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Living ring-opening metathesis polymerisation of amino ester functionalised norbornenes

Stefano C. G. Biagini[a], Martyn P. Coles[b], Vernon C. Gibson[b,*], Matthew R. Giles[b], Edward L. Marshall[b] and Michael North[a]
[a]Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK
[b]Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, South Kensington, London SW7 2AY, UK
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The living ring-opening metathesis polymerisation of norbornene monomers bearing amino ester residues, using the molybdenum initiators $Mo(=CHCMe_2Ph)(=N-2,6\text{-}i\text{-}Pr_2C_6H_3)(OR)_2$, {R = CMe_3, $\mathbf{I_A}$, CMe_2CF_3, $\mathbf{I_B}$, $CMe(CF_3)_2$, $\mathbf{I_C}$}, is reported. The monomers are derived from reactions of *exo*- and *endo*- himic anhydrides with the amino ester hydrochlorides of glycine (**1**), alanine (**2**) and isoleucine (**3**). The optically pure monomers derived from **2** and **3** afford optically active polymers whose optical activities are independent of *cis* content and molecular weight, indicating the absence of a cooperative effect between chiral centres along the chain. The polymers derived from the *exo* monomers show a *cis–trans* vinylene dependence upon the ancillary alkoxide ligands of the initiator with $\mathbf{I_A}$ giving high *trans* contents and $\mathbf{I_C}$ giving high *cis*. The *cis/trans* content for the *endo* polymers show relatively little or no dependence upon the initiator. Poly(*exo*-**1**) is exceptional in its ability to incorporate various hydrocarbons in the solid state, including hexane and methane. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: metathesis; molybdenum; amino ester)

INTRODUCTION

Naturally occurring macromolecules exhibit well-defined conformations accordant upon their monomer sequence. Well-known examples include the α-helix and β-sheets adopted by proteins and the base-pair double helix of DNA. The primary, secondary and tertiary structures of a biopolymer perform a crucial role in determining its physical and chemical properties and hence its biological function and activity.

In attempting to synthesise artificial analogues of biopolymers it is therefore advantageous to have the highest possible command over the polymer assembly and consequently the resultant polymer architecture. The living ring-opening metathesis polymerisation (ROMP) of strained norbornene monomers using well-defined transition metal initiators allows a high level of control over many aspects of macromolecular assembly[1–4] and is particularly tolerant of a wide range of functionalities of biological relevance. Also, it is possible to assemble highly ordered, stereoregular backbones by sagacious choice of ligands at the propagating transition metal centre[5].

The first applications of ROMP methodology to the synthesis of highly functionalised polymers of biological relevance have been reported recently[6–10]. Herein we describe the results of our studies into the polymerisation of a range of amino ester functionalised norbornenes, aspects of which have been communicated previously[6].

RESULTS AND DISCUSSION

The monomers and initiators employed in this study are shown in *Scheme 1*. The monomers were prepared from the *exo*- and *endo*-isomers of himic anhydride, using a previously published procedure[11].

The polymerisations were initially monitored by n.m.r. spectroscopy after mixing 10 equivalents of monomer with the initiator in a sealed n.m.r. tube. Characteristic multiplets in the region δ11.5–13.0 ppm, attributable to the alkylidene proton of a propagating polymer chain, were observed in each case (*Table 1*). The observation of a singlet resonance due to unconsumed initiator is a common feature of all these reactions, indicating that k_p, the rate constant of propagation, is greater than k_i, the rate constant of initiation. Monitoring of the reaction of $\mathbf{I_A}$ with the least sterically hindered monomer *exo*-**1** showed that 40 monomer equivalents are required to consume the initiator. Also, the *endo* monomers polymerise appreciably slower than their *exo* counterparts. For example, 150 equivalents of *exo*-**1** are polymerised in *ca.* 60 min whereas a similar quantity of *endo*-**1** takes *ca.* 90 min. This difference is most likely a consequence of unfavourable steric interactions between the amino ester group in the *endo* isomer and the ancillary alkoxide ligands of the initiator.

The monomers are readily polymerised on a 0.5–1.0 g scale in CH_2Cl_2 with all three initiators. Characterising data for the resultant polymers are collected in *Table 1*. All are formed in moderate to high yield with reasonably narrow molecular weight distributions. A MALDI-TOF mass spectrum of a low molecular weight sample of poly(*exo*-**1**) prepared using $\mathbf{I_B}$ is shown in *Figure 1*, confirming the monomer repeat unit and the presence of neophylidene ($CHCMe_2Ph$) and benzylidene end-groups arising from the initiating alkylidene and benzaldehyde terminating agents respectively. The distribution of peak intensities confirms a narrow molecular weight distribution (M_w/M_n = 1.05)

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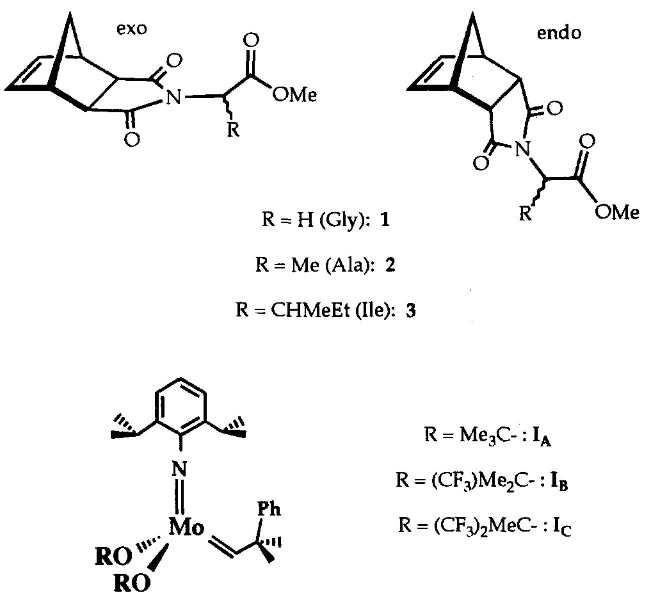
*To whom correspondence should be addressed.



Scheme 1 Monomers and initiators employed in this study

commensurate with a well-controlled, living polymerisation process.

