ROMP of *n*-alkyl norbornene dicarboxyimides: from classical to well-defined initiators, an overview

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Abstract

The ring opening metathesis polymerisation (ROMP) of *n*-alkyl norbornene dicarboxyimides using a wide range of initiators has been extensively studied. ROMP of *exo-n*-alkyl norbornene dicarboxyimides with classical initiators WCl_6/Me_4Sn (**I**) and $MoCl_5/Me_4Sn$ (**II**) gave polymers with 63% and 85% *trans* vinylene content, respectively. In contrast, the *endo*-isomer could not be polymerised in any of several attempts. Both *exo*- and *endo-n*-alkyl norbornene dicarboxyimides were polymerised using well-defined initiators $Mo(CH-t-Bu)(N-2,6-i-Pr_2C_6H_3)(OCMe_3)_2$ (**III**) and $Mo(CHCPhMe_2)(N-2,6-i-Pr_2C_6H_3)(OCMe(CF_3)_2)_2$ (**IV**). In the case of *exo* isomers, **III** gave polymers with 97% *trans* vinylene content and **IV** gave polymers with about 30% *trans* vinylene content. In the case of *endo* isomer, **III** gave polymer with 93% *trans* vinylene content and **IV** gave polymer with 57% *trans* vinylene content. The living nature of these polymerisations was confirmed by synthesising AB diblock copolymers by sequential addition of monomers. Both *exo-* and *endo-n*-alkyl norbornene dicarboxyimides were also polymerised using well-defined initiator $RuCl_2(CHPh)(PCy_3)_2$ (**V**). The polymers obtained from *exo* and *endo* monomers contain 82% and 100% *trans* vinylene content respectively. The course of the polymerisation reactions using well-defined initiators **III**–**V** were followed by ^1H NMR and both the initiator and propagating alkylidenes signals were observable. The multiplicity and broadening of the backbone resonances in ^{13}C NMR, in all cases, is consistent with a multiplicity of overlapping environments associated with *atactic* microstructures. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The ring opening metathesis polymerisation (ROMP) of substituted norbornenes and norbornadiene derivatives using classical initiators WCl_6/Me_4Sn (**I**) and $MoCl_5/Me_4Sn$ (**II**) is a well-established process [1–6]. It is established that substituents such as chloro, fluoro, cyano, esters and other hetero-atom containing func-tionalities can be tolerated by some, although by no means all, classical initiators [7–13].

The well-defined metathesis initiators $Mo(CH-t-Bu)(N-2,6-i-Pr_2C_6H_3)(OCMe_3)_2$ (**III**) and $Mo(CHCPhMe_2)(N-2,6-i-Pr_2C_6H_3)(OCMe(CF_3)_2)_2$ (**IV**) developed by Schrock [14–28] have proved useful in ROMP of cyclic and bicyclic olefins. They tolerate a wide range of functionalities, are stable and active in a variety of solvents and, in some cases, have been shown to produce polymers with well-defined microstructures, for example, virtually all
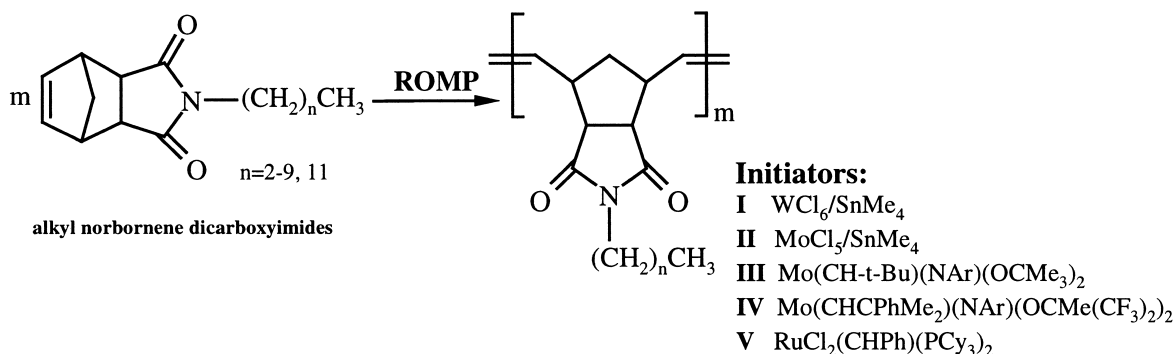
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Fig. 1. Polymerisation of *n*-alkyl norbornene dicarboxyimides using ROMP initiators I–V.

trans and highly *tactic* [18] or all *cis* with a *tactic* bias of ∼75% [19].

