

Letter

# Hydrogenation of PhCH<sub>2</sub>CHO catalyzed by ruthenium complex containing “polymer-attached” ligand prepared by living ring-opening metathesis polymerization

Kotohiro Nomura\*, Hiroyuki Ogura, Yukio Imanishi

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received 3 October 2001; accepted 12 January 2002

## Abstract

Various pyridine ligands attached to the polymer chain end could be prepared by the living ring-opening metathesis polymerization (ROMP) using well-defined the Schrock-type molybdenum-alkylidene initiator of Mo(CHCMe<sub>2</sub>Ph)(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(O<sup>t</sup>Bu)<sub>2</sub>, and the possibility for use of this ligand in catalysis has been examined for hydrogenation of PhCH<sub>2</sub>CHO in the presence of Ru(acetylacetonato)<sub>3</sub> (Ru(acac)<sub>3</sub>) (in xylene, at H<sub>2</sub> 10 atm). Significant increase in the activity was observed if the above polymer was employed as the ligand, although the activity decreased upon the addition of pyridine or 4-methylpyridine instead. The prepared catalyst could be recovered by pouring the reaction mixture into methanol, and could be reused without decrease in the activity. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Polymer supported catalyst; Hydrogenation; Ruthenium; Ring-opening metathesis polymerization (ROMP)

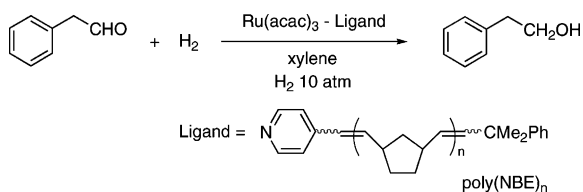
## 1. Introduction

Considerable attention has been devoted to the studies concerning polymer [1,2] or dendrimer ([3] supported catalysts, not only due to that there still exists practical concern in using homogeneous catalysts such as separation of the products from catalyst and ligand [4], but also due to that these supported catalysts play a crucial role in combinatorial and parallel synthesis which have become common in modern organic chemistry. Traditionally, insoluble polymer resins such as divinylbenzene crosslinked polystyrene

have been used as a support for homogeneous catalysts since they can easily be isolated by filtration [1a]. However, several shortcomings such as nonlinear kinetic behavior, unequal distribution and/or access to the chemical reaction, solution problems still remain due to the heterogeneous reaction nature (Recent reviews concerning soluble polymer ligands [2]).

As an attempt to combine the advantages and to minimize the disadvantages associated with homogeneous and heterogeneous catalysts, use of soluble polymer supported ligand has attracted considerable attention [2]. However, we believe, examples in use of ligand attached to the polymer chain end as well as synthesis of ligand by the controlled living polymerization technique (Use of ROMP polymer as the ligand, for example [5]) still have been limited

\* Corresponding author. Tel.: +81-743-72-6041;  
fax: +81-743-72-6049.  
E-mail address: nomurak@ms.aist-nara.ac.jp (K. Nomura).



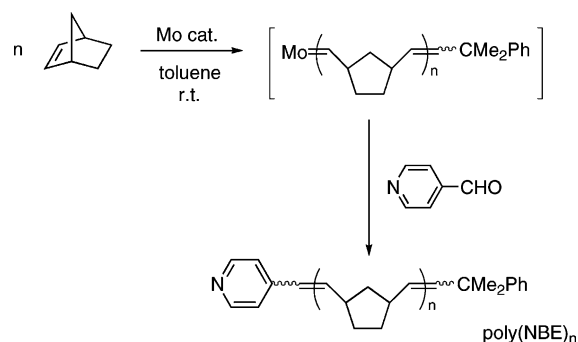
Scheme 1.

so far. Since, we recently demonstrated that poly(macromonomer(s)) could be precisely synthesized by repeating living ring-opening metathesis polymerization (ROMP) using well-defined Schrock type molybdenum initiator [6], also since we reported ruthenium catalyzed organic reactions such as exclusive reduction of aromatic nitro group under CO/H<sub>2</sub>O conditions [7], hydrogenation of ester under low hydrogen pressure [8], we have thus combined these chemistry and explored the possibility to expand the ring-opening metathesis polymerization (ROMP) technique for synthesis of ligand attached to the polymer chain end [5]. We thus chose ruthenium catalyzed hydrogenation of PhCH<sub>2</sub>CHO as the model reaction (Scheme 1), and we wish to introduce our unique preliminary results concerning ruthenium catalysis containing polymer-attached pyridine ligand in this paper.