The effect of reaction time upon M_w/M_n for the polymerisation of **2** using the *t*-butoxide and hexafluoro-*t*-butoxide initiators is shown in *Table 2*. The polydispersity of $\mathbf{I_A}$-initiated poly(*exo*-**2**) does not change significantly between 2 and 20 h. However, with $\mathbf{I_C}$ a noticeable increase is observed, a consequence of secondary metathesis reactions at this highly electrophilic molybdenum centre. In general, therefore, reaction times have been kept to a minimum; even so, a small degree of secondary metathesis cannot be excluded, especially for the $\mathbf{I_B}$ and $\mathbf{I_C}$-initiated polymerisations, and this may be the principal cause of the slight broadening of the molecular weight distributions in certain cases.

Exo-**1** undergoes ROMP with the three initiators to give polymers of different stereochemistries in a manner well documented for 2,3-bis(trifluoromethyl)norbornadiene[12–14]. Initiator $\mathbf{I_A}$ gives a predominantly *trans* polymer (95%) and, as the alkoxide ligands become progressively more electron-withdrawing, so the *cis* content of the polymer increases (*Table 1*). The *cis/trans* content of the polymers is readily determined from ^{1}H n.m.r. spectra, in which the resonances attributable to the *cis* and *trans* olefinic protons are well separated. The ^{1}H n.m.r. spectrum of poly (*exo*-**1**) prepared using initiator $\mathbf{I_A}$ is shown in *Figure 2*. Distinct resonances attributable to the *cis* and *trans* olefinic hydrogens can be seen in the range δ5–6 ppm. The ^{13}C n.m.r. spectrum of poly(*exo*-**1**) generated using $\mathbf{I_A}$ has been assigned with the aid of DEPT and HETCOR experiments and is shown in *Figure 3*. The sharp nature of the resonances is consistent with a high level of stereoregularity, and the relative intensities of the *trans* and *cis* olefinic resonances at δ131.9 and δ133.2 ppm confirm the very high *trans* content. The low frequency region (*Figure 3c*) includes signals at δ45.69 and δ45.85 ppm which originate from C1, C4 carbons adjacent to a *trans* olefinic bond. The *cis* C1, C4 resonance appears as a small signal at *ca.* 41.0 ppm which becomes more intense in the spectra of poly(*exo*-**1**) obtained using $\mathbf{I_B}$ and $\mathbf{I_C}$. The methylene bridge carbon C_7 has been shown to provide a useful probe of tacticity in polymers derived from bis(trifluoromethyl)norbornadiene[12,14]. For poly(*exo*-**1**) two resonances are observed for C_7, at δ41.70 and 41.92 ppm, indicating that the polymer is not highly tactic.

The ^{13}C n.m.r. spectra of all three samples of poly(*exo*-**1**)

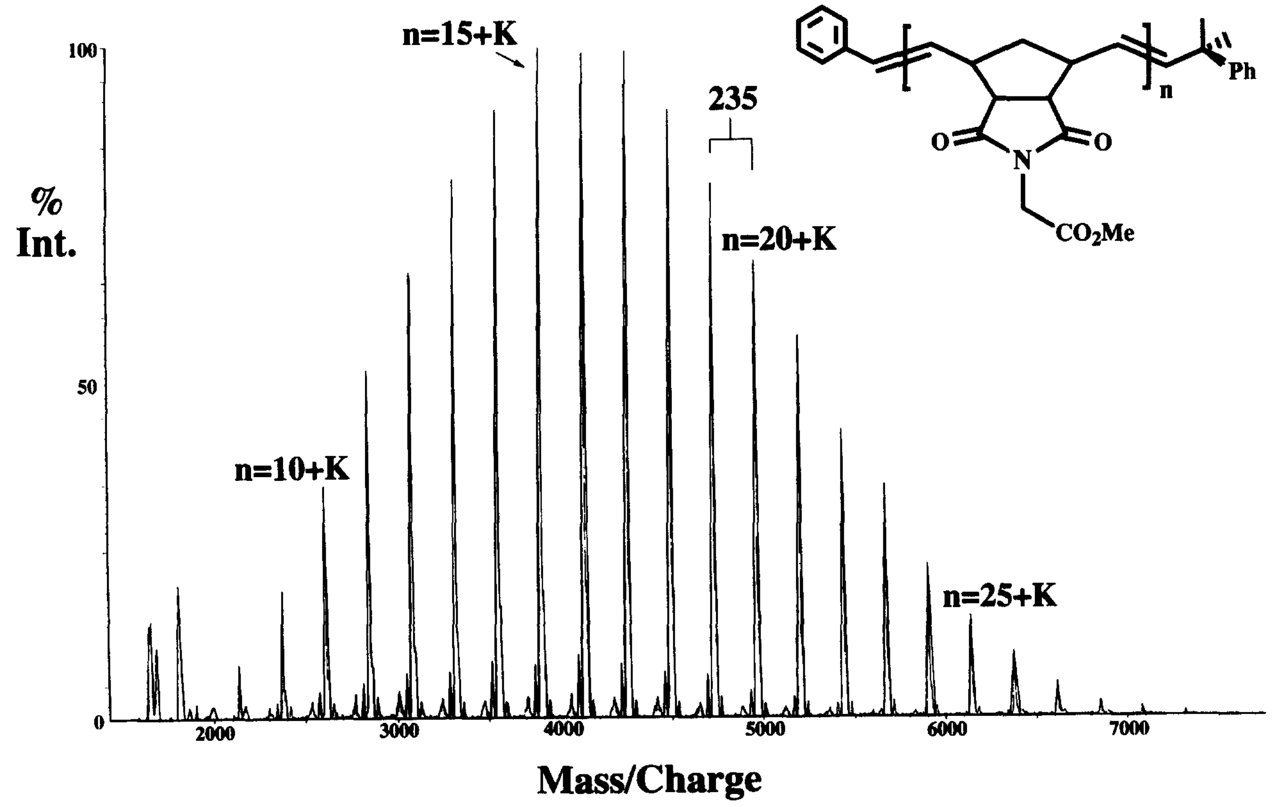


Figure 1 MALDI–TOF mass spectrum of poly(*exo*-**1**) initiated by $\mathbf{I_B}$

Table 1 Characterising data for poly(**1**–**3**)