The recent introduction by Grubbs [29–36] of the well-defined initiator $RuCl_2(CHPh)(PCy_3)_2$ (**V**) has had a tremendous impact on ROMP due to its remarkable stability towards functional groups and protic media and its ease of handling.

The work reported here describes the synthesis and characterisation of *exo*- and *endo*-*n*-alkyl norbornene dicarboxyimides monomers and ROMP of these monomers using classical and well-defined initiators (I–V, Fig. 1). This study is part of our ongoing programme of work directed towards the synthesis and characterisation of polymeric materials via RIM-ROMP and RTM-ROMP.

2. Experimental

2.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannular techniques or in a conventional nitrogen-filled glove-box. CHN analysis was performed using a Carlo Erba 1106 elemental analyser. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz (^{1}H) and 100.6 MHz (^{13}C); chemical shifts are referenced to the residual proton impurity of the deuterated solvent. Gel permeation chromatographic (GPC) analyses were performed on chloroform or THF solutions using a GBC-LC 1110 HPLC pump, a PL-DG 802 degasser, an ERC 7515A RI detector, a PL-DCU data capture unit and 3 PLgel columns (each 300 mm long) with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5 μm styrene-divinyl benzene beads). The eluent was chloroform (flow rate 1 ml/min). The system was calibrated using polystyrene standards (Polymer Laboratories) ranging from 1000–1,000,000 g/mol. Infrared spectra were recorded using a Perkin Elmer 1720-X series FTIR. Differential Scanning Calorimetry was performed using a Perkin Elmer DSC 7 differential scanning calorimeter. Thermogravimetric analysis was carried out using a Rheometric Scientific TG-760 thermobalance.

2.2. Reagents

Chlorobenzene (Analar grade) was distilled from P_2O_5 under dry nitrogen. Deuterated dichloromethane and dichloromethane were stirred over phosphorus pentoxide and vacuum distilled immediately prior to use. Benzaldehyde was fractionally distilled and dried over 4 Å molecular sieve. WCl_6, $MoCl_5$ and tetramethyl tin were purchased from Aldrich Chemical and used without further purification. The well-defined ROMP initiators, Mo(CH-*t*-Bu)(*N*-2,6-*i*-

$Pr_2C_6H_3)(OCMe_3)_2$ (**III**) and $Mo(CHCPhMe_2)$-(N-2,6-i-$Pr_2C_6H_3)(OCMe(CF_3)_2)_2$ (**IV**), [14,15] and $RuCl_2(CHPh)(PCy_3)_2$, (**V**) [30–32], were prepared following the published methods. 2,3-Bis(trifluoromethyl)norbornadiene, BTFMND, used as a comonomer for block copolymerisation reactions was prepared using the published route [4]. *Exo-* and *endo-n*-alkyl norbornene dicarboxyimides were synthesised as described previously [37]. General polymerisation procedure using classical initiators **I** and **II** and also well-defined initiators **III** and **IV** were similar to those reported earlier [37,38]. General copolymerisation procedure using initiator **III** was as described previously [38].

2.3. General polymerisation procedure using well-defined initiators **V**

The polymerisation reactions, depending on the amount of monomer used, were carried out in the Glove Box at ambient temperature in sample vials or small flasks (50 ml) equipped with magnetic stirrers. For NMR scale reactions monomers (10 equivalents, 30 mg) and initiator (10 mg) were dissolved in CD_2Cl_2 (0.40 ml each) in different vials. The initiator solution was added to the monomer solutions. The reaction mixtures were stirred for a few minutes and were then transferred into a screw capped NMR tube and were analysed by ^{1}H NMR spectroscopy immediately. The reaction mixtures were monitored until the monomer was consumed completely.

For preparative scale polymerisation monomers (1.5 g) and initiator (10 mg) were dissolved in CH_2Cl_2 (25 ml for monomers and 5 ml for initiator) in different flasks. The initiator solution was added to the monomer solution and stirred for the required time. Ethyl vinyl ether (10 equivalents with respect to initiator) was added to terminate the polymerisation reaction and the mixture was stirred for 30 min. The mixture was taken out of the Glove Box and added dropwise to a 10-fold excess of methanol.

Any precipitate was collected by filtration, dried, re-dissolved in chloroform and re-precipitated by dropwise addition of a concentrated solution to a vigorously stirred excess of methanol. The polymer products were isolated by filtration and dried under reduced pressure on the vacuum line at room temperature for 8 h, then in a vacuum oven at 40°C for 72 h.

