

# Ring-Opening Metathesis Polymerization of Cyclohexenyl Norbornene in Air and Protic Media Using Ruthenium-Based Catalysts

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**ABSTRACT:** Optimized ring-opening metathesis polymerization (ROMP) conditions for cyclohexenyl norbornene (CHNB) have been determined. ROMP of CHNB was carried out with ruthenium trichloride hydrate and ruthenium benzylidene catalysts. The effects of mol % catalyst, type of catalyst, use of a dissolution aid (for  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ ), reaction time and temperature on conversion and gel time were investigated. ROMP with 0.0027 mol % ruthenium benzylidene at room temperature gave CHNB conversions ranging from 97 to 99% with gel times of ca. 24 min. With ruthenium trichloride hydrate and using ethanol as a dissolution aid, only 60–80% conversions with gel times of ca. 43 min occurred at 55–60°C. The obtained polyCHNB's were crosslinked or not, depending on ROMP conditions. All polyCHNB' exhibited 5% weight loss at ca. 420 and 430°C under nitrogen and air atmospheres, respectively. The DSC measured glass transition temperature of all polyCHNB samples was 105°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 183–190, 1998

**Key words:** ring-opening polymerization; ROMP; poly(cyclohexenyl norbornene); ruthenium trichloride hydrate; ruthenium benzylidene

## INTRODUCTION

The ultimate goal of this project is to explore approaches to inexpensive hydrocarbon matrix composites combining the unique features of ROMP of cycloolefins with the excellent properties of the polymer produced. Hydrocarbon polymers are good alternatives for use as composite matrices due to low dielectric constants, excellent chemical resistance, and hydrophobicity. With respect to optimum property performance in composites, very high conversion and controllable gel times to allow resins to infuse the reinforced shape completely are required.

Organometallic catalysts are often inactivated by

oxygen, water, and heteroatom-containing substances.<sup>1</sup> These limitations were recently overcome with new ROMP catalysts,  $\text{RuCl}_3(\text{hydrate})$  and  $\text{OsCl}_3(\text{hydrate})$ , in the polymerization of 7-oxanorbornene derivatives.<sup>2</sup> This discovery has generated much interest in polymerizations of cycloolefins using ruthenium-based catalysts. Our main effort is toward glass fiber-reinforced composites where water absorption on the glass surface is deleterious to interphase properties and catalyst activity. As a result, the choice of ROMP catalyst is limited, and only moisture- and oxygen-tolerant catalysts can be used. A new catalyst, ruthenium benzylidene ( $\text{RuCl}_2(\text{Bis}(\text{tricyclohexyl phosphine})\text{benzylidene ruthenium(IV) dichloride}) (= \text{CHPh})(\text{PCy}_3)_2$ , **1**) exhibits remarkable stability toward oxygen and moisture, and is conveniently prepared in high yields in a one-pot reaction.<sup>3,4</sup> Here we report results of an investigation of reaction variables on CHNB

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conversion and gel time using **1** and ruthenium trichloride hydrate ( $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$ ), **2**, a readily available and inexpensive alternative.

## EXPERIMENTAL

Cyclohexenyl norbornene (**3**, CHNB, 81–88% endo isomer) was provided by Shell Chemical Co., USA, and used without further purification. Ruthenium trichloride hydrate ( $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$ ), chlorobenzene, ethanol, and 5-norbornene-2-methanol were purchased from Aldrich and used as received. The ruthenium benzylidene catalyst,  $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ , was supplied by Mark Watson and Dr. K. B. Wagener at the University of Florida, Gainesville, FL.

### Polymerizations

#### With $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$

In a 20-mL vial equipped with a septum, 2 vol % (based on CHNB) 5-norbornene-2-methanol (**4**) or ethanol was added to ruthenium trichloride hydrate (varied from 0.0003 g,  $1.45 \times 10^{-6}$  mol, to 0.02 g,  $9.64 \times 10^{-5}$  mol). After the catalyst was completely dissolved, 2 vol % chlorobenzene and CHNB (varied from 1 mL, 0.0055 mol, to 3 mL, 0.017 mol) were injected into the vial. The monomer mixture was nitrogen-purged for 1 min and then placed in a 55 or 80°C oil bath, depending on the ROMP conditions used. The bulk polymerization was continued for a specific time, i.e., from 1 to 72 h. Crude products were light- to dark-green and rubbery or stiff, depending on conditions. Two methods of evaluating CHNB conversion were used; i.e., bulk gravimetric (total yield) or thermogravimetric analysis (TGA, relative yield).

