Ring-Opening Metathesis Polymerization of Bicyclo[2.2.1]hepta-2,5-diene (Norbornadiene) Initiated by New Ruthenium(II) Complex

Esra Evrim Yalçınkaya,[1] Osman Dayan,[2] Mehmet Balcan,[1] Çetin Güler[1]

[1]Chemistry Department, Faculty of Science, Ege University, Bornova, 35100 Izmir, Turkey
[2]Laboratory of Inorganic Synthesis and Molecular Catalysis, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

Correspondence to: E. E. Yalçınkaya (E-mail: esra.evrim.saka@ege.edu.tr)

ABSTRACT: The polymerization of norbornadiene (NBD) initiated by a novel ruthenium (Ru)(II) complex (**3**) containing 1,1′-pyridine-2,6-diylbis[3-(dimethylamino)prop-2-en-1-one] (**1**) as ligand has been investigated. Ru complexes exhibit more catalytic activity in the ring-opening metathesis polymerization (ROMP) of NBD when activated with trimethylsilyldiazomethane (TMSD). The influence of the various experimental parameters such as reaction time and temperature, nature of the solvent and catalyst, ratio of the NBD/Ru, and TMSD addition has been investigated. The polymers have been obtained in high yields with a relatively low polydispersity index for ROMP and a high $\bar{M}_n$ and $\bar{M}_w$ values in a monomodal distribution. Their structures have been determined by means of FTIR and ^{1}H-NMR spectroscopy. Thermal properties have been determined via thermogravimetric analysis and DTG methods. The NBD polymerization results that initiated by Ru-based catalyst coordinated to amine ligand have been compared to initiated by [RuCl$_2$(p-cymene)]$_2$. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Norbornadiene (NBD) can serve as monomer for the synthesis of high-molecular-mass polymers with widely varying structure. This cyclic compound gives quite different chemical polymer structures, and the resulting variation of properties can be achieved by the selection of various catalyst systems. The cyclolinear structures are formed in the presence of ring-opening metathesis polymerization (ROMP) catalysts (e.g., based on Mo, W, Re, or Ru compounds) by opening of the strained five-membered-ring NBD, and thus, the polymer can be synthesized.[1–4]

Although olefin metathesis was discovered as early as 1955,[5] it has only achieved a leading role in synthetic methodology in the last decade. This is mainly attributed to advances in the field of catalysis and organometallic chemistry, which have been heavily influenced by the work of Grubbs and coworkers[6–8] and Schrock et al.[9] in developing well-defined transition metal–carbene complexes.[10,11] The most notorious representative of new generation of olefin metathesis catalysts is the metal–alkylidene complex RuCl$_2$(=CHPh)(PCy$_3$)$_2$ developed by Grubbs and coworkers.[12,13] This complex, along with similar monometallic and bimetallic species, has found numerous applications in

ROMP over the past few years.[14,15] Delaude et al. found that the dimeric ruthenium (Ru) catalyst [RuCl$_2$(p-cymene)]$_2$ was capable of ROMP-functionalized NBDs in the presence of trimethylsilyldiazomethane (TMSD) as the cocatalyst.[16] This research group also showed that readily available Ru complexes of the type RuCl$_2$(arene)(PR$_3$) are versatile and efficient promoters for the ROMP of both strained and low-strain olefins when activated by a suitable carbene precursor such as TMSD.[17,18] ROMP of NBD by using Ru complexes of the type [Ru(η^5-C$_9$H$_7$)Cl(1,5-cyclooctadiene)] was reported by Alvarez et al.[19] with a high molecular weight and narrow polydispersity index (PDI) at room temperature (RT).

The growing interest in the development of new polymers formed from ROMP has stimulated researchers to search new catalysts for this reaction. Although it is reasonable to assume that Grubbs-type complexes are powerful catalysts for olefin metathesis, new catalysts must be formulated with the design of new materials,[20,21] especially using transition metal complexes with different ligands.[21,22] Thus, the properties of the polymers depend on the ligands coordinated to the metal center not directly engaged in reaction. The most commonly used ancillary ligands are the phosphines and amine ligands, where they tune