## 2. Results and discussion

### 2.1. Synthesis of polymer-supported ligand

ROMP of norbornene (NBE) was performed in toluene at room temperature, and Mo(CHCMe<sub>2</sub>Ph)



Scheme 2.

(*N*-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(*O*<sup>*t*</sup>Bu)<sub>2</sub> was used as the initiator (Scheme 2).<sup>1</sup> 4-Pyridinecarboxaldehyde was chosen not only to terminate the polymerization quantitatively, but also to introduce pyridine moiety into the chain end of ring-opened poly(norbornene) quantitatively. This is an established method as we also previously demonstrated for synthesis of poly(macromonomer(s)) by repeating the ROMP with this molybdenum-alkylidene initiators [6], and pyridine moiety could be introduced by cleaving the polymer–metal bond via Wittig-like reaction with the aldehyde [6,9–11]. As also presented in the previous reports [6,9–11], the yields were almost quantitative in all cases (>95%), and the resultant polymer could be isolated as the white precipitate by pouring the reaction mixture into cold methanol. The resultant polymer was also identified by <sup>1</sup>H NMR spectrum [6,11]<sup>2</sup> as the ring-opened structure containing a mixture of *cis*- and *trans*-olefinic double bonds.

As shown in both Table 1 and Fig. 1, the *M*<sub>n</sub> value measured by GPC versus polystyrene standard increased linearly by varying the (NBE)/Mo molar ratios, whereas the *M*<sub>w</sub>/*M*<sub>n</sub> values were narrow

<sup>1</sup> Typical polymerization procedure is as follows: a toluene solution of Mo(CHCMe<sub>2</sub>Ph)(*N*-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(*O*<sup>*t*</sup>Bu)<sub>2</sub> (80 μmol in toluene 1.0 g) was added in one portion to a rapidly stirred toluene solution (4.0 g) containing prescribed amount of norbornene at room temperature, and the reaction mixture was stirred for 30 min. The polymerization was quenched by adding 4-pyridinecarboxaldehyde in excess amount after the consumption of monomers, stirred for 1 h for completion. The resultant solution was poured dropwise to stirred cold methanol (~200 ml), affording white-pale yellow precipitate. The polymer was collected by filtration, and was then dried in vacuo. Yield >95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.18 and 5.32 (m, 2H olefinic), 2.76 and 2.37 (br.s, 2H), 1.85 and 1.04 (m, 2H), 1.78 and 1.33 (m, 4H). Peaks corresponding to the polymer chain end [6,11] could also be observed: δ 8.52 and 8.47 (d, pyridine), 6.42 (m, Py–CH=CH–), 6.24 (dd, Py–CH=CH–), 5.56 (d, PhMe<sub>2</sub>CCH=CH–), and 5.33 (m, PhMe<sub>2</sub>CCH=CH–). Other resonances corresponding to phenyl group were also observed.

<sup>2</sup> <sup>1</sup>H-NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, <sup>1</sup>H), and all chemical shifts are given in ppm and are referenced to tetramethylsilane. GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm Ø) were calibrated with polystyrene standards.

Table 1  
Synthesis of ring-opened poly(norbornene)s with Mo(CHCMe<sub>2</sub>Ph)  
(*N*-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(*O*<sup>*t*</sup>Bu)<sub>2</sub> initiator<sup>a</sup>

Run no.	NBE/Mo <sup>b</sup>	Time (min)	$M_n$ ( $\times 10^{-4}$ ) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
1	25	5	0.47	1.20
2	50	10	0.79	1.24
3	100	30	1.29	1.22
4	100	30	1.45	1.19
5	200	30	2.63	1.10

<sup>a</sup> Conditions: in toluene, monomer concentration = ca. 0.20–0.35 mmol/ml, norbornene 83 mg (run 2), room temperature.