#### With $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$

Ruthenium benzylidene (varied from 0.0002 g,  $2.43 \times 10^{-7}$  mol, to 0.001 g,  $1.22 \times 10^{-6}$  mol) was added to neat CHNB monomer (varied from 1 mL, 0.0055 mol, to 3 mL, 0.017 mol) in a 20-mL vial equipped with a septum. Nitrogen was bubbled through the CHNB mixture for 1 min, then it was placed in the 45°C oil bath or held at room temperature, depending on the conditions. CHNB was bulk polymerized for a specific time, i.e., from 1 to 72 h. Crude products appeared as colorless and soft rubbery or light purple-pink stiff and glassy

materials depending on ROMP conditions used. Conversion was again evaluated using gravimetric or thermogravimetric analysis.

### Methods of Evaluating Conversions of PolyCHNBs Formed with Both Catalysts

#### For Gravimetric Analysis

In each set of experiments, several CHNB mixtures were prepared under the same conditions in separate reaction vials. When the desired reaction times were reached, vials were taken out, and the crude polymer products were then dissolved in chloroform containing 1 wt % 2,6-di-*tert*-butyl-4-methylphenol (BHT) as antioxidant. The polymer solutions were precipitated into acetone to remove residual monomer. The precipitates were vacuum-dried at 50°C for 24 h. The conversions were evaluated using the following equation:

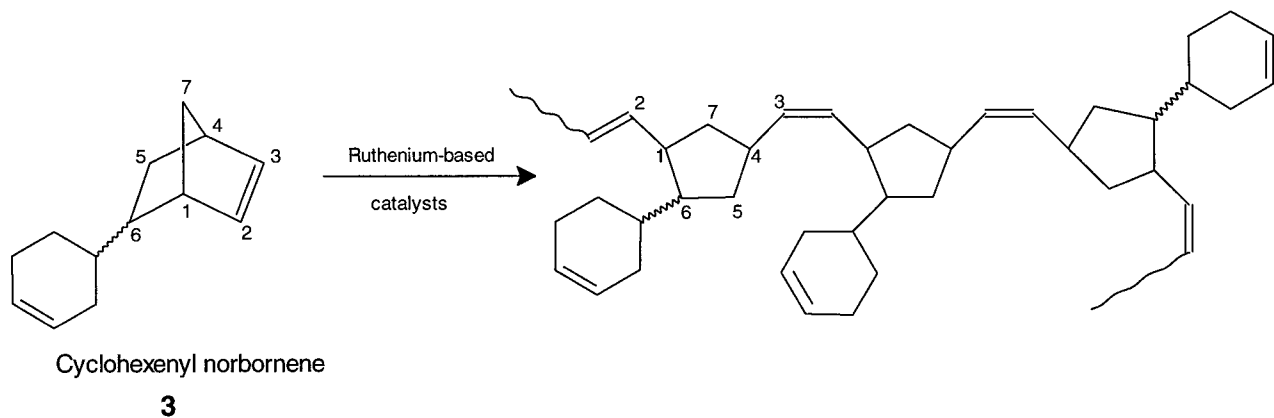
$$\% \text{ conversion} = \frac{\text{weight of dried polyCHNB}}{\text{original weight of CHNB}} \times 100$$

#### For Thermogravimetric Analysis (TGA)

For each experiment, CHNB was polymerized in one vial and small aliquots were removed with a spatula when the desired reaction times were reached. TGA was used to measure the weight loss of CHNB monomer during heating; this occurred at ca. 250°C, while the polymer was stable until ca. 410°C. From the initial and second plateaus in the TGA trace, a percent conversion was calculated by subtracting the wt % of lost monomer from 100% total crude product giving the percent conversion.

