Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 47 (2006) 3292–3297
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and ring opening metathesis polymerisation of isoxazolino- and isoxazolidino-norbornenes

James J. Murphy [a], James G. Hamilton [b], R. Michael Paton [a,*]

[a] *EaStCHEM, School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[b] *School of Chemistry, The Queens University of Belfast, Belfast BT9 5AG, Northern Ireland*

Received 12 May 2005; received in revised form 14 February 2006; accepted 7 March 2006
Available online 3 April 2006

Abstract

Isoxazolino- and isoxazolidino-norbornenes, prepared by cycloaddition to norbornadiene of nitrile oxides and nitrones, respectively, undergo ring opening metathesis polymerisation (ROMP) initiated by the Grubbs ruthenium alkylidenes **1** and **2**. The structures of the resulting polymeric isoxazolines were established from their NMR spectra by comparison to polynorbornene and to model isoxazolines prepared by nitrile oxide cycloaddition to cyclopentene. The average degree of polymerisation was regulated using an acyclic chain transfer agent (hex-1-ene) affording products with av DP = 4–157, and with narrow molecular weight distributions (PDI = 1.45–1.65). Oligomeric analogues (n = 4,16) with saturated backbones were prepared by reduction with *p*-toluenesulfonyl hydrazide.

Keywords: Heterocyclic polymer synthesis; ROMP; Ruthenium alkylidene initiators

1. Introduction

There is much current interest in the synthesis of novel functionalised polymers by ring opening metathesis polymeristion (ROMP) [1]. For this purpose, the ruthenium benzylidene initiators **1** and **2**, developed by Grubbs et al. [1a] have proved to be of particular value as they show good functional group tolerance and facilitate living polymerisations leading to well-defined products. Ring strained norbornene monomers, which can be prepared by Diels–Alder cycloaddition of cyclopentadiene to the appropriate funtionalised dienophile, show good reactivity with these initiators [2] and have been used to prepare polymers bearing various pendant groups including sulfonyl halides, [3] penicillins, [4] nucleic acid bases, [5] and monosaccharides [6]. We have adopted an alternative approach to funtionalised norbornenes that involves cycloaddition of nitrile oxides and nitrones to norbornadiene, [7] and now report that the resulting isoxazoline and isoxazolidine adducts readily undergo ROMP.

* Corresponding author. Tel.: +44 131 6504714.
E-mail address: r.m.paton@ed.ac.uk (R. Michael Paton).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.03.027

2. Experimental details

2.1. Materials and measurements

Norbornene, norbornadiene, cyclopentene, ethyl vinyl ether and *p*-toluenesulfonyl hydrazide were purchased from Aldrich and used as received. The Grubbs ruthenium initiators bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride **1** and the *N*-heterocyclic carbene-coordinated rutheniumbenzylidene complex **2** were purchased from Strem Chemicals. Dichloromethane was distilled over calcium hydride under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX250 and Bruker avance 360 instruments. The NMR samples were prepared by dissolving 50 mg of polymer in 0.5 ml of $CDCl_3$. Gel Permeation Chromatography (GPC) molecular weight measurements were recorded using a Perkin–Elmer Systems isocratic pump 250 and a Perkin–Elmer Systems LC-30 RI detector, with a 5μ column and a 5μ mixed bed Perkin–Elmer PL column connected in series, and with a flow rate 0.5 ml/min at ambient temperature using THF as the mobile phase. Samples were dissolved in THF at a concentration of 25 mg/ml. The system was calibrated using low dispersity polystyrene standards.

2.2. Synthesis of monomers[1]

2.2.1. exo-3-Ethoxycarbonyl-3a,4,5,6,7,7a-hexahydro-4, 7-methanobenzo[d]isoxazole (**6a**)

The title compound was prepared by cycloaddition of ethoxycarbonylformonitrile oxide **3a** to norbornadiene. A solution of triethylamine (0.72 g, 7.3 mmol) in diethyl ether (10 ml) was added over 8 h by means of a motorised syringe to a solution of norbornadiene (1.75 g, 19 mmol) and ethyl chloro-oximidoacetate (**4a**) [8] (0.67 g, 4.3 mmol) in diethyl ether at 0 °C for 1 h and then at room temperature for 9 h. After filtering through Celite the mixture was concentrated in vacuo. Dry flash chromatography of the residue afforded the cycloadducts as white crystalline solids.

