Facile Synthesis of Vinyl Copolymers with Optical Activity Arising from the Configuration of Stereogenic Carbon Atoms in the Main Chain

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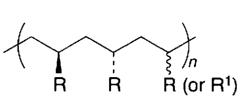
Hydrolytic cleavage of the alkyl chiral auxiliaries from copolymers of diborneyl and dimenthyl fumarates each with styrene, yields optically active vinyl copolymers of fumaric acid and styrene in which the chirality is due to the main chain.

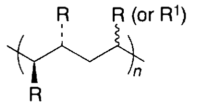
Traditionally, even in the case of isotactic chains, optical activity in vinyl polymers arising from the configuration of sterogenic carbon atoms in the main chain has been discounted as a result of the inherent symmetry in such macromolecules. Wulff, however, argued[1] and subsequently demonstrated[2] that such a source of optical activity is possible providing that appropriate stereogenic centres are suitably distributed along the polymer chain. The simplest symmetry argument involves a regularly repeating triad of stereogenic centres in which the first two are of opposite configuration to each other and the third is randomised or is a completely different structural unit, **I**. Recently Okamoto and Nakano have very elegantly reviewed this and other approaches which have been made in asymmetric polymerizations.[3]

The strategy adopted by Wulff was to use a chiral template in the form of a di-4-vinylphenyl boronate derivative of D-mannitol, and to polymerize this with various achiral vinyl comonomers. To achieve the required triad placement of stereogenic centres, sufficient of the template comonomer must undergo a regio- and enantio-selective cyclopolymerization, with the comonomer as the third member of the triad. Remarkably, this does indeed occur and, following removal of the sidechain chiral template and deboronation of the resultant copolymers, optically active styrene copolymers are obtained. As a route to widely exploitable main-chain optically active vinyl polymers this is not, however, particularly convenient.

It occurred to us that the regular placement of three stereogenic centres in a repeating triad arrangement could be achieved most easily by copolymerization of an electron-deficient 1,2-disubstituted alkene with an electron-rich vinyl monomer to produce the well known 1 : 1 alternating copolymers **II**, *e.g.* in the copolymerization of styrene and maleic anhydride.[4] If the 1,2-disubstituted alkene were to carry bulky chiral auxiliaries, there would be a real possibility of enantio-selective opening of the double bond during copolymerization to yield repeating triads closely analogous to those described by Wulff.[1] Subsequent hydrolytic cleavage of the auxiliaries would yield polymers with optical activity arising from the configuration of the carbon atoms in the main chain. In the course of the present work, Dhal *et al.*[5] reported a closely related strategy (see below).

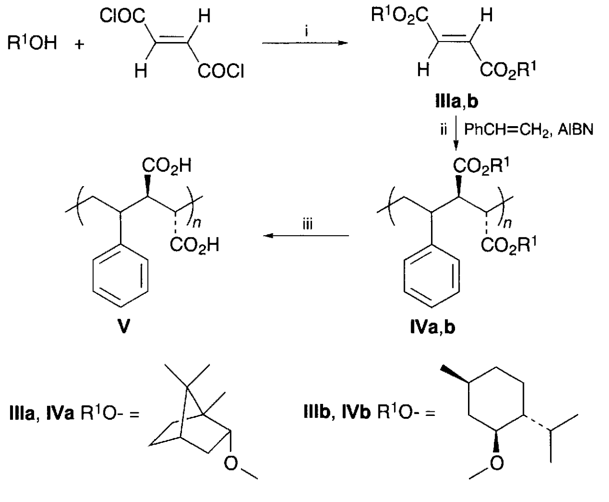


I



II

We have now synthesised the di-[(1*S*)-*endo*]-(−)-borneyl ester **IIIa** and the di-[(1*R*)(1*S*)(5*R*)]-(−)-menthyl ester **IIIb**[6] of fumaric acid (Scheme 1). Each of these have been copolymerized with styrene in a 1 : 1 molar ratio in toluene using azobis(isobutyronitrile) (AIBN) as the free radical source. The copolymers **IVa,b** were isolated as white powders and are soluble in tetrahydrofuran (THF) and chloroform, but insoluble in methanol. ^{1}H NMR analysis of the copolymers (Table 1) shows the ratio of styrene : fumarate residues in the polymers to be *ca.* 2 : 1 so that the structures **IVa,b** are idealised. A number of different batches of each diester were prepared and utilised



Scheme 1 Synthesis of chiral fumarate diesters and their optically active copolymers with styrene. *Reagents and conditions*: toluene reflux, N_2, overnight [yields: **IIIa** = 54%, $[\alpha]_D^{25}$ −52.3; **IIIb** = 58%, $[\alpha]_D^{25}$ −96.3]; ii, see Table 1 footnotes; iii, see text.

