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mosphere. The crude product was obtained by distillation under a reduced pressure. It was purified carefully by fractional distillation at 58 °C (2 mmHg) [lit.[15] 61 °C (0.3 mmHg)] to give 8.9 g (55 mmol, 83%) of colorless liquid 1: ^{1}H NMR (60-Hz, CCl_4) δ 7.58, 7.17 (4 H, m, phenyl), 6.67 (1 H, 2d, vinyl CH), 5.69, 5.19 (2 H, 2d, J = 11, 18 Hz, vinyl CH_2), 4.40 (1 H, m, SiH), 0.33 (6 H, d, $SiCH_3$).

In order to remove impurities in monomers, benzylmagnesium chloride (5 mL, 0.5 M solution in THF) was added to 1 (5.0 g) at 0 °C under a nitrogen atmosphere, and the mixture was stirred for 10 min. It was then degassed and distilled on the vacuum line into the ampules fitted with breakseals. Thus, 1 distilled from THF solution was obtained and stored at 0 °C until ready for use. Similarly, styrene, α-methylstyrene, and isoprene were purified and stored in the ampules with breakseals.

Polymerization Procedure. All the polymerizations were carried out at −78 °C with shaking under high vacuum conditions ($\sim 10^{-6}$ mmHg) in an all-glass apparatus equipped with breakseals. The polymerization of 1 was usually completed within less than 5 min and was terminated with methyl iodide after 5–10 min of the polymerization. The polymers were precipitated by adding a large excess of methanol. They were redissolved in THF, precipitated into methanol 2 additional times, and freeze-dried.

Block copolymerizations and the treatment of the resulting copolymers were also performed in a similar manner as above.

Determination of Actual Anion Content by Titration. The concentration of 2 was determined by colorimetric titration with the standardized methyl iodide in a sealed reactor through breakseals under vacuum. The operations were conducted by the method as previously reported.[13]

Instruments for Measurements. ^{1}H NMR (60-MHz) spectra were recorded with a JEOL-PMX 60 instrument. Gel permeation chromatograms (GPC) were obtained with a Toyo Soda HLC-802 instrument with UV or refractive index detection, THF being the elution solvent. Vapor-pressure osmometry (VPO) measurements for the number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. IR spectra were run with a Jasco IR-G spectrophotometer.

Registry No. 1, 4556-72-3; 1 (homopolymer), 28851-90-3; (1)(styrene) (block copolymer), 107985-72-8; (1)(isoprene) (block copolymer), 107985-71-7; 4-$H_2C{=}CHC_6H_4MgCl$, 7459-73-6; $(H_3C)_2SiHCl$, 1066-35-9; oligo(α-methylstyryl)dilithium, 57486-16-5; oligo(α-methylstyryl)disodium, 37244-89-6; oligo(α-methylstyryl)dipotassium, 52219-57-5.

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Oligomerization of Vinyl Monomers. 22. Oligomerization and Polymerization of Vinyl Phenyl Sulfoxide via Stereospecific and Stereoelective Vinyl Addition Reactions

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ABSTRACT: The oligomerization and polymerization of racemic and highly optically enriched vinyl phenyl sulfoxide (3) were carried out in THF at −78 °C. Dimer and trimer stereochemistry was consistent with the stereospecific addition of 3 to an ion pair epimer of 1-lithio(phenylsulfinyl)ethane (2) or 1-lithio-1,3-bis(phenylsulfinyl)butane (4), where the stereoelectivity for one enantiomer of 3 over the other was large. The polymerization of racemic 3 resulted in the formation of an apparently atactic polymer. In contrast, the polymerization of highly optically enriched 3 resulted in the formation of an apparently highly stereoregular polymer. These results are shown to be consistent with a process where many chain-end epimers may participate in the polymerization and each epimer undergoes vinyl addition stereospecifically and stereoelectively. However, the formation of a stereoregular polymer from optically active monomer requires that the chirality of the ion pair influence the stereoelectivity.

Introduction

In the anionic polymerization of vinyl monomers of the structure $CH_2C(R)C(Y){=}X$, where X = O or N, Y = O, N, or C and R = H or alkyl stereoregulation is often observed.[1] This has been attributed in some cases to intramolecular chelation of the counterion by the penultimate group[2] as shown in Figure 1 for the case of the living dimer of 2-vinylpyridine. For this reason the polymerization of vinyl sulfoxides is interesting. The sulfur–oxygen bond is strongly polar with a bond moment of 4.76 D[3] and coordinates strongly with metal ions. Furthermore the sulfinyl group is chiral and the reactions of lithio-α-sulfinyl carbanions with electrophiles tend to be stereoselective.[4]

We have prepared oligomers and polymers from vinyl phenyl sulfoxide (3) using 1-lithio-1-(phenylsulfinyl)ethane (2) as the initiator in THF at −78 °C. With extensively purified 3, complete conversion of monomer to polymer was possible.[5] Optically active polymer was prepared from optically active monomer. This was possible since sulfoxides are configurationally stable under neutral and basic conditions.[6] Because 3 is configurationally stable under the polymerization conditions a stereoelective[7] polymerization is possible.

Recently we have reported the formation of the dimer of 3.[8] Stereoelective addition of S_S-3 to R_S-2[9] with the stereoselective formation of an S chiral carbon was ob-

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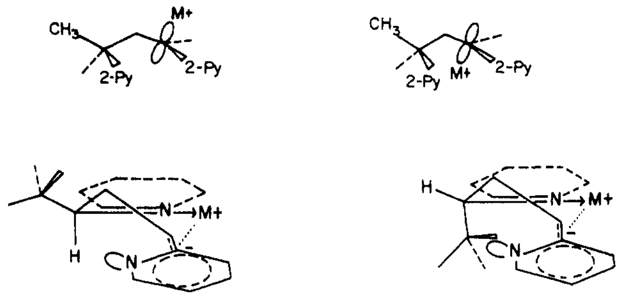


Figure 1. Chelation of an ion pair of the living dimer of 2-vinylpyridine by the penultimate pendant group.

served. The methylation stereochemistry of the resulting dimer carbanion (**4**) was dependent upon the time–temperature profile of the carbanion solution.[10] This was shown to be consistent with the formation of ion pair epimers,[11] similar to that shown in Figure 1, which did not interconvert at −78 °C but did so at higher temperatures and reacted stereospecifically.[10]

This paper reports our findings on the oligomerization and polymerization of **3**. We shall present a model for the addition of **3** to **2**. Trimerization and polymerization will also be discussed with emphasis on the number of stereoisomers or stereoisomeric triads observed. The experimental results for dimerization and trimerization are used to formulate the assumptions used in modeling the polymerization process, those being the kinetics and thermodynamics of the equilibrium between the ion pair epimers of the growing chain and the stereospecificity and stereoelectivity of their reaction with the vinyl monomer. These effects on the apparent stereoregularity of the polymer from racemic and optically active monomer will be considered.