Compound **6a**. (0.60 g, 67%) (mp 62–63 °C); δ_H (200 MHz, $CDCl_3$) 1.30–1.36 (3H, m, OCH_2CH_3), 1.60 (2H, s, H-8), 3.20 (1H, d, $J_{4,3a}=0.6$ Hz, H-4), 3.25 (1H, d, $J_{7,7a}=1.3$ Hz, H-7), 3.53 (1H, dd, $J_{3a,7a}=8.3$ Hz, $J_{3a,4}=0.6$ Hz, H-3a), 4.21–4.36 (2H, m, OCH_2CH_3), 4.97 (1H, dd, $J_{7a,7}=1.3$ Hz, $J_{7a,3a}=8.4$ Hz, H-7a), 6.00 (1H, dd, $J_{5,6}=5.7$ Hz, $J_{5,4}=3.2$ Hz, H-5), 6.28 (1H, dd, $J_{6,5}=5.8$ Hz, $J_{6,7}=3.0$ Hz, H-6); δ_C (63 MHz, $CDCl_3$) 13.9 (OCH_2CH_3), 42.7, (C-8), 45.0, (C-4), 49.7 (C-7), 56.0 (C-3a), 61.7 (OCH_2CH_3), 91.7 (C-7a), 134.6 (C-5), 140.3 (C-6), 150.9 (C-3), 160.5 (CO_2); *m/z* (EI) found: M^+, 207.09719 $C_{11}H_{13}NO_3$ requires M^+, 207.09737.

Compound **5a**. (0.13 g, 16%) (mp 61–62 °C); δ_H (200 MHz, $CDCl_3$), 1.30–1.36 (3H, m, OCH_2CH_3), 1.60 (2H, s, H-8), 3.29 (1H, d, $J_{4,3a}=4.2$ Hz, H-4), 3.34 (1H, d, $J_{7,7a}=4.1$ Hz, H-7), 4.02 (1H, dd, $J_{3a,7a}=9.3$ Hz, $J_{3a,4}=4.2$ Hz, H-3a), 4.21–4.36 (2H, m, OCH_2CH_3), 5.39 (1H, dd, $J_{7a,7}=4.1$ Hz, $J_{7a,3a}=9.4$ Hz, H-7a), 5.82 (1H, dd, $J_{5,6}=5.7$ Hz, $J_{5,4}=3.2$ Hz, H-5), 6.09 (1H, dd, $J_{6,5}=5.8$ Hz, $J_{6,7}=3.0$ Hz, H-6); δ_C (63 MHz, $CDCl_3$) 13.9 (OCH_2CH_3), 42.7, (C-8), 45.0, (C-4), 49.7 (C-7), 56.0 (C-3a), 61.7 (OCH_2CH_3), 90.7 (C-7a), 134.9 (C-5), 138.3 (C-6), 150.7 (C-3), 156.4 (CO_2); *m/z* (EI) found: M^+, 207.08959 $C_{11}H_{13}NO_3$ requires M^+, 207.08954.

2.2.2. exo-3-Phenyl-3a,4,5,6,7,7a-hexahydro-4, 7-methanobenzo[d]isoxazole (**6b**) [9,10]

The title compound was prepared from norbornadiene (1.75 g, 19 mmol) and benzohydroximoyl chloride **4b** (0.68 g, 4.3 mmol) as described above. Dry flash chromatography of the residue afforded the cycloadducts as white crystalline solids.

Compound **6b**. (0.50 g, 54%); mp 62–63 °C (63.5–64.5 °C); δ_H (200 MHz, $CDCl_3$), 1.63 (2H, s, H-8), 3.14 (1H, d, $J_{4,3a}=1.4$ Hz, H-4), 3.26 (1H, d, $J_{7,7a}=1.3$ Hz, H-7), 3.76 (1H, dd, $J_{3a,7a}=8.2$ Hz, $J_{3a,4}=1.4$ Hz, H-3a), 4.97 (1H, dd, $J_{7a,7}=1.2$ Hz, $J_{7a,3a}=8.2$ Hz, H-7a), 6.08 (1H, dd, $J_{5,6}=5.5$ Hz, $J_{5,4}=3.2$ Hz, H-5), 6.34 (1H, dd, $J_{6,5}=5.8$ Hz, $J_{6,7}=3.0$ Hz, H-6), 7.41–7.35 (3H, m, ArH), 7.71–7.69 (2H, m, ArH); δ_C (63 MHz, $CDCl_3$) 42.9 (C-8), 44.9 (C-4), 49.7 (C-7), 57.4 (C-3a), 89.2 (C-7a), 126.2 (C-5), 128.5 (C-6), 129.0 (PhC), 139.8, 135.3, 129.6 (PhCH), 155.3 (C-3).

