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Mainchain optically active vinyl copolymers *via* transition metal complex-templated asymmetric free radical polymerisation

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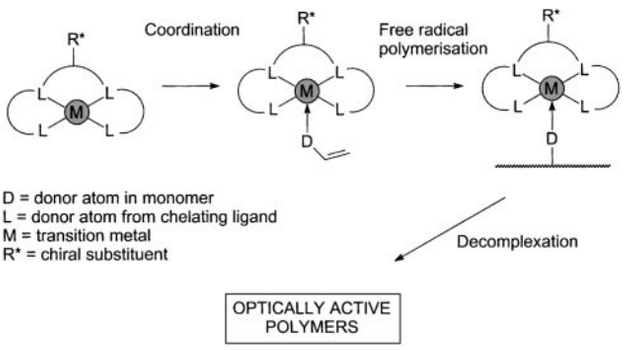
4-Vinylpyridine coordinated to optically pure Cu(II) amino acid salicylidene Schiff-base complexes as chiral templates has been copolymerised using standard free radical procedures with styrene, indene and 1,2-dihydronaphthalene. Following isolation of the copolymer products and decomplexation from the Cu(II) complexes the copolymers with indene and 1,2-dihydronaphthalene proved to be optically active. Each copolymer has an optical rotation at 589 nm which has a sign opposite to that of the original Cu(II) Schiff-base complex and to the copolymer still coordinated to the Cu(II) complex. In contrast the 4-vinylpyridine with styrene displays no optical rotation. Systematic experiments have confirmed that the chiral Cu(II) complexes induce a net asymmetry in the mainchain of the copolymers, and that the configuration of the stereogenic carbon centres on the backbone is the source of the asymmetry. A tentative mechanism is proposed to explain the nature of the induction process in these novel asymmetric free radical copolymerisations.

Introduction

Vinyl and related polymers which are optically active solely as a result of the configuration of stereogenic carbon centres in the main chain are rare.[1] They represent a class of materials of importance because of their unique properties and their potential for exploitation in nonlinear optics, liquid crystals, chiral chromatography and asymmetric catalysis. Synthesis of such main chain optically active vinyl (co)polymers *via* a simple free radical mechanism remains problematical. A number of ingenious strategies[1–3] have been implemented to date to circumvent the inherent complex symmetry properties (*e.g.* glide reflection and mirror planes) associated with stereoregular macromolecular systems (*NB* isotacticity and syndiotacticity do *not* convey optical activity on a polymer). The most successful approach remains that of Wulff whereby a chiral auxiliary or template is attached to an achiral monomer prior to polymerisation, and then removed afterwards to leave a main chain optically active polymer. Recently Wulff and Zweering have extended this approach to poly(α-olefins).[4]

Unfortunately use of a covalently bound chiral auxiliary is not particularly simple in synthetic terms, nor versatile with respect to the everyday vinyl monomers to which the approach can be applied. A technologically exploitable methodology must be convenient, applicable to a wide range of monomers, and allow the facile release of the product optically active polymer once the asymmetric induction step is achieved.

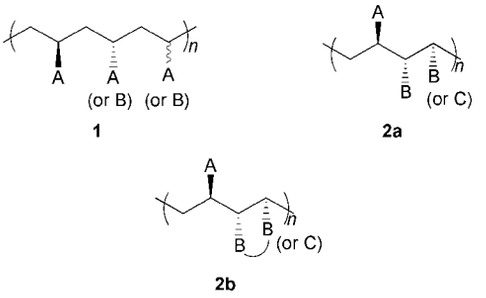
We recently made a preliminary disclosure of an entirely novel strategy[5] aimed at simplifying the chiral auxiliary approach. We used a chiral metal complex to orientate a coordinated monomer, followed by facile decomplexation after free radical polymerisation, to yield a main chain optically active copolymer. The conceptualised strategy is illustrated in Scheme 1. We now report in more detail on our elaboration of this approach.



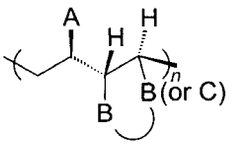
Scheme 1 Chiral transition metal complex-templated asymmetric free radical vinyl polymerisation.

Results and discussion

We argued earlier[5] that if a chiral vinyl monomer (A)–metal complex were to be polymerised with an achiral vinyl (A or B) or with a 1,2-disubstituted acyclic or cyclic (BB or BC) alkenyl monomer then there would be a strong likelihood that nonsymmetric Wulff-type[1] triads **1** or related diads **2a** and **2b** respectively would be formed along at least some sections of the polymer backbone.† The stereoselective chemical processes

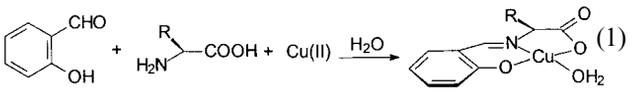


†Since free radical attack on cyclic alkenes usually occurs as a *trans* process **2b** is perhaps more clearly represented as



required to produce appropriate stereogenic centres on the polymer backbone leading to net symmetry breaking, and hence finite optical activity, will be different for **1**, **2a** and **2b**, and indeed will be less demanding in this sequence. Since in general 1,2-disubstituted acyclic alkenes do not readily participate in the free radical chain reactions that yield polymers or copolymers, we chose to examine styrene, along with indene, and 1,2-dihydronaphthalene, as three comonomers for interacting with coordinated 4-vinylpyridine, targeting **1** and **2b** as potential optically active copolymers. As in our preliminary report we chose amino acid salicylaldehyde Schiff-base complexes of Cu(II) as the enantiocontrolling centre.