the substitution lability of metal complexes via a systematic variation of their steric and electronic properties.[23] Although many studies of ROMP of NBDs with Mo- and W-containing catalysts[24–26] and also Grubbs catalysts have been carried out to date,[6–8] there is still demand for stable and easily handled complexes prepared from cheap starting materials, which make them preferred catalyst precursors. There has been rarely report of the Ru(II)–amine complexes as catalyst for ROMP of NBD. Moreover, there are scarcely any studies of NBD synthesis with the newly synthesized Ru-based catalyst coordinated to amine ligand by ROMP with reporting ^{1}H-NMR and FTIR spectroscopy, thermal analysis, molecular weight, and investigation of experimental parameters. This article aims to contribute to development of Ru(II)–amine complexes that are able to catalyze ROMP of the highly strained NBD with high yield. To further sustain these observations, we have launched a detailed study of the polymerization of NBD in the presence of new Ru-based catalytic system with TMSD and compared this new catalyst with well-known $[RuCl_2(p\text{-cymene})]_2$ catalyst to determine the influence of the ligand on this polymerization. Also, we report the polymerization of NBD under a variety of experimental conditions in this article.

EXPERIMENTAL

Materials

All reactions and manipulations were performed under an argon (Ar) atmosphere by using conventional Schlenk tube techniques. Ar gas was dried by passing through P_2O_5 (97%, Aldrich). The $[RuCl_2(p\text{-cymene})]_2$ (**2**) was prepared according to the method given in the literature[27]; the structure and the purity of the dimer were checked with FTIR and ^{1}H-NMR spectroscopy. NBD was supplied by Aldrich and distilled from CaH_2 and dried over P_2O_5 under Ar gas before use. Commercial-grade solvents were also dried under Ar atmosphere and distilled before use. Solutions of the catalyst were freshly prepared for each reaction. All of the chemicals used were reagent grade. TMSD (Aldrich) was supplied as $2M$ solution in hexanes. This solution was further diluted by addition of a suitable solvent.

Characterization Techniques

^{1}H-NMR (400 MHz) spectra were recorded on a Varian Unity 400 Spectrometer. FTIR spectra were obtained with a Perkin Elmer Pyris 1 FTIR Spectrometer. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and PDI ($\bar{M}_w/\bar{M}_n$) of the polymers were determined by gel permeation chromatography (GPC). GPC analysis of the polymers was performed on a Hewlett-Packard HPLC system with a differential refractometer detector. Tetrahydrofuran (THF) served as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities were reported versus monodisperse polystyrene standards. Thermal degradation was studied with a thermogravimetric analyzer (Perkin Elmer Pyris 1 TGA/DTA) by the heating of samples from ambient temperature to 1000°C at 10°C/min under a 10 bar dry N_2.

Synthesis of 1,1′-Pyridine-2,6-diylbis[3-(dimethylamino)prop-2-en-1-one] (1)

This compound was synthesized according to a modified literature procedure.[28] 2,6-Diacetylpyridine (0.5 g, 3 mmol) was dis-

solved in 10 mL of toluene in the Schlenk tube. Then, 3 mL of N, N-dimethylformamide dimethylacetal was added and stirred over night at 80–90°C in Ar atmosphere. The solvent was filtered by cannula wire, and the residue was dried *in vacuo* at RT. Orange color solid, 80% yield: ^{1}H-NMR (CDCl₃) δ (ppm) 8.12 (t, 1H, $J = 6.4$, pyridine-H_p), 7.91–7.98 (m, 4H; pyridine-H_m, $HC{=}N(CH_3)_2$), 6.59 (d, 2H, $J = 12.4$, O=C—CH), 3.21–2.98 (ss, 12H, $N(CH_3)_2$). ^{13}C-NMR (CDCl₃) δ (ppm) 183.5, 154.8, 148.9, 137.5, 123.62, 89.7, 37.3. FTIR (cm^{-1}) 3099, 3053, 2911, 1645, 1632, 1584, 1494, 1395, 1261, 1129, 1057, 993, 897, 783.

