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Journal of Molecular Catalysis A: Chemical 190 (2002) 109–116

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Synthesis and ring-opening metathesis polymerization of eight-membered unsaturated lactams and related monomers

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Received 24 August 2001; accepted 28 January 2002

Abstract

Novel eight-membered ring unsaturated lactams were synthesized and tested as monomers for the ruthenium-catalyzed ring-opening metathesis polymerization (ROMP). The reaction of a N-protected cyclic alkeneamine was also investigated. The Grubbs' benzylidene complexes $RuCl_2(=CHPh)(PCy_3)_2$ or $RuCl_2(=CHPh)(PCy_3)(IMesH_2)$ and selected ruthenium–arene species bearing either phosphine or stable Arduengo-type *N*-heterocyclic carbene ligands served as catalyst precursors. In most cases, isomerization of the starting materials took place and only 1-benzyl-1-aza-2-ketocyclooct-5-ene afforded a polymeric product. This polyamide was characterized by numerous analytical techniques.

Keywords: Ruthenium; Nylon; Carbene

1. Introduction

Over the past few years olefin metathesis polymerization has made an increasingly significant impact on the material arena. The ring-opening metathesis polymerization (ROMP) of cycloolefins, in particular, has emerged as a powerful tool for macromolecular engineering, because it often allows a high degree of control over the molecular weight and polydispersity of the polymer chains. The living nature of ROMP also permits the addition of a second monomer at the end of a growing chain, thus leading to block copolymers of known stoichiometries. These developments may largely be attributed to the discovery of well-defined ROMP initiators in which the active site is incorporated within a relatively robust transition-metal complex and is shielded from outside interactions by a protective array of ancillary ligands. These new, well-behaved, single-component catalysts can be fine-tuned through ligand modification in order to react in predictable and controlled ways [1–3]. More importantly, the advent of low oxophilicity catalyst precursors based on ruthenium has extended the application field of ROMP to a large set of monomers that encompasses a variety of organic functionalities, resulting in (co)polymers with novel properties [4–7].

Surprisingly, the ROMP of unsaturated cyclic amides (lactams) has received only little attention so far, although various reports describe the successful

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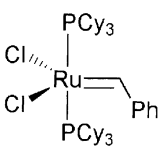
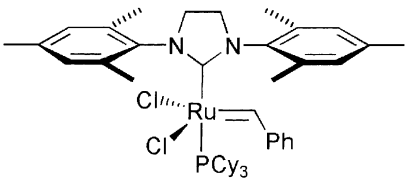
1381-1169/02/$ – see front matter
PII: S1381-1169(02)00222-4

polymerization of norbornene-5-amides or norbornene-5,6-dicarboximides and their N-substituted derivatives [8–11], thereby, confirming the tolerance of ruthenium-based catalysts toward amide and imide functional groups. Polymers containing both olefinic bonds and amido groups in their backbones have been used as membranes [12], fibers [13,14], and resins [12]. They can be crosslinked through their olefinic bonds to afford heat-resistant resins. However, the synthesis of unsaturated polyamide chains remains a relatively unploughed field, and the rare examples described in the literature usually consist in polycondensation reactions, involving either unsaturated dicarboxylic acids or unsaturated diamines [15–17]. To the best of our knowledge, no unsaturated polyamide has ever been prepared by the ROMP of a lactam monomer.

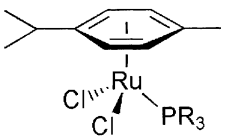
To investigate whether late transition-metal catalysts could offer a new entry to unsaturated polyamide materials, we have undertaken a study of the ROM polymerization of unsaturated lactams and of related monomers in the presence of various ruthenium-based initiators. In this article, we report on the synthesis and on the ROMP of new eight-membered ring unsaturated lactams. Results obtained with a *N*-protected cyclic alkeneamine are also discussed. The catalyst precursors are the first and second generation Grubbs' benzylidene complexes (**1**) [18,19] and selected ruthenium–arene complexes associated either with phosphine ligands (**2**) [4,20] or with stable Arduengo-type *N*-heterocyclic carbene ligands (**3**) [21,22], respectively.



