

Synthesis of Polypentenamer and Poly(Vinyl Alcohol) Using Phase Separable PIB Second Generation Hoveyda-Grubbs Catalyst

Mohammed Al-Hashimi,^{*,[a]} Robert Tuba,^[a] Hassan S. Bazzi,^{*,[a]} Robert H. Grubbs^{*,[b]}

Abstract: Equilibrium ring opening metathesis polymerization (ROMP) of strained cyclic olefins using a soluble supported second generation Ru complex has been investigated. Cycloolefin homo- and copolymers are of great academic and industrial importance due to their interesting applications as packaging materials, adhesives in coatings and optoelectronics. The supported complex exhibits good chemical stability and was effective in ROMP of strained cyclic olefins. In addition, the complex is easily phase separated from the product resulting in lower residual ruthenium in the final polymer product compared with the homogeneous complex.

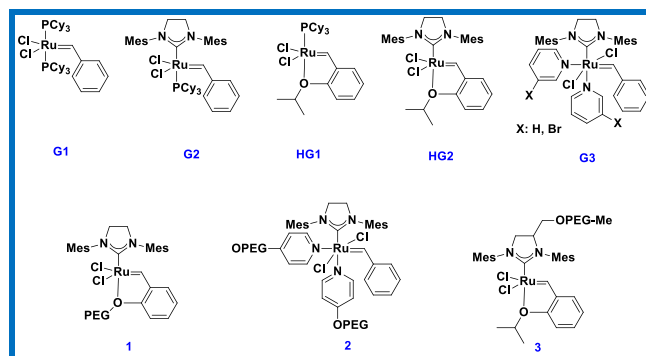


Figure 1- Classical and selected immobilized ruthenium-based olefin metathesis catalysts.

Introduction

Ring opening metathesis polymerization (ROMP) of strained cyclic olefins using well-defined metal alkylidene catalyst such as tungsten, molybdenum and ruthenium are of great academic and industrial interest.^{1–9} Over the last decade ruthenium based catalysts have attracted considerable attention because of their remarkable efficiency, stability and excellent tolerance towards a variety of functional groups (Figure 1).^{10–15}

The removal of heavy metal residues from the polymer chain, simple catalyst separation, recovery of the catalyst and minimal complex leaching are decisive criteria both from an economic and environmental aspect. Therefore, developing an economical and efficient method that separates Ru catalyst residues from the product is of great interest. To date, various strategies to solve the problems associated with Ru contamination has been reported.^{16–18} However, even after a single chromatography step the residual ruthenium in the final product in some cases is still too high 2–2400 ppm.

Some of the most commonly employed strategies to obtain supported metathesis catalysts consist of immobilizing the ruthenium alkylidene complex on to insoluble polymers,^{19–22} soluble polymers,^{23–26} inorganic supports,^{27–29} perfluorinated^{30,31} and ionic-liquid tags.^{32–35} (Figure 1).

Herein we will focus on the use of soluble polymer supported N-heterocyclic carbene (NHC) Ru metathesis catalysts. In 2001, Barrett et al. reported on the synthesis of a boomerang second generation polystyrene bound alkylidene, the catalyst was used for various ring closing metathesis (RCM) reactions.³⁶ Quantitative conversion to the desired product was reported, however fast reduction in catalytic activity was observed. Blechert et al. described the use of polymer bound Hoveyda-Grubbs ruthenium catalyst. The supported catalyst was found to have impressive activity in RCM and tandem RCM of a variety of diallyl malonates and seven membered ring precursors. Low levels of ruthenium contamination was reported.²⁵ In 2003, Lamaty et al. prepared a supported soluble poly(ethylene glycol) (PEG) catalyst **1**, following the earlier work by Yao et al.³⁷ Thus prepared the first generation Hoveyda-Grubbs catalyst onto PEG, without significant loss of activity. However, no Ru leaching data was reported. The resulting PEG Ru catalyst was reported by Lamaty to display high catalytic activity in the RCM of tosyl diallylamine and excellent recyclability.²⁶ Moreover, the residual Ru contamination in the ring-closed product was not reported. Emrick et al. also reported the synthesis of PEG substituted Ru catalyst **2**, it was found to be very effective in polymerizing cyclic olefins. The aim was to design a ROMP catalysts that was effective in water.³⁸ A related approach in 2005 was reported by Grubbs et al. They synthesized a water soluble first generation Ru catalyst supported on PEG. The supported catalyst was successfully utilized for both ROMP of strained cyclic olefins and a series of RCM transformations in both water and methanol.³⁹ Two years later Grubbs et al. reported an alternative approach by immobilizing PEG on the backbone of the NHC ligand, thus affording the PEG supported second generation catalyst **3**, which was used to catalyze a variety of model ROMP, RCM and cross metathesis reactions. Furthermore, the catalyst affords the product with low ruthenium contamination.⁴⁰ Bergbreiter et al. utilized polyethylene oligomers (PEolig) bound second-generation Ru catalyst for