Synthesis of (3)

$[RuCl_2(p\text{-cymene})]_2$ (**2**) (0.1 g, 0.16 mmol) was dissolved in dry dichloromethane (10 mL) and subsequently amine ligand (**1**) (0.088 g, 0.32 mmol) was added slowly. The reaction mixture was stirred at RT for a night in Ar atmosphere (Scheme 2). The solution was concentrated by removing half of the solvent *in vacuo*. The final product was precipitated in diethylether, filtered, and dried *in vacuo* at RT. Brown solid, 90% yield (0.17 g): ^{1}H-NMR (CDCl₃) δ (ppm) 8.75 (t, 1H, $J = 8.0$, pyridine-H_p), 8.20 (d, 2H, $J = 7.8$, pyridine-H_m), 7.60 (d, 2H, $J = 6.2$, $HC{=}N(CH_3)_2$), 6.30 (d, 2H, $J = 6.8$, O=C—CH), 5.25–5.45 (dd, 4H, $J_1 = 5.6$; $J_2 = 6.0$, arom.), 3.05–3.15 (ss, 12H, $N(CH_3)_2$), 2.75 (m, 1H, C$H(CH_3)_2$), 2.20 (s, 3H, CH_3), 1.15–1.20 (d, 6H, $J = 7.2$, CH(C$H_3)_2$). ^{13}C-NMR (CDCl₃) δ (ppm) (p-cymene) 103.9, 103.5, 86.7, 83.6, 30.6, 21.1, 18.5; (ligand) 186.7, 160.1, 154.6, 138.1, 127.9, 91.5, 41.3. FTIR (cm^{-1}) 3048, 2962, 2865, 1640, 1623, 1523, 1489, 1473, 1394, 1362, 1242, 1142, 1083, 1056, 1010, 976, 949, 897, 784, 714. Anal. calcd. for $RuC_{25}H_{33}Cl_2N_3O_2$ (579.52): C, 51.75; H, 5.69; N, 7.24%. Found: C, 51.05; H, 5.35; N, 6.81%.

Polymerization of NBD

In a typical ROMP experiment, 0.04 mmol (0.023 g) of the catalyst solution in 3 mL of dry CH_2Cl_2 was transferred into a Schlenk tube under Ar and stirred for a few minutes. A total of 8 mmol of NBD monomer was injected into the catalyst solution and stirred for a few minutes before 1 mL of 0.1M TMSD in the reaction solvent (CH_2Cl_2) (0.1 mmol) was added dropwise over a 30-min period. The reaction mixture was kept at RT and was also refluxed at 40°C for different time periods ([Ru]/[NBD] = 1/200). Then, the polymer was precipitated in large amount of methanol by adding dropwise and stirring vigorously. The precipitated polymer was filtered and washed with small portions of methanol several times. It was dried *in vacuo* overnight and characterized by FTIR, GPC, and ^{1}H-NMR spectroscopy. ^{1}H-NMR (400 MHz, CDCl₃): δ 5.6–5.2 (m, 4H), 3.6 (s, 1H), 3.2 (s,1H), 2.3 (s, 2H), 1.2 (s, 2H). FTIR (cm^{-1}) 3380, 2962, 2915, 1681, 1425, 865.

RESULTS AND DISCUSSION

The synthesis of 1,1′-pyridine-2,6-diylbis[3-(dimethylamino)-prop-2-en-1-one] (**1**) ligand is given in Scheme 1. The band assignment for the FTIR spectrum of ligand was as follows: olefinic C—H stretching band in C=CH and aromatic C—H stretching band at about 3000 cm^{-1}; C—H stretching in CH_3 and C—H stretching in CH_2 at about 2900 cm^{-1}; C—H stretching in N—CH_3 at about 2800 cm^{-1}; C=O diketones carbonyl
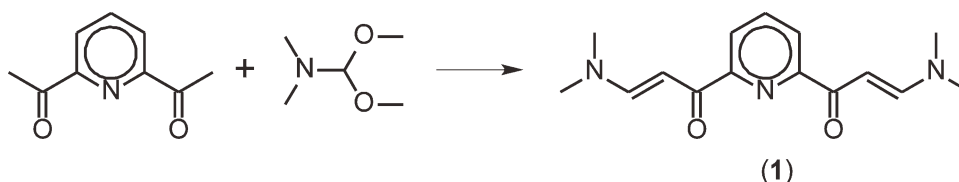
Scheme 1. Synthetic route of 1,1′-pyridine-2,6-diylbis[3-(dimethylamino)prop-2-en-1-one] (**1**).

absorption band at 1655–1635 cm^{-1}; C=C in pyridine ring at 1600–1585 cm^{-1}; C=C in chain and C=N in pyridine ring at 1680–1620 cm^{-1}; C—C in pyridine ring at 1500–1400 cm^{-1}; and C—N in ring at 1335–1020 cm^{-1}. Further bands were shown by aromatic rings in the fingerprint region between 1225 and 950 cm^{-1}.

