The polynorbornene was extracted with toluene.

## 3. Results and discussion

### 3.1. Homopolymerization studies

Homopolymers of norbornene, cyclopentene and benzonorbornadiene were formed using catalyst 1 and polynorbornene was formed using catalyst 2 under a range of conditions and their  $\sigma_c$  values (Tables 2 and 3) were determined by analysis of the  $^{13}\text{C}$  NMR spectra recorded of the polymers. The  $\sigma_c$  values are an indication of the *cis* content of the polymer.

The  $\sigma_c$  values obtained for the all homopolymers formed in dichloromethane for catalysts 1 and 2 (Tables 2 and 3) are low, indicating that both 1 and 2 are *trans* directing. This confirms previous results obtained on 1 by Rooney and co-workers [13], and on 2 by Dixneuf and co-workers [5]. This is in contrast to catalyst 3 (Fig. 1) which has previously been shown to be *cis* directing [13]. It has previously been proposed that if a ring opened metathesis polymer is formed with a high concentration of *cis* units then the propagating species is very reactive, whereas a low concentration of *cis* units is indicative of a propagating species with lower reactivity [13]. This

proposal is in agreement with the literature as previous mechanistic studies have shown that the higher activity of catalyst 3 over 1 is based on its increased ability to propagate [8]. Here we have determined that catalyst 2 also has a low ability to propagate. In fact our studies show that catalyst 2 has a lower reactivity than catalyst 1. This is shown by the fact that under room temperature conditions in dichloromethane we were unable to form a homopolymer of cyclopentene using 2 whereas catalyst 1 forms polycyclopentene quantitatively. We propose that the inability of catalyst 2 to polymerize cyclopentene is associated with the low reactivity of the initiation metallacarbene and also of propagating species formed with this monomer. This proposal is supported by the information obtained from the co-polymerization studies.

Catalyst 1 polymerized norbornene in three ionic liquids containing the BMIM<sup>+</sup> (1-butyl-3-methylimidazolium) cation and the BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and OTf<sup>-</sup> anion under biphasic conditions using toluene as the other solvent and using the neat ionic liquid. Under both sets of conditions it was found that the lowest yield of polymer was recovered using BMIMPF<sub>6</sub>. The lowest yield of polymer was also obtained from this solvent using catalyst 2 under biphasic conditions. These findings are consistent with previous studies carried out by Dixneuf and co-workers who found that BMIMPF<sub>6</sub> was a poor solvent for a different metathesis reaction catalysed using 2 [4] and may simply be due to catalyst decomposition. During the course of this study we investigated the stability of catalyst 1 in ionic liquids by monitoring changes in the UV/vis spectrum of the solution of the catalyst held at room temperature as a function of time. It was observed that after 1 h catalyst 1 had decomposed in BMIMPF<sub>6</sub> whereas it was stable in BMIMBF<sub>4</sub> over the same time period. This decomposition may arise due to trace impurities in the BMIMPF<sub>6</sub> ionic liquid. The  $\sigma_c$  values for polynorbornene show similar values for catalyst 1 using dichloromethane and a biphasic ionic liquid system. This indicates that there is little change in the propagating species under these two sets of conditions. This may suggest that the catalyst was not held in the ionic liquid during the reaction and that homogeneous catalysis was actually taking place in the toluene solution. For catalyst 2 which is ionic and is known to remain in the ionic liquids; effective recycling of the catalyst has been achieved under biphasic conditions [5]. The most significant change in  $\sigma_c$  values was observed when using BMIMOTf/toluene which produced polynorbornene with a  $\sigma_c$  value of 0.29 compared to 0.14 for DCM. This finding complements the study carried out by Dixneuf and co-workers on a ring closing metathesis reaction of the diene diallyltosylamide which showed that the highest yield of product was formed using catalyst 2 with the triflate anion [4]. In our studies catalyst 2 contains a triflate anion but will undergo anion exchange in the BMIMBF<sub>4</sub> and BMIMPF<sub>6</sub>. The present study gives further evidence that the nature of the anion is important in the catalytic activity of 2 and again we observe a relationship for a Ru catalyst which forms a propagating species which is more *cis* directing with an increase in its overall catalytic activity.

