Amino Acid derived Homochiral Polymers *via* Ring-opening Metathesis Polymerisation

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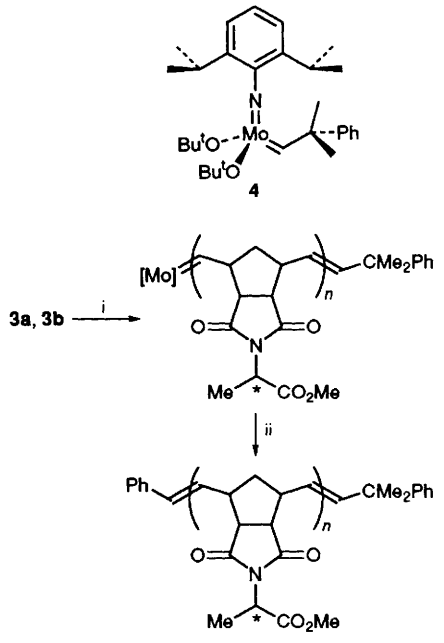
Homochiral norbornene monomers derived from amino acids undergo ring-opening metathesis polymerisation with [Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$Pr$^i_2$-2,6)(OBu^t)$_2$] to give homochiral polymers with narrow molecular mass distributions.

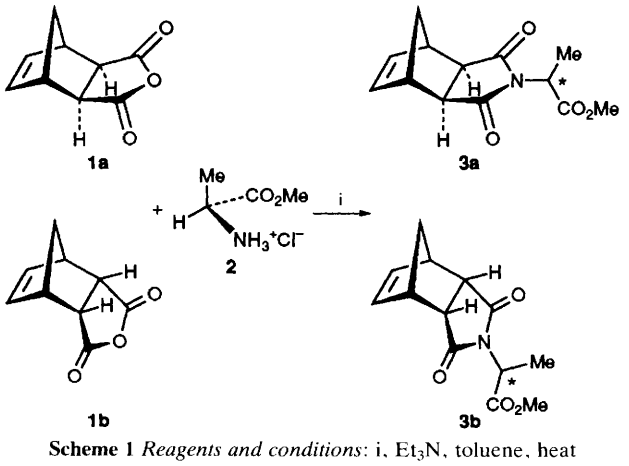
Naturally occurring polymers such as proteins and nucleic acids occur with very well defined primary, secondary and tertiary structures, and these are of fundamental importance in determining the biological and chemical properties of the polymer. There is growing academic and commercial interest in synthetic biopolymers, whose structure–activity relationships are also likely to be closely dependent upon all aspects of their molecular architecture. It is therefore vital to obtain the maximum possible level of control over the assembly of such macromolecules. Ring-opening metathesis polymerisation (ROMP) of strained cyclic alkenes using well-defined metal alkylidene initiators[1] allows control over many aspects of the polymer assembly, including its molecular mass and molecular mass distribution,[2] alkene backbone configuration[3] and tacticity.[4] The application of ROMP methodology to highly functionalised biopolymers has not previously been addressed. Therefore, we have initiated a project aimed at the synthesis and ROMP of amino acid and peptide derived norbornenes, with the ultimate aim of utilising the chirality and molecular recognition capacity of the amino acid or peptide to control the architecture of synthetic polymers. Here, we describe the synthesis of homochiral polymers derived from norbornenes functionalised with optically pure alanine ester residues.

Each optical isomer of the *exo*- and *endo*-norbornene monomers† **3a,b** were synthesised by treatment of L-, D- or DL-alanine methyl ester **2** with either the *exo* **1a** or *endo* **1b** anhydrides according to Scheme 1. That no racemisation occurred during this monomer synthesis was shown by the additional preparation of monomers derived from both DL- and L-isoleucine. Commercially available DL-isoleucine is actually a racemic mixture of both diastereomers, so the norbornene derivatives derived from the racemic isoleucine show two sets of peaks in both the ^{1}H and ^{13}C NMR spectra. The monomers derived from L-isoleucine, however, gave a single set of peaks, indicating that no epimerisation of the α-centre had occurred within the detection limits of NMR spectroscopy.

The polymerisation was initially investigated on an NMR scale by adding 10 equiv. of the monomer to initiator **4** in deuteriated benzene. In all cases, a ^{1}H NMR signal was observed in the range δ 11–12 attributable to the propagating metal alkylidene hydrogen of a living polymer chain[2] (Scheme 2). The polymerisations were then carried out on a preparative scale, the monomer being added to a rapidly stirring solution of the initiator **4** in toluene. After 15–24 h, the living polymers were quenched by the addition of benzaldehyde and the resultant polymer was isolated by precipitation from hexane.† GPC data, *cis*/*trans* content and specific rotations are collected in Table 1. In all cases, the molecular mass distribution is reasonably narrow and the vinylene linkages in the polymer backbone are predominantly *trans* (77–91%), as expected for the *tert*-butoxide initiator.[3,4] The polymers derived from the optically active monomers D- and L-**3a** and D- and L-**3b** are



Scheme 2 *Reagents and conditions*: i, **4**, toluene, room temp.; ii, PhCHO, room temp.



Scheme 1 *Reagents and conditions*: i, Et_3N, toluene, heat

Table 1 Physical parameters of the polymers derived from **3a** and **3b** using initiator **4**

Monomer (equivalents)	σ_c[a]	$[\alpha]_D^{20}$	M_n(found)[b]	M_n(calc.)	PDI (M_n/M_w)
L-**3a** (21)	0.08	−31	9065	5316	1.25
D-**3a** (54)	0.09	+34	10199	13349	1.13
DL-**3a** (85)	0.10	—	43030	21063	1.15
L-**3b** (46)	0.22	−52	21379	11608	1.28
D-**3b** (54)	0.20	+54	19581	13472	1.18
DL-**3b** (60)	0.23	—	18298	15027	1.29

[a] σ_c = %*cis*/100. [b] M_n and M_w were determined by gel permeation chromatography recorded on 0.1–0.3% m/v samples using a Waters differential refractometer R401 fitted with a Waters 590 pump and 3 PLgel 5 mm mixed columns previously calibrated using commercially available polystyrene standards (Polymer Laboratories) in the molecular mass range 162 to 1.03 × 10^6 ($CHCl_3$ flow rate = 1 cm^3 min^{-1}).

themselves optically active, and they can be considered as artificial peptides in which the amide backbone has been replaced by an all carbon system.

In summary, we have shown that it is possible to prepare optically pure norbornenes derived from amino acids, and to use them as monomers for ROMP. The resulting polymers are optically active, have narrow molecular mass distributions, and the geometry of the alkenes can be controlled. Our studies in this area are currently being extended to the use of other amino acids and peptides within the norbornene monomers, and will be reported in due course.

The authors thank the EPSRC Innovative Polymer Synthesis Initiative for a studentship to M. P. C., the Interdisciplinary Research Centre in Polymer Science and Technology for polymer characterisation services, and the EEC-Erasmus scheme for grants to L. M. and D. Z.

Received, 8th September 1994; Com. 4/05476H

Footnote

† All new compounds gave satisfactory spectral and analytical data

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