The amino acid salicylaldehyde Schiff-base complexes of Cu(II) are well known[6] and optically active complexes are easily



(1)

prepared [eqn. (1)]. Furthermore the stable, generally square planar, geometry about the metal centre[7] seemed to offer a good opportunity for coordination of a nitrogen-containing donor monomer[8] such as 4-vinylpyridine. Furthermore Schiff-base complexes with Cu[9] and Co[10] metal centres that contain pendant vinyl groups have been shown to undergo facile free radical polymerisation in the preparation of molecularly imprinted polymer networks,[10] and in forming enzyme mimics.[9] In addition other metal complexes containing polymerisable functional groups have been shown to form polymers readily under normal free radical conditions.[11]

In the event our ideas proved correct when a 4-vinylpyridine complex of *N*-salicylidene-(*S,S*)-(+)-isoleucinato Cu(II) (**3a**) formed *in situ* was copolymerised with indene, followed by decomplexation. The 4-vinylpyridine–indene copolymer **P1** (Scheme 2) so formed displays a *negative* optical rotation at 589 nm whereas the starting complex **3a**, the Schiff-base–polymer adduct **4**, as well as (*S,S*)-isoleucine itself, all show a *positive* optical rotation of varying magnitude at this wavelength. This switch in optical rotation is unequivocal evidence of asymmetric induction during the free radical polymerisation and an excess of diads **2b** must be present in the copolymer as the source of asymmetry.

Amino acid salicylaldehyde Schiff-base complexes of Cu(II)

Seven Cu(II) monohydrate complexes **3** were synthesised by methods based on that published by Smith *et al.*[6] Yields were in the range ~30–75%. In addition to the synthesis of the (*S,S*)-isoleucinato **3a**, the (*S*)-alaninato **3b**, the (*S*)-*tert*-leucinato **3c**, the (*R*)-phenylglycinato **3d**, the (*R*)- and (*S*)-valinato **3e** and **3f** and the (*S*)-serinato **3g** complexes (Table 1) were prepared. Unsuccessful attempts were also made to isolate the (*S*)-asparaginato and (*S*)-glutamic acid analogues. The former was

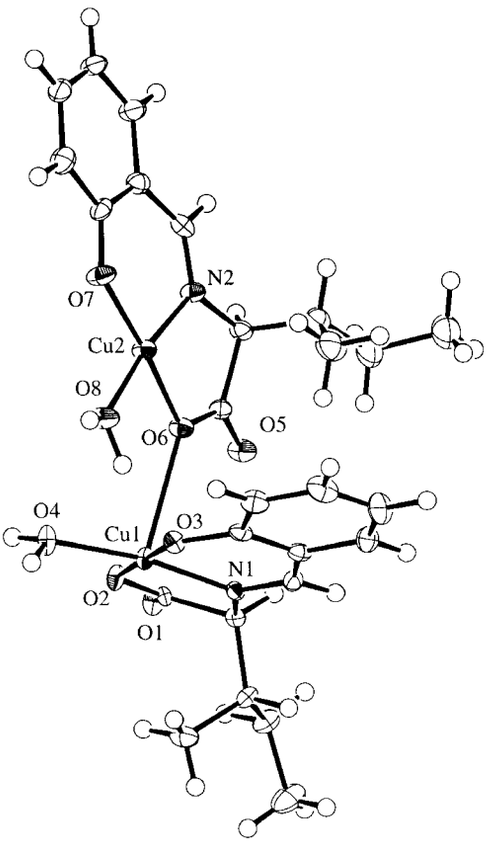


Fig. 1 X-Ray crystal structure of *N*-[salicylidene-(*S*,*S*)-(+)-isoleucinato] Cu(II) monohydrate, **3a**. ORTEP view of **3a** with 50% probability ellipsoids. Selected distances (Å) and angles (°) Cu1–O2 1.914(3), Cu1–O3 1.910(3), Cu1–O4 1.936(3), Cu1–O6 2.584(3), Cu1–N1 1.924(3), Cu2–O6 1.944(3), Cu2–O8 1.878(3), Cu2–O8 1.914(3), Cu2–N2 1.907(4), Cu2–C23* 3.561(5), Cu2–C24* 3.378(5), Cu1–O6–Cu2 126.5(1), where * is $0.5-x$, $-y$, $-0.5+z$.

isolated as a light green powder (68%) but proved to be insoluble in all common solvents; the latter was a green solid (45%) which yielded satisfactory elemental microanalytical data, but displayed no optical rotation. In addition attempts to isolate the (*S,S*)-isoleucinato based ligand in the absence of Cu(II) failed. Relevant data for the seven useful complexes are summarised in Table 1. In general these were obtained as green powders or ill-defined solids; only **3a** and **3f** were clearly crystalline displaying melting points ~230 °C (decomp.); the others darkened and slowly decomposed on heating. The quality of the crystals from **3a** allowed a single crystal X-ray structure to be determined (Fig. 1), confirming the expected square planar geometry, and showing this species to exist as a dimer in the solid state with the sp^3 carboxylate oxygen of one

Table 1 Copper(II) amino acid salicylidene Schiff-base monohydrate complexes **3**