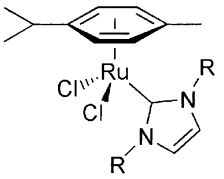
1a



1b



2a: $PR_3 = PCy_3$
2b: $PR_3 = P\text{-}i\text{-}Pr_3$



3a: R = Mes
3b: R = Cy

Cy = cyclohexyl Mes = mesityl (2,4,6-trimethylphenyl)

2. Experimental

2.1. Materials and methods

Solvents (Et_2O, THF, pentane) were freshly distilled over $LiAlH_4$, acetonitrile was stored over molecular sieve 4A and was freshly distilled prior to use. Potassium *tert*-butoxide and $LiAlH_4$ of 95% purity were used without any further purification. All other chemicals were reagent grade and used as received from commercial suppliers.

Polymerizations were carried out under inert atmosphere using standard Schlenk techniques. Gel permeation chromatographic (GPC) analyses of the polymers were performed in THF on a Hewlett-Packard HP 1090 instrument equipped with a HP 1037A refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μm; pore sizes: 100 000, 10 000, 1000, and 100 Å). The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively) were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ with TMS as internal standard. GC/MS analyses were performed on a HP 6890 chromatograph equipped with a fused silica capillary column (30 m, i.d. 0.25 mm, 0.25 μm thickness, 5% Ph Me siloxane) coupled to a HP 5973 mass selective detector. Elemental analyses were carried out on a EuroVector EA3000 instrument at the Institute of Industrial Chemistry, Technical University of Szczecin. Melting and boiling points are uncorrected.

2.2. Synthesis of monomers

2.2.1. 4-Cycloheptenone (4)

This unsaturated ketone was prepared according to the literature [23–25], bp 40–43 °C/2.5 Torr (lit. bp

60 °C/12 Torr [25]). ^{13}C NMR (δ ppm): 24.10, 42.46, 129.51, 213.72. MS (70 eV): *m/z* (%) 110 (M^+, 74), 92 (16), 82 (24), 81 (25), 68 (59), 67 (100), 54 (27), 53 (29), 41 (19), 39 (28).

*2.2.2. 4-Cycloheptenone oxime (**5**)*

The procedure of Wilson and Sawicki was followed [26], mp 56–59 °C (lit. mp 56–58 °C [26]). ^{13}C NMR (δ ppm): 23.03, 27.92, 28.66, 31.35, 129.09, 129.77, 163.21.

*2.2.3. 4-Cycloheptenone oxime tosylate (**6**)*

The procedure of Wilson and Sawicki was followed [26], mp 80–82 °C (lit. mp 83–84 °C [26]). ^{13}C NMR (δ ppm): 21.70, 22.74, 27.89, 29.48, 31.07, 127.05, 128.68, 128.72, 129.41, 129.53, 130.24, 172.06.

*2.2.4. 1-Aza-2-ketocyclooct-5-ene (**7a**)*

The procedure of Wilson and Sawicki was followed [26], mp 89–91 °C (lit. mp 88–89 °C [26]). ^{13}C NMR (δ ppm): 24.62, 30.28, 34.53, 40.52, 126.91, 129.24, 176.90.

