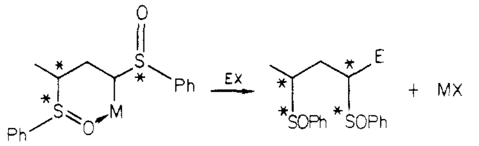
Communications to the Editor

Oligomerization of Vinyl Monomers. 16. Stereoselection and Stereoelection in the Anionic Dimerization of Vinyl Phenyl Sulfoxide

Alkylation and other electrophilic reactions of lithio-α-sulfinyl carbanions have been demonstrated to be generally quite stereoselective.[1] For this reason, the anionic polymerization of vinyl sulfoxides may be of interest. In such a process, the resulting polymer may be expected to be stereoregular for several reasons. First, the stereochemistry of monomer addition is expected to be influenced by the sulfur adjacent to the carbanion. Additional stereochemical control is expected by the chiral carbon and sulfur atoms β and γ to the carbanion, respectively. This is all the more plausible since coordination of metal counterion with the γ-sulfoxide is expected, in analogy with the polymerization of polar monomers such as methacrylates[2] and 2-vinylpyridines,[3] where such coordination has been shown to strongly affect the stereochemistry (eq 1). In addition,



(1)

such a polymerization may be expected to be stereoelective; i.e., it may show a stereochemical correlation between the chirality of the sulfur of the carbanion site and that of the vinyl monomer.[4] We therefore decided to investigate the stereochemistry of anionic polymerization of vinyl phenyl sulfoxide.

$$CH_3CH_2SOPh + \underset{1}{CH_3Li} \rightarrow \underset{2}{CH_3CHLiSOPh} + CH_4 \quad (2)$$

$$2 + CH_2CHLiSOPh \xrightarrow[THF/-78\ °C]{} \underset{3}{CH_3CH(SOPh)CH_2CH(SOPh)Li} \quad (3)$$

$$3 + EX \xrightarrow[THF/-78\ °C]{} \underset{4a,b}{CH_3CH(SOPh)CH_2CH(SOPh)E} + LiX \quad (4)$$

a, E = H; **b**, E = CH_3

Past attempts to polymerize this monomer by anionic initiation have resulted in low yields of polymer (<10%).[5] We have recently carried out the successful anionic polymerization of vinyl phenyl sulfoxide using **2** as initiator in THF at −78 °C. Conversions are generally high (~ 100%). Unfortunately, analysis of stereochemistry of the polymer prepared from racemic monomer is not simple, as there are six possible stereoisomeric dyads in the polymer as opposed to the two (meso and racemic) dyads in the absence of a chiral sulfur. We therefore decided to investigate the stereochemistry of anionic dimerization in order to reduce the stereochemical complexity (eq 3).

Results and Discussion. Dimerization was carried out by the reaction of (*R*)-ethyl phenyl sulfoxide with 1 equiv of methyllithium in THF at −78 °C (eq 2). The resulting carbanion **2** was allowed to react with *rac*-vinyl phenyl sulfoxide (eq 3) by vapor-phase distillation of monomer onto the carbanion to form dimer **3**, which was reacted wtih CH_3OH or CH_3I (eq 4). The resulting dimers **4** were isolated from the oligomer mixture by preparative liquid chromatography. Proton (400 MHz) and carbon-13 (25 MHz) analysis of dimer **4a** indicated the formation of two of the four possible stereoisomers in a ratio of about 4:1. It is clear, therefore, that the addition of the monomer is either highly stereoselective (formation of *RsR* and *RsS* isomers) or highly stereoelective (formation of *RrR* and *RsR* or *RrS* and *RsS* isomers).[6] Analysis of dimer **4b** formed by reaction of optically active (*R*)-**2** with 1 equiv of racemic monomer followed by methylation of **3** (eq 4) indicated the presence of only four of the six possible stereoisomers in a 77:13:7:3 ratio.[7] The major isomer exhibited equivalent methine protons and an ABX_2 pattern for the CH_2 group consistent with meso isomers **6** (*RrsS*) or **7** (*RsrS*). The third most abundant isomer exhibited a simple methylene triplet expected for the racemic dimers **8** (*RrrR*) or **9** (*RssR*). NMR analysis showed the other two isomers to be unsymmetrical. The stereochemistry of the meso compound was determined to be that of **7** by X-ray analysis of a single crystal obtained from an acetone–H_2O mixture (Figure 1).

