Chiral Polymerization

Transfer of Chirality from (−)-Sparteine Zinc(II) (Meth)acrylate Complexes to the Main Chains of Their (Meth)acrylate Polymer Derivatives**

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Optically active polymers represent a class of materials of importance because of their unique properties and potential application as chiral chromatographic stationary phases, as supports for or ligands in asymmetric catalysts, and as components in nonlinear optical and liquid-crystalline materials. However, vinyl and related polymers that are optically active as a result of the configuration of their main chains, rather than chiral side-chain substituents, are very rare as this requires very special stereoregular symmetries of consecutive repeat units.

In general, symmetry operations are more difficult to recognize in a long polymer chain made up of uniformly repeating units than in low-molecular-weight compounds. Wulff, however, recognized that only one specific sequence of eight possible hexad sequences of a homopolymer of a monosubstituted vinyl monomer is chiral.[1] Not surprisingly it is extremely difficult to control a vinyl polymerization to introduce such a chiral hexad sequence in a polymer backbone. One of the methods proposed by Wulff to reduce this difficulty was to introduce a second repeat unit in the polymer backbone to help break down the overall symmetry. For such copolymers, triad sequences (Figure 1) in which a syndiotactic

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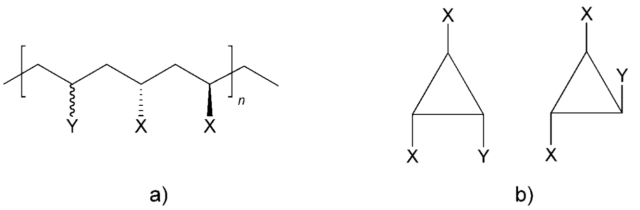


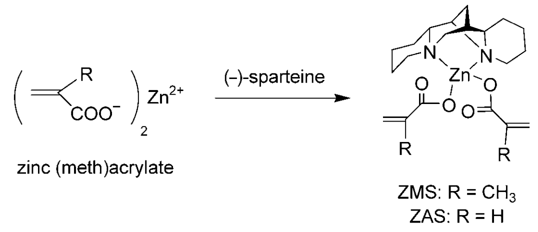
Figure 1. Chiral triad in a linear chain (a) and in a ring structure (b) (see Reference [1]).

(or racemic) diad sequence of one comonomer is spaced apart by a repeat unit of another comonomer would be chiral.[1] Indeed Wulff et al. went on to complete some extremely elegant syntheses that involved the use of covalently bound chiral templates to confirm that his rationalizations were correct.[1,2]

Kakuchi and Obata,[3] Sivaram and co-workers,[4] and Sherrington and co-workers[5] have subsequently used essentially the same synthetic strategy with different templates to confirm the generality of Wulff's approach. In all of these cases, multifunctional vinyl monomers have been covalently bonded to a chiral moiety and then polymerized, followed by cleavage and washing away of the template, to produce main-chain chiral polymers.

Although this strategy has been valuable, the use of covalently bound chiral templates is not particularly convenient nor is it versatile, as, in effect, specifically functionalized monomers need to be synthesized. A more attractive methodology in this context would be one that exploited a noncovalently or more weakly bound chiral template that could be readily synthesized and later easily removed from the polymer product once asymmetry is induced. If in addition such a template could be employed with a routinely available monomer, then the potential for application would be far greater. Preliminary work on this alternative noncovalent approach was carried out by Sherrington and co-workers,[6] who showed that hydrogen bonding and metal coordination also can be exploited in synthesizing carbon–carbon main-chain optically active polymers. However, to date, these approaches have been useful only for a very limited number of monomers and the levels of specific optical rotation that have been reported is limited. Herein, we report the use of metal coordination as the source of weaker interaction between the chiral template and the monomer, with the latter being simply a methacrylate or acrylate anion.

