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Increasing Molecular Weight Parameters of a Helical Polymer through Polymerization in a Chiral Solvent

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In this communication, we demonstrate that polymerization in a chiral solvent can affect the molecular weight (MW) distribution of the product by perturbing the balance of helical screw senses of the growing chains. Specifically, for the Wurtz-type synthesis of polymethylphenylsilane (PMPS) in either (*R*) or (*S*)-limonene, the weight-average MW of the product was twice that of PMPS synthesized in (*R/S*)-limonene.

To date, chiral solvents in polymer syntheses have largely been used to influence the tacticity of the polymer.¹ However, a number of polymers adopt helical conformations with alternating *P*- and *M*-screw sense segments of varying lengths. In solution, these are in dynamic equilibrium. Both forms are chiral and optically active, but as there is no enantiomeric excess of either, the polymer solutions are optically inactive.² An imbalance, and hence optical activity, can be induced in this distribution by the incorporation of chiral groups as substituents or constituents of the chain or by the influence of external agents such as complexing molecules or chiral solvents.^{3,4} Manipulation of the enantiomeric balance by chiral solvation during a polymerization process has not been investigated to date.

Polysilanes are most commonly synthesized by the Wurtz-type reductive-coupling of the corresponding dichloro-diorganosilane using Na metal in a high boiling solvent such as toluene (Figure 1a).⁵ Despite having the appearance of a step-growth polymerization, it has been shown to be predominantly a chain reaction. The vast majority of polysilanes adopt helical conformations in solution.⁶ Using PMPS as a model system, it has been demonstrated that the balance of helical screw senses is the main determinant of the chain growth polymerization mechanism,⁷ the termination of chain growth at temperatures higher than 60 °C being consequent on a helical reversal (see Figure 1b) reaching the Na surface. A back-biting reaction then ensues, a low MW cyclosilane is eliminated, the polymer chain detaches from the surface and growth ceases. These processes give rise to an intermediate MW fraction (I_p). Alternatively, adjacent reversals that are further from the sodium surface can meet and mutually annihilate. When helical reversals annihilate within a chain, the probability of continued chain growth is enhanced, ultimately giving rise to a high MW fraction (H_p).

On the basis of the foregoing, it is reasonable to expect that the propagation and termination processes should be directly affected by perturbing the distribution of helical screw senses (and hence helical reversals) by employing a chiral solvent for the polymerization. It has been previously demonstrated for PMPS that dissolution in a chiral solvent induces an enantiomeric excess of one screw sense.⁸ Chiral solvents are expensive and generally unavailable in the quantities needed even for small-to-medium scale polymerizations. However, one exception is limonene, which is suitably inert, is readily available in both enantiomeric forms, and is relatively inexpensive. Thus, polymerizations of dichloromethylphenylsilane (DCMPS) were performed in both (*R*) and (*S*)

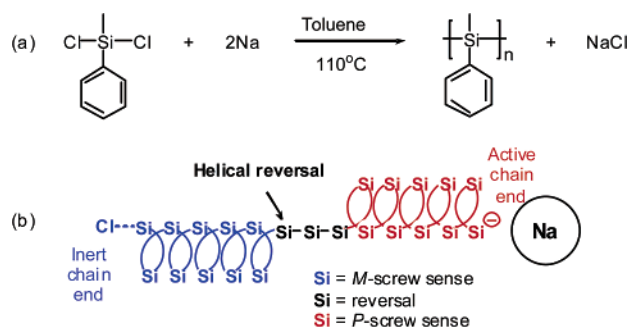


Figure 1. (a) Standard Wurtz-type synthesis of polymethylphenylsilane, and (b) representation of *P* and *M* helices in the growing polymer chain.

Table 1. Average Yields, Molecular Weights, and Polydispersity Indices from the Synthesis of PMPS in Optically Active and Inactive Limonene at Various Temperatures

temp./°C	limonene solvent	yield/%	M_n	M_w	M_w/M_n
70	active	16	1610	24 100	15.5
70	inactive	17	1600	22 000	14.3
80	active	25	1400	50 000	37.0
80	inactive	25	1100	40 800	37.0
90	active	24	1700	80 000	50.2
90	inactive	17	1700	39 200	22.9

enantiomers of limonene and in racemic mixtures of the two enantiomers at 23, 40, 60, 70, 80, and 90 °C. The standard procedure involved reacting a sodium sand with DCMPS in limonene ((*S*)-(–), (*R*)-(+) or (*S/R*)-(±)) under dry $N_{2(g)}$ for 2 h. Quenching of the reactions was achieved by the slow addition of ethanol. The polymerizations were repeated 4–6 times in the optically inactive and 4–8 times in the optically active solvents at each temperature. The data given in Table 1 are averages of these results (full MW parameters for all polymeric products can be found in the Supporting Information, Tables SI 1–5).⁹ The product mixtures were characterized using size-exclusion chromatography and the average MW parameters for the polymerizations conducted at 70, 80, and 90 °C are given in Table 1.^{10,11}

Comparison of the paired (active/inactive) molecular weight parameters of products of the reactions show that as the temperature is raised, higher MW products are favored by conducting the reaction in optically active limonene. More revealing of this trend is the changed profile of the MW distributions over the same temperature range (Figure 2).