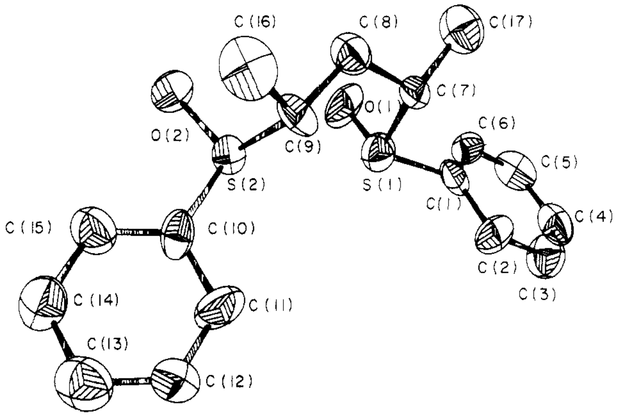
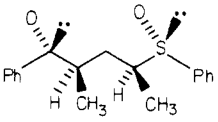
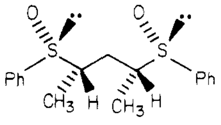


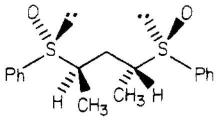
Figure 1. X-ray structure of the *RsrS* (meso) dimer.



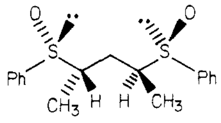
(*RrsS*)-**6**



(*RsrS*)-**7**



(*RrrR*)-**8**



(*RssR*)-**9**

The formation of both *RsrS* and *RssR* (or *RrrR*) isomers suggests that the process is not highly stereoelective. The formation of only two isomers of **4a** indicates, therefore, that the monomer addition is highly stereoselective, consistent with the formation of the *RssR* (racemic) dimer **4a**. The configurations of the other two isomers of **4b** are thus reasonably assigned as *RsrR* (13%) and *RssS* (3%), and the two stereoisomers of **4a** must be *RsS* (major) and *RsR* (minor) (Scheme I).

The observed stereoelection is only apparent as it is based on the stereochemistry of the isolated dimer. Under the conditions of the experiment, the formation of higher oligomers and the possible variation in the enantiomeric excess of the monomer during the reaction should influence the result. The addition reaction was repeated with *rac*-**2**

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Scheme I

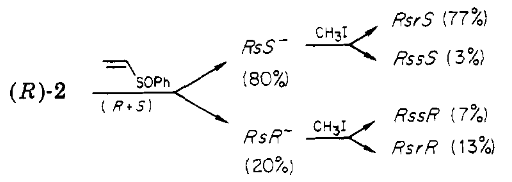

Table I
Stereoelection Observed for the Addition of *rac*-Vinyl Phenyl Sulfoxide to Dimer Anion (*R*)-2

run	[α]$_D$ of 1, deg	[2]/[monomer]	[(*RsS*)-4a]/[(*RsR*)-4a]^a	% dimer^b in oligomer mixture
1	+194	1	4	
2	0	2.0	12	>97
3	0	1.0	12	>90
4	0	1.0	13	>90

[a] Determined as the 25-MHz ^{13}C intensities of the methyl carbon. [b] Computed from areas under the LC trace of the separated oligomers.

as well as racemic monomer under conditions where virtually only dimeric anion was formed ([2]/[monomer] $\geq$ 1). Thus, the observed stereoelection represents the true stereoelectivity of 2 toward the monomer enantiomers. The results (Table I) show that the stereoelectivity under these conditions is about 12/1 in favor of the *R/S* (or *S/R*) addition.

In conclusion, the anionic dimerization of vinyl phenyl sulfoxide according to eq 3 has been demonstrated to occur with very high (>98%) stereoselectivity and high (92%) stereoelectivity. Inspection of Scheme I indicates that methylation of the RsS⁻ dimer anion occurs with considerable stereoselectivity (96%) to produce a carbon of *R* stereochemistry, whereas the corresponding methylation of the RsR⁻ anion is similar but much less stereoselective (65%). Results on the methylation stereochemistry of these anions as well as on the higher oligomers and polymers will be reported in the near future.

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Registry No. (*R*)-**2**, 88180-52-3; (*RsS*)-**4a**, 88180-50-1; (*RsR*)-**4a**, 88243-84-9; (*RsrS*)-**4b**, 88180-51-2; (*RssS*)-**4b**, 88243-85-0; (*RssR*)-**4b**, 88243-86-1; (*RsrR*)-**4b**, 88243-87-2; (±)-CH$_2$=CHS(O)Ph, 88180-53-4.

