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Ring opening metathesis polymerisation of *n*-alkyl norbornene dicarboxyimides using well-defined initiators

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Exo-n-alkyl norbornene dicarboxyimides and *endo-n*-octyl norbornene dicarboxyimide were polymerised by ring opening metathesis polymerisation using well-defined initiators Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and Mo(CHCPhMe$_2$)(NAr)(OCMe$(CF_3)_2)_2$. Using Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and Mo(CHCPhMe$_2$)(NAr)(OCMe$(CF_3)_2)_2$ as initiators with the *exo*-monomers gave polymers with 97% *trans* and 70% *cis* vinylene content, respectively, and with the *endo*-monomer gave polymers with 93% *trans* and 57% *trans* vinylene content. In both cases the ^{13}C n.m.r. spectra were complex indicating that these polymers are essentially atactic. ^{1}H n.m.r. Spectroscopy and GPC analyses of polymeric materials prepared from *exo*- and *endo*-monomers demonstrated that the initiator carrying t-butoxy ligands gives fairly well-defined living polymerisation; whereas with the initiator bearing fluorinated ligands propagation is significantly faster than initiation which leads to much higher molecular weights than expected on the basis of monomer to initiator ratio and a broadening of the molecular weight distribution. The living character of these systems was confirmed by the synthesis of AB diblock copolymers via sequential addition of monomers. A series of block copolymers were prepared using *exo-n*-alkyl norbornene dicarboxyimides as monomer and 2,3-bis(trifluoromethyl)norbornadiene as comonomer. The glass transition temperatures of the polymers obtained from *endo*-monomers are significantly higher than those of the poly(*exo-n*-alkyl norbornene dicarboxyimide)s, probably as a consequence of a stiffer less mobile backbone resulting from the *endo* repeat units. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ROMP; living polymerisation; poly(*n*-alkyl norbornene dicarboxyimide)s)

INTRODUCTION

The work described in this paper was undertaken as part of a wider programme which is directed towards the synthesis of new polymers.

Recently we reported that *exo-n*-alkyl norbornene dicarboxyimides undergo ROMP using classical initiator systems derived from molybdenum pentachloride and tungsten hexachloride activated by tetramethyl tin[1]. 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 polymer samples with higher *trans* content exhibit lower T_g which is consistent with greater backbone mobility in the polymer with higher *trans* content. Thermal analysis of the samples prepared showed that there was a trend to lower T_g with increasing length of pendant alkyl group which is what is expected if the pendant group is large enough to give internal plasticisation. All the polymers prepared exhibited monomodal molecular weight distributions with polydispersity indices of the order of 2–3.5 and number average molecular weights in the range 40 000–60 000. Also we reported that, in contrast to the *exo*-isomers, *endo-n*-alkyl norbornene dicarboxyimides could not be ring open polymerised using either the $MoCl_5/SnMe_4$ or the $WCl_6/SnMe_4$ systems, in any of several attempts[1].

Well-defined metathesis initiators of the general type $M(NAr)(CHR')(OR'')_2$ ($M = W$ or Mo, $R' = CMe_3$ or $CPhMe_2$, $R'' = OCMe_3$ or $OCMe(CF_3)_2$ and Ar = 2,6-i-$Pr_2C_6H_3$) have proved useful in ROMP of cyclic and bicyclic olefins[2–5]. Molybdenum initiators have been employed most often to prepare polymers from a variety of norbornenes and norbornadienes[6–24]. 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 *trans* and highly *tactic*[11] or all *cis* with a *tactic* bias of ~75%[13].

It has been reported that norbornene containing esters, cyano, acetate and related functionalities can be polymerised in a living manner employing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ as initiator to give polymers with narrow polydispersities[9,25]. Gibson *et al.*[26,27] have recently reported the ROMP of amino acid substituted norbornene monomers, producing homochiral polymers with narrow molecular weight distribution and good control over double bond geometry. However, to the best of our knowledge there are no reports in the literature on the ROMP of *n*-alkyl norbornene dicarboxyimides using well-defined initiators.

In this paper we describe ring opening metathesis polymerisation of norbornene dicarboxyimide derivatives using well-defined Schrock initiators. The work reported here clearly demonstrates that *exo*- and *endo-n*-alkyl norbornene dicarboxyimides are polymerised in a living and well-defined manner using Mo(CH-*t*-Bu)(NAr)-$(OCMe_3)_2$ or Mo(CHCPhMe$_2$)(NAr)(OCMe$(CF_3)_2)_2$ as initiators.