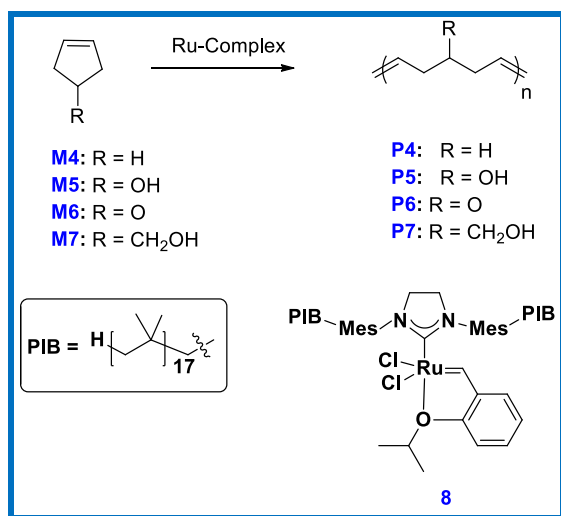
[a] Dr. M. Al-Hashimi, Dr. R. Tuba, Prof. H. S. Bazzi
Department of Chemistry
Texas A&M University at Qatar
P.O. Box 23874, Doha, Qatar.
E-mail: mohammed.al-hashimi@qatar.tamu; hassan.bazzi@tamu.edu

[b] Prof. R. H. Grubbs
The Arnold and Mabel Beckman Laboratories of Chemical
Synthesis, Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125,
United States
E-mail: rhg@caltech.edu

various RCM reactions. The catalyst displayed relatively high recyclability up to 10 times with no significant loss of activity and low levels of Ru leaching was reported.⁴¹

Despite these efforts, very little attention has been focused on using soluble polymer bound alkylidene Ru complexes in ROMP to prepare products with lower Ru contamination. Moreover, ROMP is a robust method for synthesizing functionalized polymers, producing totally linear materials. Inspired by those reports we turned our attention to synthesize functionalized and non-functionalized polypentenamers. Moreover, well defined poly(Vinyl Alcohol) (PVA) copolymers with the aim to combine a simple purification step with low Ru contamination in the final product. To the best of our knowledge, ROMP of cyclopentene and its functionalized derivatives via soluble NHC Ruthenium supported catalysts has not been reported.

Polypentenamer **P4** can be synthesized via ROMP of cyclopentene **M4**, respectively (Scheme 1). There is remarkable interest in synthesizing well defined functionalized and non-functionalized linear polymers because of their interesting properties. For example trans polypentenamer is an excellent rubber vulcanisate having similar physical properties to that of natural rubber.^{42,43} Poly(vinyl alcohol) **P5** based block copolymers have found considerable potential in optoelectronics, coatings, as adhesives, and in dispersion systems, moreover, PVA derivatives such as Nelficon A is widely used in contact lenses.⁴⁴⁻⁴⁷



Scheme 1 - Ring-opening metathesis polymerization of monomer **M4-7**.