Compound **5b**. (0.15 g, 16%); mp 61–63 °C (62–64 °C); δ_H (200 MHz, $CDCl_3$) 1.56 (2H, s, H-8), 3.36 (2H, br s, H-7,4), 4.13 (1H, dd, $J_{3a,7a}=9.5$ Hz, $J_{3a,4}=4.0$ Hz, H-3a), 5.41 (1H, dd, $J_{7a,7}=4.2$ Hz, $J_{7a,3a}=9.5$ Hz, H-7a), 5.92 (1H, dd, $J_{5,6}=5.8$ Hz, $J_{5,4}=3.0$ Hz, H-5), 6.16 (1H, dd, $J_{6,5}$ 5.8 Hz, $J_{6,7}=3.4$ Hz, H-6), 7.34–7.41 (3H, m, ArH), 7.65–7.72 (2H, m, ArH); δ_C (63 MHz, $CDCl_3$) 46.7, (C-8), 47.7 (C-4), 48.7 (C-7), 57.0 (C-3a), 87.3 (C-7a), 126.4 (C-5), 128.5 (C-6), 129.2 (PhC), 134.9, 133.9, 129.6 (PhCH), 156.4 (C-3).

2.2.3. exo-4-Methyl-5^{exo}-phenyl-3-oxa-4-azatricyclo[5.2.1.$0^{2,6exo}$]dec-8-ene (**15**) (70%) [11]

The title compound was prepared by reaction of norbornadiene with *C*-phenyl-*N*-methyl nitrone as previously reported.

2.3. Polymer synthesis

The general methods used for the preparation of the homopolymers and block copolymers are illustrated by the following examples:

2.3.1. Polymerisation of ethoxycarbonylisoxazolino norbornene **6a**

A solution of initiator **2** (5.0 mg, 0.0058 mmol) in dichloromethane (1.0 ml) was added by syringe to a solution of **6a** (100 mg, 0.48 mmol) in dichloromethane (1.0 ml). After 2 h the reaction was terminated by addition of ethyl vinyl ether (20 mg, 0.28 mmol), and the mixture added dropwise to methanol containing 2,6-di-*tert*-butyl-4-methylphenol (5 mg). The resulting white precipitate, **9a** was recovered by filtration, washed with methanol and dried: δ_H (500 MHz, $CDCl_3$) 1.43 (3H, m, $CO_2CH_2CH_3$) 1.62–1.98 (2H, m, H-7), 3.05 (2H, m, H-1,4 (t)), 3.23 (2H, m, H-1,4 (c)), 3.65 (1H, m, H-6), 4.33 (2H, m, $CO_2CH_2CH_3$) 4.89–5.23 (1H, m, H-5), 5.42–5.77 (2H, m, H-2,3); δ_C (90 MHz, $CDCl_3$) 14.2 ($CO_2CH_2CH_3$), 39.2 (C-7), 43.6, 46.5, 50.7 (C-1,4), 57.4 (C-6), 62.0 ($CO_2CH_2CH_3$), 94.6 (C-5), 130.0–134.3 (C-2,3), 153.6 (C-3a), 160.5 ($CO_2CH_2CH_3$).