### Characterization

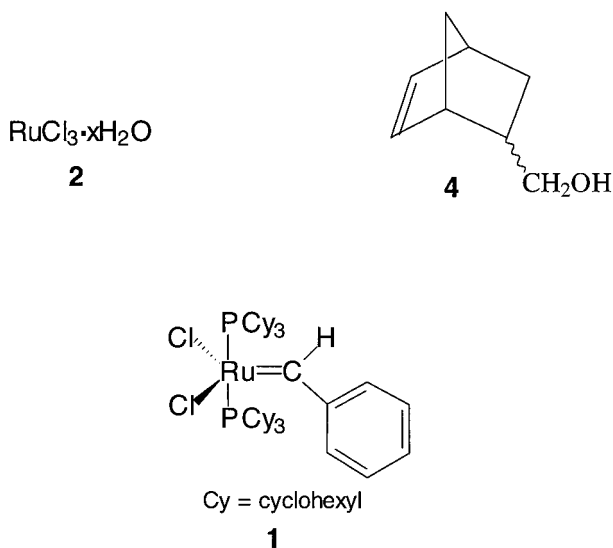
The microstructure of polyCHNB was measured using a Mattson Instruments Galaxy Series FT-IR. TGA analysis employed a SDT 2960 Simultaneous DTA-TGA, TA Instruments, at a heating rate of 20°C/min from 30 to 550°C under air or nitrogen atmosphere. Glass transition temperatures ( $T_g$ s) of all polyCHNB samples were obtained with a DSC 2920 differential scanning calorimeter, TA instruments, at a heating rate of 10°C/min from 30 to 300°C under nitrogen.



**Scheme 1** Ring opening metathesis polymerization of cyclohexenyl norbornene (CHNB), **3**.

## RESULTS AND DISCUSSION

The overall goal of this study was to maximize the conversion of CHNB and control gel time. Keeping in mind that the polymerization conditions have to be applicable to composite fabrication, only air- and moisture-tolerant catalysts were employed. In our study, ROMP was conducted using both ruthenium trichloride hydrate and ruthenium benzylidene. As previously stated, 99–100% conversion and gel time in hours were the prime targets. The overall process for ROMP of CHNB is given in Scheme 1.



**Scheme 2** Chemical structures of ruthenium trichloride hydrate, **2**, ruthenium benzylidene, **1**, and 5-norbornene-2-methanol, **4**.

## General Observations

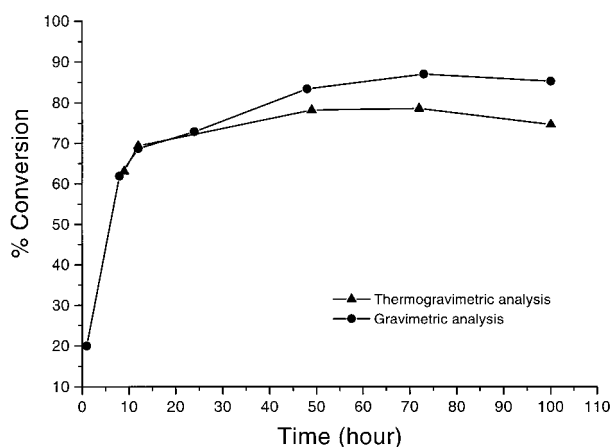
Behavior of the two catalyst systems (Scheme 2) examined was very different. Chlorobenzene acts as a cocatalyst with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  and without it the ROMP of CHNB does not take place. 5-Norbornene-2-methanol and ethanol were chosen as dissolution aids and used in minimal quantity because bulk polymerizations were desired. 5-Norbornene-2-methanol was chosen because its structure can be incorporated into the polymer backbone, reducing the volatile organic contents. With  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , complete solubility of poly-CHNB in chloroform was dependent on ROMP conditions. Some samples completely dissolved while others only swelled due to different degrees of crosslinking. Regardless of degrees of polymer solubility, all polymer mixtures were precipitated into acetone to remove the residual monomer and catalyst. The chloroform-swollen insoluble poly-CHNBs were cut into pieces to enhance surface area for residual monomer to diffuse out before adding to acetone. After cleanup, polyCHNBs polymerized with 0.02–1.0 mol % catalyst remained dark green in color, while samples obtained with less than 0.01 mol % catalyst appeared as fluffy white solids.