In our search for a new noncovalent or more weakly bound template–monomer system, two chiral (−)-sparteine zinc (meth)acrylate complexes ZMS and ZAS (Scheme 1) were prepared by mixing a solution of (−)-sparteine in methanol with commercially available zinc(II) methacrylate or zinc(II) acrylate (Aldrich), respectively, in chloroform. Addition of cold diethyl ether to the mixtures led to crystallization of the products. The structures of the white crystalline products (yields: 82 % ZMS and 92 % ZAS) were deduced by elemental microanalysis, FTIR and ^{1}H and ^{13}C NMR spectroscopy, single-crystal X-ray crystallography (Figure 2), and polarimetry (Table 1). The specific rotations of ZAS proved to be 6–8-times higher than those of ZMS (Table 1). The solution copolymerization of each complex with styrene (St; Scheme 2) using AIBN as initiator (2 wt % relative to total C=C content) in methanol at 70 °C (oil-bath temperature) under a nitrogen atmosphere for 20 h resulted in the spontaneous precipitation of the polymer products **1a**, **3a**, **5a**, and **7a** (Table 2), which were collected by simple filtration and washed repeatedly with methanol. These copolymers were insoluble in all organic solvents tested, which is perhaps not surprising as both ZMS and ZAS are in effect difunctional monomers and so are likely to yield cross-linked products on (co)polymerization. Surprisingly, however, when dichloroethane (DCE) was used as the polymerization solvent (Table 2), even after 20 h of reaction the reaction mixtures remained homogeneous and the products **2a**, **4a**, **6a**, and **8a** had to be recovered by precipitation in excess methanol. These copolymers were readily resoluble in DCE and chloroform which, together with the absence of any signals from pendent vinyl groups in the ^{1}H NMR and FTIR spectra, is most easily explained in terms of the ZMS and ZAS comonomers undergoing selective cyclopolymerization of



Scheme 1. Synthesis of (−)-sparteine Zn (meth)acrylate complexes, ZMS and ZAS.

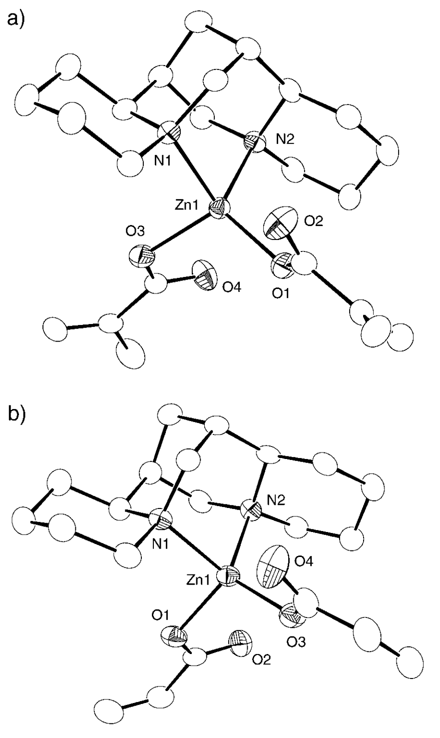
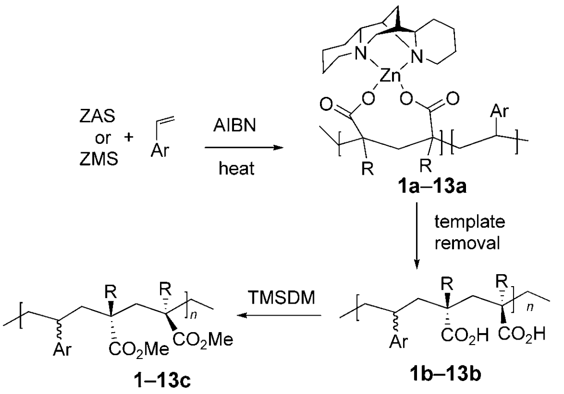


Figure 2. Molecular structures of (−)-sparteine Zn (meth)acrylate complexes a) ZMS and b) ZAS, from single-crystal X-ray diffraction studies.

Table 1: Optical activities of ZMS and ZAS, and their respective copolymers with styrene and 2-vinylnaphthalene.