Experimental Section

Tetrahydrofuran was distilled from Na/K alloy with benzophenone as an indicator. Methyllithium, low halide, was purchased from Alpha. Racemic **3** was purchased from Aldrich and purified as previously described.[10] Ethyl phenyl sulfoxide (**1**) and optically active **3** were synthesized and purified as previously described.[10] Methyl phenyl sulfoxide (**9**) was synthesized in an analogous fashion by the reaction of ethyl phenyl sulfinate and methyl magnesium iodide in ether. It was purified by flash chromatography on a 15 × 1 cm column of 400-mesh silica gel by elution with a 3/2 hexane/acetone mixture followed by distillation from CaH_2 at 91–93 °C and at $<1 \times 10^{-2}$ mmHg. The crystalline solid was stored under vacuum and used to prepare a solution in THF. The solution was separated into tubes equipped with break-seals prior to use.

The oligomers were prepared by high-vacuum techniques as previously described.[10] Isolation of the various oligomers was carried out by preparative liquid chromatography. Separation resulted from a programmed elution from 100% hexane to 40% hexane/60% methylene chloride (10% methanol) in 400 min using an Altex Model 110-A chromatograph with a LOBAR "B" LiChroprep Si 60 column. The NMR spectra of the isolated oligomers were recorded on either a Nicolet NT-300 or a JEOL FX100 NMR spectrometer. Optical rotations were measured in acetone using a Randolf Model 70 polarimeter.

Polymerization was carried out in a fashion similar to the oligomerization, with the appropriate **3**/**2** ratio. For instance, a solution of **2** in THF at −78 °C was mixed rapidly with a solution of racemic **3** in THF at −78 °C such that the resulting solution was 5.6×10^{-2} M in **3** and 2.8×10^{-4} in **2**. After the solution was left standing for 12 h, excess 90%-enriched ^{13}C-labeled methyl iodide was distilled through the vacuum line onto the solution. The solvent and unreacted methyl iodide were then removed under high vacuum.

Samples for NMR analysis were prepared by distilling $CDCl_3$ onto the polymer residue, distilling the solvent from the resulting solution, and repeating this process 2 more times. The $CDCl_3$ solution of this polymer residue yielded ^1H or ^{13}C NMR spectra with no signals for THF or methyl iodide. Infrared analysis of the polymer was carried out on a Perkin-Elmer 281 IR spectrometer. The poly(vinyl phenyl sulfoxide) was oxidized to a poly(vinyl sulfone) by stirring for 24 h in a thirtyfold excess of 30% hydrogen peroxide in glacial acetic acid. After filtration the polymer was dried on the vacuum line. The NMR samples for poly(vinyl phenyl sulfone) were prepared in an analogous fashion to those of poly(vinyl phenyl sulfoxide). Infrared spectra were recorded. The optical rotation of optically active polymer was measured in chloroform.

IR (KBr pellet) poly(vinyl phenyl sulfoxide) 3030 m, 2970, w, 2940 w, 1635 m, 1475 m, 1440 s, 1315 w, 1260 w, 1080 s, 1040 vs, 1000 m, 745 s, 685 cm^{-1} s.

IR (KBr pellet) poly(vinyl phenyl sulfone) from racemic sulfoxide 3060 m, 2950 m, 1625 w, 1585 m, 1475 m, 1440 s, 1300 vs, 1130 vs, 1080 vs, 1020 m, 995 m, 930 w, 845 w, 760 m, 740 s, 685 cm^{-1} s.

IR (KBr pellet) poly(vinyl phenyl sulfone) from optically active sulfoxide 3060 m, 2960 m, 1625 w, 1590 m, 1475 m, 1440 s, 1305 vs, 1240 w, 1135 vs, 1090 vs, 1000 m, 930 w, 850 w, 760 m, 740 s, 685 cm^{-1} s.

Results

Oligomerization was carried out by rapidly mixing THF solutions of **3** and **2** at −78 °C (eq 1 and 2). The resulting carbanion solution was divided into two or three portions. Each portion was terminated with different electrophiles (eq 3). The dimer, trimer, and, in some cases, tetramer were isolated by preparative liquid chromatography.[12] Higher oligomers and stereoisomers of a given oligomer were separable in some cases.[13]

$$\underset{\mathbf{1,\ 9}}{\mathrm{RCH_2S(O)Ph}} \xrightarrow{\mathrm{CH_3Li/THF\ -78\ ^\circ C}} \underset{\mathbf{2,\ 10}}{\mathrm{RCHLiS(O)Ph}} + \mathrm{CH_4} \qquad (1)$$

$$\mathbf{2,\ 10} + \underset{\mathbf{3}}{\mathrm{CH_2CHS(O)Ph}} \xrightarrow{\mathrm{THF\ -78\ ^\circ C}} \underset{\mathbf{4,\ 5,\ 11}}{\mathrm{R[CH(S(O)Ph)CH_2]_{\mathit{n}}CH(S(O)Ph)Li}} \qquad (2)$$

$$\mathbf{4,\ 5,\ 11} + \mathrm{EX} \xrightarrow{\mathrm{THF\ -78\ ^\circ C}} \underset{\mathbf{6b,\ 7a,b,\ 8a,b,\ 12a}}{\mathrm{R[CH(S(O)Ph)CH_2]_{\mathit{n}}CH(S(O)Ph)E + LiX}} \qquad (3)$$

for **1, 2, 4, 5, 6, 7, 8** $R = CH_3$ for **9, 10, 11, 12** $R = H$

for **6** $n = 0$ for **4, 7, 11, 12** $n = 1$ for **5, 8** $n = 2$

for **a** $E\text{–}X = H\text{–}OCH_3$

for **b** $E\text{–}X = CH_3\text{–}I,\ ^{13}CH_3\text{–}I$, or $CD_3\text{–}I$

As the molar ratio **3**/**2** and the optical purity of **3** and **2** increased, the proportion of dimer in the resulting mixture decreased.[14] Within the range of **3**/**2** used, **7a** or **7b** was always the major component of the oligomer mixture. It was found to be well in excess of 90 mol % using **3**/**2** = 1, in which case little **1** was isolated upon protonation of the mixture. At a **3**/**2** ratio of two, tetramer and pentamer constituted a much larger portion of the oligomerization mixture than did trimer. Thus dimerization is very rapid relative to the formation of trimer which, in turn, is slow relative to the formation of tetramer and higher oligomers.

Dimerization. The methylation of **2** with CD_3I gave two diastereomers of **6b** in a ratio of 1.5 independently of the time–temperature profile of the carbanion solution. In contrast, the addition of **3** to **2** occurred with only the formation of an *S* methine carbon α to an *R* sulfur within the detection limits of our analysis.[15] As the ion pair of **2** should exist in two epimeric forms (Figure 2), these observations would be consistent with two equilibrating

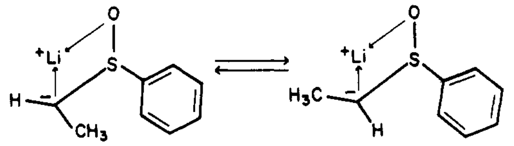


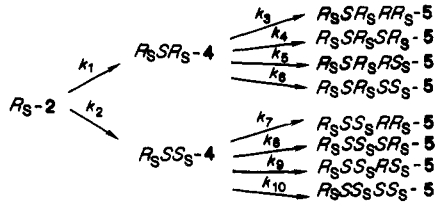
Figure 2. Diastereomeric ion pair epimers of 1-lithio-1-(phenylsulfinyl)ethane.