Crosslinked polymers were obtained only in polymerizations with 0.05 mol % or higher of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , possibly through olefin addition processes of the cyclohexenyl group during or after ring-opening metathesis polymerization. Wagener and co-workers proposed that olefin addition through the pendant five-membered ring contributes to the formation of crosslinked polydicyclopentadiene and the cyclohexene moiety of

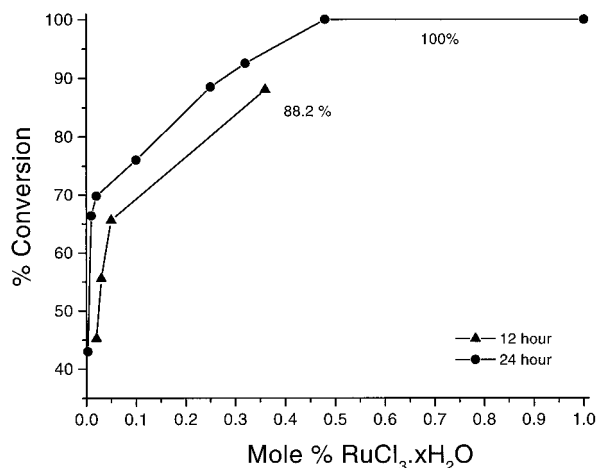
CHNB should be even less prone to ring opening.<sup>5</sup> The exact mechanism leading to crosslinking of polyCHNB has not yet been determined, but certainly can involve oxidative processes.

Ruthenium benzylidene normally decomposes when exposed to reactive species in air and moisture, but is stable by itself in the presence of both. Therefore, ROMP with this catalyst normally requires degassing the system. Under conditions used here, however, ruthenium benzylidene readily polymerized CHNB without system degassing. In addition, while the purple-pink ruthenium benzylidene only partially dissolved in CHNB monomer, the catalyst promoted ROMP without dissolution aids. All polymers obtained with this catalyst were completely soluble in chloroform, regardless of the ROMP conditions employed. After precipitating into acetone, white powder polymers were obtained. It should be noted, however, that during polymer cleanup, polymers dissolved in chloroform occasionally underwent oxidation, resulting in crosslinked products. To prevent this, 1 wt % 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as an antioxidant.

Molecular weight estimates of polyCHNBs were attempted with a size-exclusive chromatography (SEC). However, the polymer solutions would not pass through a 0.2- $\mu\text{m}$  filter, even though they appeared visually to be dissolved in tetrahydrofuran (THF). Possible reasons could be that lightly crosslinked polymers were formed, or



**Figure 1** A comparison of conversions of polyCHNB evaluated by gravimetric (●) and thermogravimetric (▲) analyses. PolyCHNBs in both batches were polymerized at 55–60°C with 0.02 mol %  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  using ethanol as a dissolution aid.



**Figure 2** The effect of mol %  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  on conversion of CHNB polymerized at 80°C for 12 (×) and 24 (■) h, using 5-norbornene-2-methanol as a dissolution aid.

that THF is not a good enough solvent for very high molecular weight polyCHNBs.

### Conversions and Gel Times

In the early stage of this study, the conversions of CHNB were evaluated by gravimetric analysis. However, this method was time consuming and not economical, because a lot of solvent was consumed during polymer cleanup.

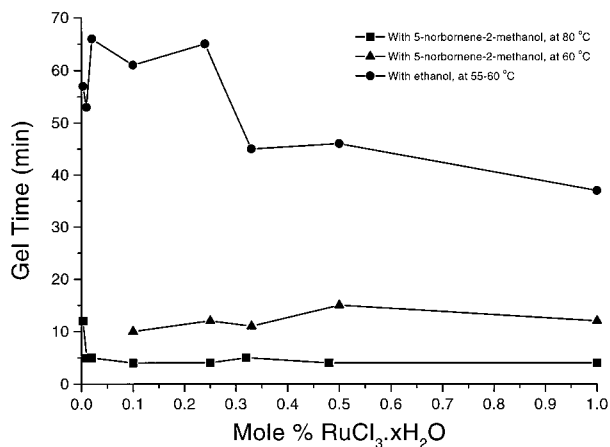
A thermogravimetric analysis (TGA) was used later; the conversions reported here were evaluated with both methods. A comparison of conversions measured by gravimetric and TGA analyses is given in Figure 1. Conversions of polyCHNB within the first 24 h measured by either method were almost identical. After 24 h, conversions by TGA showed ca. 1–10% higher values. Because there were only minor differences for conversions measured by the two methods, TGA is preferred based on sample size needed and simplicity. Moreover, with the gravimetric technique, dissolving polymers in chloroform was always impractical, especially when higher amounts of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  were used that tended to give crosslinking.