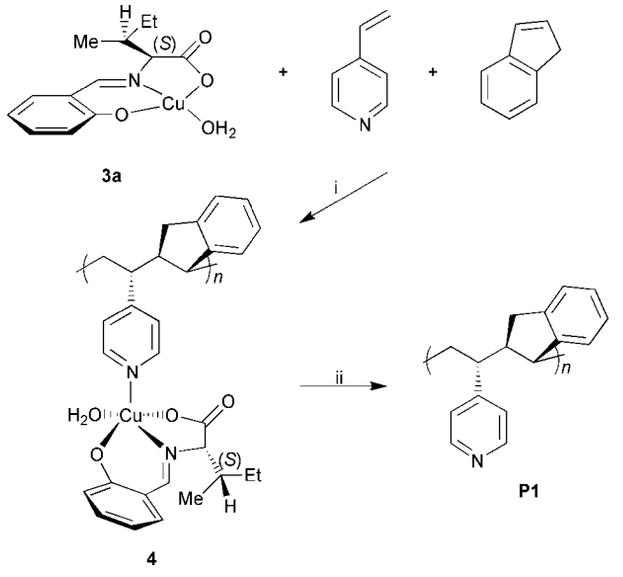
				Specific optical rotation[c], [α]/deg dm^{-1} g^{-1} cm^3			Microanalytical data found (calculated) (%)		
Cu(II) complex (configuration)	R	Yield (%)	Appearance	436 nm	589 nm	Concn (MeOH)/ 10^{-2} g cm^{-3}	C	H	N
3a (*S*)	(*S*)-2-Me-propyl	56	Dark green crystals[b]	−755.6	+126.7	0.018	49.65 (49.6)	5.5 (5.4)	4.4 (4.45)
3b (*S*)	CH_2Ph	42	Pale green powder[a]	−2113.0	+17.4	0.023	57.0 (55.1)	4.2 (4.3)	4.4 (4.0)
3c (*S*)	*tert*-Butyl	73	Dark green powder[a]	−2213.0	+373.0	0.015	49.7 (49.6)	5.4 (5.4)	4.35 (4.45)
3d (*R*)	Phenyl	32	Green solid[a]	+1958.0	−94.7	0.019	50.9 (53.8)	4.0 (3.9)	3.8 (4.2)
3e (*R*)	Isopropyl	51	Pale green powder[a]	+881.8	−181.8	0.011	50.1 (47.9)	4.6 (5.0)	4.9 (4.65)
3f (*S*)	Isopropyl	70	Green needles[b]	−727.8	+185.2	0.018	50.9 (47.9)	4.7 (5.0)	4.8 (4.65)
3g (*S*)	CH_2OH	35	Light green powder[a]	−264.7	+162.3	0.017	39.1 (41.6)	3.75 (3.8)	4.4 (4.85)

[a]Decomposed slowly on heating. [b]Mp 230–231 °C (decomp.). [c]No measurement possible at 365 nm because light absorption too strong.

Table 2 Optical activity data for copolymer–Schiff-base Cu(II) complexes

Cu(II) complex template	Cu(II) complex of copolymer	Specific optical rotation[a], [α]/deg dm^{-1} g^{-1} cm^3 436 nm	589 nm	Concn (MeOH)/10^{-2} g cm^{-3}
3c	**P3**	−1172.4	+286.2	0.029
3f	**P5**	−688.2	+76.5	0.017
3e	**P6**	+568.4	−110.5	0.019
3a	**P9**	−500.0	+55.6	0.018
3a	**P10**	−626.7	+86.7	0.015
3a	**P12**	−455.6	+38.9	0.018
3a	**P13**	−518.2	+81.8	0.011
3a	**P14**	−611.1	+66.7	0.018

[a]Polymer complexes absorb too strongly at 365 nm to allow any measurement.



Scheme 2 Asymmetric free radical copolymerisation of 4-vinylpyridine and indene induced by coordination to a chiral Cu(II) isoleucine Schiff-base complex. *Reagents and conditions*: i) AIBN, MeOH, reflux, N_2; ii) 2 M HCl then NH_3(aq).

molecule coordinating to a fifth axial site on the copper centre of another.

The complexes based on (*S*) amino acids all display a positive Cotton effect (*i.e.* the sign of the optical rotation changes from negative to positive as the wavelength of light increases; 436 nm negative, 589 nm positive). Likewise complexes based on (*R*) amino acids display a negative Cotton effect. All polymer-bound Cu(II) amino acid Schiff-base complexes **4** (see Table 2) exhibit similar Cotton effects to the free complexes.

The complexes **3a**–**g** proved to be insoluble in most organic solvents and water but did dissolve well in methanol. Furthermore when a stoichiometric equivalent of pyridine was added to suspensions of **3a**, **3f** and **3g** in a non-solvent such as dichloromethane, tetrahydrofuran or toluene, then blue-green isotropic solutions formed readily. This is good evidence that pyridine becomes strongly coordinated to the complexes. Furthermore when pyridine was added to methanol solutions of the same complex a colour change from dark green to blue-green occurred. Despite this visual observation little change could be seen in the UV/VIS spectra recorded during this process, suggesting that no major change in geometry of the metal centre occurs when the pyridine molecule is coordinated. All attempts to isolate pyridine complexes for X-ray crystal structure determination failed and so for the time being we do not know whether 4-vinylpyridine displaces a water molecule and occupies a square planar coordination site, or if it coordinates axially to the Cu(II) centre.

Structure **4** in Scheme 2 is therefore drawn so only for illustration, and does not imply a proven square planar arrangement with axially coordinated pyridine.