*2.2.5. 1-Methyl-l-aza-2-ketocyclooct-5-ene (**7b**)*

Lactam **7a** (1.3 g, 10.4 mmol), potassium *tert*-butoxide (2.66 g, 22.5 mmol), and crown ether 18C6 (96 mg) were stirred in THF (30 ml) for 15 min at room temperature. Methyl iodide (5.8 g, 40.9 mmol) in THF (3 ml) was added dropwise within 2 h and the resulting mixture was further stirred overnight. GC/MS showed the total conversion of **7a**. The reaction mixture was then diluted with Et_2O (20 ml), water (2 ml) was added, and the mixture was acidified with 5% aqueous HCl. The organic layer was separated and the aqueous phase was extracted with Et_2O (3 ml × 20 ml). The combined extracts were dried over $MgSO_4$ and the solvents were removed under reduced pressure (water pump). A vacuum distillation afforded **7b** as a colorless liquid. Yield 0.79 g (84%); bp 73–75 °C/1.5 Torr. ^{1}H NMR (δ ppm): 2.41–2.48 (m, 4H), 2.76 (t, J = 7.5 Hz, 2H), 2.88 (s, 3H), 3.61 (t, J = 6.5 Hz, 2H), 5.47–5.52 (m, 1H), 5.72–5.79 (m, 1H). ^{13}C NMR (δ ppm): 26.43, 28.81, 35.40, 36.52, 49.86, 127.69, 131.02, 175.31. MS (70 eV): *m/z* (%) 139 (M^+, 60), 110 (47), 84 (18), 83 (12), 82 (17), 81 (8), 68 (36), 67 (23), 54 (59), 44 (100), 42 (31), 39 (20). Anal. Calc. for $C_8H_{13}NO$ (139.20): C, 69.03; H, 9.41; N, 10.06. Found: C, 68.94; H, 9.40; N, 9.93%.

*2.2.6. 1-Ethyl-l-aza-2-ketocyclooct-5-ene (**7c**)*

Lactam **7a** (1.0 g, 7.99 mmol), potassium *tert*-butoxide (2.08 g, 17.6 mmol), and crown ether 18C6 (116 mg) were stirred in THF (20 ml) for 15 min at room temperature. Ethyl iodide (2.50 g, 16.0 mmol) in THF (3 ml) was added dropwise within 2 h and the resulting mixture was further stirred overnight. GC/MS indicated a ca. 60% conversion of **7a**. A second portion of potassium *tert*-butoxide (2.18 g, 18.5 mmol) was added to the flask before ethyl iodide (2.62 g, 16.8 mmol) in THF (3 ml) was added dropwise, then stirred overnight as described immediately above. Conversion of **7a** reached ca. 90% at this stage, as evidenced by GC/MS. To reach 100% conversion, the addition-stirring step was repeated once more with 2.20 g of potassium *tert*-butoxide (18.6 mmol) and 3.05 g of ethyl iodide (19.6 mmol). The reaction mixture was then diluted with Et_2O (20 ml), water (2 ml) was added, and the mixture was acidified with 5% aqueous HCl. The organic layer was separated and the aqueous phase was extracted with Et_2O (3 × 20 ml). The combined extracts were dried over $MgSO_4$ and the solvents were removed under reduced pressure (water pump). A vacuum distillation afforded **7c** as a colorless liquid. Yield 0.91 g (74%); bp 80–82 °C/1 Torr. ^{1}H NMR (δ ppm): 1.12 (t, J = 7.2 Hz, 3H), 2.25–2.52 (m, 4H), 2.78 (t, J = 7.5 Hz, 2H), 3.36 (q, J=7.2 Hz, 2H), 3.59 (t, J = 6.6 Hz, 2H), 5.47–5.53 (m, 1H), 5.74–5.80 (m, 1H). ^{13}C NMR (δ ppm): 13.00, 25.11, 27.95, 34.67, 41.61, 46.17, 126.42, 129.45, 173.68. MS (70 eV): *m/z* (%) 153 (M^+, 51), 138 (26), 125 (9), 124 (16), 96 (9), 71 (8), 68 (26), 67 (16), 58 (100), 54 (36), 53 (9), 42 (21), 39 (13). Anal. Calc. for $C_9H_{15}NO$ (153.22): C, 70.55; H, 9.87; N, 9.14. Found: C, 70.50; H, 9.64; N, 9.27%.