Monomer	Initiator	Propagating alkylidene (δ ppm)[a]	σ_c^b	T_g (°C)[c]	$[\alpha]_D^{20}$ (°)[d]	M_n (calc)[e]	M_n (obs)[f]	M_w/M_n^f
exo-**1**	$\mathbf{I}_\mathrm{A}$	11.4 (d)	0.05	151	—	23820	32400	1.12
	$\mathbf{I}_\mathrm{B}$	12.4 (d)	0.46	145	—	13780	19000	1.21
	$\mathbf{I}_\mathrm{C}$	13.0 (m)	0.71	140	—	30570	42500	1.23
endo-**1**	$\mathbf{I}_\mathrm{A}$	11.9 (d)	0.19	192	—	19670	20500	1.27
	$\mathbf{I}_\mathrm{B}$	11.8 (m)	0.24	192	—	20620	37300	1.21
	$\mathbf{I}_\mathrm{C}$	12.3 (m)	0.36	197	—	23700	24200	1.27
exo-DL-**2**	$\mathbf{I}_\mathrm{A}$	11.54 (t)	0.09	154	0	13740	22900	1.15
	$\mathbf{I}_\mathrm{B}$	11.90 (m, br)	0.41	146	0	16440	19300	1.25
	$\mathbf{I}_\mathrm{C}$	12.40 (m, br)	0.71	138	0	19140	23200	1.15
exo-D-**2**	$\mathbf{I}_\mathrm{A}$	11.54 (t)	0.08	153	+ 34	13740	20500	1.16
	$\mathbf{I}_\mathrm{B}$	11.90 (m, br)	0.41	146	+ 38	16440	19400	1.26
	$\mathbf{I}_\mathrm{C}$	12.37 (m, br)	0.74	138	+ 34	19140	18100	1.10
exo-L-**2**	$\mathbf{I}_\mathrm{A}$	11.54 (t)	0.07	153	− 31	13740	27100	1.27
	$\mathbf{I}_\mathrm{B}$	11.89 (m, br)	0.43	147	− 35	16440	19500	1.51
	$\mathbf{I}_\mathrm{C}$	12.36 (m, br)	0.73	137	− 30	19140	20000	1.07
endo-DL-**2**	$\mathbf{I}_\mathrm{A}$	11.93 (m)	0.10	192	0	13740	18300	1.28
	$\mathbf{I}_\mathrm{B}$	12.36 (m, br)	0.10	192	0	16440	41000	1.60
	$\mathbf{I}_\mathrm{C}$	12.99 (m, br)	0.10	192	0	19140	43800	1.56
endo-D-**2**	$\mathbf{I}_\mathrm{A}$	11.92 (m)	0.10	190	+ 54	13740	19600	1.18
	$\mathbf{I}_\mathrm{B}$	12.35 (m, br)	0.10	189	+ 50	16440	30600	1.25
	$\mathbf{I}_\mathrm{C}$	12.99 (m, br)	0.10	188	+ 52	19140	33000	1.12
endo-L-**2**	$\mathbf{I}_\mathrm{A}$	11.91 (m)	0.10	195	− 52	13740	21400	1.28
	$\mathbf{I}_\mathrm{B}$	12.35 (m, br)	0.10	191	− 50	16440	28600	1.20
	$\mathbf{I}_\mathrm{C}$	13.00 (m, br)	0.10	189	− 51	19140	35200	1.10
exo-DL-**3**	$\mathbf{I}_\mathrm{A}$	11.5 (d) 11.6 (d)	< 0.05	137	0	26460	59200	1.21
	$\mathbf{I}_\mathrm{B}$	11.9 (m)	0.56	123	0	19110	38900	1.20
	$\mathbf{I}_\mathrm{C}$	12.5 (m)	0.75	116	0	22930	50200	1.13
exo-L-**3**	$\mathbf{I}_\mathrm{A}$	11.5 (m)	< 0.05	118	− 57	9380	13300	1.27
	$\mathbf{I}_\mathrm{B}$	11.9 (m)	0.55	129	− 61	22800	24200	1.17
	$\mathbf{I}_\mathrm{C}$	12.4 (m)	0.77	125	− 59	40570	57900	1.23
endo-DL-**3**	$\mathbf{I}_\mathrm{A}$	11.7 (d, br)	0.06	190	0	12200	40600	1.25
	$\mathbf{I}_\mathrm{B}$	12.1 (d, br)	0.05	188	0	32230	46700	1.17
	$\mathbf{I}_\mathrm{C}$	12.9 (m)	0.07	188	0	21070	39600	1.20
endo-L-**3**	$\mathbf{I}_\mathrm{A}$	11.7 (d) 11.8 (d)	0.08	188	− 79	20600	67700	1.44
	$\mathbf{I}_\mathrm{B}$	12.1 (d, br)	0.06	204	− 72	22340	35100	1.25
	$\mathbf{I}_\mathrm{C}$	12.7 (m)	0.12	194	− 67	10500	38900	1.05

[a] ^{1}H n.m.r. chemical shifts in $CDCl_3$ for monomers **1** and **3** and in C_6D_6 for monomer **2**.

[b] Determined from ^{1}H n.m.r. spectrum for the *exo* polymers and ^{13}C n.m.r. spectrum for the *endo* polymers.

[c] Measured by d.s.c.

[d] Optical rotations measured for the monomers: *exo*-D-**2**, +43°; *exo*-L-**2**, −43°; *endo*-D-**2**, +22°; *endo*-L-**2**, −25°; *exo*-L-**3**, −51°; *endo*-L-**3**, −43°.

[e] Determined from the monomer to initiator ratio.

[f] Determined by g.p.c. analysis in chloroform solution relative to polystyrene standards; a correction factor (which is different for each polymer) is thus required in comparing M_n (calc) with M_n (obs).

include signals due to *n*-hexane, the solvent from which the samples were precipitated, even though each sample was dried in a vacuum oven at 50°C for 24 h prior to analysis. We shall return shortly to discuss this feature in more detail.

The polymerisations of the *exo*-**2** and *exo*-**3** monomers proceed with a similar *cis/trans* dependence upon the alkoxide ligands of the initiator, although no hexane incorporation has been detected in any of these materials. The ^{13}C n.m.r. of poly(*exo*-L-**3**) is noteworthy because it shows none of the *allo*-isoleucine resonances observed in the spectra of poly(*exo*-DL-**3**), thus demonstrating that epimerisation at the α stereogenic centre does not occur during polymerisation, within the limits of detection of n.m.r. spectroscopy.

The *endo* monomers also readily undergo polymerisation with $\mathbf{I}_\mathrm{A}$–$\mathbf{I}_\mathrm{C}$, although they show a much less pronounced dependence of *cis/trans* content on the initiator employed. Examination of the ^{13}C n.m.r. spectra of poly(*endo*-**1**) in the C1, 4 region (*cis* δ40.2–41.0; *trans* δ44.9–45.8 ppm) reveals a *trans* bias in all cases, ranging from 81% ($\mathbf{I}_\mathrm{A}$) to 64% ($\mathbf{I}_\mathrm{C}$). The polymers obtained from *endo*-**2** and *endo*-**3** exhibit even less *cis/trans* variation, the *endo*-**2** materials invariably giving *cis* vinylene contents of *ca.* 90%, whilst the poly(*endo*-**3**) samples give *trans* contents between 88 and 95%.