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EXPERIMENTAL

General

All manipulations of solvents, catalysts, monomers and polymerisation reactions were carried out using standard vacuum line techniques or under an atmosphere of dry, oxygen-free nitrogen in a Glove Box (Braun). n.m.r. spectra were recorded using a Varian VXR400S (^{1}H @ 399.95 MHz and ^{13}C @ 100.58 MHz). Chemical shifts are reported in parts per million with respect to the internal reference tetramethylsilane. GPC traces were recorded for solutions in chloroform using a Waters 590 HPLC pump, a Waters R401 RI detector and three PLgel columns with pore size of 10^2, 10^3 and 10^5 Å (flow rate 1 $cm^3 min^{-1}$). Solutions (0.1–0.3% w/v) were filtered through a Whatman WTP type 0.2 μm filter to remove particulates before injection. The columns were calibrated using polystyrene standards (Polymer Laboratories Ltd) ranging from 162 to 2.31×10^6 g mol^{-1}. 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 Stanton Redcroft TG-760 thermobalance. CHN analysis was performed using a Carlo Erba 1106 elemental analyser.

Reagents

Deuterated dichloromethane was stirred over phosphorous pentoxide and vacuum distilled immediately prior to use. Dichloromethane used as polymerisation solvent was dried by prolonged reflux over phosphorous pentoxide, freshly distilled and degassed before use. Benzaldehyde was fractionally distilled and dried over a 4 Å molecular sieve. The ROMP initiators, Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$, were prepared following the published methods[2,3]. 2,3-Bis(trifluoromethyl)-norbornadiene, BTFMND, used as a comonomer for block copolymerisation reactions, was prepared using the published route[28]. *Exo*- and *endo*-*n*-alkyl norbornene dicarboxyimides were synthesised as described previously[1].

General polymerisation procedure

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. Monomers and initiators were dissolved in the same solvent in different vials. The monomer solution was added to the initiator solution in the reaction vials or flasks. To terminate the polymerisation reaction benzaldehyde (10 equivalents with respect to initiator) was added to the reaction mixture 4 h after mixing the monomer and initiator solutions, and the resulting solution 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, redissolved in dichloromethane and reprecipitated 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.

General copolymerisation procedure

The polymerisation procedure for the synthesis of block copolymers is very similar to the procedures adopted for the synthesis homopolymers described above. In a typical n.m.r. scale experiment, *exo*-*n*-heptyl norbornene dicarboxyimide (monomer A) (0.135 g, 0.516 mmol) was dissolved in deuterated dichloromethane (0.45 ml) and Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ (0.0063 g, 0.0129 mmol) was dissolved in the same solvent (0.45 ml). The monomer solution was added to the initiator solution and stirred for 5–6 min. The reaction mixture was transferred into an n.m.r. tube fitted with a Young's Teflon tap. The reaction was followed by ^{1}H n.m.r. until all the initiator and all the monomer were consumed completely. The n.m.r. tube was then taken into the Glove Box and the solution was poured into a new sample vial. BTFMND (monomer B) (0.118 g, 0.56 mmol) in deuterated dichloromethane (0.2 ml) was added to the living polymer solution. The reaction was followed by ^{1}H n.m.r. in the same manner until all monomer B was converted to polymer. At this stage benzaldehyde (5-fold excess) was added to terminate the polymerisation and the mixture was stirred for 30 min. The block copolymers were recovered following the procedure described above for homopolymers.