Although little difference is observed for the paired products at 70 °C, the MW of the product prepared in optically active limonene is more than twice that obtained in racemic limonene at 90 °C, and this is seen to arise from a redistribution of the intermediate MW fraction (I_p) to the high MW fraction (H_p). At 70 °C, the proportions of H_p and I_p are essentially the same regardless of the optical activity of the limonene. At 90 °C, as evidenced in Figure

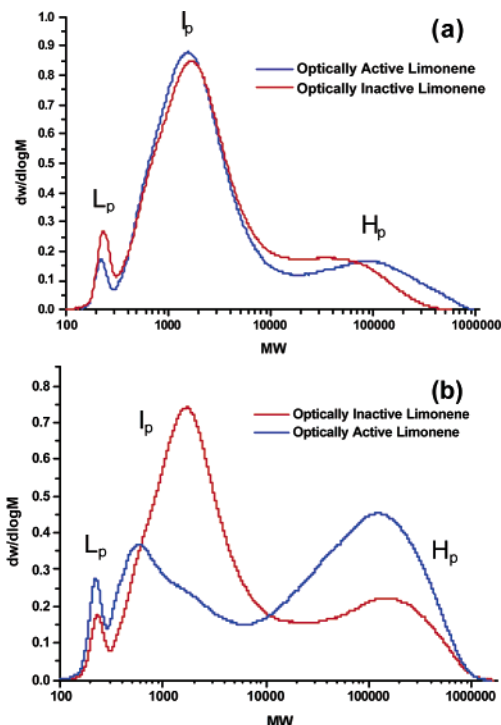


Figure 2. Typical molecular weight distributions obtained for PMPS prepared by Wurtz-type reductive-coupling in optically active and inactive limonene at (a) 70 °C and (b) 90 °C.

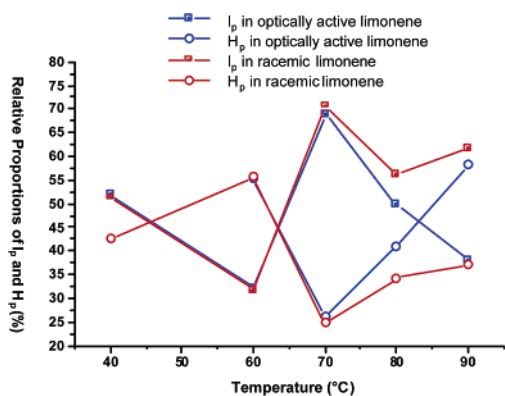


Figure 3. Variation in the relative proportions of intermediate (I_p) and high (H_p) molecular weight fractions of PMPS synthesized in optically active and optically inactive limonene with temperature.¹³

3, there is a dramatic increase in H_p to ~58% for the polymer formed in the chiral solvents, against ~37% for that formed in the racemic mixture solvent.¹²

We believe the increase in the relative fractions of the high MW materials is a direct consequence of the perturbation of the distribution of helices within PMPS dissolved in the optically active solvent. UV-vis analysis of PMPS in the limonenes and THF at room temperature showed a clear increase in conformational order consistent with preferential helix formation, and circular dichroic spectra indicated helical excesses in both the (*R*)- and (*S*)-limonene

(see Supporting Information for typical UV and CD spectra). The mechanism of the Wurtz polymerization developed by McLeish et al. predicts that the probability of termination can be reduced by (i) increasing the rate of interaction between helical reversals, (ii) reducing the reversal diffusion rate, or (iii) reducing the reversal formation rate and thereby the incidence of reversals.⁷ Of these possibilities, it would seem most likely that by inducing an enantiomeric excess of one screw-sense over the other, it is the incidence of the helical reversals that is reduced in chiral solvents.

A full discussion of the results presented here in the context of the polymerization model will be presented in a forthcoming publication.

Acknowledgment. We thank Professor Robert West for fruitful discussions and pointing us in the direction of limonene.

Supporting Information Available: Experimental procedure for polymer synthesis; full tables of MW parameters and fractions for all products (Tables SI 1–5); a plot of M_w vs temperature (Figure SI 1); variation of relative MW fractions with temperature, error bars included (Figure SI 2); UV-vis and CD spectra and data for PMPS in various solvents (Table SI 6, Figures SI 3–5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- There was no significant difference in the MW parameters of the products from the (*R*)- and (*S*)-limonene. Consequently, the average of 4–8 values were used for the purpose of comparison. The results for the racemic limonene polymerizations are averages of 3–4 reactions. A full comparison between the results obtained in (*R*) and (*S*)-limonene will be presented in a forthcoming publication.
- The back-biting mechanism leading to termination only becomes significant above 70 °C. A full discussion of reactions conducted at temperatures below 70 °C will be presented in a forthcoming publication.
- No incorporation of the solvent into the polymer chain or effect on stereoregularity was observed by spectroscopic analysis of the PMPS. The chemical structures and tacticities of the polymers were identical to that observed for previous reported samples of PMPS.
- The % L_p , I_p , and H_p were consistently defined and analysed as MWs <1000 = L_p , between 1000–10 000 = I_p and >10 000 = H_p .
- For clarity, error bars were omitted from Figure 3. See supporting information for comparative plots of I_p and H_p with temperature showing the results of error calculations.

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