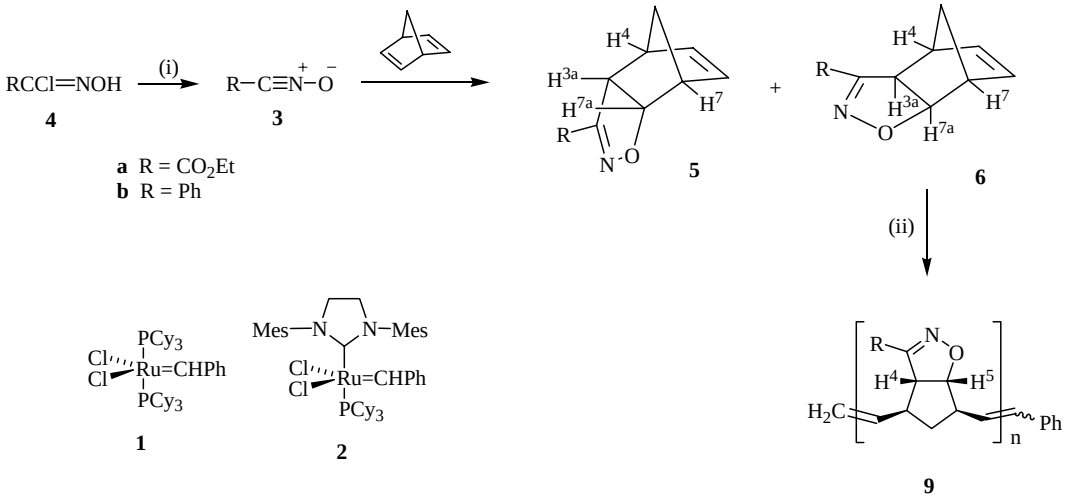
2.3.2. Polymerisation of phenylisoxazolinonorbornene **6b**

The polymerisation of **6b** with **1** was performed in the same manner, affording a polymeric product, **9b**, which was recovered by filtration, washed with methanol and dried: δ_H (500 MHz, $CDCl_3$) 1.22, 1.92 (2H, m, 7-H), 2.66, 2.89 (2H, br d, 1,4-H), 3.77 (1H, br s, 6-H), 4.89 (1H, m, 5-H), 5.44 (2H, m, H-2,3), 7.28, 7.63 (5H, br d, Ph); δ_C (63 MHz, $CDCl_3$) 26.6, 27.3 (C-7), 43.6, 48.2, 50.1 (C-1,4), 58.5 (C-6), 92.0 (C-5), 127.9, 128.4, 129.0, (PhCH, PhC), 130.3–134.5 (C-2,3), 159.5 (C=N).

2.3.3. Copolymerisation of cyclopentene and phenylisoxazolinonorbornene **6b**

Using initiator **1** (5 mg, 0.006 mmol), cyclopentene (17 mg, 0.24 mmol) was polymerised for 24 h, after which the second

[1] All new compounds were characterised by their ^1H and ^{13}C NMR spectra and their elemental compositions established by HRMS and/or combustion analysis.



Scheme 1. Reagents and conditions: (i) ET_3N, Et_2O, 0–20°C; (ii) **1** or **2**, CH_2Cl_2, 20°C.

monomer **6b** (51 mg, 0.24 mmol) was added to the reaction mixture. After stirring for a further 24 h the mixture was heated at 50 °C for 6 h and the reaction terminated by addition of ethyl vinyl ether. The block copolymers were isolated using the same procedure as that for the homopolymers.

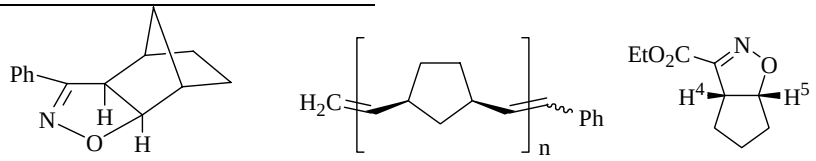
2.4. Hydrogenation reactions

A sample of the polymer **9a** (100 mg, 0.48 mmol) was dissolved in chlorobenzene and to the solution was added *p*-toluenesulfonyl hydrazide (2 g, 10.5 mmol). The mixture was heated at reflux at 130 °C with stirring for 4 h and then precipitated into methanol to afford a grey polymeric solid, which was recovered by filtration, washed with methanol and dried: δ_H (500 MHz, $CDCl_3$) 0.81 (3H, br s, CH_3), 1.18–1.30 (5H, m, H-7, $CH_3CH_2O_2C$), 1.50 (4H, m, H-2,3), 1.95 (8H, m, $3\times CH_2$, H-7), 2.72 (2H, m, H-1,4), 3.41 (1H, m, H-6), 4.26 (2H, m, $CH_3CH_2O_2C$), 4.71 (1H, m, H-5); δ_C (90 MHz, $CDCl_3$) 11.2 (CH_3), 13.2 ($CO_2CH_2CH_3$), 20.4, 20.6, 28.0, 28.3 (CH_2), 30.8, 32.7 (C-2,3), 37.4 (C-7), 44.1, 47.2 (C-1,4), 56.3 (C-6), 60.9 ($CO_2CH_2CH_3$), 93.9 (C-5), 152.9 (C=N), 160.0 ($CO_2CH_2CH_3$).