Copolymerisations involving 4-vinylpyridine complex of 3a

Initial copolymerisations involving 4-vinylpyridine and **3a** proved difficult to work-up, and in particular to achieve full decomplexation and separation of the Cu component from the copolymer. However, an efficient and convenient protocol was developed (see Experimental section). Preliminary experiments exploring maleic anhydride, methyl methacrylate and indene respectively as a comonomer yielded some copolymers with small optical rotations which appeared to decay on leaving solutions to stand. Such effects have been reported before in the case of poly(3-methyl-4-vinylpyridine) prepared as a sense selective helix, where it was proposed that the helical superstructure unfolds in solution.[12] Be this as it may the copolymers involving indene did give consistent and stable optical rotation data and so this system was examined in more detail.

Table 3 4-Vinylpyridine–indene copolymers prepared using different chiral Cu(II) template complexes[a]

Copolymer	Cu(II) template complex	^{1}H NMR composition 4-Vpy : indene[b]	Specific optical rotation[c], [α]/deg dm^{-1} g^{-1} cm^3 436 nm	589 nm	Concn (MeOH)/ 10^{-2} g cm^{-3}	Microanalytical data found (%) C	H	N
P1	**3a**	3 : 1	−4.0	−1.2	0.32	80.4	6.7	10.6
P2	**3b**	11 : 5	−14.5	−3.5	0.31	79.2	6.6	10.0
P3	**3c**	19 : 5	−3.9	−1.9	0.31	77.8	6.6	10.4
P4	**3d**	2 : 1	0	0	0.31	NR[d]	NR	NR
P5	**3f**	3 : 1	−4.2	−2.3	0.31	78.1	6.8	10.1
P6	**3e**	14 : 5	+5.0	+2.4	0.34	81.0	6.1	9.5

[a]See Experimental section for further details. [b]Feed composition: 5 mmol each of template, **3**, 4-Vpy and indene in CH_3OH; $[monomer]_{total}$ = 1.0 M. [c]Light absorption too strong at 365 nm to allow measurement. [d]Not recorded.

Copolymerisations of indene with 4-vinylpyridine complexes of 3a–d, 3f

Copolymerisations of 4-vinylpyridine (4-Vpy) coordinated with **3a**–**d**, **3f** respectively and indene are reported in Table 3. In each polymerisation the mole feed composition 4-Vpy : indene was 1 : 1. The resultant copolymer compositions determined from ^{1}H NMR spectra show a significant enrichment in 4-Vpy residues, typically 4-Vpy : indene being in the range 2 : 1 to 4 : 1. The copolymer structures are therefore far from the idealised 1 : 1 alternation indicated by **2b**, and almost certainly indene residues are separated by random sequences of 4-Vpy residues of varying length. Nevertheless in each case the resultant copolymers, fully decomplexed from the Cu(II) centres, are optically active. This is in contrast to a control copolymer of 4-Vpy and indene prepared similarly but in the absence of Cu(II) complex, which was optically inactive. Another potentially important control is a copolymerisation in the presence of the (*S,S*)-isoleucine salicylaldehyde Schiff-base ligand in the absence of Cu(II). However, attempts to isolate this free ligand proved unsuccessful and we conclude that this rather unstable species cannot alone be responsible for the observed asymmetric induction.

Each of the copolymers (**3a**–**d**, **3f**) prepared in the presence of Cu(II) complexes displays a negative optical rotation (at 589 nm) whereas the Cu(II) complexes from which they are derived, and the corresponding copolymers still complexed to the Cu(II) centres, display positive rotations (Tables 1 and 2). The exception to this is copolymer **P4** derived from **3d** which displays no measurable optical activity. In practice complex **3d** was only sparingly soluble in methanol even in the presence of 4-Vpy, and the polymerisation was at least in part heterogeneous. It is perhaps not surprising therefore that enantiocontrol was disturbed in this case.

Interestingly the optical rotation of the copolymers **P1**–**P6** does not seem to vary greatly with the size (bulkiness) of the substituent on the amino acid residue in the Cu(II) complex employed. This is perhaps not surprising since the rotation will be determined by the number of chiral diads **2b** present in the backbone. While the degree of induction at each asymmetric bond formation step (see mechanism later) may be influenced to some extent by the amino acid substituent, overall the statistical distribution of the diads **2b** will probably be a more important factor in controlling the observed optical rotation, and that this seems to be similar for all the copolymers is not unreasonable.

The effect of varying the mole feed composition in polymerisations was examined using indene and 4-Vpy complexed with **3a**. The data obtained are shown in Table 4. For the series **P1**, **P7**, **P8** and **P11** for a fixed level of **3a** and 4-Vpy each of 5 mmol, the level of indene was increased from 5 to 25 mmol. Despite this, and other variations **P9** and **P10**, the copolymer composition determined from ^{1}H NMR spectra appears to reach a limiting level of 4-Vpy : indene of $\sim$2 : 1. There is some indication that the optical rotation of the resultant copolymers (*e.g.* at 436 and 589 nm) does show a tendency to increase with increase of indene in the feed.