Results and Discussion

We and Register et al. have previously reported on the equilibrium ring opening metathesis polymerization of cyclopentene **M4** using various well defined non-supported Ru catalysts **G1**, **G2** and **G3**.⁴⁸⁻⁵⁰ Herein, we extend our study towards the ROMP of cyclopentene and its functionalized

derivatives using phase separable PIB second generation Ru complex **8**. The increased stability and robustness of the soluble Ru complex **8** facilitates an easy separation of the product from the ruthenium complex. Moreover, avoiding laborious column chromatography/ multiple precipitations in achieving highly pure polymers. We have already showed that PIB-supported Ru complex **8** is useful in RCM⁵¹ and ROMP of several substituted oxanorbornenes.⁵² We report the results of our initial studies for the ROMP of cyclopentene **M4**, by exploring the feasibility of using a soluble polymer-bound Ru catalyst. The ROMP of strained cyclic olefins is mainly enthalpy-driven.⁵³ On the other hand, less strained cyclopentene is thermodynamically less favored to polymerize. Whereby, the monomer conversion is dependent on the reaction temperature and not the catalyst activity, resulting in a monomer-polymer equilibrium.^{54,55}

PIB Ru complex **8** was prepared following previously published protocols. The catalytic activity of complexes **HG2** and **8** were evaluated for the equilibrium ROMP of monomer **M4** at two different temperatures. In all cases the reaction was performed in THF under an inert atmosphere, using 0.225 mol % catalyst loading for 60 min to furnish polymer **P4** (Table 1, entries 1-4). The polymerizations were terminated by quenching the reaction mixture with excess ethyl vinyl ether. At this point, the % conversion was determined by ¹H NMR spectroscopy recorded in THF-d₈, wherein resonances at δ 5.69 ppm for the cyclic olefin monomer was replaced by a new chemical shift at δ 5.35 ppm indicated polymer formation.

Table 1 summarizes the conversion for ROMP of monomer **M4**, molecular weight distribution and the polydispersity index of the polymers, were determined using GPC analysis. Interestingly, the use of PIB Ru complex **8** at 0 °C achieved 82% monomer conversion in less than 5 min, no significant change in conversion was seen over 60 min. The result was comparable to the non-supported complex **HG2** giving 84% conversion. Furthermore, the average molecular weights of the polymer and the PDI's using complex **8** ($M_w = 51,700$ g/mol, PDI = 1.6, entry 1) and complex **HG2** ($M_w = 59,500$ g/mol, PDI = 1.7, entry 2) are quite comparable. However, carrying out the reaction at room temperature resulted in 70% conversion for both complexes, affording polymers with low molecular weights and broad PDI's (entry 3 and 4), even at longer reaction times (2 h) no improvement was seen. We attribute the low molecular weight of the polymers to the very fast equilibration rate. The trans/cis double bond ratio in the polymer chain was determined from ¹³C NMR spectroscopy. The olefinic peaks of the polymer appear at $\delta = 130.93$ ppm (trans) and 130.30 ppm (cis) are in accord with previous reports, both complexes resulted in polymer **P4** having a slight excess of trans ratio (trans/cis ~80:20).^{8,49}

In view of these encouraging results, and to examine the scope of complex **8** we decided to investigate the ROMP of several functionalized cyclopentene monomers **M5-M7**. According to our theoretical calculations as depicted in Figure 2 the hydroxyl functionalized cyclopentene **M5** has the highest strain energy