*2.2.7. 1-tert-Butoxycarbonyl-1-aza-2-ketocyclooct-5-ene (**7d**)*

Lactam **7a** (1.25 g, 10.0 mmol), di-*tert*-butyldicarbonate (3.45 g, 15.8 mmol), and 150 mg of 4-dimethylaminopyridine (DMAP) in acetonitrile (3 ml) were stirred for 24 h at room temperature (GC/MS analysis showed the presence of unreacted starting material after 3 h). The solvent was then removed under reduced pressure. Flash chromatography of the residue (SiO_2, Et_2O) afforded an oil which slowly solidified. Crystallization from pentane afforded colorless crystals

of **7d**. Yield 1.32 g (59%); mp 60–61 °C. Concentration of the mother liquor afforded a further crop of less pure material (0.27 g, 12%). ^{1}H NMR (δ ppm): 1.52 (s, 9H), 2.25–2.36 (m, 4H), 2.94–2.97 (m, 2H), 3.52–3.55 (m, 2H), 5.72–5.83 (m, 2H). ^{13}C NMR (δ ppm): 24.89, 26.50, 28.22, 41.55, 44.18, 82.02, 129.74, 131.03, 153.06, 182.46. MS (70 eV): *m/z* (%) 225 (M^+, 0.1), 170 (22), 125 (37), 124 (11), 109 (9), 96 (19), 69 (13), 68 (14), 67 (9), 57 (100), 56 (12), 54 (13), 41 (25), 39 (12). Anal. Calc. for $C_{12}H_{19}O_3N$ (225.29): C, 63.98; H, 8.50; N, 6.22. Found: C, 64.13; H, 8.48; N, 6.04%.

*2.2.8. 1-Trimethylsilyl-l-aza-2-ketocyclooct-5-ene (**7e**)*

To lactam **7a** (0.50 g, 4.0 mmol) dissolved in THF (5 ml), 2 M lithium diisopropylamide in heptane/THF/ethylbenzene (2 ml, 4.0 mmol) was added with a syringe, and the resulting suspension was stirred for 30 min. Solvents and diisopropylamine were removed under vacuum and the flask was pressurized with argon before THF (5 ml) and chlorotrimethylsilane (1.5 ml, 11.8 mmol) were added. The reaction mixture was stirred for 2 h at room temperature. Solvents and other volatile components were then removed under vacuum and the residue was extracted with pentane (2 × 10 ml). Evaporation of the solvent yielded 0.50 g of an oily product (63%). ^{1}H NMR (δ ppm): 0.18 (s, 9H), 2.27–2.42 (m, 4H), 2.66–2.72 (m, 2H), 3.44 (t, J = 6.5 Hz, 2H), 5.42–5.49 (m, 1H), 5.70–5.80 (m, 1H). ^{13}C NMR (δ ppm): 0.03, 24.46, 30.41, 36.21, 42.68, 126.68, 129.21, 180.98. Due to its high reactivity toward water, no satisfactory microanalysis could be obtained for **7e**, but its purity was checked by GC analysis.

*2.2.9. 1-Benzyl-l-aza-2-ketocyclooct-5-ene (**7f**)*

Lactam **7a** (1.4 g, 11.19 mmol), potassium *tert*-butoxide (3.4 g, 28.8 mmol), and crown ether 18C6 (100 mg) were stirred in THF (12 ml) for 15 min at room temperature. Benzyl chloride (2.05 g, 16.2 mmol) in THF (2 ml) was added dropwise within 2 h and the resulting mixture was stirred overnight. GC/MS showed the total conversion of **7a**. The reaction mixture was then diluted with Et_2O (10 ml), water (2 ml) was added, and the mixture was acidified with 5% aqueous HCl. The organic layer was separated and the aqueous phase was extracted with Et_2O (3 × 20 ml). The combined extracts were dried over $MgSO_4$ and the solvents were removed under reduced pressure (water pump). The residue was crystallized from Et_2O-pentane, affording colorless crystals of **7f**. Yield 1.85 g (77%); mp 56–58 °C. Chromatography of the concentrated mother liquors (SiO_2, acetone) afforded an additional 0.34 g (14%) of product. ^{1}H NMR (δ ppm): 2.32–2.50 (m, 4H), 2.82 (t, J = 7.1 Hz, 2H), 3.52 (t, J = 7.1 Hz, 2H), 4.54 (s, 2H), 5.39–5.45 (m, 1H), 5.74–5.81 (m, 1H), 7.24–7.32 (m, 5H). ^{13}C NMR (δ ppm): 25.02, 27.33, 34.89, 45.39, 49.02, 126.63, 127.33, 128.25, 128.41, 128.48, 129.37, 173.98. MS (70 eV): *m/z* (%) 215 (M^+, 64), 132 (8), 124 (7), 120 (48), 118 (7), 91 (100), 68 (8), 65 (11), 54 (10). Anal. Calc. for $C_{14}H_{17}NO$ (215.30): C, 78.10; H, 7.96; N, 6.51. Found: C, 78.10; H, 7.96; N, 6.51%.