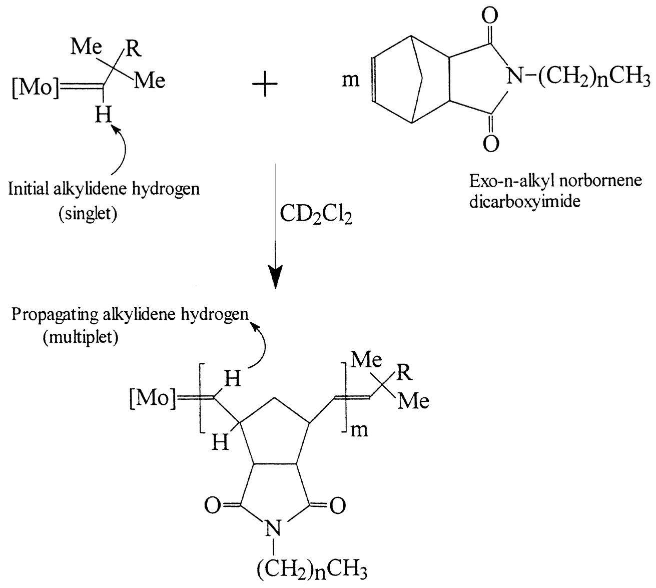
RESULTS AND DISCUSSION

Homopolymer synthesis

Exo-*n*-alkyl norbornene dicarboxyimides undergo living ROMP with Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$. The polymerisation reactions were followed by ^{1}H n.m.r. spectroscopy. The singlet resonance due to the initiator alkylidene hydrogen is replaced by a set of downfield resonances assigned to the propagating alkylidene hydrogens of the living oligomers, see *Scheme 1*. ^{1}H n.m.r. Spectra obtained 5 min after the addition of 10 equivalents of *exo*-*n*-octyl norbornene dicarboxyimide to either Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ or $Mo(CHCPhMe_2)$ $(NAr)(OCMe(CF_3)_2)_2$ solutions in deuterated dichloromethane (CD_2Cl_2) showed the singlet peaks at 11.22 and 12.21 ppm due to the initial alkylidene hydrogens of the molybdenum t-butoxide and hexafluoro-*t*-butoxide initiators, respectively. The multiplet peaks due to the propagating alkylidene hydrogens were also seen at, respectively, *ca*. 11.60 and 12.60 ppm. At the same time at which these peaks developed, peaks associated with the polymers appeared in the spectra at chemical shifts comparable to those established during the earlier study of these polymerisations initiated with classical initiators[1].

A series of experiments established that for the t-butoxide initiator, increasing the amount of monomer, eventually resulted in complete consumption of initiator. This, in principle, allows well-defined living polymerisation of these monomers with this initiator. By contrast with the hexafluoro-*t*-butoxide initiator there was always a significant percentage of initiator left even at high monomer concentration, which indicates that for this initiator, although there is no termination reaction the rate of propagation is significantly faster than the rate of initiation which leads to a broadening of molecular weight distribution (see below). The polymerisation reactions were repeated on larger scales, typically using between 0.4 and 1.0 g of monomers. The amounts of reagents, reactions times and yields of recovered polymer for typical experiments are recorded in *Table 1*.

All polymers obtained were soluble in chloroform, dichloromethane, tetrahydrofuran and insoluble in methanol and pentane. Films could be cast from solution. The infra-red spectra of all the poly(*exo*-*n*-alkyl norbornene



Scheme 1 Schematic for living polymerisation of norbornene dicarboxyimides with well defined initiators; $n = 6, 7, 8, 9$ and 11, R = Me or Ph

Table 1 Experimental details for the polymerisation of *exo*-*n*-alkyl norbornene dicarboxyimides using (A) Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and (B) $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ as initiators

Initiator system	Monomer $n =$	[M] g, (mmol)	[I] g, (mmol)	[M]:[I]	Time (h)	Yield (%)
A	6	0.5, (1.94)	0.022, (0.046)	42	3	78
	7	0.6, (2.18)	0.021, (0.044)	50	4	75
	8	0.54, (1.86)	0.015, (0.038)	49	3.5	76
	9	0.55, (1.82)	0.020, (0.042)	43	4	84
	11	1.15, (3.47)	0.031, (0.063)	55	3	92
B	6	0.52, (1.98)	0.038, (0.049)	40	3.5	81
	7	0.50, (1.82)	0.022, (0.028)	65	3	79
	8	0.40, (1.39)	0.014, (0.018)	78	4	76
	9	0.57, (1.88)	0.015, (0.019)	100	4.2	72
	11	0.44, (1.33)	0.015, (0.019)	70	4	83

dicarboxyimide)s samples obtained using either initiator were very similar. As expected, peaks characteristic of the imide at 1771 and 1700 cm^{-1} were prominent features of all the spectra. ^1H n.m.r. and ^{13}C n.m.r. spectra of poly(*exo*-*n*-alkyl norbornene dicarboxyimide)s obtained using Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ as initiator were in agreement with the structures proposed and showed a generally similar pattern of chemical shifts. The analysis revealed that the polymers have a *trans* vinylene content greater than 97%. The complexity of the signals excludes a *tactic* microstructure so the polymer can be assigned an *atactic* microstructure (spectra are not reproduced in this manuscript but are available in Ref. 29).