In the case of **P9** and **P10** attempts were also made to produce very low molecular weight polymers by employing high levels of free radical initiator (49 and 24 mass% respectively). It was hoped that telomers might allow more exact molecular structural evaluation of the proposed chiral diads **2b** to be achieved using ^{1}H and ^{13}C NMR spectroscopy. However the copolymers produced seemed superficially to be physically similar to the other samples, and there was no obvious narrowing of the broad resonances generally seen in the ^{1}H NMR spectra. All attempts to secure data on the molecular weight of the copolymers by GPC analysis failed as a result of the strong sorption of the samples to the GPC column packing. Even the use of *m*-cresol as eluent at 120 °C was unsuccessful. Difficulties in securing GPC analysis of 4-Vpy polymers have been recognised already.[12]

The influence of the total monomer concentration in polymerisations was also examined using indene (10 mmol) and 4-Vpy complexed with **3a** (5 mmol) in various volumes of methanol. The results obtained are shown in Table 5. The copolymer composition determined from ^{1}H NMR spectra did show a shift in the mole ratio 4-Vpy : indene of $\sim$3 : 1 at low total monomer concentration to $\sim$2 : 1 at high total monomer concentration despite the comonomer mole ratio being constant.

Finally in this series of copolymers in order to confirm that enantiocontrol is indeed imposed by the configuration of the Cu(II) complex, the effect of using the (*R*) and (*S*) forms of the same Cu(II) template was examined. The (*R*)- and (*S*)-valinato species **3e** and **3f** were exploited in this context. The data obtained, copolymers **P5** and **P6**, are shown in Table 3. The copolymer compositions determined from ^{1}H NMR spectra are very similar. Most importantly the sign of the optical rotation of the two copolymers is different indicating that the induced asymmetry from the (*S*)-valinato complex is the opposite of that from the (*R*)-valinato complex, and that the source of induction is unambiguously the Cu(II) centre in each case.

Copolymerisations of 1,2-dihydronaphthalene and styrene with 4-Vpy complexes of 3a

The results of copolymerisations in which indene was replaced by styrene or 1,2-dihydronaphthalene are shown in Table 6. In the case of the latter comonomer the results are similar to those found using indene and the optical activity of copolymers **P16** and **P17** almost certainly arises from an excess of non-symmetric diads **2b** in the polymer mainchain. Crucially, however, when a non-cyclic analogue of indene and 1,2-dihydronaphthalene, *i.e.* styrene, is the comonomer, the resultant copolymer shows no optical activity and is presumed to lack any net asymmetry. In this instance any asymmetry has to arise from triads **1** (and higher *n*-ads) as argued by Wulff,[1] and the use of the 4-Vpy complex of **3a** alone is not sufficient to control the configuration of two styryl residues. This result tends to confirm the likely mechanism of enantiocontrol in the case of 1,2-disubstituted cyclic and acyclic alkene comonomers (see later).

Copolymerisations of indene with 2-vinylpyridine (2-Vpy) or *N,N*-diallylisopropylamine replacing 4-Vpy

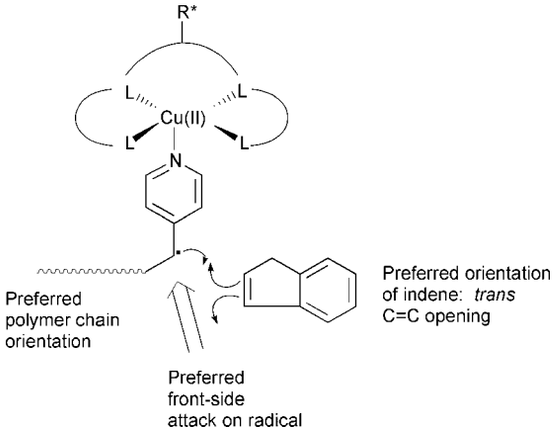
Attempts to copolymerise indene with 2-Vpy or *N,N*-diallylisopropylamine each complexed with **3a** were unsuccessful. No copolymer could be isolated from the various reactions attempted. In the case of the diallylic amine this is perhaps not too surprising since allylic residues tend to undergo favourable H atom abstraction rather than radical addition, and indeed are often free radical polymerisation inhibitors. The exception to this are diallylic ammonium salts in water which do undergo a facile cyclopolymerisation, where the allylic H atoms are believed to be protected by local hydrophobic effects.[13] In principle coordination of the diallylic amine to a Cu(II) centre would also reduce the electron density adjacent to the allyl groups (as does quaternisation) and polymerisation in water might be more successful with this comonomer.

Lack of copolymerisation involving 2-Vpy might arise for two reasons. Firstly if the pyridine N atom does indeed successfully coordinate to the Cu(II) centre of **3a**, the vinyl group on the *ortho* position may simply be too sterically hindered to participate in copolymerisation. A second possibility arises from an early report that Cu^{2+} causes a reduction in the rate of polymerisation of 4-Vpy, but essentially totally inhibits polymerisation of 2-Vpy.[14] Further work is needed to evaluate these possibilities.