The effect of the polymer structures upon their physical properties is highlighted by the glass transition temperatures measured by differential scanning calorimetry (d.s.c.). Each

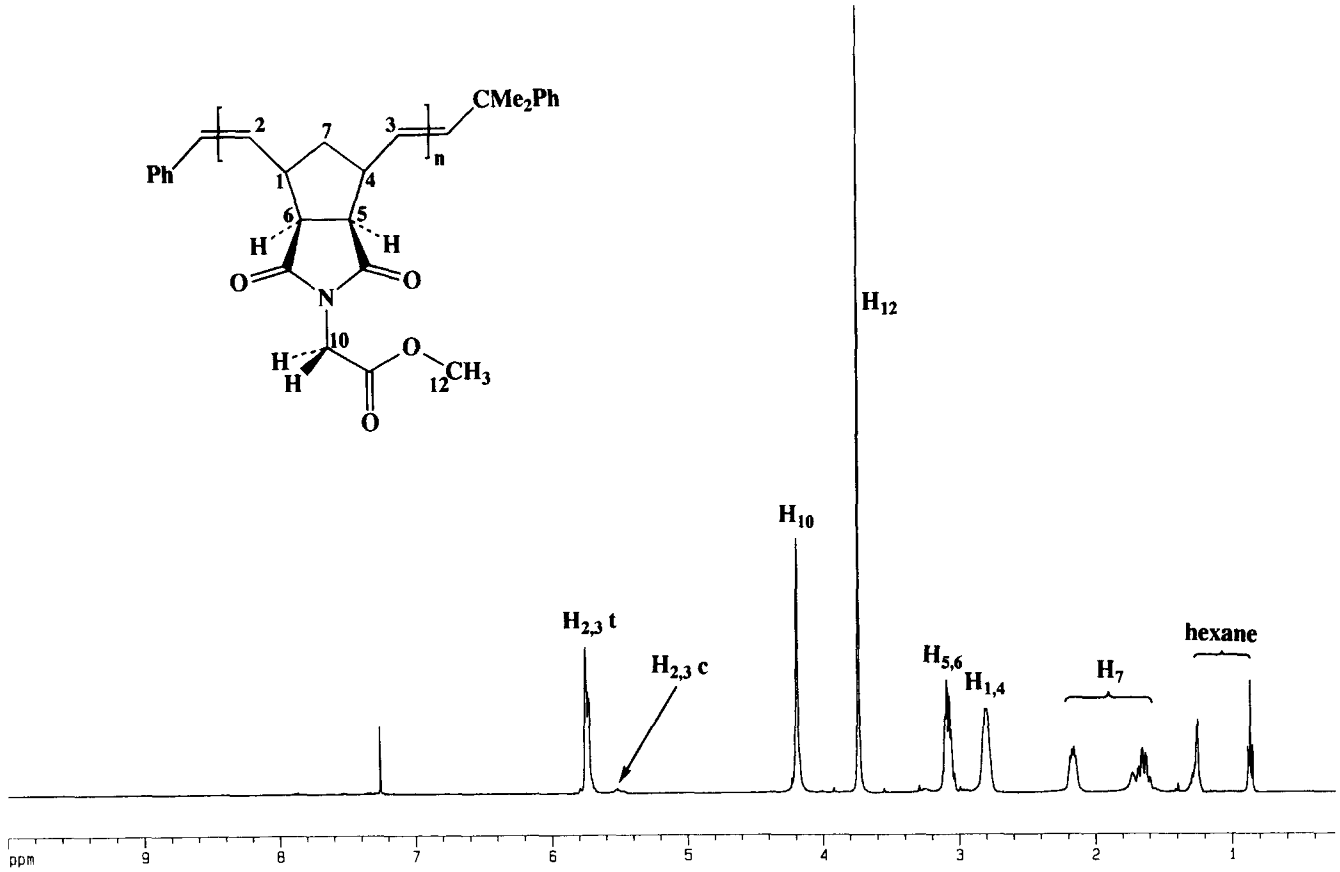


Figure 2 400 MHz ^{1}H n.m.r. ($CDCl_3$) spectrum of poly(*exo*-**1**) initiated by $\mathbf{I_A}$

Table 2 Dependence of polydispersity on reaction time for poly(*exo*-**2**)

Monomer	Initiator	Time of polymerisation (h)	M_w/M_n
exo-DL-**2**	$\mathbf{I_A}$	2	1.15
		20	1.15
exo-D-**2**	$\mathbf{I_A}$	2	1.16
		20	1.13
exo-L-**2**	$\mathbf{I_A}$	2	1.27
		20	1.25
exo-DL-**2**	$\mathbf{I_C}$	0.5	1.15
		20	1.32
exo-D-**2**	$\mathbf{I_C}$	0.5	1.11
		20	1.41
exo-L-**2**	$\mathbf{I_C}$	0.5	1.06
		20	2.00

set of *endo* polymers show relatively steady T_gs, in the region of 190°C, reflecting their similar *cis/trans* contents. The *exo* polymers, however, with their widely differing *cis/trans* contents, exhibit T_gs over a wider temperature range (120–150°C, *Table 1*), the T_g increasing with increase in *trans* content. A similar trend in T_g with *cis/trans* content has been observed for poly(bis(trifluoromethyl)norbornadiene)[13].

The ROMP of enantiomerically pure isomers of **2** and **3** gives rise to polymers with homochiral centres (*Table 1*). Their optical rotation values are independent of the *cis/trans* content in the polymer backbone and also the molecular weight of the polymer. Samples of poly(*endo*-D-**2**) of M_n 5900 and 53 920 gave optical rotations of + 50° and + 51° respectively. These observations imply that there is no cooperative effect between the chiral centres along the polymer chain.