^1H n.m.r. and ^{13}C n.m.r. spectra for poly(*exo*-*n*-alkyl norbornene dicarboxyimide)s, derived from $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ initiator were similarly assigned. In general, the spectra displayed higher multiplicities and broader resonances than those from polymers made with the *t*-butoxide initiator and analysis established a *cis* vinylene content of about 70%. The spectra are complex and indicate that these polymers are also essentially *atactic*.

GPC traces for polymers obtained using the initiator carrying *t*-butoxy ligands show shoulders on the high molecular weight side of the main peak. The molecular weight of the shoulder was roughly twice that of the main peak. The high molecular weight components were considered to arise as a consequence of dimerisation reaction induced by traces of dioxygen accidentally introduced at the termination stage[15].

For polymerisations initiated with the complex having *t*-butoxy ligands polydispersity values fall between 1.04 and 1.1 suggesting that under these conditions well-ordered living polymerisation occurred. This conclusion is supported by the good correlation between the theoretical M_n values and those observed for the major peak. When the initiator carrying hexafluoro-*t*-butoxy ligands was used the resulting polymers showed a much broader molecular weight distribution, between 1.3 and 2.1 (see *Table 2*) and the correlation between theoretical and observed M_n values was rather poor. Invariably the observed M_n was greater than that calculated assuming a well-ordered living polymerisation. This can be explained by the observation that propagation with this initiator was much faster than initiation (as concluded from the ^1H n.m.r. analysis of the initiation process discussed earlier). A second possible explanation of the broadened polydispersity may lie in

Table 2 Molecular weight and thermal analysis data for poly(*exo*-*n*-alkyl norbornene dicarboxyimide)s obtained using (A) Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and (B) $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ as initiator

Initiator system	Polymer $n =$	[M]:[I]	GPC			DSC[a] T_g (°C)	TGA[b] 2% weight loss
			M_n calculated	M_n found	PDI		
A	6	36	9400	9300	1.08		
		42	10950	11000	1.09	65	430
		15	4150	4400	1.07		
	7	34	9360	9400	1.04		
		38	10460	10600	1.09		
		50	13870	14000	1.1	51	435
	8	36	10400	10700	1.05		
		49	14160	14200	1.08	52	435
	9	35	10600	10700	1.08		
		43	13000	13600	1.1	52	435
	11	35	11600	11700	1.08		
		55	18200	18500	1.1	50	420
B	6	25	6500	7400	1.4		
		40	10400	12400	1.5	67	420
	7	65	17900	19900	1.3		
		44	12100	13300	1.5	53	440
	8	49	14000	22100	2.1		
		78	22300	32300	1.5	51	445
	9	100	30300	41500	1.5		
		80	24200	27200	1.4	56	445
	11	70	23000	25000	1.3	66	445

[a] Approx. 5 mg samples, scanned from 0 to 300°C @ 10°C min^{-1}.
[b] Approx. 5 mg samples, under dry nitrogen @ 10°C min^{-1}.

secondary, or cross metathesis, between the more reactive propagating chain end and double bonds in the polymer backbone; however, this is probably a minor effect because these polymer chains are fairly highly sterically shielded.

DSC and thermogravimetric analysis for the poly(*exo*-*n*-alkyl norbornene dicarboxyimide)s prepared are summarised in *Table 2*. All the polymers displayed similar thermal stabilities and similar glass transition temperatures. The small differences observed may be a consequence of molecular weight and/or tacticity differences but do not justify detailed analysis. Under the experimental protocol adopted (*Table 2*) a 2% weight loss was observed for all polymers at about 435°C. Glass transition temperatures were in the range 50–70°C and no evidence of crystalline melting point was detected.