Sample[a]	Solvent[b]	Specific optical rotation, $[\alpha]^{23}$ [deg dm^{-1} g^{-1} cm^3] $\lambda = 365$ nm	$\lambda = 436$ nm	$\lambda = 589$ nm
ZMS	CH_3OH[c]	−12.0	−9.5	−5.5
ZAS	$CHCl_3$[c]	−98.0	−61.5	−30.5
1b (St-co-MAA)	THF	+0.95	+0.65	+0.20
1c (St-co-MMA)	$CHCl_3$	+1.65	+1.05	+0.40
2a (St-co-ZMS)	$CHCl_3$	−2.95	−2.15	−1.00
2b (St-co-MAA)	THF	+1.25	+0.60	+0.25
2c (St-co-MMA)	$CHCl_3$	+2.70	+0.80	+0.40
3b (St-co-AA)	THF	+1.45	+0.50	+0.00
3c (St-co-MA)	$CHCl_3$	+0.40	+0.20	+0.00
4b (St-co-AA)	THF	+3.10	+1.20	+0.50
4c (St-co-MA)	$CHCl_3$	+1.75	+0.75	+0.00
5b (St-co-AA)	THF	+1.60	+0.75	+0.20
5c (St-co-MA)	$CHCl_3$	+1.65	+0.80	+0.50
6a (St-co-ZAS)	$CHCl_3$	−14.90	−9.80	−5.40
6b (St-co-AA)	THF	+2.40	+1.10	+0.45
6c (St-co-MA)	$CHCl_3$	+1.25	+0.30	+0.10
7b (St-co-AA)	THF	+1.10	+0.50	+0.00
7c (St-co-MA)	$CHCl_3$	+1.40	+0.70	+0.50
8b (St-co-AA)	THF	+2.00	+0.90	+0.30
8c (St-co-MA)	$CHCl_3$	+0.90	+0.25	+0.15
9b (2VN-co-MAA)	THF[d]	+10.80	+4.50	+2.10
10b (2VN-co-MAA)	THF[d]	+8.15	+3.50	+1.40
10c (2VN-co-MMA)	THF[d]	+11.40	+5.80	+2.50
11b (2VN-co-AA)	THF[d]	+24.40	+12.40	+4.60
12b (2VN-co-AA)	THF[d]	+23.00	+11.30	+4.60
12c (2VN-co-MA)	THF[d]	+19.20	+10.00	+3.80
13b (2VN-co-AA)	THF[d]	+12.80	+6.20	+1.70

[a] Copolymer compositions: ZMS = sparteine zinc methacrylate; ZAS = sparteine zinc acrylate; St = styrene; MAA = methacrylic acid; MMA = methyl methacrylate; AA = acrylic acid; MA = methyl acrylate; 2VN = 2-vinylnaphthalene. [b] 0.5–1.5 g/100 mL. [c] 2.0 g/100 mL. [d] 0.25 g/100 mL.



Scheme 2. Ideal cyclopolymerization of chiral zinc (meth)acrylates ZMS (R = Me) and ZAS (R = H) with vinyl arene monomers (Ar) to yield main-chain chiral Ar-MAA and Ar-AA copolymers, followed by methylation of the latter to yield main-chain chiral Ar-MMA and Ar-MA copolymers. AIBN = azobis(isobutyronitrile); TMSDM = (trimethylsilyl)-diazomethane.

their two vinyl groups, as elegantly demonstrated by Wulff with his covalently templated bis-styrylboronate comonomer.[1] Whether or not some ZMS- or ZAS-derived segments are incorporated with insertion of one or more styrene segments between the (meth)acrylate segments is impossible for us to say. However homopolymerization of ZMS in DCE and copolymerization of ZMS with methyl methacrylate in DCE both result in gelation, which suggests that in these two polymerization processes the reaction of the various methacrylate functions is statistical and results in cross-linked products. In contrast, in copolymerizations of ZMS or ZAS with the electron-rich monomer styrene in DCE, the latter plays an important role in generating linear soluble copolymers.

We believe therefore that copolymerization of styrene with ZMS or ZAS in DCE results in the formation of at least some Wulff-type chiral triads (Figure 1; Y = St, X,X = ZMS or ZAS) in the backbone of the resultant copolymers and most likely with some of these triads also present in the copolymers prepared in methanol as well. The workup of **1a**–**8a** (see Table 2 and Supporting Information) destroys the template Zn complex and removes the Zn and (−)-sparteine components to yield the corresponding styrene–(meth)acrylic acid copolymers St-MAA and St-AA (**1b**–**8b**; Scheme 2 and Table 2). This was confirmed by the appearance of the signal for CO_2H and disappearance of the resonances for (−)-sparteine in the ^1H NMR spectrum, by the appearance of a peak for the C=O group of the carboxylic acid in the FTIR spectrum, and by the absence of nitrogen upon elemental analysis of the products. Copolymers **1b**–**8b** were readily soluble in THF, consistent with the loss of any cross-links arising from removal of bridging Zn centers in ZMS- or ZAS-derived segments. Polarimetric measurements of solutions of copolymers **1b**–**8b** showed small but definite dextrorotatory specific optical rotation (Table 1), in contrast to the levorotatory rotations of (−)-sparteine, ZMS, ZAS, and the unpurified template-containing copolymers **2a** and **6a** (Table 1). Furthermore compounds **2b**, **4b**, **6b**, and **8b**, which were derived respectively from **2a**, **4a**, **6a**, and **8a**, with the latter group prepared as a soluble species in DCE, consistently show a greater specific rotation than **1b**, **3b**, **5b**, and **7b**, which were each derived respectively from **1a**, **3a**, **5a**, and **7a**, with the latter group formed as precipitates in MeOH (Table 2).