Thermogravimetric analyses (t.g.a.) on all the polymer samples show a substantial weight loss in the temperature range 380–580°C, corresponding to the elimination of all the maleimide groups. The encapsulation of *n*-hexane within the polymers of *exo*-**1** is also revealed by t.g.a. Under a steady stream of nitrogen the solvent is released in the temperature range 150–180°C, close to the T_g of the polymer (*Figure 4*). Furthermore, if the samples of poly(exo-**1**) are redissolved and subsequently precipitated from either excess *n*-pentane or *n*-heptane, the C_5 and C_7 hydrocarbons are incorporated. A branched hydrocarbon such as 2,2,4-trimethylpentane can also be trapped, as can cyclohexane. The polymer was also found to incorporate methane and 2,2-dimethylpropane by bubbling the gas through a CH_2Cl_2 solution of the polymer until the solvent had evaporated. The methane can be detected by n.m.r. spectroscopy and the t.g.a. trace shows that this hydrocarbon too is not released until the polymer is warmed to a temperature in excess of 150°C. However, encapsulation does not occur for ethylene, methanol, acetone, carbon dioxide, dichloromethane or 1-chlorohexane.

Cis/trans contents

Schrock and co-workers have demonstrated the origin of *cis/trans* stereochemistry in polymers derived from the four-coordinate molybdenum initiators[14]. The invariably high levels of *trans* content in the polymers prepared from the *endo* monomers suggests that the steric hindrance of the amino ester groups forces most of the propagation to occur via the highly reactive anti rotamers (*Figure 5*(a)), even for the fluorinated initiators. Any deviation from an all-*trans* microstructure most probably reflects the statistical probability of the *endo* monomer approaching the metal centre in the '7-*anti*' manner, i.e. with the 7-methylene group of the norbornene fragment pointed away from the imido group. Alternatively, the monomer may always approach in a '7-*anti*' manner and the polymerisation proceed via the thermodynamically more stable syn rotamer[14] (*Figure 5*b).

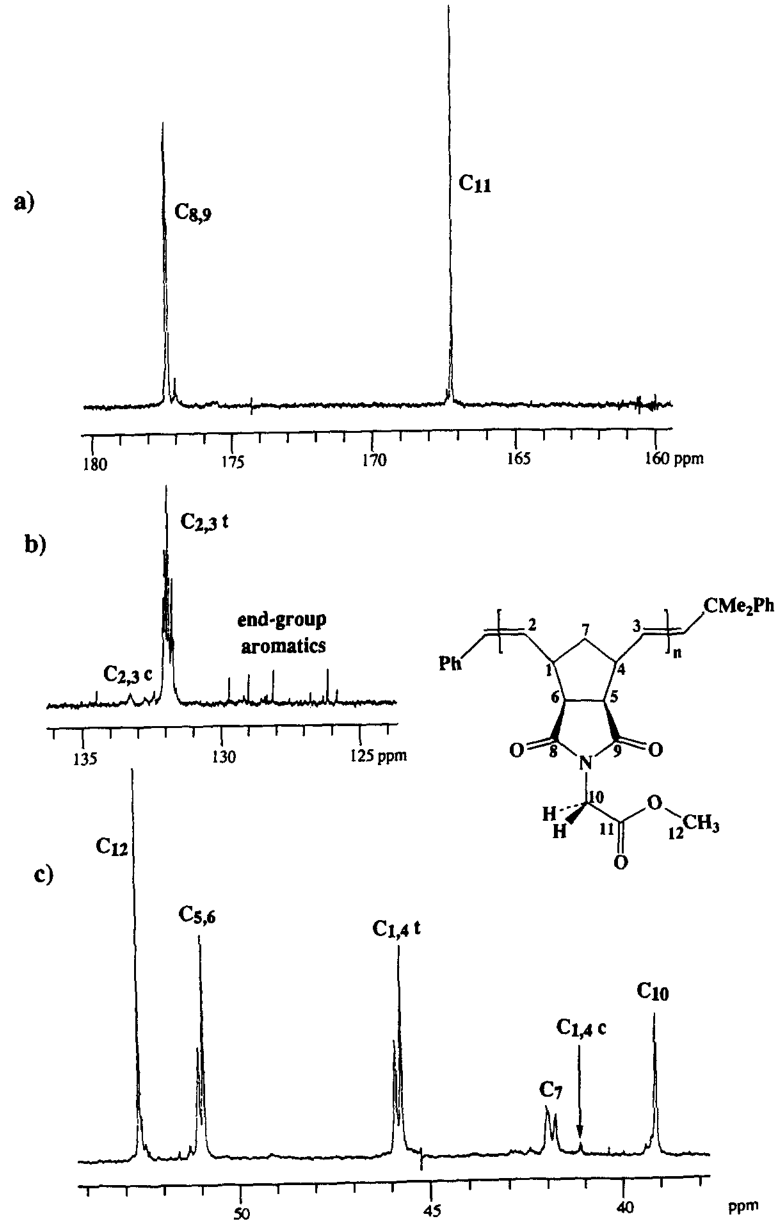


Figure 3 100 MHz ^{13}C n.m.r. (CDCl$_3$) regions for poly(*exo*-**1**) initiated by $\mathbf{I_A}$

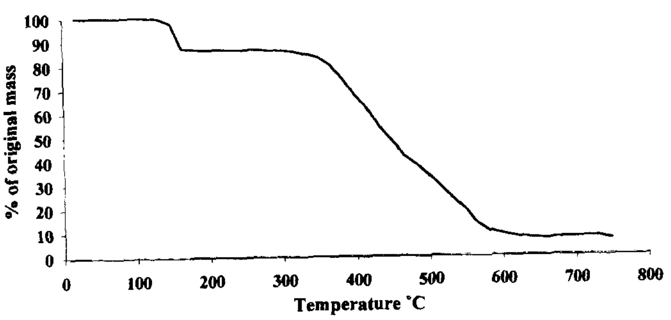


Figure 4 T.g.a. trace for poly(*exo*-**1**) initiated by $\mathbf{I_A}$

Stereochemical invariance of the *endo* polymers would again be a consequence.

*Solvent incorporation by poly(exo-***1***)*

The ability of poly(*exo*-**1**) to bind certain hydrocarbons is exceptional in the series of polymers described here, and is fairly unusual for poly(norbornenes) in general. There appears to be a minimum chain length required to capture the hydrocarbon. For example, a sample of poly(*exo*-**1**) with $M_n = 21300$ incorporates 28% hexane (expressed as a molar percentage) whilst an identical polymer derived from just 20 monomer equivalents showed no incorporation. Also, similar molar quantities of hexane are incorporated irrespective of the *cis/trans* content of the polymer. Since the coiling of the high *cis* and high *trans* polymers would be expected to be substantially different, this observation points to polymer coiling being relatively insignificant. An alternative explanation, therefore, is that the solvent or gas may be trapped between the polymer chains, possibly in crystalline regions. X-ray powder diffraction studies, however, have thus far proved inconclusive in establishing the degree of crystallinity in samples of poly(*exo*-**1**) and further investigations will be required. Nevertheless, it is clear that the nature of the amino ester must play a key role in the hydrocarbon incorporation since the polymers derived from *exo*-**2** and *exo*-**3** display no tendency to incorporate hexane. It is possible, therefore, that substituents larger than hydrogen may block the channels or pockets that might otherwise be available to incorporate small hydrocarbon molecules. Such channels or pockets do not appear to be present in poly(*endo*-**1**) since this too does not incorporate guest molecules.

