

# Transition metal complex-templated asymmetric free radical polymerisation

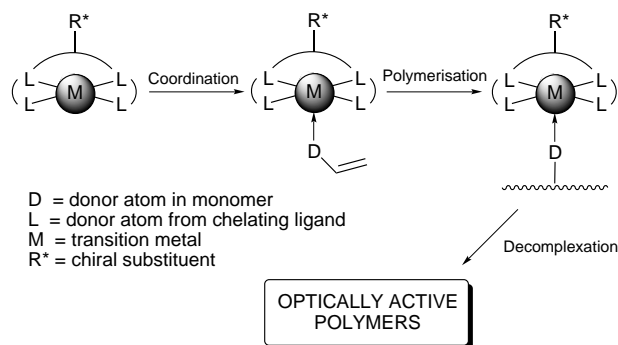
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For the first time an amino acid Schiff base copper complex has been used as a chiral template—auxiliary for the induction of configurational asymmetry into the backbone of 4-vinylpyridine-co-indene polymers, yielding main chain optically active macromolecules *via* free radical polymerisation.

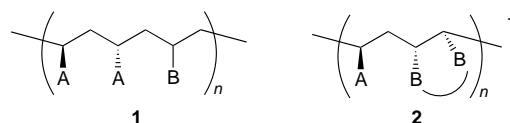
The synthesis of vinyl polymers whose optical activity arises solely as a result of the configuration of stereogenic carbon centres in the main chain is of increasing importance because of their unique properties and potential applications in (second order) nonlinear optics, liquid crystals, ferroelectrics and asymmetric catalysis.<sup>1</sup> Whereas main chain optically active (co)polymers employing non-alkene comonomers (*e.g.* CO, epoxides) have been prepared using optically active metal complex initiators, the synthesis of main chain optically active vinyl (co)polymers *via* a simple free radical mechanism remains problematical. To date, a number of ingenious strategies<sup>1–3</sup> have been reported which circumvent the inherent complex symmetry properties (*e.g.* glide reflection and mirror planes) associated with stereoregular macromolecular systems (*note* isotactic and syndiotactic vinyl polymers are *not* optically active), and therefore lead to main chain optically active polymers. Unfortunately, however, the majority<sup>1,2</sup> suffer from various disadvantages (such as multistep syntheses of monomers, expensive reagents/starting materials or products that are not readily amenable to functionalisation) that render them unsuitable for commercial exploitation. Thus for 'asymmetric synthesis polymerisation' (whereby a chiral auxiliary, or template, is attached to an achiral monomer prior to polymerisation and then removed afterwards to leave optically active polymer)<sup>2</sup> to achieve viability in a commercial process or as a routine laboratory procedure, the auxiliary must be of low cost, readily attached to everyday monomers and easily removed from the newly formed polymer.

We now adumbrate a novel and highly expedient strategy for preparing main chain optically active polymers in which the chiral auxiliary is a transition metal salicylidene–amino acid Schiff base complex. A vinyl monomer containing a suitable donor group (*e.g.* a vinylpyridine) will coordinate to the metal centre, thus forming a chiral monomer unit. Upon completion of the polymerisation the template complex, being attached only through relatively weak dative bonds, should be easily removed, thus liberating the vinyl polymer (Scheme 1).



Scheme 1

If a chiral monomer complex of this type were copolymerised with achiral monosubstituted or cyclic 1,1-disubstituted vinyl (or related) compounds, we realised that there would be a strong likelihood that nonsymmetric Wulff-type<sup>1</sup> triads (**1**) or related diads (**2**), respectively, would be formed along at least some sections of the polymer backbone. Should this in fact be the case, any such polymers would display optical activity as a result of the main chain configuration.



Accordingly, we have now synthesised the copper(II) amino acid Schiff base complex **3** from (*S,S*)-(+)-isoleucine, salicylaldehyde and copper(II) acetate in aqueous solution (see Table 1).<sup>4</sup> The amino acid was chosen because of its non-functionalised alkyl side chain, which provides steric bulk on the 'upper' face of the complex without the possibility of any undesirable side reactions occurring. Copper Schiff base complexes have long been known<sup>5</sup> and generally possess square planar geometry about the metal. Furthermore, such complexes have a high affinity for, and are readily coordinated by, one or two pyridine molecules to form five- or six-coordinate species.<sup>5</sup> Precedent exists for the free-radical polymerisation of transition metal complexes without any adverse interactions with the metal (*e.g.* electron transfer from a radical centre): copper<sup>6,7</sup> and cobalt<sup>8</sup> Schiff base complexes have been used to prepare imprinted polymer networks containing enzyme mimetic or chiral binding cavities, respectively.

Polymerisations were performed, under an inert atmosphere, in (deoxygenated) MeOH solutions of **3**, 4-vinylpyridine (4-VPy) **4** and indene (IN) **5** with AIBN (1 wt%) as the radical source (Scheme 2). Evaporation of the solvent gave dark green Schiff base–polymer adducts **6**; these were not characterised except for measurement of the specific rotation in one case (see Table 2, entry 4). These adducts were broken down through acid hydrolysis before the free polymers were precipitated from the acidic aqueous solution by basifying with aqueous ammonia. Further reprecipitation from MeOH solutions into aqueous ammonia produced the polymers **7** as off-white powders. Attempts to measure the molecular weights of **7**, using gel permeation chromatography, have so far failed because the copolymers appear to be absorbed onto the poly(styrene-divinylbenzene) column packings. This is a recognised problem

Table 1 Data for the copper(II) amino acid Schiff base complex **3** and (*S,S*)-(+)-isoleucine