Table I
Protonated Dimers Isolated for Various Compositions of 2 and 3[a]

run	$[\alpha]^{25}_D$ 1	3	3/2	R_SSS_S-7a/ R_SSR_S-7a
1	+194	0	1.0	4
2	+194	0	2.2	12
3	+194	0	3.6	>20
4	0	0	0.5	12
5	0	0	1.0	12
6	0	0	1.0	13
7	0	0	2.2	>20
8	+146	+446	0.56	4
9	+146	+446	1.0	0.36
10	+194	+474	1.0	0.28
11	+194	+474	1.5	0.33

[a] Determined by ^{1}H or ^{13}C NMR spectroscopy in $CDCl_3$ at room temperature.

Scheme I



forms that undergo methylation and vinyl addition stereospecifically. For instance, methylation of the sulfinyl carbanion 4 was previously shown to occur stereospecifically and syn to the cation.[10] In that case the stereoselection was found to be dependent on the 3/2 molar ratio used and the time–temperature profile of the carbanion solution. Since methylation of 2 occurs with very little stereoselectivity, the two ion pair epimers probably interconvert readily with little difference in their rates of methylation. Hence the addition of 3 to 2 appears to occur much more rapidly with one epimer than the other.

The observed R_SSS_S-**7a**/R_SSR_S-**7a** ratio varied with the initial 3/2 ratio and the optical purity of 3 and 2 (Table I). The composition of the isolated dimer reflects both the formation and the consumption of the dimeric carbanion (Scheme I). Thus the true stereoelectivity of dimerization is revealed only when little trimer or higher oligomers are formed from racemic reagents, since kinetic resolution of the reagents would be reflected in the product distribution. This condition was realized for 3/2 molar ratios less than or equal to 1, and a moderately high stereoelectivity of 12 was observed.

The dependence of stereoelectivity on ion pair chirality was investigated by the addition of 3 to lithio(phenylsulfinyl)methane (10),[16] where the epimers are not diastereomeric. In contrast to the case of the addition of 3 to 2, dimerization is not rapid relative to trimerization in this case. Therefore no conditions were found where the ratio R_SS_S-**12a**/R_SR_S-**12a** necessarily reflected the true stereoelection of 3 by 10. However, the stereoelection can be inferred by the kinetic resolution of 10 due to stereoelective dimerization. Thus a mixture of optically active 3 ($[\alpha]^{25}_D$ = +446) and 2 equiv of racemic 10 was protonated, and 9 was isolated by preparative liquid chromatography. No optical activity could be detected for the isolated 9. Apparently little if any stereoelection occurred when 10 was used rather than 2, and it is therefore suggested that ion pair chirality has a strong influence on the stereoelectivity of dimerization.

Table II
Methylation Stereochemistry for Various Compositions of 2 and 3[a]

run	$[\alpha]^{25}_D$ 1	3	3/2	R_SSS_SR-7b/ R_SSS_SS-7b	R_SSR_SR-7b/ R_SSR_SS-7b
1	0	0	0.5	0.48	
2	0	0	1.0	0.55	
3	0	0	2.2	>20	
4	+194	0	1.0	25	1.9
5	+146	+446	0.5	1.0	0.28
6	+146	+446	1.0	1.3	2.6

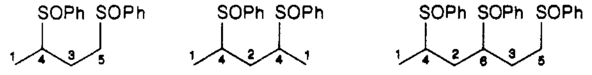
[a] 0.05 M in 2 with addition of methyl iodide 15 min after mixing 2 and 3 at −78 °C in THF.

As reported previously,[10] methylation of 4 yielded up to four diastereomers of **7b** with the relative proportions of these dependent upon the 3/2 ratio, the optical purities of 3 and 2, and the time–temperature profile of the solution. Variation of the time–temperature profile of the carbanion solution resulting from a 3/2 ratio of 1 or less showed that the R_SSS_S-4-*pro-S* and R_SSR_S-4-*pro-S* epimers were favored kinetically and the epimers R_SSS_S-4-*pro-R* and R_SSR_S-4-*pro-R* were favored thermodynamically. When the 3/2 ratio increased to 1, the ratio R_SSS_SR-**7b**/R_SSS_SS-**7b** increased slightly. However, when the 3/2 ratio was 2 or more only R_SSS_SR-**7b** was observed (Table II). Thus it could be concluded that the consumption of ion pair R_SSS_S-4-*pro-S* was faster than R_SSS_S-4-*pro-R*. No evidence of equilibration of the ion pair epimers was observed at −78 °C after the complete consumption of 3, for 3/2 ratios of 1 or less. At a 3/2 ratio of 1, the oligomer mixture was almost all dimer, with an R_SSS_S-**7a**/R_SSR_S-**7a** ratio of 12 after protonation and an R_SSS_SS-**7b**/R_SSS_SR-**7b** ratio of 1.8. Therefore, R_SSS_S-4-*pro-R* was about 33 mol % of the living oligomer mixture (12/13 × 1/2.8 × 100%). At a 3/2 ratio of 2, dimer was in excess of 50 mol % of the oligomer mixture, and the only methylated dimer isolated was R_SSS_S-**7b**. Thus R_SSS_S-4-*pro-R* was more than 50 mol % of the living oligomer mixture. Therefore at least 17% of the total living dimer, or 27% of the R_SSS_S-4-*pro-S* present after the first vinyl addition, was converted to the thermodynamically favored R_SSS_S-4-*pro-R* prior to methylation of the carbanion solution resulting from mixing 2 equiv of 3 with 2. Thus epimerization of R_SSS_S-4-*pro-S* to R_SSS_S-4-*pro-R* is a significant mode of its depletion. To determine whether the R_SSS_S-4-*pro-R*/R_SSS_S-4-*pro-S* ratio was affected by vinyl addition in conjunction with epimerization, trimerization must be examined.

Trimerization. The elucidation of trimer configuration is inherently difficult. Since the addition of 3 to 2 occurs witth absolute stereoselectivity only 8 of the 16 protonated trimers, **8a**, and 12 of the 16 methylated trimers (Figure 3), **8b**, may be formed. None of the trimer stereoisomers is symmetric. Furthermore, trimer is always a minor component of the oligomer mixture. Therefore the determination of trimer stereochemistry may only confirm vinyl addition to any particular ion pair epimer of 4. To rule out the addition of monomer to any epimer of 4 requires the elucidation of all higher oligomers, since the trimer composition is always influenced by its consumption by vinyl addition.