Methylation of copolymers **1b**–**8b** using (trimethylsilyl)-diazomethane (TMSDM) in a 1:3 mixture of methanol/THF under nitrogen at room temperature yielded quantitatively the corresponding styrene–methyl (meth)acrylate copolymers St-MMA and St-MA (**1c**–**8c**; Scheme 2). These were isolated by precipitation into hexane and were characterized by microanalyses and also FTIR and ^1H NMR spectroscopy. The specific rotation values of **1c**–**8c** are also dextrorotatory (Table 1). As a control, copolymers were synthesized with styrene using achiral zinc methacrylate or zinc acrylate in methanol. The polymers precipitated from solution as they formed and were decomplexed by stirring with dilute HCl to

Table 2: Copolymerization of ZMS and ZAS with styrene and 2-vinylnaphthalene to yield main-chain chiral (meth)acrylate copolymers.

Monomers (mole ratio)	Copolymerization[a] Solvent	Copolymer	Isolated yield [%]	Solubility	Template-removal method[b]	After template removal Copolymer	Recovery [%]	Solubility	Composition[c]	Copolymer after methylation
ZMS/St 1:2	MeOH[d]	**1a**, precipitate	53	insoluble	A	**1b**	47	THF, DMSO	St/MAA 1.6:1.0	**1c**
	DCE[d]	**2a**, solution	37	DCE, $CHCl_3$	A	**2b**	26	THF, DMSO	St/MAA 1.6:1.0	**2c**
ZAS/St 1:1	MeOH	**3a**, precipitate	32	insoluble	B	**3b**	32	THF, DMSO	St/AA 1.0:1.0	**3c**
	DCE	**4a**, solution	30	DCE,[e] $CHCl_3$[e]	B	**4b**	28	THF, DMSO	St/AA 0.9:1.0	**4c**
ZAS/St 1:2	MeOH	**5a**, precipitate	43	insoluble	B	**5b**	46	THF, DMSO	St/AA 1.4:1.0	**5c**
	DCE	**6a**, solution	33	DCE, $CHCl_3$	B	**6b**	34	THF, DMSO	St/AA 1.3:1.0	**6c**
ZAS/St 1:3	MeOH	**7a**, precipitate	50	insoluble	B	**7b**	49	THF, acetone	St/AA 1.7:1.0	**7c**
	DCE	**8a**, solution	32	DCE, $CHCl_3$	B	**8b**	31	THF, acetone	St/AA 1.8:1.0	**8c**
ZMS/2VN 1:1	DCE	**9a**, solution	45	DCE, $CHCl_3$	B	**9b**	39	THF, acetone	2VN/MAA 1.1:1.0	–
ZMS/2VN 1:2	DCE	**10a**, solution	43	DCE, $CHCl_3$	B	**10b**	45	THF, $CHCl_3$	2VN/MAA 1.5:1.0	**10c**
ZAS/2VN 1:1	DCE	**11a**, solution	40	DCE, $CHCl_3$	B	**11b**	42	THF, DMSO	2VN/AA 1.3:1.0	–
ZAS/2VN 1:2	DCE	**12a**, solution	46	DCE, $CHCl_3$	B	**12b**	47	THF, acetone	2VN/AA 3.0:1.0	**12c**
ZAS/2VN 1:4	DCE	**13a**, solution	46	DCE	B	**13b**	45	THF, $CHCl_3$	2VN/AA 6.0:1.0	–

[a] Conditions: AIBN = 2 wt% of total C=C content, 24 h, 70°C (oil-bath temp), concentration of C=C in solution = 1 M. [b] See Supporting Information. [c] From elemental analysis. [d] 20 h, concentration of C=C in solution = 0.75 M. [e] Partially soluble.

yield St-MAA and St-AA copolymers, both of which exhibited no optical rotation.