3. Results and discussion

3.1. Synthesis of monomers

A wide range of *exo-* and *endo-n*-alkyl norbornene dicarboxyimide monomers, shown in Fig. 1, was synthesised and recovered as white solids or colourless liquids. Satisfactory elemental analysis (Table 1) ^{1}H and ^{13}C NMR spectroscopy confirmed their structures and purity. The infrared spectra of the monomers synthesised were all very similar and showed characteristic peaks at ca. 1760, 1690 cm^{-1} (asymmetric and symmetric C = O stretching), 1400 cm^{-1} (C–N stretching).

3.2. ROMP with classical initiators

Exo-n-alkyl norbornene dicarboxyimides monomers undergo ROMP using initiator sys-

Table 1
Elemental analyses for *n*-alkyl norbornene dicarboxyimides

Monomer $n =$, isomer	C % found (calculated)	H % found (calculated)	N % found (calculated)
2, exo	70.12 (70.22)	7.73 (7.37)	6.41 (6.83)
3, exo	71.23 (71.21)	7.79 (7.81)	6.30 (6.39)
4, exo	72.25 (72.07)	8.16 (8.21)	6.07 (6.00)
5, exo	72.68 (72.84)	8.63 (8.56)	5.65 (5.66)
5, endo	72.69 (72.84)	8.53 (8.56)	5.61 (5.66)
6, exo	73.64 (73.53)	8.99 (8.87)	5.35 (5.36)
7, exo	74.13 (74.15)	9.02 (9.15)	5.23 (5.09)
7, exo	74.08 (74.15)	9.41 (9.15)	4.75 (5.09)
8, exo	74.75 (74.69)	9.58 (9.41)	4.75 (4.84)
9, exo	75.60 (75.21)	9.81 (9.63)	4.68 (4.62)
11, exo	76.17 (76.08)	10.05 (10.04)	4.26 (4.23)

tems **I** and **II**, in chlorobenzene at 40°C to 60°C, Table 2. The infrared spectra of the product polymers were all very similar and, as expected, peaks characteristic of the imide group at ca. 1770 and 1700 cm^{-1} were prominent features of all the spectra.

The ^{1}H NMR spectra of the polymers were in agreement with the structures proposed and showed a generally similar pattern of chemical shifts and intensities. The most useful and detailed structural characterisation of the polymers was carried out using high resolution of ^{13}C NMR spectroscopy [37]. In general, the initiator system **I** gave polymers with about 63% *trans* vinylene content whereas the initiator system **II** gave polymers with about 85% *trans* vinylene content. The overall conclusion from the ^{13}C NMR analysis was that the polymers obtained are atactic.

The results of DSC analysis (Table 2) revealed that the polymer samples with higher *trans* content exhibit lower Tg, which would be consistent with greater backbone mobility associated with higher *trans* content. There is a also trend to lower Tg with increasing length of pendant alkyl group, which is what would be expected if the pendant group is large enough to give an internal plasticisation effect. A 2% weight loss was observed by TG between 399°C and 414°C for all the polymers obtained, while the maximum weight loss was observed at about

570°C (Table 2). All polymers prepared gave unimodal distributions with dispersity indexes of the order of 2 to 3.5 (Table 2).

By contrast, the *endo-n*-alkyl norbornene dicarboxyimides would not undergo ROMP using either the initiator system **I** or the initiator system **II**, in any of several attempts [37].

3.3. ROMP with well-defined molybdenum initiators

The ROMP of *exo-n*-alkyl norbornene dicarboxyimides and *endo-n*-octyl norbornene dicarboxyimide using the well-defined Schrock molybdenum initiators of the types **III** and **IV** has been successfully established [38], Table 3.

^{1}H NMR spectra obtained 5 min after the addition of 10 equivalents of exo-*n*-octyl norbornene dicarboxyimide to either **III** or **IV** in deuterated dichloromethane (CD$_2$Cl$_2$) showed the singlet peaks at 11.22 and at 12.21 ppm due to the initial alkylidene hydrogens of the **III** and **IV**, respectively. The multiplet peaks due to the propagating alkylidene hydrogens were also seen at, respectively, ca. 11.60 and 12.60 ppm. Increasing the amount of monomer eventually resulted in the complete consumption of the initiator. This, in principle, allows well-defined living polymerisation of these monomers with these initiators.