*2.2.10. 1-Benzyl-1-aza-4-cyclooctene (**8**)*

Lactam **7f** (1.0 g, 4.64 mmol) dissolved in THF (10 ml) was added dropwise to $LiAlH_4$ (0.35 g, 8.76 mmol) in THF (10 ml) under nitrogen. The reaction mixture was then refluxed for 6 h. After cooling to room temperature, water (10 ml) was added dropwise and the resulting mixture was extracted with Et_2O (3 × 50 ml). The combined extracts were washed with 10% aqueous HCl (2 × 20 ml). They were stirred with charcoal and filtered. A concentrated potassium hydroxide solution (from 5 g of KOH in 5 ml of water) was added to the filtrate and the resulting mixture was extracted with Et_2O (3 × 50 ml). The ether solution was dried over KOH pellets and the solvent was removed under vacuum. A bulb-to-bulb distillation afforded **8** as a colorless oil. Yield 0.79 g (84%); bp 125–130 °C (bath temp.)/1 Torr. ^{1}H NMR (δ ppm): 1.44 (br s, 2H), 2.24 (br s, 4H), 2.66 (br s, 4H), 3.77 (s, 2H), 5.63–5.78 (m, 2H), 7.21–7.38 (m, 5H). ^{13}C NMR (δ ppm): 24.39, 27.93, 29.01, 52.20, 56.07, 61.96, 126.78, 128.11, 128.75, 129.55, 130.18, 132.66. MS (70 eV): *m/z* (%) 201 (M^+, 24), 200 (39), 173 (10), 172 (21), 146 (15), 134 (6), 110 (18), 91 (100), 81 (7), 65 (12), 42 (8), 41 (6). Anal. Calc. for $C_{14}H_{19}N$ (201.31): C, 83.53; H, 9.51; N 6.96. Found: C, 83.40; H, 9.40; N, 6.82%.

2.3. Typical polymerization procedure

Complex **2a** (0.0059 g, 10^{-2} mmol) and a lactam monomer (1 mmol) were placed in a flask under

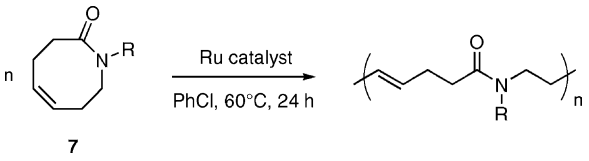
argon before dry chlorobenzene (1 ml) and tetradecane (0.0080 g, GC internal standard) were added. The mixture was stirred for 5 min at 60 °C, then 0.3 ml of trimethylsilyldiazomethane (TMSD, 0.1 M in chlorobenzene, 3×10^{-5} mmol) were added via a syringe. The solution was stirred for 24 h at 60 °C and conversion was monitored by gas chromatography. After cooling to room temperature, the reaction mixture was poured in a large volume of *n*-heptane. The precipitated polymer was dried overnight under vacuum and analyzed by GPC and NMR spectroscopy.