References and Notes

(1) T. Durst, R. Viau, and M. R. McClory, *J. Am. Chem. Soc.*, **93**, 3077 (1971); T. Durst, R. Viau, R. Vanden Elgen, and C. H. Nguyen, *Chem. Commun.* 1334 (1971); T. Durst, *J. Am. Chem. Soc.*, **91**, 1034 (1969); J. F. Bielmann and J. J. Vicens, *Tetrahedron Lett.*, **34**, 1399 (1978). A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe *J. Am. Chem. Soc.*, **87**, 5498 (1965); R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *ibid.*, **94**, 8795 (1972).

(2) F. A. Bovey, "Polymer Conformation and Configuration", Academic Press, New York, 1969, Chapter 2 and references therein.

(3) S. S. Huang, C. Mathis, and T. E. Hogen-Esch, *Macromolecules*, **14**, 1802 (1981) and references therein.

(4) Stereochemical nomenclature conforms with that used in organic chemistry. Thus, stereoselective addition of monomer to 2 refers to the preferential formation of a chiral carbon in 2 α to sulfur. Stereoelective reactions are defined as those in which a single reactant reacts preferentially with one of two enantiomeric reactants (monomers in this case).

(5) J. E. Mulvaney and R. A. Ottaviani, *J. Polym. Sci., Part A-1*, 8, 2293 (1970); N. Kunieda, M. Kinoshita, and M. Imoto, *J. Polym. Sci., Polym. Lett. Ed.*, **9**, 241 (1971).

(6) The Cahn–Ingold–Prelog convention is used, with upper case letters designating sulfur and lower case letters designating carbon.

(7) Determined by the relative ^{1}H NMR absorptions of the methyl doublets of CD$_3$I methylated **4b**.

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Origin of Fluorescence Emission from Poly(vinyl chloride)

Fluorescence spectroscopy has been used in the study of various aspects of several polymers and the subject has been reviewed.[1,2] Although contradictory papers have been reported[3,7], we now believe that the origin of fluorescence emission from polyolefins such as polyethylene and polypropylene can be attributed to polynuclear aromatic (PNA) impurities that are released into the atmosphere in large quantities from the combustion and pyrolysis of fuels and lubricants.[8,9]

Observation of the fluorescence emission of nondegraded poly(vinyl chloride) has been reported, but it has received little attention and the origin of the chromophoric impurities is still unclear.[1,10]

We have now come to the conclusion that the fluorescence species in nondegraded PVC also involve PNA impurities although the intensity of the fluorescence emission is very weak compared to that of the polyolefins.

All samples were commercial products containing no additives. A powdery sample (ca. 30 g) was extracted with 200 mL of an extrapure grade of hexane (Wako Pure Chemical Co. Ltd., Japan) in a Soxhlet extractor for 24 h and then dried under reduced pressure (1 mmHg) for 12 h. Sample films (ca. 0.07 mm thick) of unextracted and extracted high-density polyethylene (HDPE) and isotactic polypropylene (IPP) were prepared by vacuum pressing (see ref 8). Films of unextracted and extracted poly(vinyl chloride) (PVC) were prepared by casting from 1,2-dichloroethane solution and dried under reduced pressure at ambient temperature for 5 h (see ref 11). Fluorescence spectra were recorded with a Hitachi MPF 2A fluorescence spectrophotometer with a xenon source and photomultiplier at room temperature.

In Figure 1, fluorescence emission (λ_{ex} = 240 nm) and excitation (λ_{em} = 340 nm) spectra of PVC are shown in comparison with that of HDPE and IPP. Although the intensity of the spectra of PVC is much weaker than that of HDPE and IPP, the shape of the spectrum is almost same as that of the polyolefins. It shows excitation maxima at ca. 240 and 295 nm and an emission maximum at ca. 340 nm. The results apparently suggest that the origin of chromophoric species in PVC is analogous to that in the polyolefins.

Thus, a fluorescence emission from PVC film prepared from a powdery sample after hexane extraction was observed. As shown in Figure 2, the fluorescence emission observed in the film prepared from the unextracted PVC sample is not found after hexane extraction. However, the extract (hexane solution) shows a fluorescence emission whose shape is similar to that of the unextracted film. In

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