Table 2
Experimental details for the polymerisation of *exo-n*-alkyl norbornene dicarboxyimides using classical initiators **I** and **II**, and thermal characterisation data

Monomer *n* =	Initiator system	Temp (°C)	Time (min)	Yield (%)	GPC		DSC Tg (°C)	TG 2% wt-loss
					Mn	PDI		
4	**I**	40	5–7	75	55,000	1.9	70	401
	II	60	16–18	84	79,000	2.3	72	399
5	**I**	40	5–7	86	69,000	2.2	68	403
	II	60	16–18	77	62,000	2.1	64	399
6	**I**	40	5–7	72	44,000	2.3	61	401
	II	60	16–18	78	72,000	2.4	57	406
7	**I**	40	5–7	86	66,000	2.5	57	404
	II	40	16–18	82	49,500	1.9	56	399
9	**I**	40	5–7	69	71,000	2.4	–	414
	II	60	16–18	75	61,000	3.4	46	405

Table 3
Experimental details for the polymerisation of *exo-n*-alkyl norbornene dicarboximides using well-defined initiators **III** and **IV**, and thermal characterisation data

Initiator system	Polymer $n =$	[M]:[I]	Time (h)	Yield (%)	Mn calc.	GPC		DSC Tg (°C)	TG 2 % wt-loss
						Mn Found	PDI		
III	6	42	3	78	10,950	11,000	1.09	65	430
	7	50	4	75	13,870	14,000	1.1	51	435
	8	49	3.5	76	14,160	14,200	1.05	52	435
	9	35	4	84	10,600	10,700	1.08	52	435
	11	55	3	92	18,200	18,500	1.08	50	420
IV	6	25			6500	7400	1.4		
		40	3.5	81	10,400	12,400	1.5	67	420
	7	65	3	79	17,900	19,900	1.3	53	440
	8	78	4	76	22,300	32,300	1.5	51	445
	9	80			24,200	27,200	1.4		
		100	4.2	72	30,300	41,500	1.5	56	445
	11	70	4	83	23,000	25,000	1.3	66	445

^{1}H NMR and ^{13}C NMR spectra of polymers obtained using initiators **III** and **IV** were in agreement with the structures proposed and showed a generally similar pattern of chemical shifts. The ^{13}C NMR analysis revealed that the polymers obtained using **III** have a *trans* vinylene content greater than 97%. The spectra for polymers derived from **IV** displayed higher multiplicities and broader resonances than those from polymers made with **III** and the analysis established a *trans* vinylene content of about 30%. Both spectra are complex and indicate that these polymers are essentially *atactic* [38].

For polymerisations initiated with **III** polydispersity values fall between 1.05 and 1.1, Table 3, suggesting that under these conditions well-ordered living polymerisation occurred. This conclusion is supported by the good correlation between the theoretical Mn values and those observed for the major peak. However, when the initiator **IV** was used the resulting polymers showed a much broader molecular weight distribution, between 1.3 and 2.1 and the correlation between theoretical and observed Mn values was rather poor. This can be explained by the observation that propagation with this initiator was much faster than initiation (as concluded from the ^{1}H NMR analysis of the initiation process discussed earlier). The molecular

weight broadening may be explained, in part, to cross metathesis between the more reactive propagating chain ends and double bonds in the polymer backbone. All the polymers displayed similar thermal stabilities and similar glass transition temperatures (Table 3). The small differences observed may be a consequence of molecular weight and/or tacticity differences but do not justify detailed analysis. Glass transition temperatures were in the range 50°C to 70°C and no crystalline melting points were detected (Table 3). A 2% weight loss was observed for all polymers at about 435°C.

The *endo*-adduct also undergoes ROMP using **III** and **IV** to give high molecular weight polymer [38]. The ^{1}H NMR spectra of the living polymer solutions in deuterated dichloromethane show a multiplet signal at 11.70 and 12.34 ppm due to the hydrogens of the propagating alkylidene of **III** and **IV**, respectively. As with the exo-monomer, the polymerisation using initiator **IV** propagation occurs significantly faster than with **III**. ^{1}H NMR and ^{13}C NMR spectra of poly(*endo-n*-octyl norbornene dicarboximide), prepared using **III** and **IV** as initiators were in agreement with the structure proposed and showed a generally similar pattern of chemical shifts and intensities. The conclusion from this analysis is that the polymer obtained using **III**

Table 4
Experimental details for the polymerisation of *endo-n*-octyl norbornene dicarboxyimides using well-defined initiators **III** and **IV**, and thermal characterisation data

Initiator system	[M]:[I]	Time (h)	Yield (%)	Mn calc.	GPC		DSC Tg (°C)	TG 2% weight loss
					Mn found	PDI		
III	59	4	–	16,250	16,400	1.3	–	–
	80	4	84	–	–	–	104	465
IV	33	4	–	9100	11,700	1.8	–	–
	100	4	79	–	–	–	92	460

as initiator has 93% *trans* vinylene content and that using **IV** gave polymer with 57% *trans* vinylene content. The multiplicity and broadening of the backbone resonances, in both cases, is consistent with a multiplicity of overlapping environments associated with an *atactic* polymer. The results of GPC analysis (Table 4) for polymeric materials prepared from *endo*-monomers similarly imply that the molybdenum initiator **III** gives a fairly well-defined living polymerisation; whereas with **IV**, propagation is significantly faster than initiation, which leads to higher molecular weights than expected and a broadening of the molecular weight distribution.