From the ^{1}H-NMR spectrum of amine ligand, the peak at 8.12 ppm was assigned to CH group proton of pyridine-H_p. The peaks at 7.91–7.98 ppm were assigned to four CH groups protons of pyridine-H_m and HC=N(CH$_3$)$_2$. The δ value of two CH groups protons that O=C—CH was shown at 6.59 ppm. The signals on 3.21–2.98 ppm were assigned to four CH$_3$ groups of N(CH$_3$)$_2$.

The Ru(II) complex (**3**) containing 1,1′-pyridine-2,6-diylbis[3-(dimethylamino)prop-2-en-1-one] ligand was synthesized by starting from [RuCl$_2$(p-cymene)]$_2$ (Scheme 2). From the FTIR spectrum of the catalyst: olefinic C—H stretching in C=CH and aromatic C—H stretching at about 3040 cm^{-1}; C—H stretching in CH$_3$ and C—H stretching in CH$_2$ at about 2900 cm^{-1}; C—H stretching in N—CH$_3$ at about 2800 cm^{-1}; C=C in chain and C=N ring at about 1620 cm^{-1}; C=O diketones carbonyl absorption band at about 1640 cm^{-1}; C=C in pyridine ring at about 1523 cm^{-1}; C—C in pyridine ring at 1500–1400 cm^{-1}; and C—N in ring at 1335–1020 cm^{-1}. Further bands were shown by alkanes and alkenes in the fingerprint region between 1400 and 800 cm^{-1}.

The structural analysis of **3** was determined on the basis of ^{1}H- and ^{13}C-NMR spectra. From the ^{1}H-NMR spectra, the effect of coordination of the Ru(II) to the 1,1′-pyridine-2,6-diylbis[3-(dimethylamino)prop-2-en-1-one] ligand through the pyridyl nitrogen for **3** could clearly be seen. The protons of the pyridine ring of **3** are shifted downfield compared with free ligands (**1**). The triplet peak at 8.75 ppm was assigned to CH group proton of pyridine-H_p. The doublet peak at 8.20 ppm was assigned to other two CH group protons of pyridine-H_m. The δ value of two CH groups protons of HC=N(CH$_3$)$_2$ chain was shown at 7.60 ppm. The doublet signal on 6.30 ppm was assigned to two

CH groups of O=C—CH chain. The double doublet peaks at 5.25–5.45 ppm were assigned to four CH groups of benzene ring protons. The peaks at 3.05–3.15 ppm were assigned to four CH_3 groups of N(CH$_3$)$_2$. By calculating peak areas, the δ value of CH group proton of CH(CH$_3$)$_2$ was assigned at 2.75 ppm, CH_3 group proton of CH(CH_3)$_2$ was assigned at 2.20 ppm, and two CH_3 group protons of CH(CH_3)$_2$ were represented at 1.15–1.20 ppm. Also, the total count of carbon peaks for **3** matched well with the composition of the complex in ^{13}C-NMR spectra. When the ligand and complex carbon peaks were compared, the δ values were shifted to high values in the ^{13}C-NMR spectra especially at carbonyl and pyridine carbons.

The polymerization of NBD in dichloromethane at RT in the presence of Ru(II) complex (**3**) and TMSD catalytic system was achieved (Scheme 3). Furthermore, the influence of the various experimental parameters on the polymer yield was investigated in this study. For some conditions, however, yields were low, but these results were convincing as they were promising enough to launch a systematic study of the reaction.