<sup>b</sup> Molar ratio of NBE/Mo.

<sup>c</sup> GPC data in THF vs. polystyrene standard.

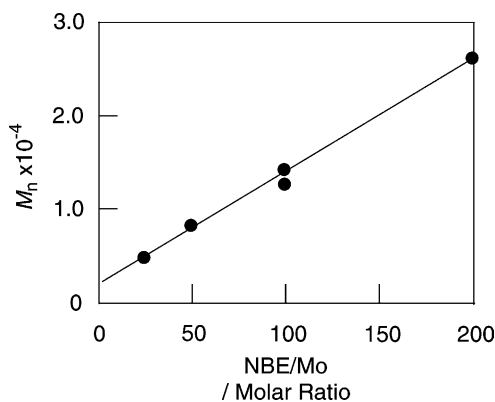


Fig. 1. Plot of  $M_n$  (by GPC in THF vs. polystyrene standard) as a function of NBE/initiator molar ratio based on results displayed in Table 1.

( $M_w/M_n = 1.10$ – $1.24$ ) (see footnote 2).<sup>3</sup> These results clearly indicate that the present polymerization took place in a living manner as established previously [6,9–11].

<sup>3</sup> The  $M_n$  values measured by GPC in THF versus polystyrene standard were somewhat higher than those calculated based on monomer/Mo molar ratios. The same trend was also seen if 4-Me<sub>3</sub>SiOC<sub>6</sub>H<sub>4</sub>CHO was used in place of 4-pyridinecarboxaldehyde, and the exact molecular weights were almost identical with those based on the initial molar ratios, which were confirmed by both <sup>1</sup>H NMR and MALDI-TOF mass spectrometry [6]. Although the attempt to measure mass spectrometry was not successful at this moment, we believe that the present polymerization proceeded with quantitative initiation efficiency as established previously in this series of ROMP chemistry.

## 2.2. Catalytic hydrogenation

Since we recently reported that the catalyst system composed of Ru(acac)<sub>3</sub> and P(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> exhibited high catalytic activity for hydrogenation of PhCH<sub>2</sub>CHO affording PhCH<sub>2</sub>CH<sub>2</sub>OH exclusively [8], we thus chose this reaction and explored the possibility for use of this soluble polymer ligand, poly(NBE), in place of P(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> under the similar conditions. Results are summarized in Table 2.<sup>4,5</sup>

The catalytic hydrogenation took place if only Ru(acac)<sub>3</sub> was added in xylene (41.0 and 69.4 turnovers, runs 7 and 10). Notable increase in the catalytic activity was observed upon the addition of the present polymer ligand (runs 11 and 12), although the addition of pyridine or 4-methylpyridine retarded the activity under the same conditions (runs 8 and 9). On the other hand, the use of poly(4-vinylpyridine) 2% crosslinked (Aldrich) in place of poly(NBE) did not show the improvement in the catalytic activity (runs 16 and 17). In addition, it seemed impossible to recover the polymer ligand due to the tiny amount (1.2 mg, run 16 in Table 2) compared to the poly(NBE)<sub>100</sub> (100 mg, run 15 in Table 2), and this should be a significant benefit to use the present *polymer attached* ligand for efficient recycling. No reaction took place if the reaction was attempted without Ru(acac)<sub>3</sub>, clearly indicating that the ruthenium catalyzes the catalytic reaction. The reaction product was PhCH<sub>2</sub>CH<sub>2</sub>OH almost exclusively, and trace amount (<1%) of PhCH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph was observed on GLC chromatogram. We believe that this is an interesting example that only the pyridine ligand attached to the ROMP polymer chain end could enhance the catalytic activity. The observed catalytic activity also depended upon molar ratio of the ligand

<sup>4</sup> The catalytic reactions were typically carried out as follows: in an autoclave (20 ml) made of stainless steel was charged Ru(acac)<sub>3</sub>, ligand, xylene, PhCH<sub>2</sub>CHO under nitrogen atmosphere [8]. The reaction mixture was stirred under H<sub>2</sub> at 150 °C for 5 h. Reaction product was then determined by GLC using an internal standard and was identified by using GLC by co-injection with the authentic samples under different conditions. Identification was made by comparison of retention time of the chromatogram (Column: DB-1 30 m, 0.25 mm  $\times$  0.25  $\mu$ m  $\phi$ ), and GC-MS (GC-MS QP 5000, Shimadzu Co. Ltd.).