### With $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$

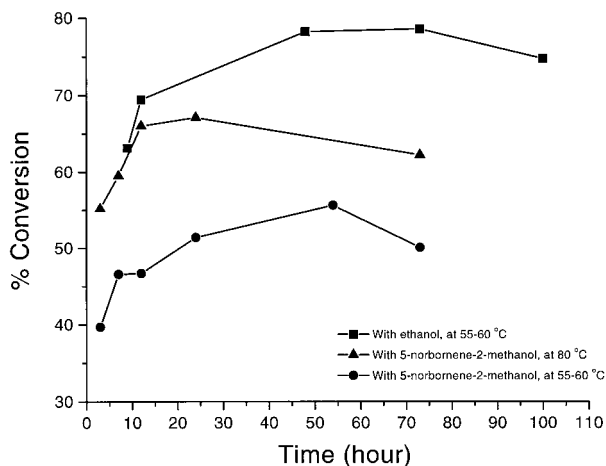
Figure 2 shows that increasing the concentration of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  to 0.5 mol % or higher allowed 100% conversions to be achieved. However, using higher amounts of catalyst led to difficulty main-

taining homogeneity of the reaction mixtures. While, ruthenium trichloride hydrate completely dissolved in both ethanol and 5-norbornene-2-methanol, complete solubility is limited by the amount of alcohol employed. In our system, conditions close to bulk polymerization were desired and the alcohol amount was kept to a minimum; i.e., to 2 vol % based on CHNB monomer used. Conversions of 68% were obtained in polymerization with 0.02 mol %  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ . Due to the balance between conversion and solubility that 0.02 mol %  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  offered, this amount of catalyst was chosen for most reactions. By varying reaction time and temperature, it was hoped that the conversion would be enhanced to essentially 100%.

In addition to conversion, gel time controls the feasibility of composite fabrication. Conditions that provide a wide time window for processing are favorable; i.e., long enough for resin to infuse fibers and wet them thoroughly before reaction causes viscosity increase and gelation. Gel time used here is not indicative of crosslinking (as it is generally), but is the time at which the polymerizing mixture of CHNB physically stopped flowing and formed a gel-like product. Gel time was not affected as much by the amount of  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  catalyst used as by dissolution aids and reaction temperatures (Fig. 3). There was no significant change in gel time for systems with 5-norbornene-2-methanol, regardless of different



**Figure 3** The effects of mol %  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ , reaction temperature and dissolution aid on gel time: CHNB was polymerized with various mol %  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  in the presence of 5-norbornene-2-methanol at 80°C (■) and 60°C (▲), and in the presence of ethanol at 55–60°C (●).



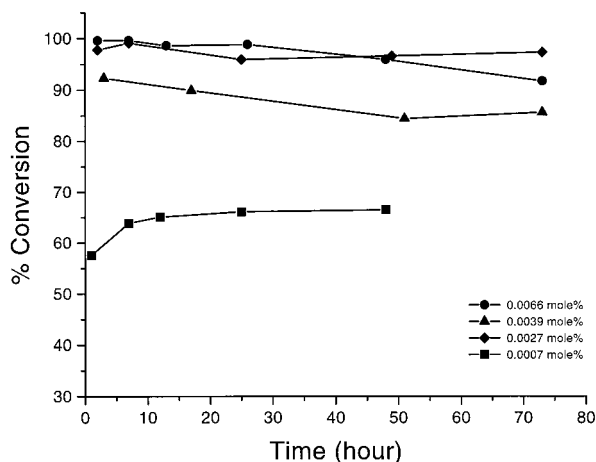
**Figure 4** The effects of dissolution aid and reaction temperature on conversion of CHNB polymerized with 0.02 mol %  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  at 55–60°C in the presence of ethanol (■), and at 80°C (▲) and 55–60°C (●) in the presence of 5-norbornene-2-methanol. PolyCHNBs exhibited gel times of 43 (■), 14 (▲), and 60 (●) minutes.

catalyst concentrations used. However, reaction temperature was important and CHNB at 80°C exhibited one-half the gel time of that reacted at 60°C. Polymerizations with 5-norbornene-2-methanol gelled much faster than those with ethanol. Polymerizations with ethanol not only gave longer gel times but also higher conversions (Fig. 4). These ranged from 70–85% after 12 h of reaction at 55°C. Polymerizations with 5-norbornene-2-methanol, on the other hand, led to conversions in the range of 50–67% with gel times of 14 min, and higher conversions were obtained at 80°C than at 60°C.