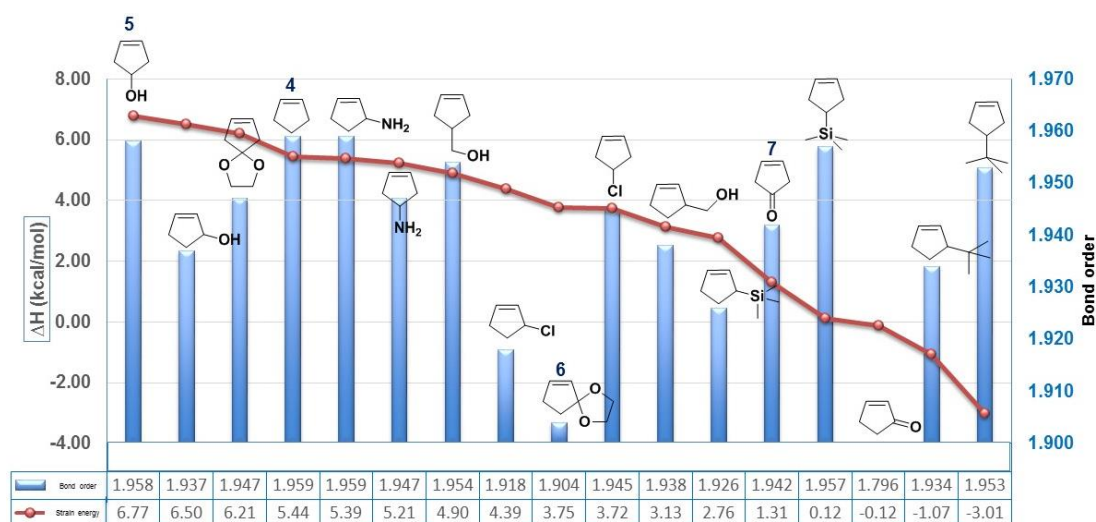


Figure 2- Density functional theory (DFT) calculations for cyclopentene **M4** and functionalized cyclopentene monomers **M5-M7**. Ring strain energy in (kcal/mol) (red square) and bond order (Green column). (Calculations were performed with Gaussian 09, DFT B3LYP/6-31G**).

6.77 kcal/mol and a bond order of 1.96. Moreover, this would result in higher monomer conversions than cyclopentene **M4** which has a slightly lower ring strain energy of 5.44 kcal/mol with the same bond order 1.96. Other functionalized derivatives that were selected for ROMP included monomers **M6** and **M7** in order to validate our predicated model. The calculated strain energy for monomer **M6** is 3.75 kcal/mol (a difference of 1.7 kcal/mol) which is slightly lower in value than that of cyclopentene **M4**, suggesting the polymerization may or may not occur under the same reaction conditions. On the other hand, ketone **M7** is predicated to have a very low strain energy 1.31 kcal/mol, implying that ROMP of the monomer is not feasible.

The hydroxyl cyclic monomer **M5** was polymerized using catalyst **HG2** and **8** under similar catalyst loading at 0 °C and room temperature, to afford polymer **P5**. The progress of the reaction was monitored using ¹H NMR spectroscopy. Interestingly, as predicated by DFT calculations a marked difference in the % conversion was observed. A higher monomer conversion is achieved at both temperatures for the ROMP of 3-cyclopentene-1-ol **M5** in comparison with ROMP of cyclopentene **M4** as depicted in Table 1 (entries 1, 3, 5 and 7). Both complexes afforded the same trans/cis ratio for **P5** ~79:21. Moreover, this was found to be very close to the ratio for **P4**. GPC analysis of polymer **P5** in THF resulted significantly in lower molecular weight polymers, this could be due to the partial solubility of polymer **P5** in THF.

ROMP of monomer **M5** at room temperature results in a slightly higher molecular weight polymer having narrow PDI ($M_w = 7,500\text{g/mol}$ and $\text{PDI} = 1.43$), while carrying out the ROMP at 0 °C affords a non-equilibrated polymer with a broader PDI ($M_w = 6,900\text{g/mol}$ and $\text{PDI} = 2.48$). PIB supported Ru complex **8** and its homogenous analogue **HG2** both display similar good performance resulting in high monomer conversion (Table 1,

entry **7** and **8**), the only difference resided in that the PIB Ru complex results in a slightly higher M_w polymer ($M_w = 7,500\text{g/mol}$) than its homogeneous counterpart ($M_w = 5,800\text{g/mol}$).

Table 1. Results for the ROMP of monomers **M4** and **M5** using Ru complex **HG2** and **8**.

Entry ^a	Polymer	T (°C)	Yield ^c (%)	M_w^d (g/mol)	PDI ^d	Ru content ppm	Ru content (%)	
1		0	40mg	82	51,700	1.57	690	11
2		0 ^b	50mg	84	59,600	1.69	ND	
3		25	45mg	71	19,800	2.74	297	5.3
4		25 ^b	60mg	70	33,400	2.92	2715	65
5		0	35mg	94	6,900	2.48	1548	21.6
6		0 ^b	45mg	96	10500	1.80	ND	
7		25	39mg	80	7,500	1.43	953	71 ^c ,15
8		25 ^b	119mg	74.4	5,800	1.57	4434	98.4
9		25 ^d	715mg	84%	3,800	1.38	2500	96

[a] The loading of complex **HG2** and **8** was 0.225 mol %. The substrate concentrations was 1.1 mmol in THF (0.4mL), and the reactions were carried out in a sealed flask under a nitrogen atmosphere for 60 min at temperatures indicated in the table.[b] Using non- supported **HG** complex. ND- not determined.
[c] Before phase separation.