The *endo*-adduct also undergoes ROMP using the molybdenum *t*-butoxide and hexafluoro *t*-butoxide initiators to give high molecular weight polymers. It should be noted that the attempted ROMP of the *endo* monomers using classical initiators, such as molybdenum pentachloride and tungsten hexachloride activated by tetramethyl tin, was unsuccessful[1]. *Endo*/*exo* selectivity in the ROMP of substituted norbornenes with ‘classical’ initiators has been reported previously[30], but never convincingly rationalised. The lack of marked *endo*/*exo* selectivity with well-defined initiators contrasts with the selectivity of the ‘classical’ initiators and is not rationalised easily. In the widely accepted mechanism of norbornene ROMP the initiator approaches the monomer from the *exo* face of the double bond, the *exo*/*endo* disposition of the substituents on the other side of the ring can have little or no steric effect but there may be an electronic effect between *endo* substituents which could increase or decrease the π donor capacity of the double bond undergoing ROMP depending on the nature of the substituent. Rationalisations based on such considerations are, at best, speculative. The exact nature of the propagating species in ‘classical’ ROMP is unknown but it may be that an *endo* monomer is capable of co-ordinating to the metal centre as a chelate destroying its reactivity, an option not possible with the *exo* isomer. The ^1H n.m.r. spectrum of the living polymer solution in deuterated dichloromethane shows a multiplet signal at 11.7 ppm due to the hydrogens of the propagating alkylidene, and at the same time peaks for the polymer appeared. For the hexafluoro-*t*-butoxide initiator the propagating alkylidene is observed as an unresolved signal at 12.34 ppm. As with the *exo*-monomers propagation with the fluorinated initiator occurs significantly faster than that for the *t*-butoxide system. The polymeric products were soluble in chloroform, dichloromethane, tetrahydrofuran and insoluble in methanol and pentane. Films could be cast from solution.

^1H n.m.r. and ^{13}C n.m.r. spectra of poly(*endo*-*n*-octyl norbornene dicarboxyimide), prepared using Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ 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 Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ as initiator has 93% *trans* vinylene content and that the multiplicities of the backbone carbon signals are consistent with an *atactic* microstructure.

The same analysis has been applied to ^1H n.m.r. and ^{13}C n.m.r. spectrum of poly(*endo*-*n*-octyl norbornene dicarboxyimide) prepared using $Mo(CHCPhMe_2)(NAr)$-

Table 3 Experimental details for the polymerisation of *endo-n*-octyl norbornene dicarboxyimide using (A) Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and (B) $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ initiators

Initiator system	[M]:[I]	Time (h)	Yield (%)	GPC M_n calculated	GPC M_n found	GPC PDI	DSC[a] T_g (°C)	TGA[b] 2% weight loss
A	59	4	—	16250	16400	1.3	—	—
	80	4	84	—	—	—	104	465
B	33	4	—	9100	11700	1.8	—	—
	100	4	79	—	—	—	92	460

[a]Approx. 5 mg samples, scanned from 0 to 300°C @ 10°C min^{-1}.
[b]Approx. 5 mg samples, under dry nitrogen @ 10°C min^{-1}.

Table 4 Experimental details for the block copolymerisation of *exo-n*-alkyl norbornene dicarboxyimides (monomer A) and BTFMND (monomer B) using Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ as initiator

Monomer A $n =$, (mmol)	Initiator mmol	[A]:[I]	Propagating alkylidene H of block-A	Monomer B mmol	[B]:[I]	Propagating alkylidene H of block-B	Yield (%)
6, (1.13)	0.0290	39	11.60	1.45	50	11.30	75
7, (1.14)	0.0280	41	11.60	1.26	45	11.30	73
8, (1.11)	0.0250	44	—	1.50	50	11.30	76
9, (1.30)	0.0300	43	—	1.65	55	11.31	78
11, (0.95)	0.0226	42	—	1.24	55	11.31	73

$(OCMe(CF_3)_2)_2$ as initiator. The conclusion from this analysis is that the initiator gave a polymer with 57% *trans* vinylene content. The multiplicity and broadening of the backbone resonances is again consistent with a multiplicity of overlapping environments associated with an *atactic* polymer. The results of GPC analysis (*Table 3*) for polymeric materials prepared from *endo*-monomers imply that the molybdenum initiator carrying *t*-butoxy ligands gives fairly well-defined living polymerisation; whereas with the initiator bearing fluorinated ligands 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 3*) are significantly higher (92–104°C) than those observed for poly(*exo-n*-alkyl norbornene dicarboxyimide)s described earlier and 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 2% weight loss for these polymers occurs at about 460°C indicating a slightly greater stability than the polymers from the *exo* monomers.