3. Results and discussion

3.1. Synthesis of monomers

Lactam **7a** was synthesized from 4-cycloheptenone (**4**) according to the literature [26] (Scheme 1). The key step was the facile Beckmann rearrangement of the tosyl oxime **6**, leading to a 62% overall yield. The starting unsaturated ketone **4** was obtained from ethyl acetoacetate and *cis*-1,4-dichlorobutene according to the indications of Descotes and co-workers [23], further modified by Wilson and Wiesler [24], and by Marshall and Royce [25]. The ^{13}C NMR spectral data for compounds **4–7a** are listed in the experimental part of this report (Section 2.2), since they were not previously published.

The new N-protected lactams **7b–f** were obtained from **7a**. The methyl, ethyl, and benzyl derivatives (**7b**, **7c**, and **7f**, respectively) were prepared by alkylation of lactam **7a** with a suitable halogeno compound in the presence of potassium *tert*-butoxide and crown ether 18C6 (Section 2.2). The trimethylsilylated lactam **7e** was synthesized from the lithium salt of **7a** and chlorotrimethylsilane, whereas the *tert*-butoxycarbonyl substituted lactam **7d** was obtained by reaction of **7a** with di-*tert*-butyldicarbonate



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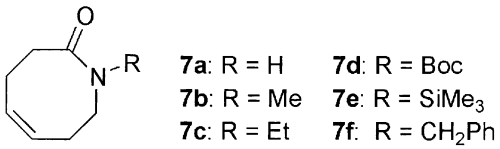
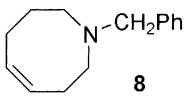
Scheme 2.

in the presence of 4-DMAP [27]. Reduction of **7f** with lithium aluminum hydride afforded the *N*-benzylated cycloalkeneamine **8**. All of these products were characterized by NMR spectroscopy and by GC/MS. The reaction yields were not optimized.





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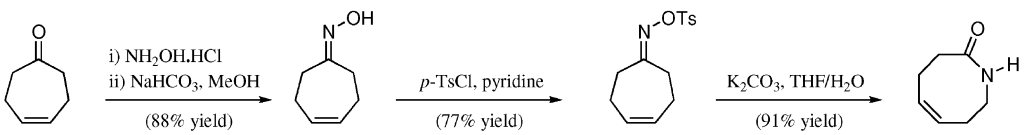
3.2. Polymerization reactions

To assess the reactivity of monomers **7a–f**, exploratory polymerization experiments were performed with two of the most active ruthenium-based ROMP initiators currently available, viz. the Grubbs' benzylidene complex **1a** (system A) [18] and the $[RuCl_2(p\text{-cymene})]_2/PCy_3$/TMSD catalytic system developed in Liège (system B) [4] (Scheme 2). In both cases, the reactions were carried out in chlorobenzene at 60 °C with a 100:1 monomer-to-ruthenium ratio. The recourse to a mixture of the $[RuCl_2(p\text{-cymene})]_2$ dimer with 2 (or more) eq. of tricyclohexylphosphine offers a convenient synthetic alternative to



4 **5** **6** **7a**

Scheme 1.

performed complex **2a**. Previous work from our group has shown indeed that the 1:2 combination of $[RuCl_2(p\text{-cymene})]_2$ and PCy_3 was equivalent to **2a** in the polymerization of cyclooctene [4]. A major difference between the two systems is that complex **1a** contains a vinylidene carbene moiety and can promote ROMP per se, whereas the 18-electron precursor **2a** needs to be further activated in situ by TMSD to generate a highly reactive coordinatively unsaturated ruthenium–carbene species that triggers the catalytic process.

3.2.1. Reaction of 1-aza-2-ketocyclooct-5-ene (7a)

The $[RuCl_2(p\text{-cymene})]_2/PCy_3$/TMSD catalytic system A was poorly active for the polymerization of this monomer. Experimental observation showed that a brown solid precipitated right from the very beginning of the reaction. This phenomenon could be easily explained either by the insolubility of polyamides in organic media or by the formation of new poorly soluble ruthenium species. The polymer yield remained very low (<0.5%), and the polymerization process was progressively supplanted by an isomerization process (ca. 10% of isomeric products after 5 h at 60 °C and 40% after 18 h at 90 °C, as determined by GC). These results prompted us to consider the protection of the amide function in order to circumvent the solubility limitations.