The glass transition temperatures of the polymers obtained from *endo*-monomers (Table 4) are significantly higher (92°C to 104°C) than those observed for poly(*exo-n*-alkyl norbornene dicarboxyimide)s described earlier. This is probably a consequence of a stiffer less mobile backbone resulting from the *endo* repeat unit stereochemistry. The 2% weight loss for these polymers occurs at about 460°C indicating a

slightly greater stability than the polymers from the *exo* monomers.

The living nature of these polymerisation reactions was confirmed by synthesising AB diblock copolymers by sequential addition of monomers (Table 5). In a typical example, exo-*n*-octyl norbornene dicarboxyimide (monomer A) (40 equivalents) in deuterated dichloromethane was polymerised using initiator **III**. The ^{1}HNMR spectrum (Fig. 2a) showed a multiplet signal at 11.60 ppm due to the propagating alkylidenes of poly(block A) and also showed that both the initiator and monomer are completely consumed [38]. A solution of BTFMND (45 equivalents) (monomer B) in the same solvent was added and was allowed to stir for 1 h. The ^{1}HNMR spectrum (Fig. 2b) showed that the multiplet peak at 11.60 ppm, due to the propagating alkylidene species of block A, was completely replaced by a doublet at 11.30 ppm due to the propagating alkylidene species of block B. This doublet is characteristic of the propagating species leading to a *syndiotactic* block with

Table 5
Experimental details for the block copolymerisation polymerisation of *exo-n*-alkyl norbornene dicarboxyimides (monomer A) and BTFMND (monomer B) using well-defined initiator **III**

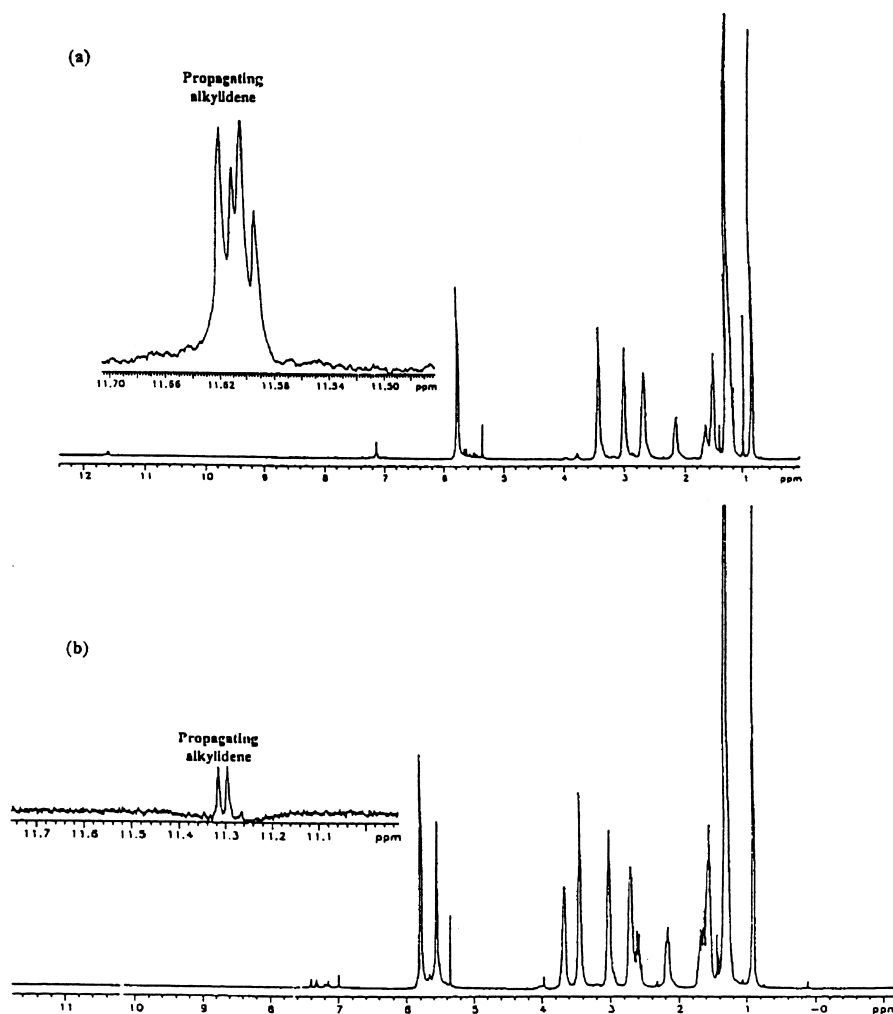| Monomer A n =	[A]:[I]	Propagating alkylidene of Block-A	[B]:[I]	Propagating alkylidene of Block-B	Yield (%)	Tg (°C) Block A	Tg (°C) Block B
6	39	11.60	50	11.30	75		
7	41	11.60	45	11.30	73	50	97
8	44		50	11.30	76		
9	43		55	11.31	78		
11	42		55	11.31	73		