3. Results and discussion

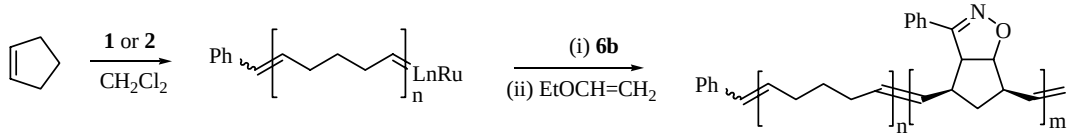
In order to minimise dimerisation to furoxans (1,2,5-oxadiazole *N*-oxides) [12], the nitrile oxides **3** were generated in situ by triethylamine-induced dehydrochlorination of the corresponding hydroximoyl chorides **4**. [13] An excess of norbornadiene was used to avoid 2:1 adducts resulting from nitrile oxide cycloaddition to both alkene units in the dipolarophile. Using this approach norbornadiene and ethoxycarbonylformonitrile oxide **3a**, generated from ethyl chloro-oximidoacetate **4a**, afforded a mixture of *endo*- and *exo*-adducts **5a** (15%) and **6a** (67%), which were separated by chromatography (Scheme 1). The individual isomers were readily identified by their characteristic ^{1}H NMR spectra.[1] For the *exo*-product **6a** the isoxazoline protons 3a–H (δ_H 3.48 ppm) and 7a–H (δ_H 4.95 ppm, $J_{3a,7a}=7.1$ Hz) have small couplings to the adjacent bridgehead protons 4-H and 7-H of 1.2 and 1.4 Hz, respectively. In contrast, for the *endo*-adduct **5a** protons 3a–H (δ_H 4.02 ppm) and 7a–H (δ_H 5.39 ppm, $J_{3a,7a}=9.9$ Hz) show larger couplings to 4-H (4.2 Hz) and 7-H (4.1 Hz). Benzonitrile oxide and norbornadiene reacted similarly to yield adducts **5b** (16%) and **6b** (54%) [9,10].

The compatibility of the isoxazoline ring system with the ROMP conditions was first established by carrying out a typical polymerisation of norbornene initiated by compound **1** in the presence of isoxazoline **7**, which was prepared from benzonitrile oxide and norbornene [14]. The resulting polynorbornene **8** was indistinguishable from an authentic sample[2] and compound **7** (94%) was recovered from the reaction mixture.



The suitability of isoxazolino-norbornenes **6a** and **6b** as monomers for ROMP was examined using the Grubbs initiators **1** and **2**. Polymerisation of **6a** using initiator **2**

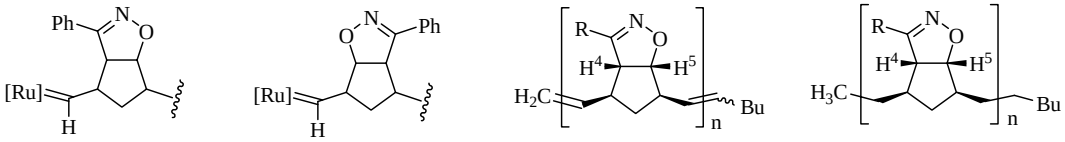
[2] Polynorbornene **8** was prepared as previously described: Amir-Ebrahimi V, Corry DA, Hamilton JG, Thomson JM, Rooney JJ. Macromolecules 2000;33:717.