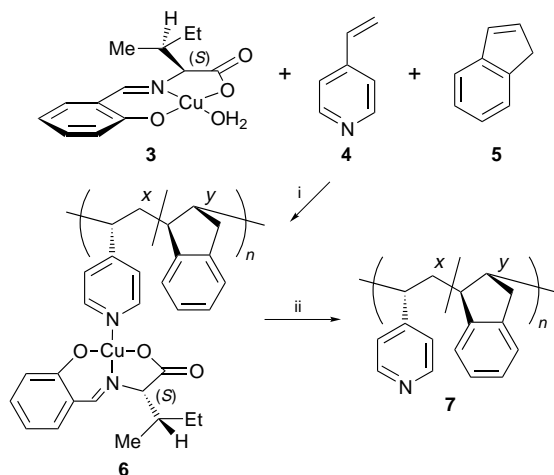
$\lambda/\text{nm}$	$[\alpha]^{25}/10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$	
	( <i>S,S</i> )-(+)-Ile	Complex <b>3</b>
365	+6.4 <sup>a</sup>	— <sup>b</sup>
436	+13.6 <sup>a</sup>	−1014 <sup>c</sup>
589	+27.1 <sup>a</sup>	+128.6 <sup>c</sup>

<sup>a</sup>  $c = 0.14 \times 10^{-2} \text{ g cm}^{-3}$  in MeOH. <sup>b</sup>  $c = 0.07 \times 10^{-2}$  and  $0.035 \times 10^{-2} \text{ g cm}^{-3}$  in MeOH. The sample absorbed too much light at these concentrations for a reading to be obtained. <sup>c</sup>  $c = 0.07 \times 10^{-2} \text{ g cm}^{-3}$ .

**Table 2** Data for poly(4-vinylpyridine-*co*-indene) copolymer **7**

Entry	Reactants/mmol			<i>T</i> /°C	<i>t</i> /h	Polymer composition <sup>a</sup> 4-Vpy:IN	[α] <sup>25</sup> /10 <sup>-1</sup> deg cm <sup>2</sup> g <sup>-1</sup>			<i>c</i> /10 <sup>-2</sup> g cm <sup>-3</sup>	Solvent	Yield/g (%)
	<b>3</b>	<b>4</b>	<b>5</b>				365 nm	436 nm	589 nm			
1	5	5	5	65	18	3:1	— <sup>b</sup>	−4.0	−1.2	0.57	MeOH	0.59 (53)
2	7.5	7.5	7.5	65	18	4:1	−6.3	— <sup>c</sup>	−2.0	0.32	MeOH	0.85 (49)
3	7.5	7.5	7.5	65	16	4:1	−6.5	— <sup>c</sup>	−2.1	0.30	MeOH	0.79 (46)
4	5.2	5.2	5.2	65	18	3:1	−5.8	−4.2 <sup>d</sup>	−2.3 <sup>d</sup>	0.31	MeOH	0.58 (51)
5	0	10	10	65	16	7:2	0	0	0	0.52	CHCl <sub>3</sub>	1.21 (54)

<sup>a</sup> Determined using <sup>1</sup>H NMR spectroscopy. <sup>b</sup> The sample absorbed too much light at this concentration for a reading to be obtained. <sup>c</sup> No readings taken. <sup>d</sup> Specific rotation of adduct **6** was −688.2 at 436 nm and +76.5 at 589 nm (*c* 0.017, MeOH).



**Scheme 2** Reagents and conditions: i, AIBN, MeOH, reflux N<sub>2</sub>; ii, 2 M HCl then NH<sub>3</sub> (aq)

with poly(4-vinylpyridine) systems<sup>9</sup> which we are currently addressing. However, the materials **7** do show all the characteristics of macromolecular systems, including broad NMR resonances and initially becoming gel-like before slowly dispersing to form isotropic solutions in organic solvents.

Each of the polymers **7a–d** which were prepared using the chiral auxiliary template displayed *negative* optical rotations at 365, 436 and 589 nm (see Table 2). The polymer **7e** which resulted from a blank control experiment (without template) was, as expected, optically inactive. Obviously, the asymmetric induction which has taken place during the polymerisation process is due to the stereogenic centre in complex **3**. In order to be absolutely certain that the optical activity observed arose from the main chain configuration of the polymers **7** we carried out a detailed study of the optical rotary properties of the complex **3** and the Schiff base-polymer adduct **6**, as well as (*S,S*)-(+)-isoleucine itself: at 589 nm all these have *positive* optical rotations of varying magnitude.

Thus we can unequivocally conclude that polymers possessing main chain optical activity have been obtained. It is important to appreciate that for a chemical process to achieve this, not only must a significant number of stereogenic centres be generated enantioselectively but it is also essential for some higher order asymmetry to be generated simultaneously. At the moment we are not able to specify precisely the configurations of the stereogenic carbon centres along the backbone although

free-radical propagation of cyclic alkenes does generally proceed *via* a *trans* reaction. The overall configurations giving rise to the observed optical activity are therefore not clear cut, but there must be an excess of the diads, **2**, in the backbone.

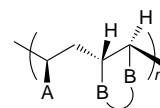
We have described a simple, low cost and effective method for the synthesis of main chain optically active polymers. To the best of our knowledge this is the first example where a chiral transition metal complex has been employed as a template for asymmetric induction during a polymerisation reaction. It is also the first instance where non-covalent interactions have been utilised to attach the chiral auxiliary. We are currently expanding the range of copolymers produced in this way, and of course considerable scope exists for exploiting chiral Schiff base (or other) metal complexes involving other amino acids and indeed other chiral molecules.

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## Notes and References

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† Since free radical attack on cyclic alkenes usually occurs as a *trans* process **2** is more clearly represented as:



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