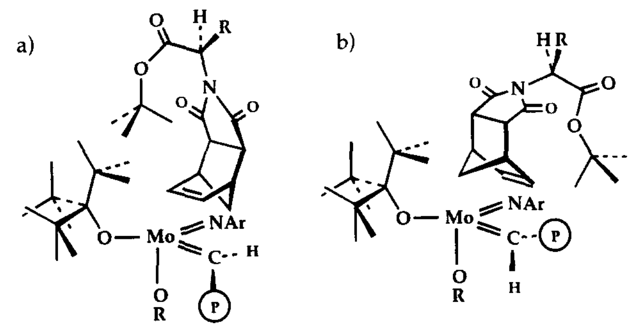
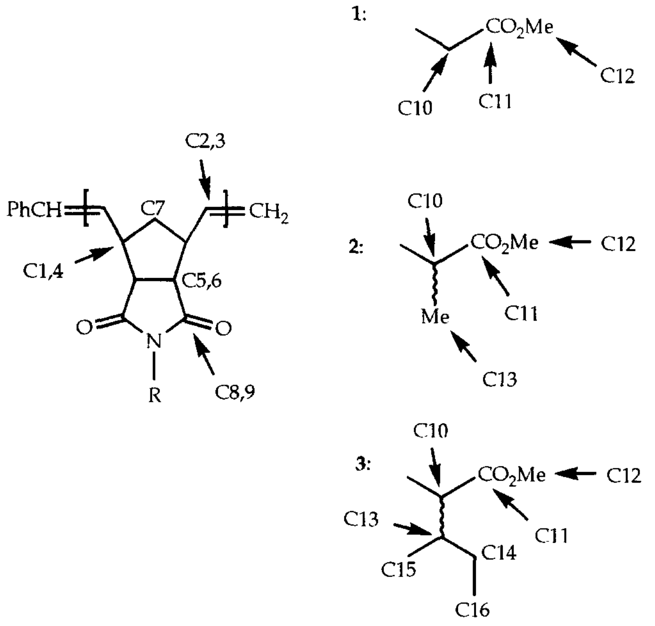


Figure 5 Possible pathways of approach of *endo* monomers to the initiator alkylidene: (a) 7-*syn* approach to *anti*-alkylidene; (b) 7-*anti* approach to *syn*-alkylidene



Scheme 2 Atom labels employed in n.m.r. assignments

CONCLUSION

A series of amino-ester derivatised norbornenes has been polymerised in a controlled manner using well-defined molybdenum ROMP initiators. The polymer derived from the glycine ester-functionalised norbornene is exceptional in this series in its ability to encapsulate a variety of hydrocarbon molecules. In future publications we shall describe extensions of this work to amino acid-containing monomers and polypeptide functionalised norbornenes.

EXPERIMENTAL

All manipulations were performed on a conventional vacuum/inert atmosphere (nitrogen) line using standard Schlenk and cannular techniques, or in an inert atmosphere (nitrogen) filled glove box.

All solvents (with the exception of *n*-hexane and methanol which were used to precipitate the polymers from solution) were dried by prolonged reflux over a suitable drying agent, being freshly distilled and deoxygenated prior to use. N.m.r. solvents ($CDCl_3$ and C_6D_6) were dried by stirring over phosphorus (V) oxide.

The three initiators, I_A, I_B and I_C, were prepared according to the procedure developed by Schrock *et al.*[15]. All the monomers were synthesised by previously published methods[6,11]. Before polymerisations were attempted the monomers were dried *in vacuo* and, if required, residual moisture was removed by passing a solution of the substrate down a short column of activated alumina.

N.m.r. spectra were recorded on a Varian VXR 400 at the University of Durham and on a Bruker AC250 at Imperial College at frequencies of 399.95 MHz for ^1H and 100.58 MHz for ^{13}C (Durham) and 250.13 MHz for ^1H and 62.53 MHz for ^{13}C (Imperial). ^1H n.m.r. chemical shifts are quoted as δ in ppm with respect to the residual protio impurity in the solvents used; ^{13}C n.m.r. shifts are quoted as δ in ppm with respect to the methyl carbons of tetramethylsilane. The following abbreviations are used in the text to describe the n.m.r. signals: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), br (broad), vbr (very broad).

Infra-red spectra (KBr windows) were obtained on a Perkin-Elmer Model 1600 *FT* i.r. spectrometer. The films were obtained by dissolving a small quantity of the polymer in either dichloromethane or chloroform and then transferring one or two drops of the viscous solution directly to the surface of the KBr plate. The solvent was then allowed to evaporate in air before the i.r. spectrum was obtained. Absorptions are abbreviated in the text as follows: vs (very strong), s (strong), m (medium), w (weak), br (broad), sh (shoulder).

G.p.c. traces were recorded on a Viscotek SEC[3] triple detector (T60) system (differential refractometer, right-angle laser light scattering and viscometer) fitted with a Knauer HPLC pump 64 and two PLgel 10 μl mixed columns, using chloroform as the column medium at a flow rate of 1 $cm^3 min^{-1}$. Samples were filtered through a 0.45 μm filter immediately prior to injection to remove particulates. The columns were calibrated using polystyrene standards (Polymer Laboratories Ltd) ranging from approximately 1560 to 1×10^6 molecular weight.

D.s.c. measurements were carried out on a Perkin-Elmer Series 7 instrument. The Series 7 measurements were carried out at the University of Durham and the calorimeter was calibrated using the dual point method (with elemental zinc and indium); samples were heated at a rate of 10°C min^{-1}. The MALDI–TOF spectrum of poly(*exo*-**1**) was measured on a Kratos Kompact Research MALDI IV spectrometer and the molecular weight distribution calculated using Kompact software.