Finally, monomers **M6** and **M7** were selected for the ROMP reaction at 0 °C and 25 °C using both Ru complexes **HG2** and **8** to support our assumptions. The % conversion was insignificant, only oligomer formation was seen by GPC analysis. This correlates to what was predicted by DFT calculations, hence, both monomers having a low ring strain energy **M6** 3.75 kcal/mol and **M7** 1.31 kcal/mol.

In general, the experimental results obtained in this study correlate really well with the DFT calculations determined for the strain energies of the cyclic olefins. Under the ROMP reaction conditions used we can hypothesize that the minimal strain energy needed to achieve high % conversion of the monomer to the polymer possibly should be above 5.2 kcal/mol as calculated using DFT.

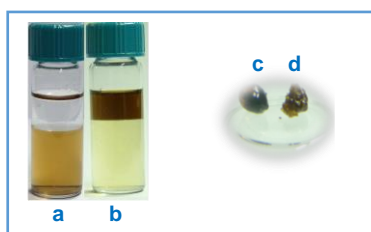


Figure 3- Images of visual comparison of the polymer phase separated product from Ru residues. (a) heptane/methanol mixture- methanol (bottom) layer contains both the Homogenous complex **HG2** and polymer product. (b) heptane/methanol mixture- heptane (top) layer contains the PIB supported complex **8** and polymer product in the methanol (bottom) layer. (c) Polymer prepared using **HG2** complex. (d) Polymer prepared using complex **8**.

A Biphasic catalyst system represents a desirable alternative to homogeneous catalytic reactions due to the practical simplicity with which the supported Ru catalyst and products can be separated. For the product purification, a straightforward procedure was used. Upon completion of the ROMP, the reaction mixture was quenched using ethyl vinyl ether and the solvent was concentrated to afford the crude product. The polymer and PIB Ru catalyst **8** residue were then separated using a biphasic system, by adding an equivolume mixture of heptane and methanol. The product polymer was insoluble in non-polar solvents, moreover, to our advantage completely soluble in methanol. Hence, the polymer was recovered in the methanol solution, while the Ru complex remained in the heptane phase. The solubility of the polymer was also explored in water, which resulted to be partially soluble. This solubility difference is evident in a visual comparison as depicted in Figure 3. While the methanol phase of the homogeneous Ru complex **HG2** was highly colored (hence, containing the polymer products and Ru residues), the methanol phase of the PIB supported complex **8** was essentially colorless containing the polymer product. Moreover, the heptane phase was colored due to the Ru residues.

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was used to determine the content of Ru leaching in the polymer products (the results are shown in Table 1). Noticeably, the residual Ru in all the products obtained using PIB Ru complex **8** were found to be lower in comparison to the polymers obtained using the non-supported Ru complex **HG2**. Consequently, the isolated polypentenamer **P4** when employing the supported complex **8** resulted in 297 ppm (5.3%) Ru contamination without precipitation (entry 3), however, the use of **HG2** complex afforded **P4** with higher Ru residues 2715 ppm (65%) even after multiple precipitations with MeOH (entry 4). Furthermore, isolated **P5** showed 15% Ru contamination with the use of complex **8** in comparison to 98.4% Ru leaching upon the use of complex **HG2** (entries 7 and 8).

The findings are particularly notable for large scale applications, in terms of its convenience providing an attractive alternative to easily separate the catalyst from the reaction products.

Conclusions

In summary, we have investigated the ROMP of non-functionalized and various functionalized cyclopentene using a soluble supported second generation Ru complex, which showed analogous activity to its homogeneous counterpart. Moreover, the practical simplicity of separating the soluble supported complex from the polymer product provides an alternative method to homogeneous catalysts.

The residual Ru contamination in the polymer products was significantly lower when using the PIB supported complex in comparison to the non-supported analogue even after the traditional method of multiple precipitations. Further studies and other investigations on different functionalized cyclic monomers using the soluble supported complex will be reported in due course.