The lack of symmetry of **8a** and **8b** makes identification of the various stereoisomers on the bases of coupling

Table III
^{13}C NMR Chemical Shifts for Dimers and Trimers



isomer	chem shifts,[a] ppm 1	2	3	4	5	6
dimers						
$R_\mathrm{S}SR_\mathrm{S}$-**7a**	10.2		23.0	57.4	52.9	
$R_\mathrm{S}SS_\mathrm{S}$-**7a**	10.0		23.7	57.7	53.5	
$R_\mathrm{S}SR_\mathrm{S}S$-**7b**	10.8	31.8		56.0		
$R_\mathrm{S}SR_\mathrm{S}R$-**7b**	11.2, 14.1	29.7		56.2, 56.4		
$R_\mathrm{S}RR_\mathrm{S}R$-**7b**	12.8	28.0		56.4		
$R_\mathrm{S}SS_\mathrm{S}S$-**7b**	10.6, 13.8	30.6		56.2, 56.4		
$R_\mathrm{S}SS_\mathrm{S}R$-**7b**	10.4	33.0		56.4		
$R_\mathrm{S}RS_\mathrm{S}S$-**7b**	14.0	30.0		56.0		
trimers **8a**						
A	10.4	27.0	21.5	55.4	52.3	59.2
B	10.7	27.4	21.9	55.8	52.8	59.6
C	10.5	27.1	22.1	56.2	51.8	59.9
D	10.4	27.3	23.4	56.7	53.2	60.1
E	10.6	25.8	21.8	55.7	52.7	59.5
F	10.7	26.9	22.5	55.6	52.9	59.8

[a] Relative to $CDCl_3$ = 77.0.

patterns in their ^1H NMR spectra very difficult. Assignment based on the chemical shifts is also very difficult. As seen in Table III, the β-sulfinyl methylene ^{13}C NMR signals of the protonated trimers are shifted upfield relative to those of dimer. This may be due to the shielding of the methylene by the penultimate sulfinyl group in a six-membered ringlike conformation that would not exist for the methylene of **7**. Shielding of the methyls by a penultimate sulfinyl group would occur with dimers as well as with trimers. Because the signals for the methyl groups are consistent for dimer and trimer, the methyl signals may be of use in assigning stereochemistry, particularly where sulfur chirality is known.

From our data a reasonable assignment can be made for the case where highly optically enriched **1** ($[\alpha]^{25}_D$ = +194°) and **3** ($[\alpha]^{25}_D$ = +474°) were used in a 1:1 molar ratio. Only one isomer of **8a** (isomer A of Table III) and two isomers of **8b** were observed. Due to kinetic resolution of **3** by stereoelective dimerization the monomer feed would be nearly pure R_S-**3** before the trimer was formed. Since $R_\mathrm{S}SR_\mathrm{S}$-**4** is more rapidly consumed by monomer addition (Table I), the resulting trimeric anion was probably either $R_\mathrm{S}SR_\mathrm{S}SR_\mathrm{S}$-**5** or $R_\mathrm{S}SR_\mathrm{S}RR_\mathrm{S}$-**5**. The two methylated trimers, **8b**, had methyl ^{13}C NMR signals at 10.4 ppm for the two initiator derived methyls and at 11.0 and 12.9 ppm for the terminal methyls. On the basis of the chemical shifts of the dimers, this would be expected for the methylation products of $R_\mathrm{S}SR_\mathrm{S}SR_\mathrm{S}$-**5** but not for $R_\mathrm{S}SR_\mathrm{S}RR_\mathrm{S}$-**5** (Table IV).

As seen in Table V, only four isomers of **8a** were observed by using racemic reagents. The observation of less than eight possible isomers may occur even if all eight are formed, since the isolated trimer composition reflects the depletion of trimeric carbanion by vinyl addition. However, it would be highly coincidental that no conditions were found under which at least five isomers were observed, particularly since two additional trimers were observed with optically active **3** and **2**.

The formation of only four isomers would be expected if only two ion pair epimers undergo nonstereoelective vinyl addition or if all of the diastereomeric ion pairs of **4** undergo stereoelective vinyl addition. The first of these two possibilities can be ruled out since the two trimers isolated from samples prepared with optically active **3** and **2** were not among the four isolated with racemic reagents (Table V). Therefore it is very likely that all of the ion pair epimers of **4** undergo stereoelective vinyl addition.

Table IV
Expected ^{13}C Chemical Shifts for the Methyl Groups of 8b[a]

8a	8b[c]	chem shift,[b] ppm init	final
A	obsd[d]	10.4	12.9/11.0
$R_\mathrm{S}SR_\mathrm{S}SR_\mathrm{S}$	2/4	10.8	12.8/11.2
$R_\mathrm{S}SR_\mathrm{S}SS_\mathrm{S}$	12/16	10.8	10.6/14.0
$R_\mathrm{S}SR_\mathrm{S}RR_\mathrm{S}$	1/4	11.2	14.1/10.8
$R_\mathrm{S}SR_\mathrm{S}RS_\mathrm{S}$	10/15	11.2	10.4/13.8
$R_\mathrm{S}SS_\mathrm{S}SR_\mathrm{S}$	6/8	10.6	13.8/10.4
$R_\mathrm{S}SS_\mathrm{S}SS_\mathrm{S}$	12/13	10.6	10.8/13.8
$R_\mathrm{S}SS_\mathrm{S}RR_\mathrm{S}$	5/8	10.4	14.1/10.6
$R_\mathrm{S}SS_\mathrm{S}RS_\mathrm{S}$	10/14	10.4	11.2/12.8

[a] The chemical shifts observed for the methyl groups of dimers **7b** that have the same relative configurations as the four chiral centers in closest proximity to the methyl groups of the trimers **8b**. [b] In ppm relative to $CDCl_3$ = 77.0. [c] Number of isomer in Figure 3. [d] Isolated from a methylated aliquot of the same reaction mixture that gave isomer **8a** A upon protonation.

Table V
Protonated Trimers 8a Isolated from Various Compositions of 3 and 2[a]

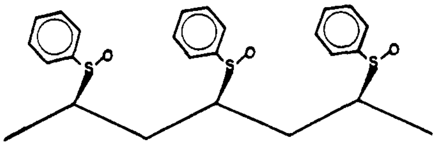
$[\alpha]^{25}_D$ 1	3	3/2	8a
+194	+474	1.0	A
+194	+474	3.0	B
+194	0	2.2	B, C, D
+194	0	3.5	C, D, E
0	0	1.0	D, E, F
0	0	2.0	C, D, F

[a] Isomers of **8a** assigned by their chemical shifts in ^{13}C NMR spectra.

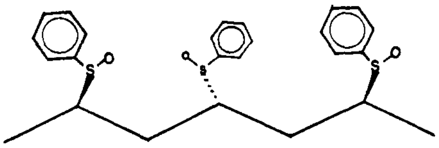
From the dimerization and trimerization results certain phenomena may be expected for the polymerization of **3**. The two epimeric chain ends should interconvert readily.[17] Both should undergo stereoelective vinyl addition stereospecifically. The stereoelection may be influenced by the ion pair chirality. Therefore the stereochemistry of polymerization is of interest under similar conditions to oligomerization.