It would appear that the propagating species formed from 1 is more reactive in the ionic liquids than in a conventional solvent. Polynorbornene formed using catalyst 1 in each of the neat ionic liquids showed an increase in its *cis* content ( $\sigma_c = 0.34, 0.21, 0.33$

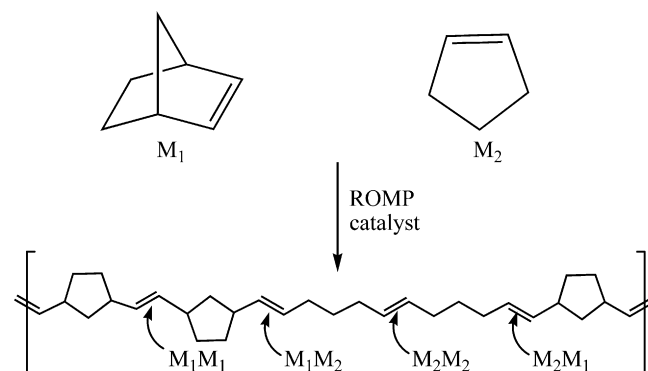


Fig. 2. The four possible types of olefin units in a co-polymer formed using norbornene and cyclopentene.

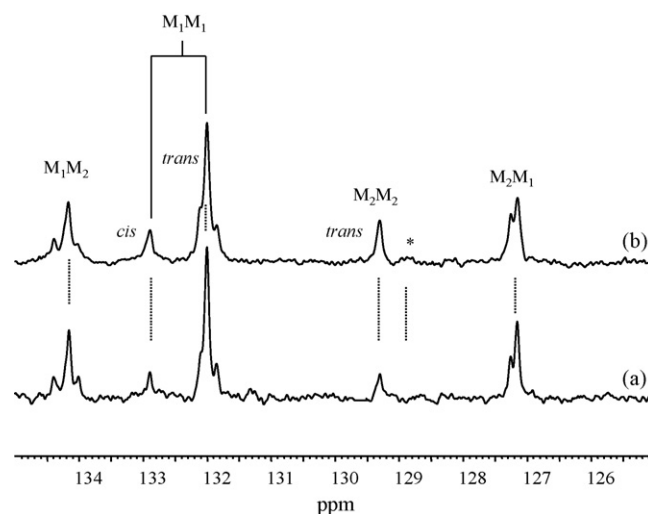


Fig. 3. Olefinic region of the <sup>13</sup>C NMR spectrum recorded of the co-polymer formed from norbornene (M<sub>1</sub>) and cyclopentene (M<sub>2</sub>) using catalyst 1 in (a) dichloromethane and (b) BMIMOTf. \* *cis* M<sub>2</sub>M<sub>2</sub> signal cannot be distinguished from the noise in the spectra.

for BMIMX X = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and OTf<sup>-</sup>, respectively) compared to the polymer formed in dichloromethane ( $\sigma_c = 0.15$ ).

### 3.2. Co-polymerization studies

Co-polymers were formed using catalyst 1 under a range of conditions and their  $r_1r_2$  and  $F_1$  values (Table 4) were determined by analysis of the <sup>13</sup>C NMR spectra recorded of the polymers. Fig. 2 shows the number of positions that the two monomers can adopt in a co-polymer and Fig. 3 shows the olefinic region of the <sup>13</sup>C NMR spectra for the norbornene (M<sub>1</sub>)/cyclopentene (M<sub>2</sub>) co-polymer formed using catalyst 1 in dichloromethane (a) and BMIMOTf (b). The  $r_1r_2$  values are an indication of whether the co-polymer is random, alternating or blocky. The  $F_1$  value quantifies the amount of

Table 4

The  $r_1r_2$  and  $F_1$  values for co-polymers formed using catalyst 1 in a range of solvent systems.