Block copolymer synthesis

The ill-defined classical initiator systems are unsuited to the preparation of block copolymers. In contrast, well-defined initiators are capable of producing block copolymers in a living manner by the sequential addition of monomers. In a typical example, 40 equivalents of *exo-n*-octyl norbornene dicarboxyimides (monomer A) in deuterated dichloromethane was added to Mo(CH-*t*-Bu)(NAr)-$(OCMe_3)_2$ in solution in deuterated dichloromethane and the ^1H n.m.r. spectrum was recorded after 30 min (*Figure 1a*). The spectrum shows a multiplet signal, probably two overlapping doublets, at 11.60 ppm due to the propagating alkylidenes of poly(block A) and also shows resonances due to the polymer. Since this initiator with this monomer gives an *atactic* polymer with greater than 97% *trans* vinylenes, the two propagating alkylidene doublets must be a consequence of either *syn*/*anti* alkylidene isomerisation or *meso* and *racemic* propagating chain end dyads. No signals due to the initiator or monomer can be seen which indicates that both are completely consumed. A solution of 45 equivalents of BTFMND (monomer B) in deuterated dichloromethane was added to the living polymerisation mixture and the ^1H n.m.r. spectrum was recorded 1 h after the addition. 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 greater than 98% *trans* vinylene content[10,11]. At the same time, peaks for the poly(block B) appeared. The intensity of the peaks for poly(block B) increased and there was a corresponding decrease in the relative intensity of the peaks associated with monomer B. The reaction was monitored until monomer B was completely converted to polymer (*Figure 1b*).

Block copolymers were successfully prepared using *exo-n*-alkyl norbornene dicarboxyimides ($n = 6$, 7, 8, 9 and 11) and the BTFMND monomer in deuterated dichloromethane (*Table 4*). The advantage of these systems is that the complete course of the copolymerisation reactions can be followed by ^1H n.m.r. spectroscopy. When the first monomer is polymerised characteristic propagating alkylidene resonances are seen in the ^1H n.m.r. spectrum. When the comonomer is added, after the complete polymerisation of the first monomer, a new propagating alkylidene signal typical of the second monomer appears (see *Table 4*). The samples were soluble in dichloromethane, chloroform, tetrahydrofuran and insoluble in methanol and pentane. All samples exhibit single mode molecular weight distribution and relatively narrow polydispersity (between 1.22 and 1.29). A DSC thermogram of the block copolymers shows two glass transition temperatures characteristics of