Polymerization. A solution of racemic **3** in THF and a solution of racemic **2** were mixed at −78 °C such that the

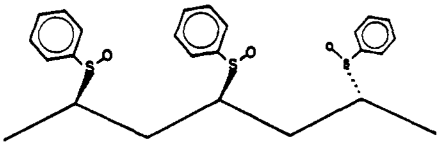
TRIMER TRIADS



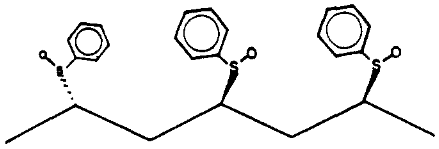
$R_SRR_SR_SS$ ($S_SSS_SS_SR$) mm $R_SSR_SSR_SS$ ($S_SRS_SRS_SR$) [$R_SRR_SRR_SR$ ($S_SSS_SSS_SS$)] 1



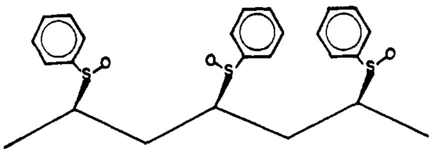
$R_SRR_SR_SS$ ($S_SSS_SS_SR$) rr $R_SSR_SRR_SS$ ($S_SRS_SSS_SR$) [$R_SRR_SSR_SR$ ($S_SSS_SRS_SS$)] 2



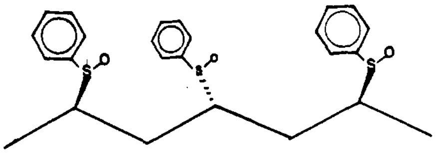
$R_SRR_SR_SR$ ($S_SSS_SS_SS$) mr $R_SSR_SSR_SR$ ($S_SRS_SRS_SS$) [$R_SSR_SRR_SR$ ($S_SRS_SSS_SS$)] 3



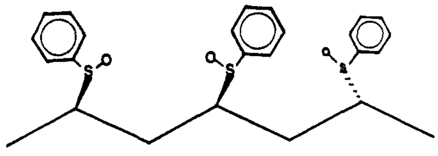
$R_SSR_SR_SS$ ($S_SRS_SS_SR$) rm $R_SRR_SSR_SS$ ($S_SSS_SRS_SR$) [$R_SRR_SRR_SS$ ($S_SSS_SSS_SR$)] 4



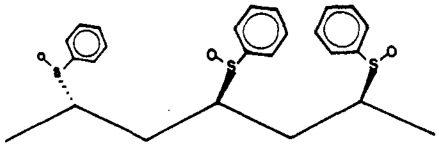
$R_SRS_SR_SS$ ($S_SSR_SS_SR$) mm $R_SSS_SSR_SS$ ($S_SRR_SRS_SR$) [$R_SRS_SRR_SR$ ($S_SSR_SSS_SS$)] 5



$R_SRS_SR_SS$ ($S_SSR_SS_SR$) rr $R_SSS_SRR_SS$ ($S_SRR_SSS_SR$) [$R_SRS_SSR_SR$ ($S_SSR_SRS_SS$)] 6

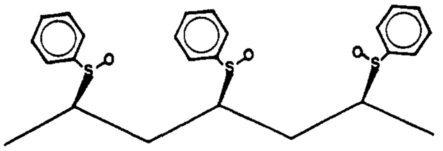


$R_SRS_SR_SR$ ($S_SSR_SS_SS$) mr $R_SSS_SSR_SR$ ($S_SRR_SRS_SS$) [$R_SSS_SRR_SR$ ($S_SRR_SSS_SS$)] 7

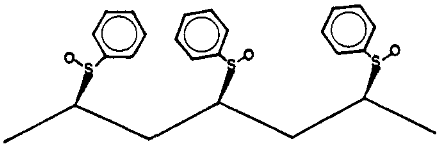


$R_SSS_SR_SS$ ($S_SRR_SS_SR$) rm $R_SRS_SSR_SS$ ($S_SSR_SRS_SR$) [$R_SRS_SRR_SS$ ($S_SSR_SSS_SR$)] 8

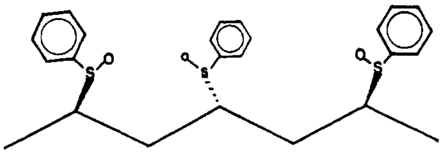
TRIMER TRIADS



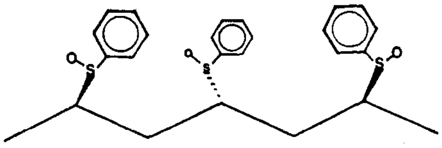
$R_SRR_SS_SS$ ($S_SSS_SR_SR$) mm $R_SSR_SSS_SS$ ($S_SRS_SRR_SR$) [$S_SRR_SRR_SR$ ($R_SSS_SSS_SS$)] 9



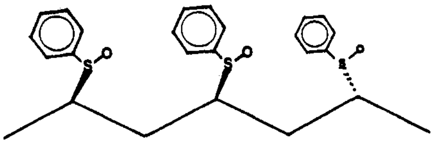
$S_SRR_SR_SS$ ($R_SSS_SS_SR$) mm $S_SSR_SSR_SS$ ($R_SRS_SRS_SR$) [$R_SRR_SRS_SR$ ($S_SSS_SSR_SS$)] 10



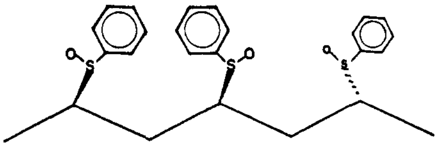
$R_SRR_SS_SS$ ($S_SSS_SR_SR$) rr $R_SSR_SRS_SS$ ($S_SRS_SSR_SR$) [$S_SRR_SSR_SR$ ($R_SSS_SRS_SS$)] 11



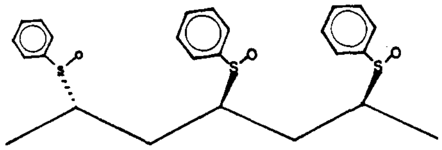
$S_SRR_SR_SS$ ($R_SSS_SS_SR$) rr $S_SSR_SRR_SS$ ($R_SRS_SSS_SR$) [$R_SRR_SSS_SR$ ($S_SSS_SRR_SS$)] 12



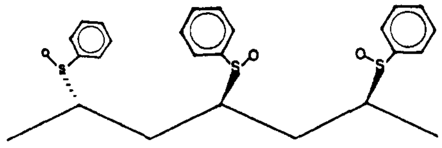
$R_SRR_SS_SR$ ($S_SSS_SR_SS$) mr $R_SSR_SSS_SR$ ($S_SRS_SRR_SS$) [$S_SSR_SRR_SR$ ($R_SRS_SSS_SS$)] 13



$S_SRR_SR_SR$ ($R_SSS_SS_SS$) mr $S_SSR_SSR_SR$ ($R_SRS_SRS_SS$) [$R_SSR_SRS_SR$ ($S_SRS_SSR_SS$)] 14



$S_SSR_SR_SS$ ($R_SRS_SS_SR$) rm $S_SRR_SSR_SS$ ($R_SSS_SRS_SR$) [$R_SRR_SRS_SS$ ($S_SSS_SSR_SR$)] 15



$R_SSR_SS_SS$ ($S_SRS_SR_SR$) rm $R_SRR_SSS_SS$ ($S_SSS_SRR_SR$) [$S_SRR_SRR_SS$ ($R_SSS_SSS_SR$)] 16

Figure 3. Stereoisomeric trimers (**8b**) and polymeric triads. Because methyl groups flank the structures, both ends of the trimers have the same priority and the central carbon is not formally a chiral center. Therefore for a given structure there are five configurations listed for the trimers (to the left of the r,m notation), although there are six configurations listed for the polymeric triads (to the right of the r,m notation). The r,m notation (racemic, meso) indicates the relative configuration of adjacent diads in the carbon backbone of the structure. The triad notation is that for the displayed triad as formed where the polymer chain resides to the left and the sulfinyl carbanion is to the right. The notation in brackets if for the same triad generated where the displayed triad is flanked by the sulfinyl carbanion to the left and the polymer chain to the right. The notation in brackets as read from left to right corresponds to the structure as viewed from right to left. This was done to highlight the fact that all triads may be generated from two diastereomerically different chain ends and is useful when determining the outcome of a polymerization (as in Schemes II-VII). Mirror image isomers are in parentheses.