<sup>5</sup> In this chemistry, we chose the  $M_n$  value calculated based on monomer/Mo molar ratio as described in the above background [6,11].

Table 2  
Hydrogenation of PhCH<sub>2</sub>CHO by Ru(acac)<sub>3</sub>-polymer ligand catalyst system<sup>a</sup>

Run no.	Ru(acac) <sub>3</sub> (mol)	Additives (A/Ru) <sup>b</sup>	PhCH <sub>2</sub> CHO (mmol)	TON <sup>c</sup>
6	–	Poly(NBE) <sub>100</sub>	2.0	–
7	0.02	None	2.0	41.0
8	0.02	4-Methylpyridine (1)	2.0	12.1
9	0.02	Pyridine (2)	2.0	21.2
10	0.005	None	2.0	69.4
11	0.005	Poly(NBE) <sub>100</sub> (1)	1.0	153
12	0.005	Poly(NBE) <sub>100</sub> (1)	1.0	144
13	0.005	Poly(NBE) <sub>100</sub> (1)	2.0	125
14	0.005	Poly(NBE) <sub>100</sub> (2)	2.0	86.0
15	0.010	Poly(NBE) <sub>100</sub> (1)	2.0	112
16	0.010	Poly(4-vinylpyridine) (1.2) <sup>d</sup>	2.0	39.6
17	0.010	Poly(4-vinylpyridine) (2.1) <sup>d</sup>	2.0	43.4

<sup>a</sup> Conditions: xylene 1.25 ml, H<sub>2</sub> 10 atm, 160 °C, 5 h, 20 ml scale autoclave.

<sup>b</sup> Molar ratio based on ruthenium.

<sup>c</sup> TON (turnover number) = PhCH<sub>2</sub>CH<sub>2</sub>OH produced (mmol)/Ru (mmol).

<sup>d</sup> Poly(4-vinylpyridine) 2% crosslinked (Aldrich).

to ruthenium, substrate charged initially (runs 12–15). The addition of P(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> did not improve the catalytic activity (runs 18–19, Table 3), although the use of this phosphine in place of poly(NBE)<sub>*n*</sub> enhanced the catalytic activity [8].<sup>6</sup>

The activity was not dependent upon the chain length of ROMP polymer ligand, because no differences were seen in the catalytic activities with various poly(NBE)<sub>*n*</sub> prepared by varying the initial monomer/Mo molar ratios (runs 13, 15, 21–23, Table 3). The olefinic double bond in poly(NBE) was hydrogenated according to the published method [12], and was used as the ligand in this catalytic reaction. No improvement in the catalytic activity was observed (runs 13 and 20), suggesting the presence of double bond in the poly(NBE) did not affect the catalytic activity.<sup>7</sup> Although the exact

reason is not clear at this moment, these are also especially interesting findings as the unique characteristics of the present ligand in this catalytic reaction.

It should be noted that reuse of the catalyst did not decrease the catalytic activity (run 24, Table 3).<sup>8</sup>

The catalyst could be collected as brown precipitate from the reaction mixture efficiently (recovered yield >98%) by pouring the reaction mixture into cold methanol (Scheme 3) because the polymer supported catalyst was insoluble in methanol. The catalytic activity (turnover number) did not change between first (run 12) and second runs (run 24), although the hydrogenation did not complete in each runs.<sup>9</sup> These results also indicate that ruthenium should be supported almost exclusively on the polymer surface probably

<sup>6</sup> For example, the activity of 384 turnovers (96% yield) after 5 h was obtained if excess amount of phosphine was added. Reaction conditions, Ru(acac)<sub>3</sub> 0.005 mmol, P(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> 0.050 mmol (phosphine/Ru = 10, molar ratio), PhCH<sub>2</sub>CHO 2.0 mmol, xylene 1.25 ml, H<sub>2</sub> 10 atm, 160 °C, 5 h (same conditions in runs 13, 18–19 except that PhCH<sub>2</sub>CHO = 2.0 mmol and excess amount of P(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> was used). The activity depended upon phosphine/Ru molar ratio [8].