Scheme 2.

afforded a solid that was identified as polyisoxazoline **9a** (75%) from its spectroscopic properties by comparison to polynorbornene **8** and compound **10** [15], which was prepared as a model for the isoxazoline units in the polymer by reaction of nitrile oxide **3a** with cyclopentene. For polymer **9a** there are characteristic peaks for the ethoxycarbonylisoxazoline moiety in the proton spectrum at δ_H 5.05 (5-H), 4.33 (OCH_2), 3.65 (4-H), and 1.43 ppm (CH_3), and in the carbon spectrum at δ_C 160.5 (C=O), 153.6 (C-3), 94.6 (C-5), 62.0 (OCH_2), 57.4 (C-4) and 14.2 ppm (CH_3). GPC analysis gave an average molecular weight of 138.4×10^3, corresponding to a polydispersity index (PDI) of 1.65 and an average degree of polymerisation (av DP) of 668. Phenylisoxazoline monomer **6b** was polymerised using both initiators **1** and **2** to afford polyisoxazoline **9b** (63% for **1**, 62% for **2**). In contrast, attempted polymerisation of **6a** using initiator **1** afforded only unreacted monomer.

For phenylisoxazoline monomer **6b**, initiated by **1** in $CDCl_3$, the progress of the polymerisation could be monitored by ^{1}H NMR spectroscopy. In addition to the sharp singlet at 19.9 ppm for unreacted initiator **1**, a broader signal was observed at 19.4–19.5 ppm, which is attributed to the carbene hydrogens of the ruthenium alkylidene end-groups of the propagating polymer [4,5,16]. The breadth of the peak can be explained, in part at least, by the presence of regioisomers **11** and **12**.[3] The detection of proton signals corresponding to the propagating species and the low PDI value is indicative of a living polymer system.



The living nature of the polymerisations using initiators **1** and **2** was demonstrated by the AB-type block copolymerisation of cyclopentene and **6b** (Scheme 2). Cyclopentene (40 equiv.) was polymerised with **1** for 24 h after which the second monomer **6b** (40 equiv.) was added to the reaction mixture. After stirring for a further 24 h the mixture was heated at 50 °C for 6 h and terminated with ethyl vinyl ether. An increase in molecular weight (M_n) from 1.5×10^3 to 7.0×10^3 was observed (measured by GPC against polystyrene standards), which corresponds to an AB block copolymer comprising cyclopentene and **6b** ($M_w/M_n=1.12$) with an av DP of $A=21$ and $B=29$, respectively. The copolymer from the analogous experiment using initiator **2** also possessed an AB structure with $A=21$, $B=107$ and a PDI = 1.33.

In order to obtain lower molecular weight polymers with greater solubility and better defined NMR spectra, a series of experiments was conducted using monomer **6a**, initiator **2**, and varying amounts of hex-1-ene as chain transfer agent [17]. The butyl and vinyl end groups in the product were clearly discernible in their NMR spectra,[4] thus allowing the average DP for the polymers/oligomers to be determined by comparison with the internal olefinic resonances. For example, using **6a**, hex-1-ene, and **2** in the ratio 160:16:1 afforded polymer **13** (R = CO_2Et) with $M_n=3.4\times10^3$, corresponding to the incorporation of 16 monomer units (Table 1, entry 3).

Samples of oligomers **13** ($n=4,16$) were converted into hydrogenated analogues **14** (89 and 83%, respectively) by treatment with *p*-toluenesulfonyl hydrazide (5 equiv.) in chlorobenzene at 130 °C, a method that has previously proved to be successful for polynorbornenes and polynorbornadienes [18]. In the ^{13}C NMR spectrum[4] of the product the absence of olefinic resonances in the region 115–140 ppm and the appearance of new peaks at 30–33 ppm indicated that the reaction had gone to completion. Characteristic signals were also present at 160 (C=O), 153 (C=N), 93 (C-5), 60–61 (OCH_2) and 56 ppm (C-4) demonstrating that isoxazoline moiety is stable to the diimide reduction conditions.

Having established that isoxazolino-norbornenes were suitable monomers for ROMP the feasibility of using the analogous isoxazolidino compounds was examined. As a

[3] The polymeric products **9**, **13** and **14** all contain regioisomeric isoxazolinocyclopentane units.

[4] Selected NMR data for polymers **13** and **14**: **13** δ_H/ppm 5.9 (vinyl CH), 4.9–5.1 (vinyl CH_2), 0.89 (butyl CH_3); δ_C/ppm 159.9, 159.5 (C=O), 152.6, 152.5 (C=N), 138.8–139.1 (vinyl CH_2), 127.3 (butyl=CH), 113.7–115.1 (vinyl CH), 92.9–94.3 (C-5), 61.0, 61.1 (OCH_2), 55.6–56.8 (C-4), 30.4, 30.5, 30.8, 31.1 (butyl CH_2), 21.2, 21.3, 26.3, 26.4 (2×butyl CH_2), 12.9, 13.1 (CH_3); **14** δ_C/ppm 160.5, 159.9 (C=O), 152.9 (C=N), 92.9, 92.5 (C-5), 61.0, 60.3 (OCH_2), 56.3, 55.7 (C-4), 30.8–32.7, 20.6, 20.4 (CH_2), 13.2 (CH_3).