Experimental Section

Materials and Reagents

PIB Ru catalyst **8** was prepared according to literature procedure.⁵² PIB (Glissopal 1000) was a gift from BASF. All other reagents were purchased from Sigma Aldrich. All reactions were carried out under argon using solvents and reagents as commercially supplied without further purification, unless otherwise stated. ¹H NMR, ³¹P NMR and ¹³C NMR spectra were recorded on a Bruker Avance II 400 spectrometer, using the residual solvent resonance of THF or tetramethylsilane (TMS) as an internal reference and are given in ppm. Number-average (M_n) and weight average (M_w) were determined by GPC analyses, which were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) mixed medium columns (LT5000L) at 35 °C with a flow rate of 1.0 mL/min. A 12-point universal calibration curve was recorded using narrow polydispersity polystyrene standards. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230–400 mesh) unless otherwise indicated. Thin-layer chromatography was performed on Merck aluminum-backed plates

precoated with silica (0.2 mm, 60 F254). ICP-MS data were obtained using a Perkin-Elmer ELAN DRCe instrument.

The ring strain energies of the substituted cyclohexene have been calculated using density functional theory (DFT) studies, which was performed using RB3LYP method at 6-31G (D) basis set using SPARTAN '10 MECHANICS PROGRAM: PC/x86 1.1.0 software.

General procedure for the ring-opening metathesis polymerization

Preparation of Polymer **P4**. In a glove box, the appropriate monomer **M4** (0.1 mL, 1.1 mmol) and the PIB-supported Ru complex **8** (0.225 mol%, 2.44×10^{-3} mmol) were weighed into a Schlenk flask and dissolved in anhydrous THF (0.4 mL), and the reaction was stirred for 1 h at the desired temperature indicated in table 1. The polymerization was terminated by injecting 0.1 mL of ethyl vinyl ether and the crude mixture was analyzed by ^1H NMR spectroscopy to determine the % monomer conversion.

Separation of PIB catalyst from product

The polymer THF solution was evaporated to dryness and the crude polymer was dissolved in MeOH (1 mL), hexane (1 mL) was added and the layers were separated. The MeOH layer was then concentrated under vacuum to afford the polymer.

Polymer (P4)

1. When using PIB-supported complex **8**;
 - at 0 °C; Yield: 40 mg; GPC: $M_w = 51,700$ g/mol, PDI = 1.57; ICP: 11% Ru leaching.
 - at 25 °C; Yield: 71 mg; GPC: $M_w = 19,800$ g/mol, PDI = 2.74; ICP: 5.3% Ru leaching.
2. When using Ru catalyst **HG2**;
 - at 0 °C; Yield: 50 mg; GPC: $M_w = 59,600$ g/mol, PDI = 1.69.
 - at 25 °C; Yield: 70 mg; GPC: $M_w = 33,400$ g/mol, PDI = 2.92; ICP: 65% Ru leaching.

^1H and ^{13}C NMR data was in agreement with previously reported work.

Polymer (P5)

3. When using PIB-supported complex **8**;
 - at 0 °C; Yield: 35 mg; GPC: $M_w = 6,900$ g/mol, PDI = 2.48; ICP: 21.6% Ru leaching.
 - at 25 °C; Yield: 39 mg; GPC: $M_w = 7,500$ g/mol, PDI = 1.43; ICP: 15% Ru leaching.
4. When using Ru catalyst **HG2**;
 - at 0 °C; Yield: 45 mg; GPC: $M_w = 10,500$ g/mol, PDI = 1.80.
 - at 25 °C; Yield: 119 mg; GPC: $M_w = 5,800$ g/mol, PDI = 1.57; ICP: 98.4% Ru leaching.

^1H NMR (400 MHz, THF- d_6) δ : 5.52 (bs, 2H), 3.45-3.60 (m, 1H), 2.67 (bs, 1H), 2.15 (s, 4H), ^{13}C NMR (100 MHz, THF- d_6) δ : 130.29, 128.86, 71.71, 41.85, 41.54.

ICP-MS Digestion Procedure

The appropriate polymer and 4 mL of concentrated nitric acid was added to a glass vial as reported previously.⁵⁶ The mixture was heated to 110 °C until the entire sample was dissolved. The solution was then allowed to stand at room temperature. At this point, the concentrated acidic aqueous solution was diluted with distilled water, and the diluted sample solution was analyzed by ICP-MS.