Fig. 2. The 400 MHz ^{1}H NMR spectra recorded in CD$_2$Cl$_2$ as solvent of (a) living poly(*exo-n*-octyl norbornene) and (b) living poly(*exo-n*-octyl norbornene dicarboxyimide-co-BTFMND).

greater than 98% *trans* vinylene content [17,18]. The reaction was monitored until monomer B was completely converted to polymer.

All samples exhibit single mode molecular weight distribution and relatively narrow polydispersity (between 1.22 and 1.29). DSC thermogram of the block copolymers show two glass transition temperatures characteristic of block A, 50°C, and block B, 97°C, indicating the incompatibility of the segments A and B in the block copolymer system.

All polymer samples prepared from *exo-* and *endo*-monomers and also the block copolymer

samples were soluble in chloroform, dichloromethane, tetrahydrofuran and insoluble in

Table 6
Experimental details for the polymerisation of *exo-n*-alkyl norbornene dicarboxyimides using well-defined initiator **V**, and thermal characterisation data

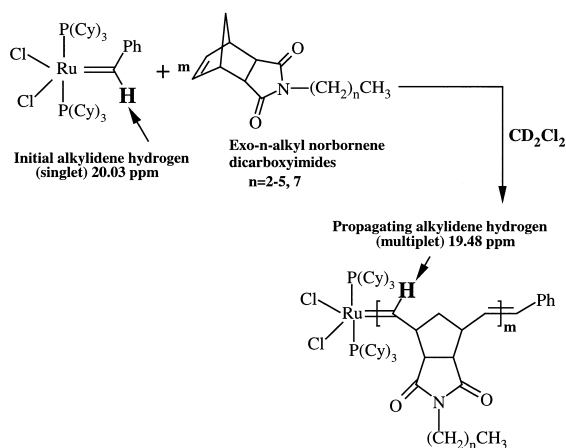| Polymer *Exo* isomer, n =	[M]:[I]	Yield (%)	GPC		DSC Tg (°C)	TG 2 % wt-loss
			Mn	PDI		
2	4000	90	453,000	1.9	139	403
3	3700	92	462,000	1.8	126	414
4	3600	91	500,000	2.0	99	400
5	3200	91	820,000	1.6	84	421
7	3700	85	492,000	1.9	58	403

Fig. 3. Schematic for living polymerisation of *n*-alkyl norbornene dicarboxyimides with well-defined ruthenium initiator.

methanol and pentane; films could be cast from solution.

3.4. ROMP with well-defined ruthenium initiator

Exo-n-alkyl norbornene dicarboxyimides undergo ROMP with the Grubbs well-defined ruthenium initiator **V** to give high molecular weight polymers (Table 6).

The polymerisation reactions were monitored by ^{1}H NMR until the monomer was consumed completely. The multiplet peak at 19.48 ppm in the spectra, due to the propagating alkylidene hydrogen of the *exo*-derived chain end, is clearly distinguished from the singlet peak of the alkylidene hydrogen of the ruthenium carbene initiator at 20.03 ppm (Fig. 3). The observation of the singlet resonance due to unconsumed initiator is a common feature of all these reactions, even where two successive 30 equivalent aliquots of the *exo*-monomer were added. It appears that for the polymerisation of *exo* monomers using initiator **V**, the propagation rate constant (k_p) is probably considerably greater than the initiation rate constant (k_i).

^{1}H NMR and ^{13}C NMR spectra of polymers prepared using **V** initiation were similar to those discussed earlier for other initiator systems. The *cis / trans* vinylene contents of the polymers were obtained using ^{13}C NMR analysis, which revealed that these polymers generally contain 82% *trans* vinylenes. DSC thermograms of these polymers exhibit Tg values similar to those observed for other initiator systems used in the work reported here. A trend to lower Tg with increasing length of pendant alkyl group is also observed (Table 6).