First, NBD monomer was polymerized in various media by ROMP. Thus, Ru(II) complex (**3**) (0.025 mmol, 0.014 g) was dissolved in 3 mL of the following organic solvents under Ar atmosphere: 1,2-dichloroethane, toluene, THF, dichloromethane, and dimethylsulfoxide. The same controlled polymerization conditions were carried out. The results of ROMP of NBD with the solvents are summarized in Table I. No precipitation took place when the reaction was carried out in dimethylsulfoxide. The polymerization of NBD using the catalyst was first examined in CH$_2$Cl$_2$ at 25°C (Table I, entry 1). The viscosity of the solution increased more rapidly with CH$_2$Cl$_2$ in comparison to the other solvents when it was stirred at 25°C, which means the reaction time was shorter. The resulting mixture was diluted and poured into MeOH by stirring continuously, giving the polymer as a white-yellow solid precipitate in a comparatively higher yield (55%). In all cases, the polymer was identified by ^{1}H-NMR spectroscopy. Because the highest yield of polymer was obtained in dichloromethane, this particular solvent was chosen as the reaction medium for all subsequent investigations.
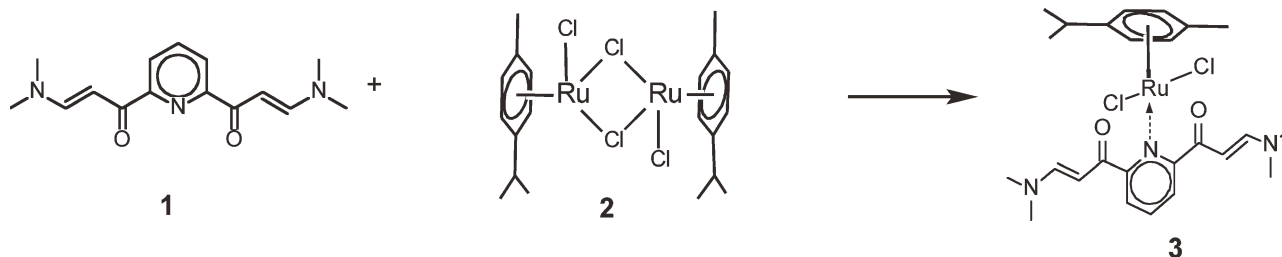
Scheme 2. Synthetic route of (**3**).
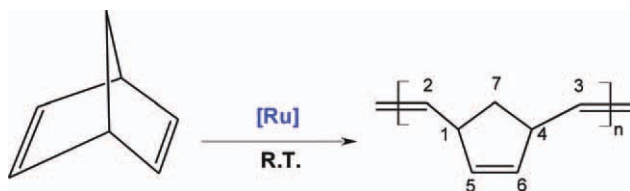
Scheme 3. ROMP of NBD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To further explore the catalytic potential of Ru(II) complex (**3**) concerning the ROMP of NBD, the monomer/catalyst ratio was increased (reactions at RT, in dichloromethane, and 18 h). The reactions were carried out for 1/200, 1/500, 1/1000, 1/1500, and 1/2000 catalyst/monomer ratio (Table II). The ratios of 50/1 and 100/1 were not preferred because of their low polymerization yield. The conversion slightly increased for Ru(II) complex (**3**), as the monomer/catalyst ratio was driven up to 1000/1 NBD with a maximum conversion of 55%. For the higher monomer/catalyst ratio, the conversions did not change significantly. As a result, optimum [M]/[C] ratio for the ROMP of NBD was found to be 1000/1.

For ROMP reactions of NBD, a linear increase of the conversion versus time was observed within the time period of 18 h at RT. After this period, the maximum conversion for NBD polymerization was reached. The solvent (CH_2Cl_2) amount was determined as 3 mL. Polymer product could not solve in any solvent when monomer was polymerized in the lower amount of solvent (<3 mL) despite the higher polymerization yield. The lower polymerization yield was obtained in the higher amount of solvent.

The polymerization reactions were carried out at RT and at 40°C reflux for 18 h in 3 mL of CH_2Cl_2 at constant [C]/[M] and other variables were kept constant. The polymerization yield was raised to 80% when the reaction was performed at reflux for 18 h. It was observed that when the reaction was carried out for 6 h at reflux, the yield was not changed. Therefore, optimum temperature was decided as for 6 h at 40°C reflux temperature because of shorter reaction time.

The role of the cocatalyst precursor on the polymerization process was emphasized. When the polymerization of NBD was tested with pure TMSD (without catalyst, 1 mL of a NBD solution in dichloromethane, and [NBD]/[TMSD] = 1000/1, RT and 40°C, and 6 h), no polymerization was observed. In a related study on the use of vinylidene–Ru complexes to catalyze

Table I. Polymerization of NBD in Various Solvents[a]

Entry	Solvent	Yield %
1	Dichloromethane	55
2	Toluene	27
3	Tetrahydrofuran	30
4	1,2-Dichloroethane	20
5	Dimethylsulfoxide	–

[a] Reactions at RT; [NBD]/[Ru] = 1000; and 6 h.