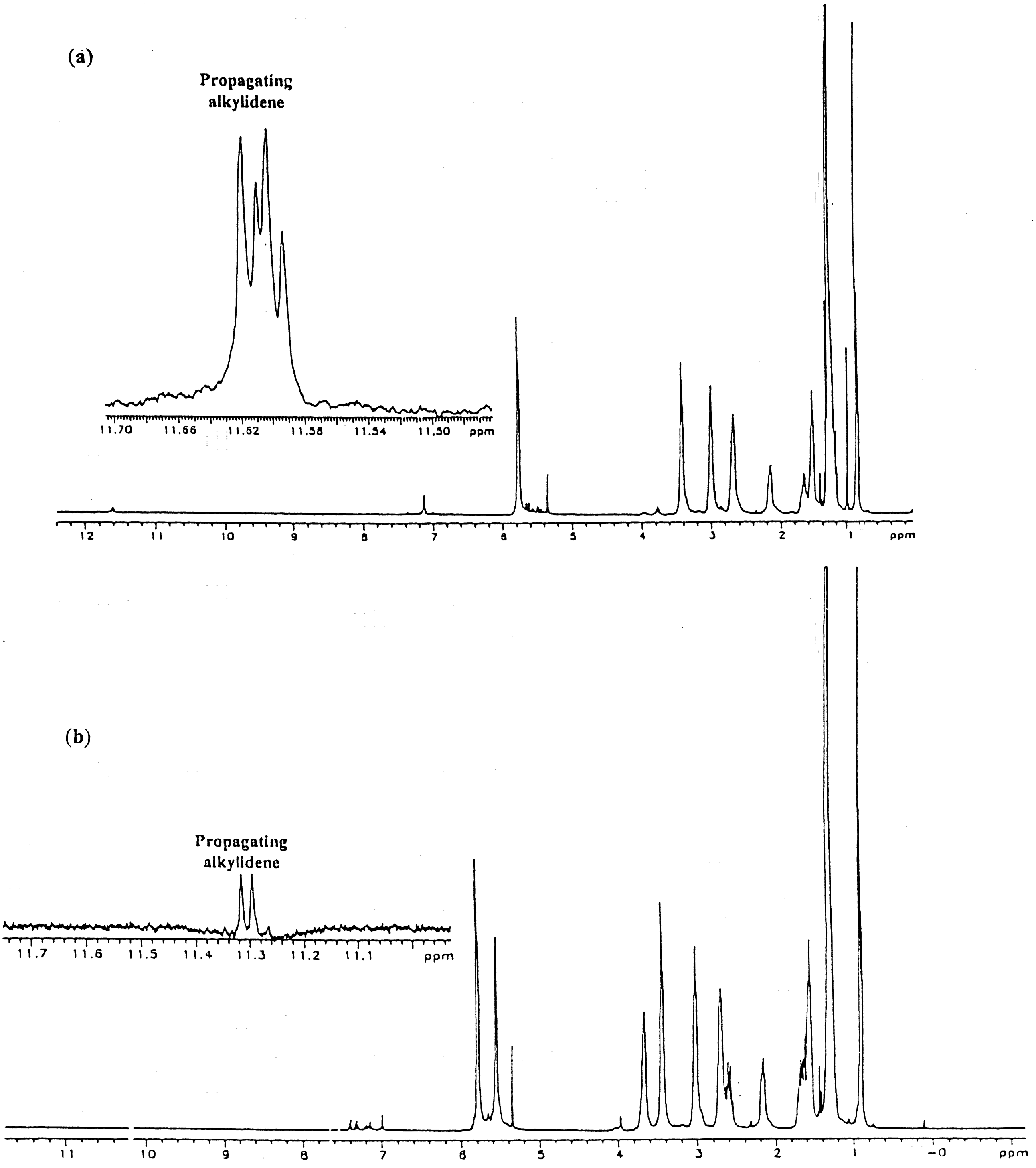


Figure 1 The 400 MHz ^{1}H NMR spectra recorded in CD_2Cl_2 as solvent of (a) living poly(*exo*-*n*-octyl norbornene dicarboxyimide) and (b) living poly(*exo*-*n*-octyl norbornene dicarboxyimide-co-BTFMND)

poly-(block A), 50°C, and poly(block B), 97°C, indicating the incompatibility of the segments A and B in the block copolymer systems.

CONCLUSIONS

The ROMP of *exo*-*n*-alkyl norbornene dicarboxyimides and *endo*-*n*-octyl norbornene dicarboxyimide using well-defined initiators of the type Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ and $Mo(CHCPhMe_2)(NAr)(OCMe(CF_3)_2)_2$ has been successfully established. The course of the polymerisation reactions was followed by ^{1}H n.m.r. and both the initiator and propagating alkylidenes signals were observable in the spectra. In general, Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ initiation gave the poly(*exo*-*n*-alkyl norbornene dicarboxyimide)s with 97% *trans* vinylene content whereas $Mo(CHCPhMe_2)$ $(NAr)(OCMe(CF_3)_2)_2$ initiation gave the same polymers with about 70% *cis* vinylene content. The spectra in both cases are complex and indicate that these polymers are essentially *atactic*. ROMP of *endo*-*n*-octyl norbornene dicarboxyimide using Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ gave polymers with 93% *trans* vinylene content and $Mo(CHCPhMe_2)(NAr)$-$(OCMe(CF_3)_2)_2$ gave 57% *cis* 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 carrying *t*-butoxy ligands gives fairly well-defined living polymerisation; whereas with the initiator bearing fluorinated ligands propagation is significantly faster than initiation which leads to much higher molecular weights than expected and a broadening of the molecular weight distribution. The molecular weight broadening may be described, in part, to cross metathesis between the more reactive fluoro substituted propagating chain end and backbone double bonds. 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 polymers obtained were monodisperse and the ^{1}H n.m.r. spectroscopic analysis indicated the absence of termination reactions, both observations being indicative of a well-behaved living polymerisation. The living nature of these polymerisations was confirmed by synthesising AB diblock copolymers by sequential addition of monomers. When the first monomer is polymerised characteristic propagating alkylidene resonances are seen in the ^{1}H n.m.r. spectrum. When the comonomer is added, after the complete polymerisation of the first monomer, a new propagating alkylidene signal typical of the second monomer appears. All samples exhibit single mode molecular weight distribution and narrow polydispersity between 1.22 and 1.29. DSC thermograms of the block copolymers show two glass transition temperatures characteristics of poly(block A) and poly(block B). This indicates the incompatibility of the segments A and B in the block copolymer systems.

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