The *endo* isomers also undergo ROMP with ruthenium initiator **V** and high molecular weight polymers are produced in low yield (Table 7). The polymerisation reactions were also monitored by ^{1}H NMR until the monomer was consumed completely. The polymerisation is appreciably slower than the polymerisation of the *exo* monomer under the same condition. A multiplet at 18.65 ppm, due to the propagating alkylidene hydrogen of the *endo*-derived chain end, and a singlet peak of the initiating hydrogen of the initiator at 20.03 ppm are clearly seen in the spectra. In this case, complete consumption of initiator was observed since the singlet alkylidene hydrogen disappeared completely after several days under the same conditions used for

Table 7

Experimental details for the comparison of the polymerisation of *exo-* and *endo-n*-alkyl norbornene dicarboxyimides using well-defined initiator **V**, and thermal characterisation data

Polymer *n* = , isomer	[M]:[I]	Conversion (%)	GPC		Trans vinylene content (%)	DSC Tg (°C)	TG 2 % wt-loss
			Mn	PDI			
5, *exo*	510	91	125,000	1.2	82	85	425
5, *endo*	510	19	50,000	1.4	100	116	330

the *exo* reaction. For the polymerisation of *endo* monomers using initiator **V**, the initiation rate constant (k_i) and propagation rate constant (k_p) appear to be much smaller than those for the *exo* monomers. The *endo*-propagating species was found to be stable over the course of the reaction, i.e. several days, and the second addition of *endo*-monomer (10 equivalents) resulted in continuation of the polymerisation. Interest-

ingly, ^{13}C NMR analysis showed that the polymers obtained contain 100% *trans* vinylenes (Fig. 4). To our knowledge, this is the first example of all *trans* polymer produced via ROMP using the Grubbs well-defined ruthenium initiator (**V**).

All the polymers obtained via ROMP of *exo*- and *endo*-monomers were soluble in tetrahydrofuran, dichloromethane and chloroform and in-
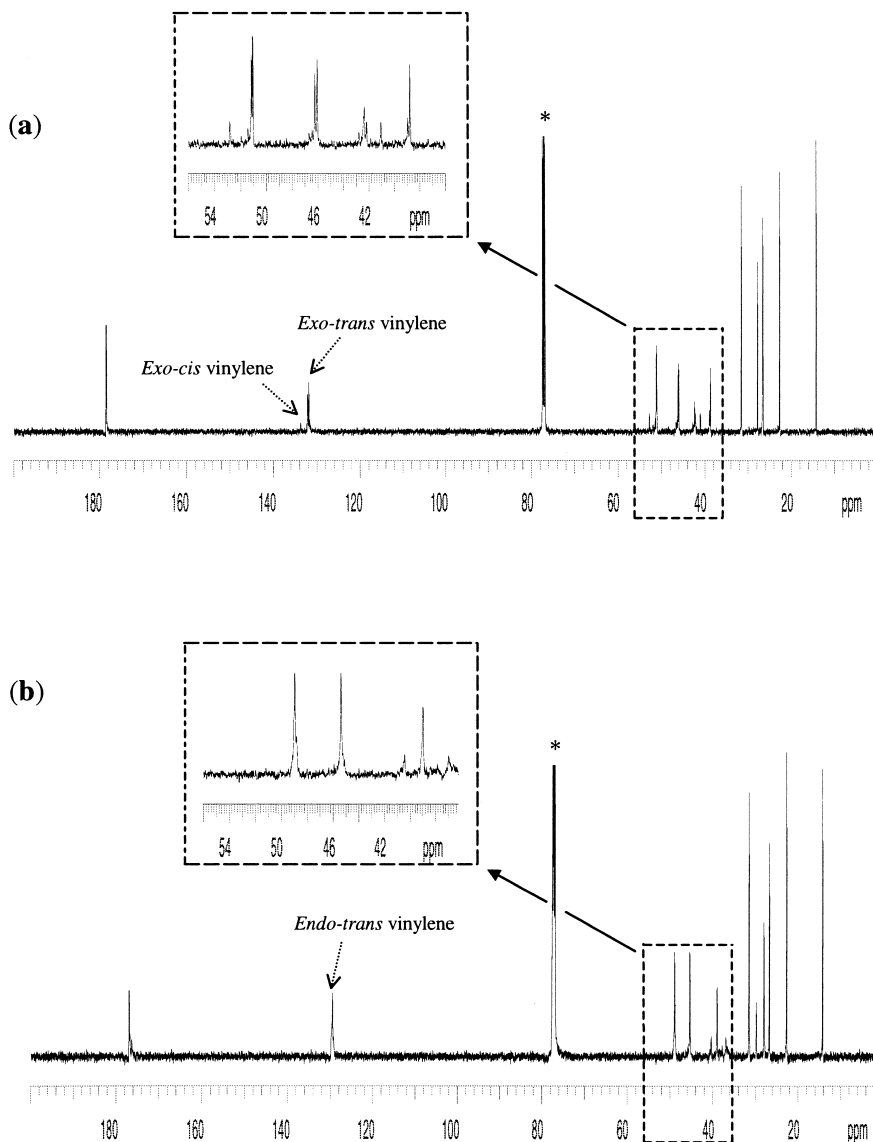