Table II. Polymerization of NBD with Various [C]/[M] Ratios[a]

Entry	[C]/[M]	Yield %
1	1/200	25
2	1/500	35
3	1/1000	55
4	1/1500	56
5	1/2000	57

[a] Reactions at RT, in CH_2Cl_2; [NBD]/[Ru] = 1000; and 18 h.

the ROMP of NBD derivatives, Katayama and Ozawa reported the unrivaled superiority of the trimethylsilylvinylidene species over various other aliphatic and aromatic derivatives.[29] Although no exact reason for this superiority was given, the authors assumed that the particularly high stability of silylvinylidene complexes might account for their outstanding catalytic activity.

However, when NBD was tested with Ru catalyst without being activated with TMSD ([NBD]/([Ru] = 1000/1, 3 mL dichloromethane, and 6 h), a conversion of 5% was observed. As the reaction was not activated by TMSD yet, the initial metal–carbene complex must have been resulted from a reaction between the catalyst and the olefin substrate. The catalyst performance is altered significantly when the reactions are initiated by a small amount of TMSD.

When a diazo compound was added to the reaction mixture, polymerization took place with no apparent induction time and high yields of polynorbornadienes (PNBDs) were obtained. We therefore assume that the diazo compound reacts with the precatalyst Ru(II)–amine complex to form a highly reactive coordinatively unsaturated Ru–carbene species that initiate the polymerization of NBD with no (or very short) observable induction time. Because of more active Ru–carbene complexes, 80% conversion was reached, which was much higher than in the case when no activator was used. The polymer exhibited a broad molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 3.53). The broadening of the molecular weight distribution was caused by the generation of multireactive sites (in the case of the activation *in situ* and by TMSD).

The rate of addition and the amount of diazo compound added to the monomer and catalyst solution at RT were investigated. As a result, it seemed to be the most efficient reaction when the original standard conditions (0.1 mmol of TMSD and 30 min addition time) were followed. Modifying the concentration of the TMSD solution or the rate of the syringe pusher used to

Table III. Properties of PNBD Formed with the Catalytic Systems (2) and (3) when Activated with a Catalytic Amount of TMSD[a]

	M_n	M_w	PDI	Yield %
[RuCl$_2$(*p*-cymene)]$_2$ (**2**)	22,450	48,600	2.16	60
Ru(II) complex (**3**)	34,300	121,300	3.53	80

[a] Reactions at 40°C reflux temperature, in CH_2Cl_2; [NBD]/[Ru] = 1000; and 6 h.
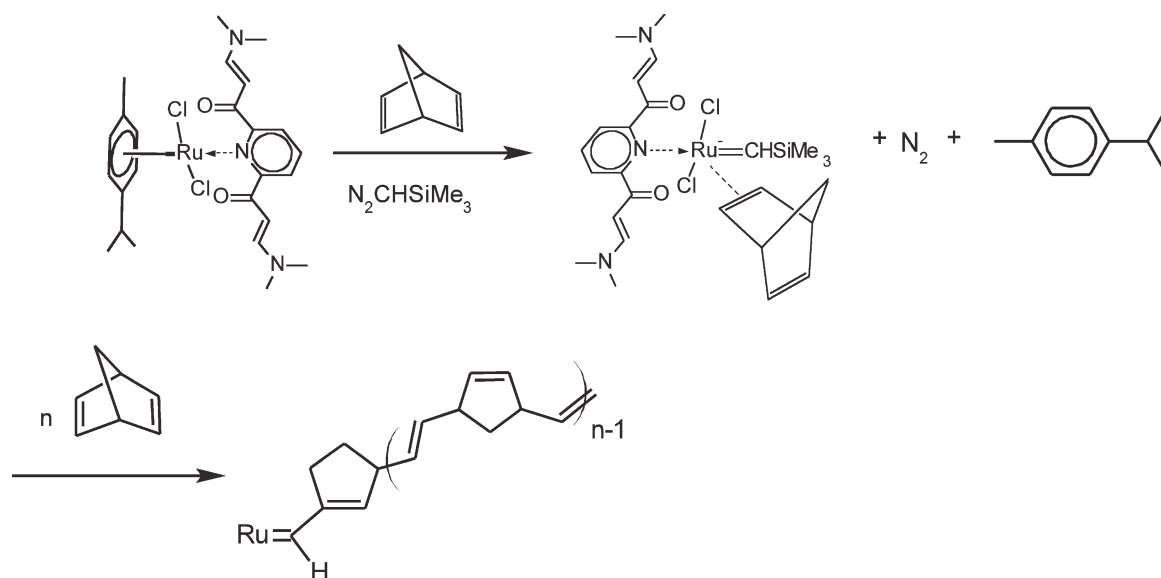
Scheme 4. Possible mechanism for the formation of the initial metal–carbene in the presence of TMSD.