<sup>7</sup> Olefinic double bonds in poly(NBE) were partly hydrogenated during the reaction. A rough estimation by calculating integration ratio of olefinic/aliphatic resonances in <sup>1</sup>H NMR spectrum of the poly(NBE)<sub>100</sub> after the reaction, less than 20% of olefinic double bonds were hydrogenated (H<sub>2</sub> 10 atm, 160 °C, 5 h, under the same conditions in run 12).

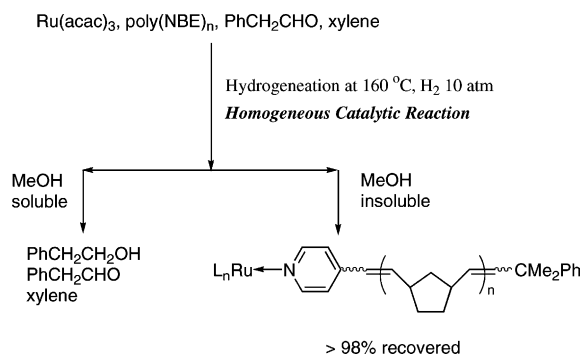
<sup>8</sup> For catalyst recycling experiment (runs 12 and 24), two independent runs were made under the same conditions in run 12. Similar catalytic activities were observed (TON = 144 (run 12) and 153, respectively), and the polymer supported catalysts could be collected as deep brown precipitate by pouring the reaction mixture into cold methanol. The isolation yields were 98% (calculated as poly(NBE) + Ru atom). The recovered catalyst was mixed and used for the next experiment (145 (run 24) and 141 (rest of the catalyst was used instead of 0.005 mmol of ruthenium under the same conditions) turnovers).

<sup>9</sup> The yields of PhCH<sub>2</sub>CH<sub>2</sub>OH were ca. 36% (runs 12 and 24) as calculated from TON and substrate charged. The reaction conditions of incomplete conversion were chosen to compare the exact catalyst performances between before and after the recycled procedure.

Table 3

Hydrogenation of PhCH<sub>2</sub>CHO by ruthenium catalysts containing polymer attached ligand<sup>a</sup>

Run no.	Ru(acac) <sub>3</sub> (mol)	Additives (A/Ru) <sup>b</sup>	PhCH <sub>2</sub> CHO (mmol)	TON <sup>c</sup>
13	0.005	Poly(NBE) <sub>100</sub> (1)	1.0	125
18	0.005	Poly(NBE) <sub>100</sub> (1) + P( <i>n</i> -Oct) <sub>3</sub> (1)	1.0	94.1
19	0.005	Poly(NBE) <sub>100</sub> (1) + P( <i>n</i> -Oct) <sub>3</sub> (2)	1.0	83.0
20	0.005	Poly(NBE) <sub>100</sub> -hydrogenated (1) <sup>d</sup>	1.0	135
13	0.005	Poly(NBE) <sub>100</sub> (1)	1.0	125
21	0.005	Poly(NBE) <sub>200</sub> (1)	1.0	121
15	0.010	Poly(NBE) <sub>100</sub> (1)	2.0	112
22	0.010	Poly(NBE) <sub>50</sub> (1)	2.0	106
23	0.010	Poly(NBE) <sub>25</sub> (1)	2.0	119
12	0.005	Poly(NBE) <sub>100</sub> (1)	2.0	144
24	0.005	Poly(NBE) <sub>100</sub> (1) reuse <sup>e</sup>	2.0	145

<sup>a</sup> Conditions: xylene 1.25 ml, H<sub>2</sub> 10 atm, 160 °C, 5 h.<sup>b</sup> Molar ratio based on ruthenium.<sup>c</sup> TON (turnover number) = PhCH<sub>2</sub>CH<sub>2</sub>OH produced (mmol)/Ru (mmol).<sup>d</sup> Olefinic double bond in poly(NBE)<sub>100</sub> was hydrogenated in advance.<sup>e</sup> Recycled catalyst was used.