Solvent	Monomers	$r_1r_2$	$f_1$	$F_1$
DCM	Norbornene (M <sub>1</sub> )/benzonorbornadiene (M <sub>2</sub> )	0.83	0.20	0.57
DCM	Norbornene (M <sub>1</sub> )/cyclopentene (M <sub>2</sub> )	0.40	0.20	0.73
DCM	Cyclopentene (M <sub>1</sub> )/benzonorbornadiene (M <sub>2</sub> )	0.25	0.50	0.50
BMIMBF <sub>4</sub>	Norbornene (M <sub>1</sub> )/cyclopentene (M <sub>2</sub> )	0.50	0.20	0.65
BMIMPF <sub>6</sub>	Norbornene (M <sub>1</sub> )/cyclopentene (M <sub>2</sub> )	0.75	0.20	0.66
BMIMOTf	Norbornene (M <sub>1</sub> )/cyclopentene (M <sub>2</sub> )	0.94	0.20	0.72

**Table 5**

The  $r_1 r_2$  and  $F_1$  values for norbornene/cyclopentene co-polymers formed using catalyst 2 with and without the addition of phenol.

Solvent	Monomers	$r_1 r_2$	$f_1$	$F_1$
DCM	Norbornene ( $M_1$ )/cyclopentene ( $M_2$ )	0.24	0.20	0.65
DCM/phenol	Norbornene ( $M_1$ )/cyclopentene ( $M_2$ )	0.52	0.20	0.67

incorporation of monomer  $M_1$  into the co-polymer compared to the feed ratio  $f_1$ .

The co-polymerization studies carried out using 1 in dichloromethane show some interesting findings. The  $F_1$  values obtained for the three co-polymers formed indicate that as is expected norbornene is more reactive than both cyclopentene and benzonorbornadiene, while when they are in direct competition for the propagating species the latter two monomers are about equal in their reactivity ( $F_1$  is equal to  $f_1$  in the case of the cyclopentene/benzonorbornadiene co-polymer). Therefore in terms of its overall relative reactivity towards the metathesis reaction it would appear that the higher steric hindrance associated with the bulky benzonorbornadiene is offset by its increased ring strain compared to cyclopentene. However, more information about the relative reactivity of the propagating species formed upon incorporation of each of the three monomers is obtained from the  $r_1 r_2$  values and is discussed below.

The  $r_1 r_2$  values for both norbornene/cyclopentene co-polymers is substantially less than 1 (0.40 for catalyst 1 (Table 4) and 0.24 for catalyst 2 (Table 5) in dichloromethane) indicating that the polymers are mainly alternating and that the alternating nature of the co-polymer is greater for the polymer formed from catalyst 2. The alternating nature is indicative of the low reactivity of the propagating species formed with both catalysts and the cyclopentene monomer. In essence what is occurring is that when a cyclopentene monomer undergoes metathesis the propagating species formed has such low reactivity that it strongly favours reaction with the more reactive norbornene monomer. This finding is in contrast to the  $r_1 r_2$  value of 0.83 determined for the co-polymer formed from norbornene/benzonorbornadiene indicating that the co-polymer has a random incorporation of the two possible monomer units. This shows that when both possible monomers form reactive propagating species there is little discrimination between the next possible unit incorporated into the polymer. Therefore the relative reactivity of the monomer units towards polymerization as determined from the  $F_1$  values obtained from the co-polymers formed using catalyst 1 indicate that norbornene > benzonorbornadiene ~ cyclopentene. However, the order of the reactivity of the propagating species P formed from catalyst 1 is that  $P_{\text{norbornene}}$  and  $P_{\text{benzonorbornadiene}}$  are highly reactive, while  $P_{\text{cyclopentene}}$  has a lower reactivity.

Strikingly, the co-polymer formed from norbornene/cyclopentene in BMIMOTf has a  $r_1 r_2$  value of 0.94 indicating that there is a random incorporation of the two monomer species. Whereas the  $r_1 r_2$  value for the same polymer formed in dichloromethane is 0.40, indicating that the polymer is tending towards an alternating structure. In contrast, as would be expected, the  $F_1$  values for the two polymers are the same indicating that overall the relative reactivity of the two monomers towards the propagating species is unchanged. Previous studies on the metathesis of 1-octene indicate that 1 shows a slightly enhanced stability and reactivity when the reaction is carried out in an ionic liquid [3]. Here we can show that this increase in reactivity does exist for catalyst 1. We would propose that the origin of this increased reactivity occurs because the viscous nature of the ionic liquid lowers the rate at which the propagating species can relax into a more stable conformation. It has previously been proposed that the lower reactivity of the  $P_{\text{cyclopentene}}$  over the  $P_{\text{norbornene}}$

species is due to its greater flexibility so it can relax more quickly into more stable conformers [13]. A theoretical study on catalyst 3 has highlighted the importance of inactive and active alkylidene conformers of the reaction intermediates in determining the reactivity of the catalyst [14]. Our study gives experimental support for this study. The more flexible propagating species is the least reactive of the species studied however, its reactivity increases when it is formed in a more viscous medium and reaction with the incoming monomer competes more favourably with conformational relaxation.