3.2.2. Reaction of N-protected amides and amines

Various eight-membered ring lactams bearing N-protecting groups have been tested as ROMP monomers using the catalytic systems A and B, respectively. Under the experimental conditions adopted the *N*-benzyl lactam **7f** was, however, the only functionalized cycloolefin that effectively underwent a polymerization (Table 1). A competing isomerization reaction also took place, as evidenced by the progressive emergence of two additional peaks in the GC chromatograms, whose retention times were close to that of

Table 1
ROMP of the *N*-benzyl lactam **7d** using various ruthenium-based catalytic systems[a]

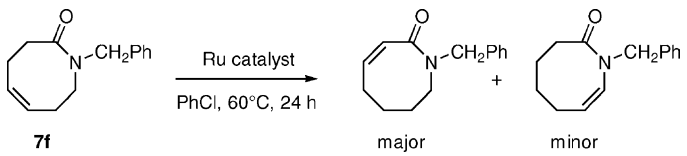
Catalyst precursor	Isolated polymer (%)[b]	Isomerization products (%)[c]
1a	13	22
1b	90	0
2a[d]	26	7
2b[d]	0	10
3a[e]	5	41
3b[e]	0	4

[a] Reaction conditions: lactam **7f** (1 mmol), catalyst precursor (10^{-2} mmol), PhCl (1 ml), 60 °C, 24 h.
[b] Precipitated from *n*-heptane.
[c] Determined by GC using tetradecane as an internal standard.
[d] Catalyst prepared in situ from $[RuCl_2(p\text{-cymene})]_2$ (5×10^{-3} mmol) and PCy_3 (2×10^{-2} mmol). TMSD (3×10^{-2} mol) was added to the reaction medium.
[e] Reaction carried out under intense visible light irradiation.

7f. The isomeric nature of these new products was confirmed by GC/MS analysis ($m/z = 215$). The two isomers showed different fragmentation patterns that are consistent with the structures proposed in Scheme 3 but were not further characterized nor isolated.

Monomers **7b–e** also went through a limited isomerization process when exposed to ruthenium complexes **1a** and **2a**, but none of them afforded any polymeric material. In the case of the *N*-benzyl amine **8**, no reaction occurred with either catalytic system A or B, and the monomer remained unchanged after 24 h at 60 °C. This result did not come as a surprise. It is notoriously difficult to polymerize basic amines, even with ruthenium-based catalysts, because of substantial catalyst poisoning [1]. The absence of any isomer peak in the GC chromatograms is more revealing and tends to prove that the formation of conjugated double bonds is the driving force of the lactam isomerization process.

Other ruthenium complexes were tested for the polymerization of the *N*-benzyl lactam **7f**. In a variation on system B, the tricyclohexylphosphine



Scheme 3.

ligand in complex **2a** was substituted with another strongly basic, sterically hindered phosphine that had led to highly active catalyst precursors for the ROMP of cyclooctene [20]. Thus, performed complex **2b** containing the triisopropylphosphine ligand was used as catalyst precursor for the ROMP of lactam **7f** in the presence of TMSD. The conversion remained, however, very low (10%) and led essentially to isomers. Two ruthenium–arene complexes bearing respectively an aryl- and an alkyl-substituted imidazol-2-ylidene ligand were also tested as catalyst precursors for the ROMP of monomer **7f**. Complex **3a**, which was an active catalyst precursor for the ROMP of cyclooctene in the presence of visible light [28], did not afford any significant yield of polyamide, but promoted rather efficiently the isomerization of the *N*-benzyl lactam. Complex **3b**, which was mainly inactive toward cyclooctene, did not afford any better results with the functionalized monomer. No polymer was isolated and isomeric products did not represent more than 4% of the starting material.