Table 4 Effect of mole fraction of indene in feed on 4-Vpy–indene copolymer produced using **3a** as the template

	Polymerisation feed composition/mmol[a]			Copolymer								
						[α]/deg dm^{-1} g^{-1} cm^3				Microanalytical data found (%)		
Copolymer	**3a**	4-Vpy	Indene	Composition[b] 4-Vpy : indene	Yield/g (%)	365 nm	436 nm	589 nm	Concn (MeOH)/ 10^{-2} g cm^{-3}	C	H	N
P1	5	5	5	3 : 1	0.59 (53)	Low E[c]	−4.0	−1.2	0.57	80.4	6.7	10.6
P7	5	5	10	11 : 5	0.59 (35)	−9.6	−5.6	−2.7	0.38	81.0	6.8	9.5
P8	5	5	15	2 : 1	0.44 (24)	−6.8	−5.0	−2.1	0.28	74.6	6.6	7.9
P9[d]	5	5	10	5 : 2	0.42 (25)	−10.3	−7.2	−2.8	0.29	80.0	7.0	9.6
P10[e]	10	10	20	2 : 1	0.99 (27)	Low E[c]	−8.0	−2.7	0.30	80.7	7.0	9.8
P11	5	5	25	2 : 1	0.22 (6)	−10.7	−8.6	−3.9	0.28	81.6	6.7	8.2

[a][monomer]$_{total}$ = 1 M in MeOH. [b]From ^{1}H NMR spectra. [c]Low energy, light absorption too strong. [d]Attempt to prepare oligomer using 5 mmol AIBN (≡49 mass%). [e]Attempt to prepare oligomer using 5 mmol AIBN (≡24 mass%).



Scheme 3 Possible mechanism for asymmetric induction during copolymer formation.

Mechanistic considerations

Indene and 1,2-dihydronaphthalene can be regarded as cyclic structural analogues of styrene. In the present context this gives rise to two major differences. Firstly opening of the C=C bond in the cyclic alkene generates two stereogenic centres and the possibility of forming diads of the form **2b** with a suitable comonomer. Each styrene monomer gives rise to only one stereogenic carbon on polymerisation and hence a triad such as **3** requires *e.g.* two styryl residues with a comonomer residue. Secondly the benzylic radical formed by addition of a propagating radical to the C=C bond in the cyclic alkenes is sterically constrained, since rotation cannot occur about the C–C single bond formed as a result of the addition. Overall the evidence in the literature is that hindered 1,2-disubstituted and cyclic alkenes undergo free radical chain propagation *via* a net *trans* opening of the C=C bond.[15]

Bearing these differences in mind and the experimental observation in the present work that indene and 1,2-dihydronaphthalene give rise to optically active copolymers with 4-Vpy, whereas styrene does not, it is possible to speculate about the origin of the enantioselection. Attack of a primary radical or propagating radical on 4-Vpy will occur at the methylene carbon with the 4-Vpy coordinated to the asymmetric Cu(II) amino acid salicylaldehyde Schiff-base complex to form the 4-Vpy derived free radical on the methine carbon. The latter is likely to be essentially sp^2 hybridised with the orientation of the growing polymer backbone controlled by the asymmetric complex (Scheme 3). Approach of *e.g.* an indene molecule to this radical centre might occur with the indene in a preferred orientation with the approach being to a preferred face of the radical, both of these preferences again being controlled by the asymmetric complex. The configuration of the first stereogenic centre derived from 4-Vpy is therefore defined. Addition of the radical will be to the C2 carbon atom of indene and the addition will be to a defined face of the molecule since the orientation and approach of the indene are both controlled. This effectively determines the configuration of the second stereogenic centre generated at the C2 carbon in indene. The radical so formed resides on the C1 carbon atom (the benzylic position) and further reaction occurs *via* a net *trans* opening of the indene C=C bond hence imposing another specific configuration on the third stereogenic centre formed. The indanyl radical formed can then attack the methylene carbon of another coordinated 4-Vpy molecule and the whole propagation cycle repeats itself, but it may also react with another indene molecule (probably with no stereochemical control). The balance of the possible propagation reactions involving both comonomers will be controlled by the reactivity ratios of the coordinated 4-Vpy and indene. Since the indene composition of copolymers fails to exceed 4-Vpy : indene ≃ 2 : 1 (Table 4), perhaps not surprisingly it seems that the coordi-

Table 5 Effect of total comonomer concentration upon magnitude of optical rotation arising in 4-Vpy–indene copolymers

		Copolymer								
				[α]/deg dm^{-1} g^{-1} cm^3				Microanalytical data found (%)		
Copolymer	Total[a] [comonomer]/ mol dm^{-3}	Composition[b] 4-Vpy : indene	Yield/g (%)	365 nm	436 nm	589 nm	Concn (MeOH)/ 10^{-2} g cm^{-3}	C	H	N
P12	0.25	14 : 5	0.14 (8)	low E[c]	−5.2	−2.1	0.20	80.6	6.8	9.6
P13	0.5	14 : 5	0.51 (30)	low E[c]	−5.5	−3.0	0.20	80.8	6.8	9.6
P7	1.0	11 : 5	0.59 (35)	−9.6	−5.6	−2.7	0.38	81.0	6.8	9.5
P14	2.0	21 : 10	0.58 (34)	low E[c]	−6.7	−2.4	0.38	81.6	6.9	8.9

[a]5 mmol each of **3a** and 4-Vpy, 10 mmol of indene in MeOH. [b]From ^{1}H NMR spectra. [c]Low energy, light absorption too strong.