#### With $\text{RuCl}_2 (= \text{CHPh})(\text{PCy}_3)_2$

ROMP using ruthenium benzylidene showed no signs of crosslinking, although molecular weights could not be estimated due to poor solubility in THF. Although ruthenium benzylidene only partially dissolved in CHNB monomer (leading to heterogeneous polymerization), it was so reactive that it enabled polymerization of CHNB under very mild conditions; i.e., 0.0027 mol % at 25°C.

ROMP of CHNB using ruthenium benzylidene was rapid and exothermic, showing temperature increases of up to 65°C. After 15 min of reaction, the temperature started dropping back to ambient, indicating high conversion. While the system was heating up, the reaction mixture changed



**Figure 5** The effect of mol % ruthenium benzylidene on conversion of CHNB polymerized with 0.0066 (◆), 0.0039 (●), 0.0027 (×), and 0.0007 (▲) at room temperature. PolyCHNBs exhibited gel times of 12 (◆), 13 (●), 24 (×), and 26 (▲) min.

from colorless to light purple-pink and became cloudy; it gelled in a matter of minutes. The heat of reaction liberated by the system was calculated by DSC as 68 J/g.

The effects of ruthenium benzylidene concentrations on conversions and gel times are illustrated in Figure 5. The gel time was essentially constant if the amount of catalyst employed was greater than 0.0039 mol %. Gel time was lengthened if much less catalyst was used, and conversions dropped (Fig. 5). Decreasing ruthenium benzylidene to 0.0027 mol % or less resulted in doubling of the gel time. Among four sets of experimental conditions, the system polymerized with 0.0027 mol % ruthenium benzylidene exhibited the best combination of conversion and gel time. ROMP at higher temperature (i.e., 45°C) showed significantly lower conversions than at room temperature (Fig. 6). Clearly, the reaction temperature affects both gel time and conversion in the polymerization with ruthenium benzylidene as well as with  $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$ . It should be noted that the small differences in conversion with time seen for some of the plots in Figures 5 and 6 are due to experimental errors and are not considered significant.

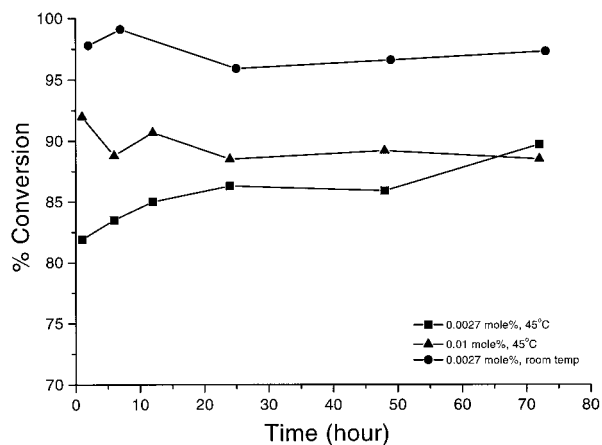
#### $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$ vs. $\text{RuCl}_2 (=CHPh)(PCy_3)_2$

Table I shows the physical appearances of crude polyCHNBs obtained with the two catalysts. The

polymers obtained with ruthenium benzylidene were glassy products, which were much stiffer than the ones obtained with  $\text{RuCl}_3 \cdot \times \text{H}_2\text{O}$  due to higher conversions. The latter produced rubbery polymers under the same conditions because residual CHNB acts as plasticizer. To have high composite performance, stiff and glassy polyCHNB is preferred. Utilizing ruthenium benzylidene in ROMP allowed much milder conditions and gave much better conversions, longer gel times, and better physical properties for bulk polymerized monomer. In addition, polyCHNBs formed with ruthenium benzylidene were more soluble in  $\text{CHCl}_3$  and little residual CHNB was present.

Clearly, ruthenium benzylidene offers far higher conversions under milder conditions and with less catalyst than ruthenium trichloride hydrate. The major drawbacks of ruthenium benzylidene are higher cost and shorter gel times (i.e., only minutes), even at room temperature. The latter makes it difficult to process the resin-catalyst mixture during composite fabrication. This catalyst is also less complex, because no dissolution aids and cocatalysts are required.