Acknowledgements

The authors gratefully acknowledge support of this work from the Qatar National Research Fund project number: NPRP X-095-1-024.

Keywords: ring opening metathesis polymerization (ROMP) • phase separable Hoveyda-Grubbs catalyst • polypentenamer • polyvinyl alcohol • Ru metathesis

- [1] A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127.
- [2] A. Demonceau, A. F. Noels, E. Saive, A. J. Hubert, *J. Mol. Catal.* **1992**, *76*, 123.
- [3] M. B. France, R. A. Paciello, R. H. Grubbs, *Macromolecules* **1993**, *26*, 4739.
- [4] A. Hejl, O. A. Scherman, R. H. Grubbs, *Macromolecules*, 2005, **38**, 7214-7218.
- [5] C. A. Busacca, D. R. Fandrick, J. J. Song, C. H. Senanayake, *Adv. Synth. Catal.*, 2011, **353**, 1825-1864.
- [6] S. Nayab, W. Park, H. Y. Woo, I. K. Sung, W. S. Hwang, H. Lee, *Polyhedron*, 2012, **42**, 102-109.
- [7] A. E. Madkour, A. H. R. Koch, K. Lienkamp, G. N. Tew, *Macromolecules*, 2010, **43**, 4557-4561.
- [8] O. Derek, B. Duz, Y. Imamoglu, *Eur. Polym. J.*, 2006, **42**, 368-374.
- [9] B. Scheibitz, A. Prager, M. R. Buchmeiser, *Macromolecules*, 2009, **42**, 3493-3499.
- [10] A. Szadkowska, C. Samojłowicz, K. Grela, *Pure Appl. Chem.*, 2011, **83**, 553-563.
- [11] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746-1787.
- [12] E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.*, 2007, **251**, 726-764.
- [13] M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565-1604.
- [14] G. O. Wilson, M. M. Caruso, N. T. Reimer, S. R. White, N. R. Sottos, J. S. Moore, *Chem. Mater.*, 2008, **20**, 3288-3297.
- [15] C. R. South, C. Burd, M. Weck, *Acc. Chem. Res.*, 2007, **40**, 63-74.
- [16] G. C. Vougioukalakis, *Chem.-Eur. J.*, 2012, **18**, 8868-8880.
- [17] W. J. Sommer, M. Weck, *Coord. Chem. Rev.*, 2007, **251**, 860-873.
- [18] M. R. Buchmeiser, *Chem. Rev.*, 2009, **109**, 303-321.
- [19] S. C. Schurer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem. Int. Ed.*, 2000, **39**, 3898-3891.
- [20] K. Mennecke, K. Grela, U. Kunz, A. Kirschning, *Synlett.*, 2005, 2948-2952.
- [21] L. Jafarpour, M. P. Heck, C. Baylon, H. M. Lee, C. Mioskowski, S. P. Nolan, *Organometallics*, 2002, **21**, 671-679.
- [22] F. M. Sinner, M. R. Buchmeiser, *Angew. Chem. Int. Ed.*, 2000, **39**, 1433-1435.