Table 6 4-Vinylpyridine–styrene and 4-vinylpyridine–1,2-dihydroxynaphthalene copolymers prepared using **3a** as chiral template complex

	Polymerisation feed composition/mmol[a]			Copolymer								
						[α]/deg dm^{-1} g^{-1} cm^3				Microanalytical data found (%)		
Copolymer	4-Vpy	1,2-DHN[c]	Styrene	Composition[b] 4-Vpy : Ar[d]	Yield/g (%)	365 nm	436 nm	589 nm	Concn (MeOH) /10^{-2} g cm^{-3}	C	H	N
P15	5	—	5	2 : 1	0.54 (69)	0	0	0	0.52	76.8	7.0	9.2
P16	5	5	—	12 : 1	0.50 (43)	−3.3	−2.3	−1.3	0.30	73.5	7.4	11.8
P17	5	25	—	3 : 1	0.42 (11)	−27.0	−19.1	−7.0	0.10	79.9	7.2	9.4

[a]5 mmol of **3a** in each. [b]From ^{1}H NMR spectra. [c]1,2-DHN = 1,2-dihydronaphthalene. [d]Ar = 1,2-DHN or styrene residues.

nated 4-Vpy is significantly the more reactive.

Overall, the above sequence of radical additions leads to the control of 3 stereogenic centres leading to diads of the form **2b**; stereochemically randomising (symmetry-inducing) factors arise only when this control is not absolute, and with the statistics of the comonomer segment placements.

When styrene is the comonomer then three monomer residues, *e.g.* one 4-Vpy and two styrene, are required to form a Wulff-type triad, **1**. Attack of a free radical on 4-Vpy coordinated to the asymmetric Cu(II) complex will be as before generating the 4-Vpy derived radical. Approach of a styrene monomer to this radical will again be to one favoured face of the radical controlled by the asymmetric complex. Hence the configuration of the first stereogenic centre (from 4-Vpy) is controlled as before. The orientation of the approach of the styrene monomer may not be as well defined as that of indene since it lacks the larger planar structure of indene. Irrespective of this however attack on the styrene molecule will occur at the methylene carbon atom and does not generate a stereogenic centre. The styrene-derived radical that forms differs from the analogous indanyl one in that free rotation can occur about the new C–C single bond. Consequently no stereochemical control can be communicated from the asymmetric 4-Vpy Cu(II) complex, and the styryl radical will undergo propagation to produce a 50 : 50 mixture of configurations at this stereogenic centre. If this reaction involves another styrene monomer then again any configurational control will be absent. If it involves a 4-Vpy monomer coordinated to the asymmetric Cu(II) complex then the 4-Vpy will undergo stereoselective double bond opening as before to produce the same configuration at the 4-Vpy derived stereogenic centre. Overall therefore the copolymer formed will consist of 4-Vpy segments with a given configuration at the stereogenic centre statistically distributed (according to reactivity ratios) amongst the styryl residues with a 50 : 50 mixture of stereogenic centres. Such a macromolecule will have a plane of symmetry (similar to an isotactic homopolymer of 4-Vpy) and so will be an optically inactive (*meso*) form. Interestingly this mechanism would predict that homopolymerisation of 4-Vpy coordinated to the asymmetric Cu(II) complex would produce an isotactic polymer, and this concept might be worth pursuing as an end in itself. Microtacticity in a methacrylic acid polymer prepared by polymerisation of this monomer coordinated to Co(III) complexes was reported 25 years ago.[16]

A very interesting structural variant relevant to these mechanistic discussions are 1,2-disubstituted acyclic alkenes such as *cis*/*trans* stilbenes and *cis*/*trans* β-methylstyrenes. These offer two prochiral centres as do the cyclic alkenes and are more than likely to undergo a *trans* opening of the C=C double bond. The difference however is that the radical formed may be able to undergo free rotation about the new C–C single bond. If the associated steric barrier is sufficiently high then the situation would be identical to that of the cyclic alkenes. In practice such alkenes do not readily undergo free radical propagation to yield polymers, and so this hypothesis cannot be tested. However, electron deficient 1,2-disubstituted alkenes such as the dialkyl fumarate and maleate esters, and indeed diesters of itaconic acid will copolymerise with suitable vinyl monomers such as styrene.[17] In extending the methodology described here therefore, and our mechanistic understanding, copolymerisation of 4-Vpy with these diesters would be a valuable starting point.

Future prospects

This work has shown quite clearly that coordination of a monomer to a suitable asymmetric metal complex is a viable template-type route to controlling the stereogenicity of carbon atoms in all carbon backbone polymers, and that the synthetic procedure and work-up are relatively straightforward. The 4-Vpy–indene and 4-Vpy–1,2-dihydronaphthalene copolymers reported here are of course very specific and not of general interest. What is required now is to extend the concept to more generally useful monomers *e.g.* methacrylic and acrylic acids, both of which are capable of coordinating to suitable asymmetric metal ion centres. In addition the approach needs modifying to allow control of the configuration of three stereogenic centres in producing Wulff-type triads **1**, and this requires the coordination of at least two monomers to the same asymmetric metal ion centre.

This development also has potential for application in low molecular weight organic synthesis, where radical addition to unsaturated molecules coordinated to asymmetric metal ion centres may offer a novel and facile method of achieving enantioselective addition.

Experimental

Materials

All materials were from commercial sources and were used as supplied except for the following. 1,2-Dihydronaphthalene was distilled under vacuum prior to use. The inhibitors were removed from indene, methyl methacrylate, 2-vinylpyridine, 4-vinylpyridine and styrene by passing each down columns of neutral alumina. Azobisisobutyronitrile (AIBN) was crystallised from a saturated solution in dichloromethane by cooling to −20 °C.