Table 1
Effect of chain transfer agent (hex-1-ene) on average number of repeat units (DP) of monomer **6a**

Entry	[Hex-1-ene]/[**6a**]	Yield (%)	σ_C	M_n ($\times 10^{-3}$)	PDI	Av no. (DP[a/b])
1	0.00	75	0.63	140	1.65	676[a]
2	0.05	96	0.64	32.9	1.45	159[a]/157[b]
3	0.10	99	0.60	3.4	[c]	[c]/16[b]
4	0.15	93	0.59	2.0	1.55	9[a]/8[b]
5	0.25	92	0.55	0.90	[c]	[c]/4[b]

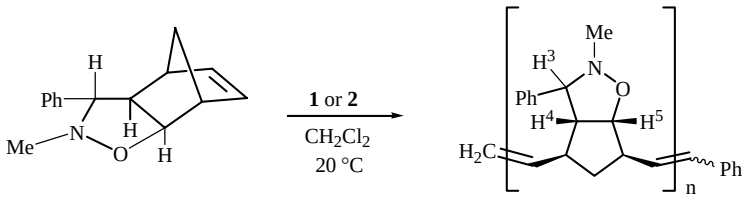
[a] Determined by GPC analysis.
[b] Determined by NMR end group analysis.
[c] Not determined.

representative example *exo*,*exo*-isoxazolidino-norbornene **15** was prepared by cycloaddition of *N*-methyl-*C*-phenylnitrone to norbornadiene [11]. Subsequent ROMP using initiator **1** afforded polymer **16** in 75% yield and average DP = 220 (Scheme 3). The product was identified from its NMR spectra, which showed characteristic proton signals at δ_H 4.41 (5-H), 3.08 (3-H), 2.49 (NMe) and 1.96 ppm (4-H), and in the carbon spectrum signals at δ_C 87.6 (C-5), 80.0 (C-3), 60.0 (C-4) and 28.7 ppm (NMe). The corresponding polymerisation using initiator **2** gave **16** in similar yield (76%) but with greater molecular weight (DP = 529).

Selected data for the polymerisations are given in Table 2. Using initiator **1** a signal was detected in the ^{1}H NMR spectrum corresponding to the propagating alkylidene compound. Polymers prepared using **2** have broad molecular weight distributions, as judged by the polydispersity index. The high propagation rates and slow initiation rates for polymerisations using **2** [19] and competing chain transfer reactions [20] result in polymers with a higher molecular weight compared with those prepared using **1**. The fraction of *cis* alkene units (σ_c) in the polymer backbone is also higher using initiator **2** [21].

4. Conclusions

These results demonstrate that the cycloadducts of nitrile oxides and nitrones with norbornadiene are suitable monomers for ring opening metathesis polymerisation and thus provide access to a new range of functionalised polymers. We are currently investigating the ROMP of isoxazolino-norbornenes prepared from glycosyl-nitrile oxides as a potential route to novel carbohydrate oligomers and polymers.



15 **16**

Scheme 3.

Table 2
Selected data for polymers derived from monomers **6a**, **6b**, **15**

Monomer[a]	Initiator[a]	Yield (%)	% *cis* content[b]	Calc. M_n[c] ($\times 10^{-3}$)	Obs. M_n[d] ($\times 10^{-3}$)	Av no. (DP)	PDI[d]	δ_H (ppm) (alkylidene)
6a	**1**	[e]	[e]	16.6	[e]	[e]	[e]	[e]
6a	**2**	75	63	16.6	138.4	668	1.65	[f]
6b	**1**	63	[f]	16.8	17.9	85	1.97	19.4
6b	**2**	75	63	16.6	138.4	668	1.65	[f]
15	**1**	75	36	18.2	57.0	251	1.84	18.6
15	**2**	76	61	18.2	111.4	490	2.37	[f]

[a] [M]/[I] = 80:1 in all cases.
[b] % *cis* content of double bonds in polymer backbone.
[c] Assuming quantitative conversion.
[d] Determined by GPC analysis.
[e] Did not polymerise.
[f] Not observable.