General procedure for n.m.r. scale reactions

In a dry box, the catalyst and the monomer (5–10 equivalents) were weighed into vials and both were dissolved in 400 μl of $CDCl_3$ (for monomers **1** and **3**) or C_6D_6 (monomer **2**). The reaction was initiated by adding the catalyst solution to the rapidly stirred monomer solution which was then stirred for 30 min at room temperature. The reaction mixture was then transferred by pipette into a sealable n.m.r. tube. The n.m.r. tube was removed from the box, flame-sealed and the spectrum recorded immediately.

General preparative scale polymerisation procedure

In a dry box, the catalyst (*ca.* 0.01 g) and the monomer (30–100 equivalents) were weighed into vials and both were dissolved in 1–2 ml of dichloromethane (for monomers **1** and **3**) or toluene (monomer **2**). The reaction was initiated by adding the catalyst to the rapidly stirred monomer solution. The solution was stirred for 1 h for *exo* monomers and for up to 1.5 h for the corresponding *endo* derivatives at room temperature. The reaction was then terminated by the addition of benzaldehyde (*ca.* 50 μl).

The polymer was isolated by precipitation from a large excess of hexane or methanol (in general, hexane is the preferred non-solvent for the *exo* polymers, methanol the preferred non-solvent for the *endo* materials). The resulting white polymer was dried *in vacuo* for 24 h at 40°C.

The numbering scheme used in the spectroscopic assignments listed below is summarised in *Scheme 2*.

Spectroscopic data for poly(exo-1)

Infra-red (thin film cast from CHCl$_3$, KBr, cm^{-1}): 3468 (w), 3058 (w, sh), 2996 (w), 2953 (m), 2588 (w), 1777 (s, sh), 1751 (vs), 1709 (vs), 1591 (sh), 1437 (w, sh), 1415 (s), 1394 (w, sh), 1367 (w), 1219 (s), 1171 (s), 1105 (w), 1074 (w), 1014 (w), 972 (w), 920 (w), 896 (w, sh), 848 (w, br), 801 (w), 768 (w), 735 (s), 702 (w, sh), 621 (w), 567 (w, br), 520 (w, br); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.74 (d (br), H_2, H_3-*trans*), 5.44 (m (br), H_2, H_3-*cis*), 4.18 (s, H_{10}), 3.73 (s, H_{12}), 3.08 (m (br), H_5, H_6), 2.79 (s (br), H_1, H_4), 2.16–1.65 (m (br), H_7), 1.24 (d, hexane), 0.86 (t, hexane); ^{13}C n.m.r. (100 MHz in CDCl$_3$, 298 K): 177.4 (C_8, C_9), 167.4 (C_{11}), 133.2 (C_2, C_3-*cis*), 131.9 (C_2, C_3-*trans*), 52.6 (C_{12}), 50.9 (C_5, C_6), 45.7 (C_1, C_4-*trans*), 41.7 (m, C_7), 41.0 (C_1, C_4-*cis*), 39.0 (C_{10}), 31.5, 22.6, 14.1 (*n*-hexane).

Spectroscopic data for poly(endo-1)

Infra-red (thin film cast from CHCl$_3$, KBr, cm^{-1}): 3670 (sh), 3467 (s, br), 2999 (s, sh), 2898 (s, sh), 2589 (w), 2331 (s, sh), 2254 (vs), 2117 (w), 1955 (w), 1777 (vs, br), 1759 (vs, br), 1438 (s, br), 1327 (s, br), 1225 (s, br), 1174 (s, br), 1097 (w), 1012 (s), 968 (s, br), 904 (s, br), 794 (w, sh), 714 (vs, br), 648 (vs), 622 (s), 560 (vs), 440 (s); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.66 (s (br), H_2, H_3-*cis* and *trans*), 4.21 (s (br), H_{10}), 3.72 (s, H_{12}), 3.24 (s (br), H_5, H_6), 2.91 (s (br), H_1, H_4), 2.27 (s (br), H_1, H_4), 1.89, 1.49 (m (br), H_7); ^{13}C n.m.r. (100 MHz in CDCl$_3$, 298 K): 175.8 (C_8, C_9), 175.4 (C_8, C_9), 167.2 (C_{11}), 129.6 (C_2, C_3-*cis* and *trans*), 52.5 (C_{12}), 49.0 (C_5, C_6), 45.3 (C_1, C_4-*trans*), 40.4 (C_1, C_4-*cis*), 39.3 (C_{10}), 38.0, 36.6 (C_7).

Spectroscopic data for poly(exo-2)

Infra-red (thin film cast from CH$_2$Cl$_2$, KBr, cm^{-1}): 3466 (w), 2952 (m), 2864 (w), 1747 (vs), 1707 (vs), 1450 (m), 1387 (vs), 1311 (m), 1230 (s, sh), 1199 (s), 1120 (m, sp), 1070 (m), 967 (m), 734 (m), 627 (m); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.72 (m, (br), H_2, H_3-*trans*), 5.52 (m (br), H_2, H_3-*cis*), 4.74 (q, H_{10}), 3.71 (s, H_{12}), 3.29 (s (br), H_5, H_6-*cis*), 3.11 (s (br), H_1, H_4-*cis*), 3.00 (s (br), H_5, H_6-*trans*), 2.71 (s (br), H_1, H_4-*trans*), 2.07, 1.60 (s (br), H_7), 1.51 (s, H_{13}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 177.4 (C_8, C_9), 169.7 (C_{11}), 133.1 (C_2, C_3-*cis*), 131.7 (C_2, C_3-*trans*), 52.7 (C_{12}), 50.6 (C_5, C_6), 47.6 (C_{10}), 45.7 (C_1, C_4-*trans*), 41.3 (C_1, C_4-*cis*), 41.7, 40.8 (C_7), 14.2 (C_{13}).

Spectroscopic data for poly(endo-2)

Infra-red (thin film cast from CH$_2$Cl$_2$, KBr, cm^{-1}): 3459 (w), 2996 (m), 2952 (m), 1749 (vs), 1703 (vs), 1452 (m), 1389 (vs), 1320 (m), 1230 (s, sh), 1202 (s), 1123 (m, sp), 1080 (m), 967 (m), 734 (m), 627 (m); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.63 (m (br), H_2, H_3-*trans* and *cis*), 4.68 (q (br), H_{10}), 3.67 (s, H_{12}), 3.20 (s (br), H_5, H_6), 2.87 (s (br), H_1, H_4), 1.84, 1.36 (s (br), H_7), 1.50 (s, H_{13}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 175.6 (C_8, C_9), 169.5 (C_{11}), 129.2 (C_2, C_3-*cis* and *trans*), 52.5 (C_{12}), 48.6 (C_5, C_6), 47.7 (C_{10}), 45.3 (C_1, C_4-*trans*), 40.3 (C_1, C_4-*cis*), 36.8, 36.3 (C_7), 14.2 (C_{13}).