The effect of varying the polymerization feed ratio of ZAS/St is also shown in Tables 1 and 2. As the proportion of ZAS in the monomer feed decreases, the optical activity of the resulting St-AA copolymers also decreases. The effect is most obvious in the copolymers prepared in DCE, that is, **4b**, **6b**, and **8b**. Reassuringly, this observation tends to confirm that the degree of induction of chirality into the carbon–carbon main chain of the copolymer is indeed controlled by the chiral ZAS or ZMS complex. Furthermore, analysis of the St-MMA and St-MA copolymers by double-detection (refractive index/light scattering) size-exclusion chromatography (SEC) confirms that the copolymers are indeed macromolecular species with number-average molecular weights, M_n, in the range 15000–50000.

Copolymerization of ZMS and ZAS, respectively, with other monomers were also evaluated, and some remarkable results were attained. Most interestingly, 2-vinylnaphthalene (2VN) was used to prepare copolymers **9a**–**13a**. Removal of the template afforded the corresponding 2VN–(meth)acrylic acid copolymers **9b**–**13b**, and methylation of selected examples of these produced the 2VN–methyl (meth)acrylate copolymers 2VN-MMA and 2VN-MA (**10c** and **12c**; Table 2). These show significantly enhanced values of specific optical rotation (Table 1) which we believe is associated, at least in part, with the increased bulk of the naphthyl group relative to the phenyl group in the analogous styrene copolymers. Also, the rotations of the methacrylate copolymers are lower than those of the corresponding acrylate species, as found with the styrene copolymers. SEC data confirmed the molecular weights of the 2VN-MMA and 2VN-MA copolymers **10c** and **12c** to be indeed in the polymeric range ($M_n \approx 15000$).

Finally, the circular dichroism spectra of some selected chiral carboxylic acid copolymers, namely **2b, 4b, 9b**, and **11b**, all showed the Cotton effect around their maximum absorption in their UV spectra (Figure 3). The styrene-based

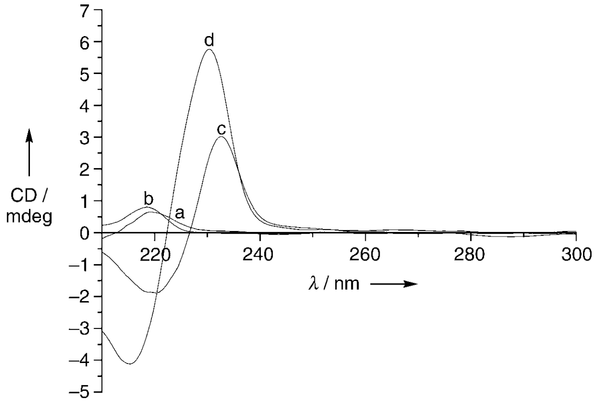


Figure 3. Circular dichroism data of chiral polymers measured in THF solution (1 mg mL^{-1}) using 0.1 mm path-length cuvette cell at room temperature. a) **2b**, b) **4b**, c) **9b**, and d) **11b**.

species **2b** and **4b** showed small but positive Cotton effects around 218 nm, whereas the 2-vinylnaphthalene-based species **9b** and **11b** showed larger, both positive and negative Cotton effects around 230 and 218 nm, respectively. A similar type of behavior was observed earlier by Wulff and Dhal[7] and Kakuchi et al.[8] for their carbon–carbon main-chain copolymers synthesized using covalently linked chiral templates.

In conclusion, a novel methodology has been developed for the synthesis of chiral vinyl polymers in which the chirality is associated only with the configuration of the backbone stereogenic centers. The methodology is somewhat more convenient than those previously reported, as a chiral (−)-sparteine Zn complex is used as an easily cleavable template and the source of asymmetry control, with chirality being transferred to the polymer main chain. If required, the complex can be prepared in situ just prior to polymerization. The method also allows the direct use of methacrylic acid and acrylic acid monomers as their respective anions, with no covalent chemical modification of these required. The liberation of the chiral copolymers from the template therefore involves only decomplexation, and the resulting macromolecules are readily available for further chemical derivatization if required as they are simple methacrylic and acrylic acid copolymers. Overall we believe the facile and core nature of the methodology will provide a convenient and cost-effective source of main-chain optically active vinyl polymers perhaps even in large quantities. The new methodology does, of course, still require a stoichiometric relationship between the chiral ligand and the (meth)acrylate monomers, and the major challenge that remains is to develop a similar templating methodology that is substoichiometric or catalytic in this respect—we are currently considering how this might be achieved.

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