Instrumentation

Specific optical rotations, [α] (in deg dm^{-1} g^{-1} cm^3) were measured when possible at 365, 436 and 589 nm in methanol solutions using a Perkin-Elmer 341 polarimeter and a 1 dm pathlength cell thermostatted at 25 °C. Infra-red (IR) spectra were recorded as thin films on, or Nujol mulls between, NaCl discs using a Nicolet Impact 400-D FTIR instrument. Unless shown to the contrary, ^{1}H NMR spectra were recorded on $CDCl_3$ solutions using a Bruker WM-250 spectrometer. Chemical shift values are quoted relative to the residual solvent

peak ($CHCl_3$, $\delta_H = 7.27$ ppm). Elemental microanalyses were performed by the Microanalytical Service in the Department of Pure and Applied Chemistry (University of Strathclyde) using a Perkin-Elmer CHN 2400 series II Analyser.

Synthesis of Cu(II) amino acid salicylidene Schiff-base complexes 3a–g

These Cu(II) complexes were synthesised as exemplified using **3a**.

***N*-Salicylidene-(*S,S*)-isoleucinatocopper(II) monohydrate, 3a.** A solution of copper(II) acetate (9.98 g, 0.05 mol) in distilled hot (70 °C) water (100 cm^3) was added to a solution of salicylaldehyde (6.61 g, 0.05 mol) and (*S,S*)-(+)-isoleucine (6.56 g, 0.05 mol) in water (100 cm^3) at approximately 60 °C. The solution became dark green immediately and was stirred at 50 °C for 1 hour and then allowed to cool before it was left at room temperature for 16 hours. The green precipitate was filtered off, washed with water, dried in a vacuum oven and recrystallised from aqueous acetic acid (50% v/v) to give dark green crystals (8.8 g, 56%). $[\alpha]_{589}^{25} = +126.7$ ($c = 0.09$, MeOH), decomposed slowly on heating, found (calc. for $C_{13}H_{15}CuNO_3 \cdot H_2O$) (%): C, 49.65 (49.6); H, 5.5 (5.4); N, 4.4 (4.45).

Complexes **3b–g** were synthesised similarly to **3a** and the relevant characterisation data are shown in Table 1.

Single crystals of compound **3a** were grown from aqueous solution and mounted using the oil-drop technique.

Crystal structure determination of 3a‡

Crystal data. $C_{13}H_{17}CuNO_4$, $M = 314.81$, orthorhombic, $a = 12.783(2)$, $b = 28.839(5)$, $c = 7.3919(9)$ Å, $U = 2724.9(7)$ $Å^3$, $T = 123(2)$ K, space group $P2_12_12_1$, $Z = 8$, μ(Mo-Kα) = 1.612 mm^{-1}, 6112 reflections measured, 5339 unique ($R_{int} = 0.0330$) were used in refinement on F^2. The final R_1 (4380 reflections with $I > 2\sigma(I)$) was 0.0375 and the final $wR(F^2)$ was 0.0981 for all reflections and 347 parameters. All reflections were measured with their Freidel mates and analysis of anomalous diffraction gave a Flack parameter of 0.006(17) indicating that the absolute configuration shown is correct. The hydrogen atoms of the water ligands were placed as found in riding modes but all other hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms.

Chiral Cu(II) Schiff-base complex-templated copolymerisations

Generic polymerisation, decomplexation and work-up procedure. The copper Schiff-base complex, 4-vinylpyridine, comonomer and initiator (2 mass% of monomers) were dissolved in methanol and the solution deoxygenated by passing a stream of nitrogen through it for 5 min. The solution was then heated to reflux under a nitrogen atmosphere for 18 h. Once cool, the solvent was evaporated to leave a dark green solid residue which was dissolved in aqueous hydrochloric acid (2 M; 25 cm^3). The pale green aqueous solution was washed with ethyl acetate (2×25 cm^3) then poured into concentrated aqueous ammonia solution (35% w/w; 100 cm^3). The precipitated polymer was collected by filtration and washed with water. Purification was effected by two reprecipitations into concentrated aqueous ammonia solution (35% w/w; 120 cm^3) from solution in aqueous hydrochloric acid (2 M; 25 cm^3) followed by a further reprecipitation into concentrated aqueous ammonia solution (35% w/w; 100 cm^3) from solution in methanol (30 cm^3). The polymer was washed thoroughly with water then dried in a vacuum oven.

Preparation of copolymer P3. As a typical example *N*-salicylidene-(*S*)-*tert*-leucinato Cu(II) monohydrate, **3c**, (1.57 g, 5 mmol), 4-vinylpyridine (0.53 g, 5 mmol) and indene (0.58 g, 5 mmol) were copolymerised in methanol (15 cm^3) as described above using AIBN (22 mg). Yield of **P3** 0.39 g (35.5%). $[\alpha]_{589}^{25} = -19$ ($c = 0.31$, MeOH), found (%): C, 77.8; H, 6.6; N, 10.4. ^{1}H NMR ($CDCl_3$), δ (250 MHz): 0.75–3.25 (a: broad multiplet, backbone C*H*, CH_2 and indenyl CH_2), 6.00–7.30 (b: broad multiplet, pyridine H3 and H5 + indene Ar*H*); 7.85–8.45 (c: broad multiplet, pyridine H2 and H6). Ratio pyridine : indene = c/2 : (b − c)/4 = 19 : 5. $[\alpha]_{589}^{25} = +286.2$ ($c = 0.029$, MeOH) for **P3** still complexed to **3c**.

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‡CCDC reference number 1145/234. See http://www.rsc.org/suppdata/jm/b0/b003007o for crystallographic files in .cif format.