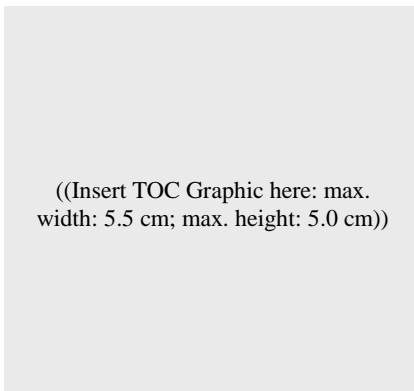
-
- [23] S. H. Hong, R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 3508-3509.
- [24] M. T. Zarka, O. Nuyken, R. F. Weberskirch, *Macromol. Rapid Commun.*, 2004, **25**, 858-862.
- [25] S. J. Connon, A. M. Dunne, S. Blechert, *Angew. Chem. Int. Ed.*, 2002, **41**, 3835-3838.
- [26] S. Varray, R. Lazaro, J. Martinez, F. Lamaty, *Organometallics*, 2003, **22**, 2426-2435.
- [27] M. Mayr, M. R. Buchmeiser, K. Wurst, *Adv. Synth. Catal.*, 2002, **344**, 712-719.
- [28] D. P. Allen, M. M. Van Wingerden, R. H. Grubbs, *Org. Lett.*, 2009, **11**, 1261-1264.
- [29] D. Fischer, S. Blechert, *Adv. Synth. Catal.*, 2005, **347**, 1329-1332.
- [30] R. Tuba, R. C. da Costa, H. S. Bazzi, J. A. Gadysz, *Acs. Catal.*, 2012, **2**, 155-162.
- [31] M. Matsugi, D. P. Curran, *J. Org. Chem.*, 2005, **70**, 1636-1642.
- [32] Q. W. Yao, M. Sheets, *J. Organomet. Chem.*, 2005, **690**, 3577-3584.
- [33] H. Clavier, N. Audic, M. Mauduit, J. C. Guillemin, *Chem. Commun.*, 2004, 2282-2283.
- [34] A. Michrowska, L. Gulajski, Z. Kaczmarska, K. Mennecke, A. Kirschning, K. Grela, *Green Chem.*, 2006, **8**, 685-688.
- [35] K. Skowerski, C. Wierzbicka, G. Szczepaniak, L. Gulajski, M. Bieniek, K. Grela, *Green Chem.*, 2012, **14**, 3264-3268.
- [36] M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock, P. A. Procopiou, *Synlett*, 2000, 1007-1009.
- [37] Q. W. Yao, *Angew. Chem. Int. Ed.*, 2000, **39**, 3896-3897.
- [38] K. Breitenkamp, T. Emrick, *J. Polym. Sci. Polym. Chem.*, 2005, **43**, 5715-5721.
- [39] J. P. Gallivan, J. P. Jordan, R. H. Grubbs, *Tetrahedron Lett.*, 2005, **46**, 2577-2580.
- [40] S. H. Hong, R. H. Grubbs, *Org. Lett.*, 2007, **9**, 1955-1957.
- [41] C. Hobbs, Y. C. Yang, J. Ling, S. Nicola, H. L. Su, H. S. Bazzi, D. E. Bergbreiter, *Org. Lett.*, 2011, **13**, 3904-3907.
- [42] A. J. Amass, *British Polymer Journal*, 1972, **4**, 327-341.
- [43] K. Sanui, R. W. Lenz, Macknigh.Wj, *Macromolecules*, 1974, **7**, 101-105.
- [44] Z. Lu, X. Huang and J. Huang, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 109-115.
- [45] G. Kostov, F. Boschet, J. Buller, L. Badache, S. Brandsadter, B. Ameduri, *Macromolecules*, 2011, **44**, 1841-1855.
- [46] K. Shimamura, Y. Munesawa, T. Uchida and N. Hikasa, *Polym. Adv. Technol.*, 2002, **13**, 205-209.
- [47] Y. C. Yu, S. J. Shin, K. D. Ko, W. R. Yu, J. H. Youk, *Polymer*, 2013, **54**, 5595-5600.
- [48] C. W. Bielawski, R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2000, **39**, 2903-2906.
- [49] R. Tuba, R. H. Grubbs, *Polym. Chem., Uk*, 2013, **4**, 3959-3962.
- [50] S. B. Myers, R. A. Register, *Polymer*, 2008, **49**, 877-882.
- [51] C. Hongfa, H. L. Su, H. S. Bazzi, D. E. Bergbreiter, *Org. Lett.*, 2009, **11**, 665-667.
- [52] M. Al-Hashimi, C. Hongfa, B. George, H. S. Bazzi, D. E. Bergbreiter, *J. Polym. Sci. Polym. Chem.*, 2012, **50**, 3954-3959.
- [53] P. Hodge, S. D. Kamau, *Angew. Chem. Int. Ed.*, 2003, **42**, 2412-2414.
- [54] S. T. Trzaska, L. B. W. Lee, R. A. Register, *Macromolecules*, 2000, **33**, 9215-9221.
- [55] E. A. Ofstead, N. Calderon, *Makromolekul Chem.*, 1972, **154**, 21-25.
- [56] M. Al-Hashimi, M. D. Abu Bakar, K. Elsaid, D. E. Bergbreiter, H. S. Bazzi, *RSC Adv.*, 2014, **4**, 43766-43771.
-

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents



*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title