All polyCHNBs, as expected, showed similar thermal characteristics and microstructures. In general, the metathesis ring-opening polymerizations of cycloolefins are stereoselective.<sup>6</sup> The degree of stereoselectivity varies with the nature of



**Figure 6** The effects of mol % of ruthenium benzylidene and reaction temperature on conversion of CHNB polymerized with 0.0027 mol % at 45°C (■) and at room temperature (●), and with mol % at 45°C (▲). PolyCHNBs exhibited gel times of 9 (●), 9 (▲), and 24 (●) minutes.

**Table I Comparison of Physical Appearance and Conversion of PolyCHNBs Formed by Ruthenium Trichloride Hydrate and Ruthenium Benzylidene**

Catalysts	Reaction Time (Hour)	Appearance <sup>a</sup>	Conversion (%)
RuCl <sub>3</sub> ·H <sub>2</sub> O	12	Dark-green and soft rubbery material	68.7
0.02 mol %	24	Dark-green and soft rubbery material	72.8
55–60°C	48	Dark-green and sturdy rubbery material	83.4
gelled in 43 min			
RuCl <sub>2</sub> (=CHPh)(PCy <sub>3</sub> ) <sub>2</sub>	7	Very stiff and clear glassy material	99.1
0.0027 mol %	25	Extremely stiff and clear glassy material	95.9
at room temperature	49	Extremely stiff and clear glassy material	96.6
gelled in 24 min			
RuCl <sub>2</sub> (=CHPh)(PCy <sub>3</sub> ) <sub>2</sub>	6	Very stiff and clear glassy material	83.5
0.0027 mol %	24	Extremely stiff and clear glassy material	86.3
45°C	48	Extremely stiff and clear glassy material	85.9
gelled in 9 min			

<sup>a</sup> CHNB smell was detected in all systems.

the catalyst and cycloolefins employed.<sup>6</sup> It has been observed that RuCl<sub>3</sub>·xH<sub>2</sub>O normally produces polymers containing almost exclusively *trans* double bonds with norbornene and a number of its derivatives.<sup>7</sup> However, a study done on both endo- and exo-dicyclopentadienes using ruthenium trichloride trihydrate (RuCl<sub>3</sub>·xH<sub>2</sub>O) found that with endo-dicyclopentadiene, the catalyst RuCl<sub>3</sub>·xH<sub>2</sub>O produced a high *cis* polymer.<sup>8</sup> In our study, polyCHNB polymerized with either RuCl<sub>3</sub>·xH<sub>2</sub>O or ruthenium benzylidene exhibited high *trans*-contents as measured by infrared spectroscopy (IR). PolyCHNB showed a strong absorption at 910 cm<sup>-1</sup> (*trans* =C—H out-of-plane deformation) and a relatively weak absorption at 661 cm<sup>-1</sup> (*cis* =C—H out-of-plane deformation).

By TGA, the 5% weight loss values were observed at ca. 420 and 430°C under nitrogen and air atmospheres, respectively. As expected, polyCHNB exhibited air oxidation due to its high content of allyl carbons in the backbone, and weight gain due to oxidation was detected at ca. 125–140°C in air. The glass transition temperature (*T<sub>g</sub>*) of all purified polymers was approximately 105°C.

## CONCLUSIONS

Crosslinked and noncrosslinked polyCHNBs were produced, depending on the catalyst and ROMP conditions. With RuCl<sub>3</sub>·xH<sub>2</sub>O, conversions were enhanced by increasing the amount of the cata-

lyst, reaction time, and temperature; using ethanol as a dissolution aid offered higher conversions than using 5-norbornene-2-methanol. The gel times were unaffected by the amount of the catalyst but decreased inversely with reaction temperature. With ruthenium benzylidene, conversions increased with decreasing reaction temperatures but essentially remained unchanged with reaction times. The gel times were mol % catalyst and temperature dependent. All polyCHNBs exhibited *T<sub>g</sub>* values around 105°C and 5% weight loss at ca. 420°C and ca. 430°C under nitrogen and air environments, respectively. The optimal ROMP condition of CHNB was with 0.0027 mol % ruthenium benzylidene at room temperature for 1 h.

To bulk-polymerize CHNB monomer, the ruthenium benzylidene catalyst offered the best combination of high conversions, moderate gel times, and desired physical properties. ROMP with ruthenium benzylidene required only small amount of the catalyst and no dissolution aids or cocatalyst. The reaction was efficiently carried out at room temperature. Therefore, for further utilizing the CHNB monomer in composite, ROMP with ruthenium benzylidene is preferred, although increasing gel time would be desirable.

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