Fig. 4. The 100 MHz ^{13}C NMR spectra recorded in CDCl$_3$ of (a) poly(*exo-n*-heptyl norbornene dicarboxyimide) and (b) poly(*endo-n*-heptyl norbornene dicarboxyimide).

soluble in methanol and pentane; films could be cast from solution.

4. Conclusion

Exo-n-alkyl norbornene dicarboxyimides monomers undergo ring opening metathesis polymerisation using classical initiators **I** and **II**. In general, molybdenum-based initiation gave polymers with about 85% *trans* vinylene content, whereas tungsten-based initiator gave polymers with about 63% *trans* vinylene content. The overall conclusion from the ^{13}C NMR analysis is that the polymers obtained are *atactic*. The polymer samples with higher *trans* content exhibit lower Tg, consistent with greater backbone mobility with higher *trans* content. Thermal analysis also shows that there is a trend to lower Tg with increasing length of pendant alkyl group, which is what would be expected if the pendant group is large enough to give an internal plasticisation. All the polymers prepared gave unimodal distribution with polydispersity indexes of 2–3.5. However, several attempts to initiate ROMP of the *endo*-monomers using either **I** or **II** were unsuccessful.

ROMP of *exo-n*-alkyl norbornene dicarboxyimides and *endo-n*-octyl norbornene dicarboxyimide using well-defined initiators **III** and **IV** has been successfully established. The course of the polymerisation reactions was followed by ^{1}H NMR and both the initiator and propagating alkylidenes signals were observable in the spectra. In general, initiation with **III** gave the poly(*exo-n*-alkyl norbornene dicarboxyimide)s with 97% *trans* vinylene content, whereas **IV** gave the same polymers with about 30% *trans* vinylene content. ROMP of *endo-n*-octyl norbornene dicarboxyimide using **III** gave polymers with 93% *trans* vinylene content and **IV** gave 57% *trans* vinylene content. The multiplicity and broadening of the backbone resonances in both cases is consistent with a multiplicity of overlapping environments associated with *atactic* microstructures. The results of GPC analysis for polymeric materials prepared from *exo*- and *endo*-monomer imply that the initiator **III** gives fairly well-defined living polymerisation; whereas with **IV** propagation is significantly faster than initiation, which leads to much higher molecular weights than expected and a broadening of the molecular weight distribution. The glass transition temperatures of the polymers obtained from *endo*-monomers are significantly higher than those observed for poly(*exo-n*-alkyl norbornene dicarboxyimide)s made under the same reaction conditions. This is probably a consequence of a stiffer, less mobile backbone resulting from the *endo* repeat unit stereochemistry. The polymerisation reactions are living, the polymers obtained show narrow polydispersities (PDI = 1.22-1.29). The living nature of these polymerisations was further confirmed by synthesising AB diblock copolymers by sequential addition of monomers. DSC thermograms of the block copolymers show two glass transition temperatures characteristic of block A and block B, indicating incompatibility of the segments A and B in the block copolymer systems.

Both *exo*- and *endo-n*-alkyl norbornene dicarboxyimide undergo ROMP using well-defined initiator **V**. The course of the polymerisation reactions was also followed by ^{1}H NMR and both the initiator and propagating alkylidenes signals were observable in the spectra. In the case of the polymerisation of *exo* monomers, the propagation rate constant (k_p) is considerably greater than the initiation rate constant (k_i) and the singlet due to alkylidene hydrogen of unconsumed initiator is observable even at high monomer concentration. By contrast, for *endo* monomers complete initiator consumption was observed. The singlet of the alkylidene hydrogen of the initiator had disappeared completely after several days under the same conditions used for the reaction of the *exo* isomer. It is noted that for the polymerisation of *endo* monomers, k_i and k_p are much smaller than those for the *exo* monomers. The *endo*-propagating species was found to be stable over the

course of the reaction, i.e. several days, and the second addition of *endo*-monomer (10 equivalents) resulted in the continuation of the polymerisation. ^{13}C NMR analysis revealed that the polymers derived from exo-monomers generally contain 82% *trans* vinylene and that polymers derived from endo monomer contain 100% *trans* vinylene, both appear to have *atactic* microstructures.

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