Table 1 Synthesis of copolymers derived from styrene and dialkylfumarates

Fumarate[a] diester	Polymerization[b] conditions	Conversion[c] (%)	Copolymers IV Styrene : Fumarate[d]			Copolymers V $[\alpha]_D$[e]
			Styrene : Fumarate[d]	$[\alpha]_D$[e]	M_w[f]	
IIIa	15 h, 80 °C	39	8 : 5	−27.5	17 150	+0.5
IIIa	11 h, 70 °C	20	19 : 10	−27.7	20 600	+1.8
IIIa	3.5 d, 80 °C	59	2 : 1	−29.9	—	+2.7
IIIa	3.5 d, 80 °C	24	3 : 1	−23.6	—	+1.0
IIIa	3.5 d, 80 °C	63	11 : 5	−27.2	—	+1.2
IIIb	7 d, 85 °C	44	13 : 5	−39.2	—	+1.0
IIIb	7 d, 85 °C	42	2 : 1	−45.1	10 650	+0.6
IIIb	15 h, 80 °C	21	9 : 5	−44.1	12 750	+1.3

[a] Different batches of diester in each case. [b] 2.5 mol dm^{-3} toluene solution, styrene : fumarate, 1 : 1, 1% *m*/*m* AIBN; vacuum. [c] Gravimetric. [d] Estimated from ^{1}H NMR spectra, Bruker WM-250. [e] Concentration = 1 g/100 ml THF, 25 °C, Perkin-Elmer 241. [f] GPC data, polystyrene equivalents.

by two of us to assess the level of reproducibility. Each copolymer displays significant *negative* optical rotation in THF solution (Table 1), and the rotations, though reduced in magnitude relative to the respective chiral monomers, are of the same sign as the latter. Though conventional hydrolysis of the esters was unsuccessful, complete cleavage of the chiral auxiliaries (indicated by ^1H and ^{13}C NMR and FTIR spectra) was achieved using powdered KOH and catalytic amounts of 18-crown-6 in refluxing xylene (1–3 d) followed by aqueous work-up. On acidification and isolation the copolymers **V** were again obtained as white powders, now insoluble in chloroform but soluble in THF and methanol. Furthermore, the copolymers **V** displayed *positive* optical rotations (Table 1). Incomplete hydrolysis resulted in copolymers still showing negative rotations. We believe that the original optical rotations of the initial copolymers **IVa,b** reflect a dominant contribution from the chiral auxiliaries present. This contrasts with the opposite optical rotations of the styrene–fumaric acid copolymers **V** which show clear evidence for a residual carbon backbone which is asymmetric as a result of the configurations of its constituent stereogenic centres induced during polymerization. The magnitude of the observed rotations is consistent with other data in the literature.[5,7]

The closely related work reported by Dhal *et al.*[5] generates main-chain asymmetric copolymers *via* hydrolyses of copolymers of achiral maleimides with optically active *p*-formyl styrene derivatives. The latter are not readily available nor are the copolymers themselves easily further exploitable. In contrast, the presently reported syntheses of simple copolymers with intrinsically asymmetric backbones utilise readily available and relatively cheap materials. The procedures are also amenable to scale-up and the carboxylic acid substituent is ideal for further facile modification. Thus, in our hands, exhaustive methylation of **V** with diazomethane generates corresponding copolymers which are again fully soluble in chloroform and whose $[\alpha]_D^{25}$ values typically becomes negative again (*ca.* -2.0 for methylated **V** derived from **IVb**). This, therefore, opens up the opportunity for developing entirely novel materials, *e.g.* chiral side-chain liquid-crystalline polymers where the mesogen itself is achiral and the source of asymmetry is the vinyl polymer backbone. The optically active fumaric acid–styrene copolymers reported here may also be useful as the basis of chromatographic chiral stationary phases, and as chiral ligands in polymer metal complex catalysts.

We acknowledge the receipt of a research assistantship for P. K. and I. H. D. from the EPSRC *via* the Innovative Polymer Synthesis Initiative. We also appreciate the molecular weight determinations carried out by RAPRA.

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