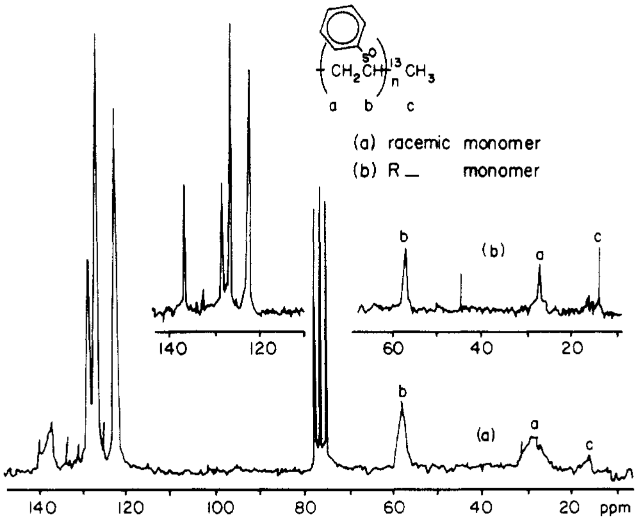


Figure 4. 25-MHz ^{13}C NMR spectra of poly(vinyl phenyl sulfoxide) in $CDCl_3$ at room temperature.

resulting solution was 5.6×10^{-2} M in **3** and 2.8×10^{-4} M in **2**. The yellow polymerization mixture became colorless after the introduction of excess 90%-enriched ^{13}C labeled methyl iodide 12 h later. The ^1H and ^{13}C NMR spectra of the polymer in $CDCl_3$ indicated that all **3** was converted to polymer and that the amount of methyl iodide consumed was within 5% of the **2** charged. Therefore there was little or no chain termination prior to introduction of the methyl iodide.[18] As seen in Figure 4a the methylene region around 30 ppm in the ^{13}C NMR spectrum is broad, suggesting the presence of many types of tetrads. Likewise the quaternary aromatic carbon signal around 140 ppm suggests the presence of many types of triads.

A portion of the polymer was oxidized to poly(vinyl phenyl sulfone). The infrared spectrum of the poly(vinyl phenyl sulfone) indicated a very high conversion of sulfoxide to sulfone. The poly(vinyl phenyl sulfone) was soluble in many polar aprotic solvents. Its ^{13}C NMR spectrum[19] in $CDCl_3$ did not suggest that it was more stereoregular than the poly(vinyl phenyl sulfoxide) from which it was made.

With optically active **3**, ($[\alpha]^{25}_D = +474$), different results were observed. Again all of **3** was converted to polymer and the amount of methyl iodide consumed was within 5% of the **2** charged. However as seen in Figure 4b all signals from the optically active polymer ($[\alpha]^{25}_D = +366$) are considerably sharper than the corresponding ones of the racemic polymer, and it was considerably less soluble in chloroform than the racemic polymer. The poly(vinyl phenyl sulfone) prepared from optically active polymer gave an infrared spectrum almost identical with that of the poly(vinyl phenyl sulfone) prepared from racemic poly(vinyl phenyl sulfoxide). However, the poly(vinyl phenyl sulfone) from optically active poly(vinyl phenyl sulfoxide) was found to be insoluble in all common solvents, consistent with a high degree of stereoregularity. Therefore it appears that a very stereoregular polymer results upon polymerization of optically active **3** but not from racemic **3**.

Discussion

The dimerization and trimerization results were consistent with a stereospecific vinyl addition reaction occurring with a high stereoelectivity. Dimerization stereoelectivity appears to be influenced strongly by ion pair chirality. A model for dimerization must account for the high stereoelection and stereoselection due to the stereospecific addition of **3** to one of the two ion pair epimers of **2**. In addition it must also account for the production of the less stable of the dimeric ion pair epimers, R_SSR_S-**4**-*pro-S* and R_SSS_S-**4**-*pro-S*.

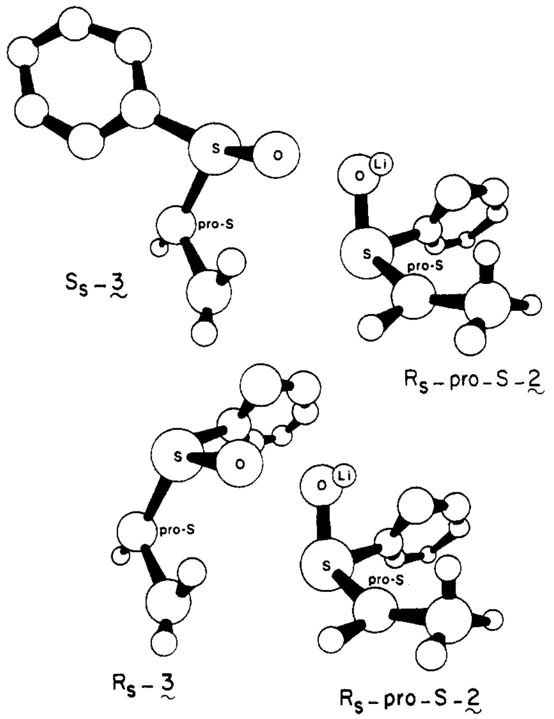


Figure 5. Monomer approach model for the addition of S_S-**3** and R_S-**3** to R_S-**2**-*pro S*.

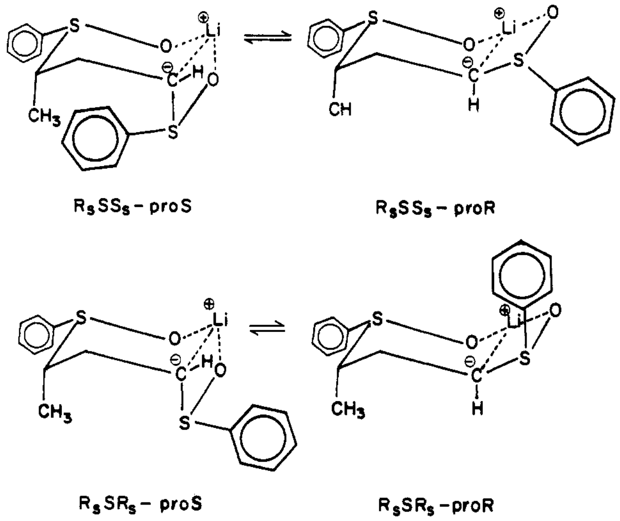
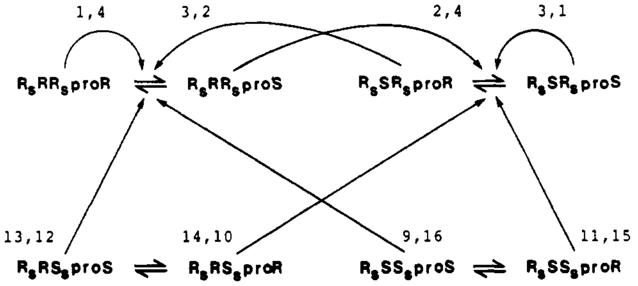


Figure 6. Chelated ion pair epimers of **4**.