Success eventually came from the recourse to the second generation Grubbs' catalyst $RuCl_2(=CHPh)(PCy_3)(IMesH_2)$ (**1b**) [19]. This ruthenium–benzylidene complex bearing a mesityl-substituted *N*-heterocyclic carbene with a saturated backbone is a much more active ROMP catalyst than its diphosphine analogue **1a** [7]. It very efficiently promoted the polymerization of monomer **7f** into the corresponding polyamide within the 24 h imparted to the reaction. GC analysis indicated that the starting material completely disappeared without concomitant isomerization, resulting in an almost quantitative yield of isolated polymer. GPC analysis in THF showed that the sticky gum formed had a relatively low molecular weight and a rather broad molecular weight distribution ($M_n = 30\,000$, $M_w/M_n = 1.47$ versus monodisperse polystyrene standards).

NMR elucidation of the microstructure of the unsaturated polyamide poly-**7f** was complicated by the possible head-to-tail, head-to-head, or tail-to-tail relative orientations of the amido groups, in addition to the *cis/trans* splitting of the olefinic double bonds. The detailed interpretation of NMR spectra is beyond the scope of this study. It can nevertheless be pointed out that ^{1}H-NMR spectroscopy confirmed the formation of the expected polymer. Comparison of the integrals for the olefinic protons (broad signal), the backbone methylene units, and the benzyl groups indicated that the amide functional groups were still fully protected. ^{13}C-NMR spectroscopy allowed to distinguish between the various types of carbon atoms, each of them giving rise to multiple peaks poorly resolved at 100 MHz. The FT–IR spectrum exhibited a strong absorption at 1634 cm^{-1}, typical of the amide carbonyl group. A thermogravimetric analysis (TGA) showed that poly-**7d** had a very high thermal stability until at least 250 °C and that a 10% weight loss occurred at ca. 340 °C. Differential scanning calorimetry (DSC) revealed a well-defined glass transition at 21 °C. No other endothermal peak was observed within the temperature range scanned (−100 to +200 °C), suggesting that the polymer does not melt before decomposition.

3.3. Deprotection of the unsaturated polyamide derived from *7f*

We have tried to deprotect the poly(*N*-benzyl lactam) derived from **7f** in order to obtain and to characterize an unsaturated polyamide chain with no substituents on the nitrogen atoms. The selective cleavage of a *N*-benzyl amide constitutes, however, a much more difficult task than the deprotection of the corresponding amine [29]. Three different methods described in the literature have been investigated but did not lead to any conclusive results. The use of pure trifluoroacetic acid at 20 °C [30] did not afford any reaction after 18 h and the starting polymer was recovered unchanged. Recourse to cerium ammonium nitrate $(NH_4)_2Ce(NO_3)_2$ in a THF/H_2O mixture for 3 h at 20 °C [31] led to a partial decomposition of poly-**7f**, but the benzyl groups were still present, as evidenced by NMR spectroscopy. Under basic conditions, bubbling dry air to introduce oxygen into a DMSO/THF solution of poly-**7f** and potassium *tert*-butoxide [32] for 3 h at 20 °C also proved unsatisfactory, as only a minute amount of *N*-protected polymer was recovered after work-up.

4. Summary

1-Aza-2-ketocyclooct-5-ene (**7a**) together with five of its *N*-protected derivatives (**7b–f**) were synthesized and submitted to ROMP conditions along with a related cyclic alkeneamine (**8**) in the presence of

various ruthenium-based catalyst precursors. These reactions led mainly to the isomerization of the starting materials and only the *N*-benzyl unsaturated lactam **7f** afforded a polymeric product. This polyamide was characterized by numerous analytical techniques. Attempts to selectively cleave the benzyl groups of poly-**7f** failed.

Acknowledgements

The financial support of the EU, through Grant TMR-HPRN CT 2000–10 “Polycat”, is gratefully acknowledged.

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