References

[1] For reviews of ROMP see (a) Trnka M, Grubbs RH. Acc Chem Res 2001; 34:18.
(b) Harned AM, Zhang M, Vedantham P, Mukherjee S, Herpel RH, Flynn DL, et al. Aldrichim Acta 2005;38:3.
(c) Nguyen ST, Trnka TM. In: Grubbs RH, editor. Handbook of metathesis, vol. 1.6. Weinheim: Wiley-VCH; 2003. p. 61–85.

[2] North M. In: Halton B, editor. Advances in strained and interesting molecules, vol. 8. Stamford: JAI; 2000. p. 145.

[3] Moore JD, Herpel RH, Lichtsinn JR, Flynn DL, Hanson PR. Org Lett 2003;5:105.

[4] Biagini SCG, Gibson VC, Giles MR, Marshall EL, North M. J Chem Soc, Chem Commun 1997;12:1097.

[5] (a) Gibson VC, Marshall EL, North M, Robson DA, Williams PJ. J Chem Soc, Chem Commun 1997;12:1095.
(b) Davies RG, Gibson VC, Hursthouse MB, Light ME, Marshall EL, North M, et al. J Chem Soc, Perkin Trans 1 2001;3365.

[6] (a) For a review see: Kiessling LL, Owen RM. In: Grubbs RH, editor. Handbook of metathesis, vol. 3.6. Weinheim: Wiley-VCH; 2003. p. 180–225.
(b) Kanai M, Mortell KH, Kiessling LL. J Am Chem Soc 1997;119:9931.

[7] Grünanger P, Vita-Finzi P. Isoxazoles: the chemistry of heterocyclic compounds, vol. 49. New York: Wiley; 1999, Part 2, p. 506 and 547.

[8] Skinner GS. J Am Chem Soc 1924;46:731.

[9] Cocu FG, Lazar R, Barbulescu N. Rev Roum Chim 1968;19:625.

[10] Ambler PW, Paton RM, Tout JM. J Chem Soc, Chem Commun 1994;2661.

[11] Boyle LW, Pergram MJ, Whitman GH. J Chem Soc (B) 1971;1728.

[12] Grundmann C, Grünanger P. The nitrile oxides. Berlin: Springer; 1971 [chapter 4].

[13] Huisgen R, Mack W. Tetrahedron Lett 1961;583.

[14] Huisgen R, Christl M, Mack W. Chem Ber 1973;106:3312.

[15] De Amici M, De Micheli C, Carrera G, Riva S. Tetrahedron: Asymmetry 1996;7:787.

[16] (a) Maughon RR, Grubbs RH. Macromolecules 1997;30:3459.
(b) Ivin KJ, Kenwright AM, Khosravi E. J Chem Soc, Chem Commun 1999;13:1209.
(c) Robson DA, Gibson VC, Davies RG, North M. Macromolecules 1999;32:6371.

[17] (a) Ivin KJ, Rooney JJ, Bencze L, Hamilton JG, Lam L-M, Lapienis G, et al. Pure Appl Chem 1982;54:447.
(b) France MB, Grubbs RH, McGrath DV, Paciello RA. Macromolecules 1993;26:4742.

[18] Al-Samak B, Amir-Ebrahimi V, Carvill AG, Hamilton JG, Rooney JJ. Polym Int 1996;85 and references therein.

[19] (a) Sanford MS, Ulman M, Grubbs RH. J Am Chem Soc 2001;123: 749.
(b) Sanford MS, Love JA, Grubbs RH. J Am Chem Soc 2001;123: 6543.

[20] (a) Bielawski CW, Grubbs RH. Angew Chem, Int Ed 2000;39:2903.
(b) Bielawski CW, Benitez D, Grubbs RH. Macromolecules 2001;34: 8610.
(c) Scherman OA, Kim HM, Grubbs RH. Macromolecules 2002;35: 5366.

[21] Amir-Ebrahimi V, Hamilton JG, Rooney JJ. In: Khosravi E, Szymanska-Buzar T, editors. Ring opening metathesis polymerisation and related chemistry. Dordrecht: Kluwer Academic Publishers; 2002. p. 45.