Only one model for dimerization could be postulated that was consistent with absolute stereoselection and a moderately high stereoelection leading to the less stable epimers of **4**. As seen in Figure 5, **3** approaches R_S-**2** syn to the cation. The reactive epimer of **2** has the methyl and phenyl groups on the same side of the plane defined by the sulfur, oxygen, lithium, and carbanion carbon. The S–O bond of **3** aligns with the O–Li bond of **2**. This arrangement maximizes electrostatic attraction and aligns the vinyl group such that R_SSR_S-**4**-*pro-S* or R_SSS_S-**4**-*pro-S* is formed if the O–Li bonds are not broken. This results in the direct formation of intramolecularly chelated dimeric carbanions. Because the phenyl group of R_S-**3** interacts with the oxygen of R_S-**2**, its addition is inhibited relative to that of S_S-**3** with R_S-**2**.

Scheme II
$\mathrm{A_SB}R_\mathrm{S}\mathrm{proD}/R_\mathrm{S}$: Case 5 of Table VI



The conversion of $R_\mathrm{S}SR_\mathrm{S}$-4-*pro-S* and $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-S* into $R_\mathrm{S}SR_\mathrm{S}$-4-*pro-R* and $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-R*, respectively, would require the breaking of the intramolecular chelation (Figure 6). The competition between intramolecular chelation and intermolecular chelation with **3** would explain why the ratio of $R_\mathrm{S}SS_\mathrm{S}R$-**7b** to $R_\mathrm{S}SS_\mathrm{S}S$-**7b** increases slightly as **3**/**2** increases to 1 and then increases dramatically as the **3**/**2** ratio exceeds 1. For **3**/**2** ratios less than 1, **3** is rapidly depleted and a considerable amount of $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-S* remains after all **3** has reacted. For **3**/**2** ratios greater than 2 a considerable amount of **3** remains after all of **2** has been consumed. Due to the low rate of trimerization relative to dimerization, intermolecular chelation of **4** by **3** may compete favorably with vinyl addition and a large amount of $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-S* is converted to the more stable $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-R*. The same arguments may be made for the consumption of $R_\mathrm{S}SR_\mathrm{S}$-4-*pro-S*.

Vinyl addition and methylation[10] both appear to occur by reaction syn to the cation. Therefore, since the trimer isolated from the reaction mixture of optically active **3** and **2** was $R_\mathrm{S}SR_\mathrm{S}SR_\mathrm{S}$-**5**, vinyl addition in conjunction with epimerization accounts for the consumption of $R_\mathrm{S}SR_\mathrm{s}$-4-*pro-S*. The same phenomena may be expected for the consumption of $R_\mathrm{S}SS_\mathrm{S}$-4-*pro-S*. Furthermore, the observation of four isomers of **8a** is consistent with all epimers of **4** undergoing stereospecific vinyl addition with a high stereoelectivity. A model for the polymerization process should be consistent with a series of stereospecific and stereoelective vinyl addition reactions.

Therefore we have considered a model for the polymerization with the following features: (1) a given pair of epimers interconverts readily during the polymerization process; (2) both epimers participate in the polymerization; (3) vinyl addition to a given epimer occurs stereospecifically and with very high stereoelectivity. The different mechanistic possibilities one must consider depend upon the number and position of the chiral centers of the growing chain that determine the stereoelectivity. We shall restrict our discussion to the cases where one or three of the last four chiral centers of the growing chain determine the stereoelectivity. The chiral ion pair will be treated as one of these centers. In order to determine the outcome of such polymerization mechanisms, one needs only to consider the four pairs of chain-end epimers, the enantiomer of monomer that is elected by each epimer, and the pair of epimers that results after vinyl addition to each epimer.

When one of the last four chiral centers determines the stereoelection of the polymerization there are eight different possible mechanisms to consider, as each of the four possible chiral centers which may control the stereoelectivity may react with a monomer of like or opposite chirality. Scheme II represents the mechanism where the stereoelection is determined by the chirality of the sulfur α to the carbanion carbon of the growing chain and the chirality of the elected monomer is identical with that of the sulfur electing it. The four pairs of epimers are placed in the four corners of a square. An arrow is drawn from each chain end to the pair of epimers that would result upon stereoelective vinyl addition to that chain end. If all four pairs of epimers are formed upon initiation, there would be 12 different triads that would be fixed at the beginning of the chain upon subsequent vinyl addition to the resulting epimers. These triads are marked as numbers adjacent to the arrows and correspond to the triad structure in Figure 3. Since the stereoelection is for the same configuration of monomer as the chain end sulfur, the two pairs of epimers at the bottom of the scheme could not be regenerated by vinyl addition and would not participate further in the polymerization. Thus, one would require an extremely sensitive technique to observe more than the four triads that would be generated throughout the polymerization. From racemic monomer, two enantiomeric atactic polymers would result. The use of optically pure monomer would result in the preparation of only one of these enantiomeric polymers.

Table VI
Stereoisomeric Triads Formed by One-Center-Controlled Stereoselective Mechanisms

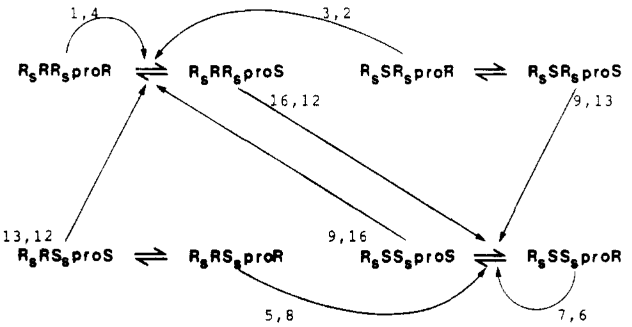
case	mechanism[a]	racemic[b]	opt active[c]	init[d]
1	$R_\mathrm{S}\mathrm{BC_SproD}/R_\mathrm{S}$	1, 2, 3, 4[f] 5, 6, 7, 8	1, 2, 3, 4	
2	$R_\mathrm{S}\mathrm{BC_SproD}/S_\mathrm{S}$	9, 10, 11, 12, 13, 14, 15, 16		
3	$\mathrm{A_S}R\mathrm{C_SproD}/R_\mathrm{S}$	1, 2, 4, 5, 6, 8, 9, 11, 13, 14, 15, 16	(1)[e]	
4	$\mathrm{A_S}R\mathrm{C_SproD}/S_\mathrm{S}$	1, 2, 3, 5, 6, 7, 10, 12, 13, 14, 15, 16	(1)[e]	
5	$\mathrm{A_SB}R_\mathrm{S}\mathrm{proD}/R_\mathrm{S}$	1, 2, 3, 4	1, 2, 3, 4	9, 10, 11, 12, 13, 14, 15, 16
6	$\mathrm{A_SB}R_\mathrm{S}\mathrm{proD}/S_\mathrm{S}$	5, 6, 7, 8		9, 10, 11, 12, 13, 14, 15, 16
7	$\mathrm{A_SBC_S}$*pro-R*/R_S	1, 4, 6, 7, 9, 12, 16	1	2, 3, 5, 8, 13
8	$\mathrm{A_SBC_S}$*pro-R*/S_S	1, 3, 6, 8, 10, 11, 14	1	2, 4, 5, 7, 15

[a] Stereoelection by one of the last four chiral centers of the growing chain for monomer: $\mathrm{A_SBC_SproD/E_S}$ where Cahn–Ingold–Prelog notation is substituted for the controlling center and the enantiomer of monomer it elects (for example, see Schemes II and III. [b] Triads of Figure 3 that may be formed throughout the chain upon polymerization of racemic monomer. [c] Triads of Figure 3 that may form by using optically pure monomer. [d] Additional triads of Figure 3 that may form as the initial triad of the chain using racemic monomer. [e] Although high polymer would not form, isotactic oligomers may be formed in a small amount with triads of structure 1 of Figure 3. [f] Two diastereomeric polymers would form, one that contains triads 1–4 and one that contains triads 5–8.