add TMSD, as distinct from literature, did not result in any significant improvement and sometimes had a detrimental influence on the polymerization outcome. Instantaneous addition of TMSD led to polymers with a more broad distribution of high molecular weights.

As a result of the experiments committed in this study, optimum conditions for polymerization were detected. Polymerization was carried out with 1000/1 as an M/C ratio, in 3 mL of dry dichloromethane, at 40°C reflux temperature, and in 6 h.

In a final set of experiments, a ROMP reaction of NBD was run by [RuCl$_2$(p-cymene)]$_2$ (**2**) and Ru(II) complex (**3**). The results obtained using these catalysts are summarized in Table III. The catalytic system with amine ligands-substituted Ru complex (**3**) was more active. The ligands also play an important role when dealing with ROMP. It is well known that the ligand nature can have profound and largely unpredictable effects on the catalytic activity of the coordination complexes in the polymerization reactions and present results strongly support this fact. It exhibited a higher molecular weight and a better catalytic activity because of the steric and electronic properties of amine ligand. The polydispersities in these catalytic systems were broad, which indicated that the polymerization was subjected to transfer reactions.

Possible mechanism for the formation of the catalytically active species in ROMP reactions is given in Scheme 4.

The most likely process for the initiation of the ROMP of NBD involves the coordination of the diene to the metal center followed by ring-opening, 1,2-hydrogen shift and alkylidene ligand formation. Such a transformation can result from the different types of coordination of NBD ligand to the metal center. In the presence of an excess of NBD, the weakly coordinating alkene bond can be substituted by NBD molecule leading to the formation of alkylidene ligand and next metallacyclobutane unit.

Structural Characterization of the PNBD

The ^{1}H-NMR spectrum of PNBD demonstrated five well-separated groups of signals. The formation of an unsaturated PNBD with characteristic signals of the olefinic protons at ca. 5.6 and 5.4 ppm appeared simultaneously (protons denoted 5,6 and 2,3). From integral ratio of the signals due to protons denoted 1,4 at δ 3.6 (*cis* double bond) and δ 3.2 (*trans* double bond) ppm appeared. H$_1$/H$_4$ = 50 : 50 was found from the integrated areas under our reaction conditions. Two protons denoted 7 appeared at δ 2.4 and 1.3 ppm.

Further proof for the successful synthesis of PNBD was obtained by FTIR analysis. The absorption bands at 2960 and 2915 cm^{-1} were attributed to olefinic C—H stretching. The intense bands of 1681 and 1425 cm^{-1} were attributed to aliphatic C=C and C—H stretching in the spectrum of PNBD, unlike from NBD monomer.

The polymer formed in high yield and had a simple unimodal molecular weight distribution as proofed by GPC analysis of the polymer. The number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$), and PDI ($\bar{M}_w/\bar{M}_n$) were determined by GPC. According to GPC trace, $\bar{M}_n$ =34,320 g/mol, $\bar{M}_w$ = 121,380 g/mol, and $\bar{M}_w/\bar{M}_n$ =3.53 results were obtained.

From the TGA of PNBD, the degradation occurred in several stages. The first stage was observed at 100°C. The second stage of decomposition commenced at 100–300°C, and the last and max decomposition stage was observed at 300–650°C. The maximum peak temperature was about 425°C. The total weight loss was about 70% at this temperature range. The remaining portion of the organic material is carbonized.