Scheme 3.

by coordination. The prepared catalyst was stable and could be handled without trouble under ordinary atmosphere (air) for a while.

Since, the molecular weight of the polymer ligand can be simply modified only by varying the monomer/initiator molar ratios, also, since the polymer main chain could be modified not only by use of substituted NBE but also by using the block copolymerization in this living ROMP chemistry using well-defined Schrock-type initiator, we certainly believe that the present approach should introduce one, new insight to study polymer supported catalysis chemistry.

## References

- [1] (a) T.W. Ford, in: Proceedings of the ACS Symposium Series 308, on Polymeric reagents and catalysts, American Chemical Society, Washington DC, 1986, p 1; (b) R.B. Merrifield, *Angew. Chem.* 97 (1985) 801.
- [2] (a) D.J. Gravert, K.D. Janda, *Chem. Rev.* 97 (1997) 489; (b) P. Wentworth, Jr., K.D. Janda, *Chem. Commun.* (1999) 1917; (c) P.H. Toy, K.D. Janda, *Acc. Chem. Res.* 33 (2000) 546; (d) P.H. Toy, T.S. Reger, K.D. Janda, *Aldrich. Acta* 33 (2000) 87; (e) C.W. Hartwig, D.J. Gravert, K.D. Janda, *Chemtracs* 12 (1999) 1; (f) D.E. Bergbreiter, *Med. Res. Rev.* 19 (1999) 439; (g) D.E. Bergbreiter, in: P.T. Anastas, L.G. Heine, T.C. Williamson (Eds.), Proceedings of the ACS Symposium Series 767 on Green Chemical Syntheses and Processes, American Chemical Society, Washington, DC, 2000, p. 182; (h) D.E. Bergbreiter, *J. Polym. Sci. Part A: Polym. Chem.* 39 (2001) 2351; (i) S. Borman, *Chem. Eng. News* 4 (2001) 49.
- [3] (a) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, *Nature* 372 (1994) 659; (b) M.A. Hearshaw, J.R. Moss, *Chem. Commun.* (1999) 1 (Review).
- [4] D.E. Bergbreiter, *Catal. Today* 42 (1998) 389.
- [5] (a) M.R. Buchmeiser, K. Wurst, *J. Am. Chem. Soc.* 121 (1999) 11101; (b) M.R. Buchmeiser, *Chem. Rev.* 100 (2000) 1565.
- [6] (a) K. Nomura, S. Takahashi, Y. Imanishi, *Polymer* 41 (2000) 4345;

- (b) K. Nomura, S. Takahashi, Y. Imanishi, *Macromolecules* 34 (2001) 4712.
- [7] (a) K. Nomura, *Chem. Lett.* (1991) 1679;  
(b) K. Nomura, *J. Mol. Catal.* 73 (1992) L1;  
(c) K. Nomura, *J. Mol. Catal. A* 95 (1995) 203;  
(d) K. Nomura, *J. Mol. Catal. A* 130 (1998) 1 (Review).
- [8] (a) K. Nomura, H. Ogura, Y. Imanishi, *J. Mol. Catal. A* 166 (2001) 339;  
(b) K. Nomura, H. Ogura, Y. Imanishi, *J. Mol. Catal. A* 178 (2002) 104.
- [9] (a) 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) 8378;  
(b) G.C. Bazan, J.H. Oskam, H. Cho, L.Y. Park, R.R. Schrock, *J. Am. Chem. Soc.* 113 (1991) 6899.
- [10] (a) R.R. Schrock, in: Y. Imamoglu (Ed.), *Metathesis Polymerization of Olefins and Polymerization of Alkynes*, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, 1998, pp. 1, 357;  
(b) R.R. Schrock, in: A. Fürstner (Ed.), *Alkene Metathesis*, Organic Synthesis, Springer, Berlin, 1998, p. 1.
- [11] G.C. Bazan, R.R. Schrock, H. Cho, V.C. Gibson, *Macromolecules* 24 (1991) 4495.
- [12] V.C. Gibson, T. Okada, *Macromolecules* 33 (2000) 655.