### 3.3. Co-polymerization using catalyst 2 and a phenol promoter

Co-polymers of norbornene and cyclopentene were formed using catalyst 2 in dichloromethane solution with and without the addition of phenol.  $F_1$  and  $r_1 r_2$  values (Table 5) were determined by analysis of the  $^{13}\text{C}$  NMR spectra recorded of the polymers.

Previous studies by Rooney and co-workers have shown that the ROMP catalytic activity of 1 is increased by the addition of phenol to the solvent [15]. A detailed study on the effect of added phenol to the catalytic activity of catalyst 1 toward self-metathesis and cross-metathesis carried out by Forman and co-workers indicates that the phenol interacts with 1 through a  $\text{PhO}\cdots\text{Cl}\cdots\text{Ru}$  interaction [16]. Phenol plays a number of roles in the metathesis cycle including lowering the rate of phosphine loss and addition and promoting the formation of the metallacyclobutane. Catalyst 2 also contains a Ru–Cl moiety and may be expected to have its activity promoted upon addition of phenol as well. Preliminary studies are reported here which show that this is the case. The co-polymerization of norbornene/cyclopentene was carried out in dichloromethane and in dichloromethane containing 5.3 mmol phenol as outlined in Section 2.3.2. In the first instance it took 1 h in order to achieve a 10% yield of polymer whereas upon addition of phenol the same yield was obtained in 10 min. Examination of the microstructure of the polymer showed that the alternating nature of the polymer was decreased upon addition of phenol with  $r_1 r_2$  having a value of 0.24 in dichloromethane and a value of 0.52 in phenol/dichloromethane solvent. This is a clear indication, as proposed by Forman and co-workers for the catalyst 1 system, that one of the roles that the phenol plays is to promote the formation of the metallacyclobutane [16]. As it indicates that the less reactive propagating species formed using the cyclopentene monomer increases its reactivity in this solvent system and therefore there is less discrimination between the more reactive monomer (norbornene) and cyclopentene as the incoming unit.

## 4. Conclusions

1. The determination of the microstructure of co-polymers gives information about the relative reactivity of the propagating species (P) in ROMP. For catalyst 1 our studies show that the propagating species formed from norbornene and benzonorbornadiene are more reactive than that formed from cyclopentene. It is proposed that the low reactivity of the  $P_{\text{cyclopentene}}$  species arises from its conformational flexibility enabling it to quickly relax into stable forms.
2. The studies on catalyst 1 in ionic liquids show that the reactivity is only increased in a neat ionic liquid. No such increase is observed under biphasic conditions, indicating that, under the latter conditions, the catalysis is occurring in the organic solvent phase. For catalyst 2 an increase in activity of the catalyst was observed in the BMIMOTf/toluene system.
3. Preliminary studies show that the activity of catalyst 2 is increased upon addition of phenol to the reaction mixture. There is interest in enhancing the activity of catalyst 2 and studies have



shown that this catalyst forms an indenylidene species which is a highly active ROM catalyst, upon addition of a strong acid [17,18]. Phenol would not react with 2 in this manner so the basis of the enhanced reactivity of 2 shown here must be due to an alternative mechanism. Further studies are underway to investigate the degree of enhancement and the mechanism of phenol promotion for catalyst 2.

4. Our studies have shown that it is possible to directly probe the reactivity of the propagating species formed in an ionic liquid. Currently there is an interest in developing tagged ruthenium ROM catalysts for anchoring in an ionic liquid [19–21]. Studies of the type outlined here would be an ideal means to investigate the reactivity of these catalysts and the influence of the nature of the ionic liquid or impurities associated with the ionic liquids on the activity of the propagating species.

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