CONCLUSIONS

Consequently, the synthesis of a new class of Ru-based catalyst coordinated to amine ligand that exhibits activity in ROMP reaction of NBDs was achieved. The ROMP activity of the

systems in this study increased dramatically when TMSD was added to activate the catalytic systems to form highly reactive coordinatively unsaturated Ru–carbene species. Under appropriate conditions, monomer conversion was 80% with a relatively broad molecular weight distribution for ROMP. These can be further narrowed by stopping the reaction at lower monomer conversions. When the new synthesized Ru-based catalyst was compared with the commercially Ru(II) arene dimer ([RuCl$_2$(p-cymene)]$_2$ (**2**)), it exhibited a higher molecular weight and a better catalytic activity because of the steric and electronic properties of amine ligand. The polymers with high molecular weight and high yield were obtained with 1000/1 as a M/C ratio when CH$_2$Cl$_2$ was used as solvent and TMSD was added to the reaction at 40°C reflux temperature.

Despite the relatively broad molecular weight distribution, the amines studied can be used as an alternative to ancillary ligands. The resulting complexes can be used for practical purposes because of several reasons; the amines are readily available from commercial products and relatively cheap according to other ligands, and the production of polymers was obtained with the higher polymerization yield.

REFERENCES

1. Grubbs, R. H.; Chang, S. *Tetrahedron* **1998,** *54*, 4413.

2. Ivin, K. J.; Laverty, D. T.; O'Donnell, J. H.; Rooney, J. J.; Steward, C. *Makromol. Chem.* **1979,** *180*, 1989.

3. Makovetsky, K. L.; Finkelshtein, E. S.; Ostrovskaya, I. Y.; Portnykh, E. B.; Gorbacheva, L. I.; Golberg, A. I.; Ushakov, N. V.; Yampolskii, Y. P. *J. Mol. Catal.* **1992,** *76*, 107.

4. Finkelshtein, E. S.; Makovetskii, K. L.; Yampolskii, Y. P.; Portnykh, E. B.; Ostrovskaya, I. Y.; Kaliuzhnyi, N. E.; Pritula, N. A.; Golberg, M. S.; Yatsenko, M. S.; Plate, N. A. *Makromol. Chem.* **1991,** *192*, 1.

5. Anderson, A. W.; Merkling, N. *G. U. S. Pat. 2,721,*189 (**1955**).

6. Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992,** *114*, 3974.

7. Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995,** *34*, 2039.

8. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996,** *118*, 100.

9. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990,** *112*, 3875.

10. Mark, H. F. Encyclopedia of Polymer Science, 3rd ed.; Wiley: Hoboken, NJ, **2004; Vol.** *11*, p 547..

11. Ivin, K. J.; Mol, J. C. Olefin Metathesis and Metathesis Polymerization; Academic Press: London, **1997;** p 317.

12. Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996,** *29*, 1789.

13. Dias, E. L.; Grubbs, R. H. *Organometallics* **1998,** *17*, 2758.

14. Schneider, M. F.; Lucas, N.; Velder, J.; Blechert, S. *Angew. Chem. Int. Ed. Engl.* **1997,** *36*, 257.

15. Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997,** *119*, 9130.

16. Delaude, L.; Demonceau, A.; Noels, A. F. *Macromolecules* **1999,** *32*, 2091.

17. Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc. Chem. Commun.* **1995,** 1127.

18. Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. F. *Macromolecules* **1997,** *30*, 3127.

19. Alvarez, P.; Gimeno, J.; Lastra, E. *Organometallics* **2002,** *21*, 5678.

20. Tolman, C.; Parshall, G. W. *J. Chem. Ed.* **1999,** *76*, 177.

21. Noels, A. F.; Graziani, M.; Hubert, A. J., Eds. Metals Promoted Selectivity in Organic Synthesis; Kluwer Academic Publishers: Dordrecht, **1991.**

22. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, **1987.**

23. Matos, J. M. *E.; Lina-Neto, B. S. J. Mol. Catal. A* **2004,** *22*, 81.

24. Colton, R. *Coord. Chem. Rev.* **1971,** *6*, 269.

25. Drew, M. G. *B. Prog. Inorg. Chem.* **1977,** *23*, 67.

26. Melnik, M.; Sharrock, P. *Coord. Chem. Rev.* **1985,** *65*, 49.

27. Bennet, M. A.; Smith, A. K. *J. Chem. Soc. Dalton Trans.* **1974,** *2*, 233.

28. Gamez, P.; Steensma, R. H.; Driessen, W. L.; Reedijk, J. *Inorg. Chim. Acta* **2002,** *333*, 51.

29. Katayama, H.; Ozawa, F. *Chem. Lett.* **1998,** 67.