Spectroscopic data for poly(endo-L-3)

Infra-red (thin film cast from CHCl$_3$, KBr, cm^{-1}): 3459 (br), 3156 (w), 2964 (vs), 2931 (vs, sh), 2877 (vs), 2256 (vs), 1751 (vs), 1707 (vs), 1426 (s), 1436 (sh), 1382 (w), 1321 (w), 1259 (w), 1196 (w, br), 994 (w, sh), 966 (s), 908 (vs), 806 (sh), 739 (s), 648 (s), 582 (s), 445 (w, br); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.61 (m (br), H_2, H_3-*cis* and *trans*), 4.35 (m, H_{10}), 3.62 (H_{12}), 3.19 (m, H_5, H_6), 2.84 (s (br), H_1, H_4), 2.30 (s (br), H_{13}), 1.79, 1.32 (m, H_7), 0.98 (m, H_{15}), 0.83 (s (br), H_{14}), 0.71 (m, H_{16}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 176.1(C_8, C_9), 168.8 (C_{11}), 129.3 (C_2, C_3-*cis* and *trans*), 57.0 (C_{10}), 52.2 (C_{12}), 48.5 (C_5, C_6), 45.6 (C_1, C_4-*trans*), 40.4 (C_1, C_4-*cis*), 37.1 (C_7), 33.6 (C_{13}), 25.6 (C_{14}), 16.9 (C_{15}), 10.9 (C_{16}).

Spectroscopic data for poly(endo-DL-3)

Infra-red (thin film cast from CHCl$_3$, KBr, cm^{-1}): 3460 (s, br), 3056 (s, sh), 2962 (vs), 2876 (s, sh), 2306 (w), 1746 (vs), 1702 (vs), 1455 (s), 1435 (s), 1384 (vs), 1320 (sh, w), 1265 (s), 1196 (s), 1135 (w), 1073 (w), 1017 (w), 967 (s), 919 (w), 895 (w), 805 (sh, w), 737 (vs), 702 (s), 582 (s); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.64 (s (br), H_2, H_3-*cis* and *trans*), 4.46 (m (br), H_{10}), 3.67 (s, H_{12}), 3.23 (s (br), H_5, H_6), 2.04 (s (br), H_1, H_4), 2.35 (s (br), H_{13}), 1.85, 1.35 (m (br), H_7), 1.04 (s (br), H_{15}), 0.94 (m (br), H_{14}), 0.82 (m (br), H_{16}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 176.1 (C_8, C_9), 168.9 (C_{11}), 129.4 (C_2, C_3-*trans*), 57.1(C_{10}- L), 55.9 (C_{10}-D), 52.3 (C_{12}), 48.6 (C_5, C_6), 45.5 (C_1, C_4-*trans*), 40.4 (C_1, C_4-*cis*), 37.0 (C_7), 34.2 (C_{13}-D), 33.6 (C_{13}-L), 27.4 (C_{14}-D), 25.6 (C_{14}-L), 16.9 (C_{15}-L), 15.8 (C_{15}-D), 11.4 (C_{16}-D), 10.9 (C_{16}-L).

Spectroscopic data for poly(exo-L-3)

Infra-red (thin film cast from CH$_2$Cl$_2$, KBr, cm^{-1}): 3465 (s), 2962 (vs, br), 2876 (sh), 2256 (s), 1774 (vs), 1750 (vs), 1706 (vs), 1463 (s), 1380 (s), 1190 (s, br), 1039 (w), 1005 (s), 968 (s), 914 (vs), 816 (w), 731 (vs, br), 647 (s), 470 (w, br); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.74 (s (br), H_2, H_3-*trans*), 5.49 (m (br), H_2, H_3-*cis*), 4.36 (m (br), H_{10}), 3.66 (s, H_{12}), 3.32, 3.18, 2.68 (m (br), H_1, H_4, H_5, H_6), 2.35 (s (br), H_{13}), 2.08, 1.52 (m (br), H_7), 1.38 (s (br), H_{14}), 1.02 (m (br), H_{15}), 0.82 (m (br), H_{16}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 177.5 (C_8, C_9), 168.9 (C_{11}), 133.4 (C_2, C_3-*cis*), 131.3 (C_2, C_3-*trans*), 57.1 (C_{10}), 52.3 (C_{12}), 50.6 (C_5, C_6), 45.9 (C_1, C_4-*trans*), 41.7 (C_1, C_4-*cis* and C_7), 33.7 (C_{13}), 25.6 (C_{14}), 16.9 (C_{15}), 10.8 (C_{16}).

Spectroscopic data for poly(exo-DL-3)

Infra-red (thin film cast from CH$_2$Cl$_2$, KBr, cm^{-1}): 2961 (s), 2876 (sh), 2256 (w), 1748 (vs), 1702 (vs), 1459 (s), 1435 (s), 1260 (w), 1189 (s), 1134 (w), 1014 (s, br), 961 (s), 787 (s), 732 (vs), 647 (w), 460 (w); ^{1}H n.m.r. (400 MHz, CDCl$_3$, 298 K): 5.71 (s (br), H_2, H_3-*trans*), 5.49 (s (br), H_2, H_3-*cis*), 4.37 (m (br), H_{10}), 3.66 (s, H_{12}), 3.32, 3.19 (m (br), H_1, H_4, H_5, H_6-*cis* and *trans*), 2.36 (s (br), H_{13}), 1.28, 1.18 (m (br), H_7), 1.05 (m, H_{15}), 0.91 (m, H_{14}), 0.83 (m, H_{16}); ^{13}C n.m.r. (100 MHz, CDCl$_3$, 298 K): 177.6 (C_8, C_9), 169.0 (C_{11}), 133.4 (C_2, C_3-*cis*), 131.5 (C_2, C_3-*trans*), 57.1 (C_{10}-L), 56.1 (C_{10}-D), 52.3 (C_{12}), 50.6 (C_5, C_6), 45.8 (C_1, C_4-*trans*), 41.6 (C_1, C_4-*cis* and C_7), 34.3 (C_{13}-D), 33.7 (C_{13}-L), 27.3 (C_{14}-D), 25.6 (C_{14}-L), 17.0 (C_{15}-L), 15.5 (C_{15}-D), 11.3 (C_{16}-D), 10.9 (C_{16}-L).

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