Table VI summarizes the results one would expect for the eight one-center-controlled mechanisms, where the result of Scheme II is case 5 of this table. The results of polymerization of racemic and optically active **3** are not consistent with one-center control of stereoelectivity by the ultimate (cases 5 and 6), or penultimate (cases 1 and 2), sulfur or with control by the penultimate chiral carbon (cases 3 and 4). In these cases, although many different triads would be expected with racemic monomer, the use of optically pure monomer would not result in a stereoregular polymer. If the chiral ion pair determines the stereoelection (cases 7 and 8), a polymer from racemic monomer should exhibit many different triads and a purely isotactic polymer should result upon the polymerization of optically pure monomer. As seen for case 7 (Scheme

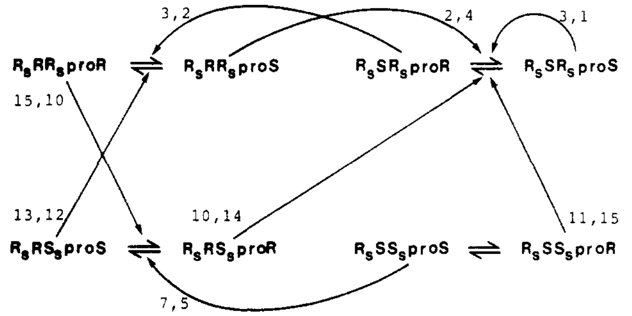
Scheme III

A_SBC_S*pro-R*/R_S: Case 7 of Table VI



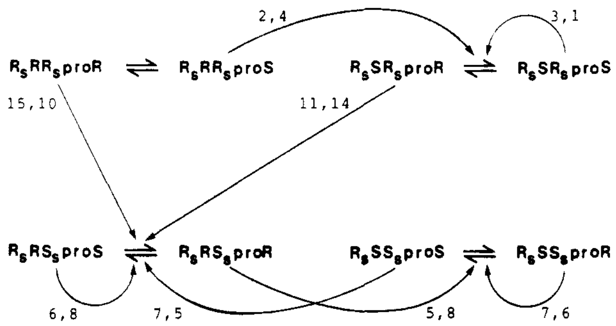
Scheme IV

A_SRR_S*pro-S*/R_S, A_SRR_S*pro-R*/S_S, A_SRS_S*pro-S*/S_S, A_SRS_S*pro-R*/S_S: Case 27 of Table VII



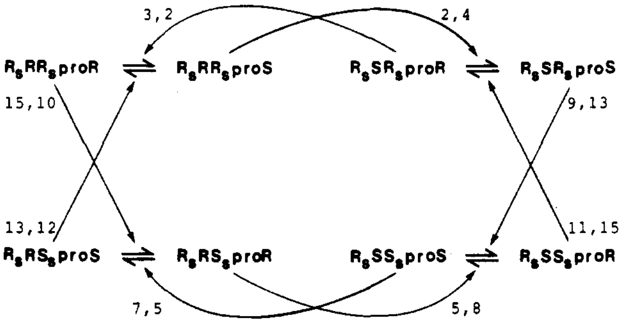
Scheme V

R_SBR_S*pro-R*/S_S, R_SBR_S*pro-S*/R_S, R_SBS_S*pro-R*/R_S, R_SBS_S*pro-S*/R_S: Case 18 of Table VII



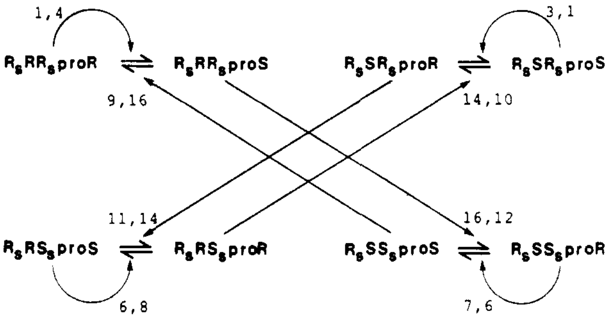
Scheme VI

R_SRC_S*pro-S*/R_S, R_SSC_S*pro-R*/R_S, R_SSC_S*pro-S*/S_S, R_SRC_S*pro-R*/S_S: Case 35 of Table VII



Scheme VII

A_SRR_S*pro-S*/S_S, A_SRS_S*pro-R*/S_S, A_SRS_S*pro-S*/R_S, A_SRR_S*pro-R*/R_S: Case 40 of Table VII



III), in which a *pro-R* ion pair elects an R_S monomer, eight different triads would form with racemic monomer. With pure R_S monomer only the R_SRR_S-*pro-R* and R_SRR_S-*pro-S* chain ends would be present after the second vinyl addition, and only the R_SRR_S-*pro-R* epimer would undergo vinyl addition, resulting in an isotactic polymer.

There are no unique two-center-controlled stereoelective mechanisms. Thus if the last two pendant phenyl sulfinyl groups control the stereoelection, the resulting polymerization is equivalent to control by either the ultimate or the penultimate group. For example, the case in which chain end R_SR_S elects R_S monomer and chain end R_SS_S elects S_S monomer is equivalent to the case where the ultimate pendant phenyl sulfinyl group elects monomer of the same configuration (Scheme II).

There are 40 three-center-controlled mechanisms that are not equivalent to a one-center-controlled mechanism. Four diastereomerically different types of chain ends must be considered to define the stereoelection. Of these unique three-center-controlled mechanisms there are 32 cases (Table VII, 1–32) where three of the four chain ends elect the same enantiomer of monomer, and eight cases (Table VII, 33–40) where two of the four chain ends elect the same enantiomer of monomer. As in the case of the one-center-controlled mechanisms, an influence by the ion pair chirality on the stereoelection is necessary to produce an apparently atactic polymer from racemic monomer and a stereoregular polymer from optically pure monomer.

Where three of the four diastereomerically different chain ends elect the same monomer, an influence by the ion pair chirality is not a sufficient condition to ensure the formation of a stereoregular polymer from optically active monomer. For example, as seen in Scheme IV (case 27 of Table VII) where the ultimate sulfur and the two chiral carbons determine the stereoelectivity, an atactic polymer would form from racemic monomer and a different atactic polymer would result from optically pure monomer. Furthermore, where an isotactic polymer is formed with optically active monomer, an isotactic triad with like sulfur configuration (triad 1 of Figure 3) need not be present in a detectable amount in the atactic polymer from racemic monomer as seen in Scheme V (case 18 of Table VII). This occurs because with racemic monomer the chain-end epimers with the configurations R_SSR_S-*pro-S* and R_SSR_S-*pro-R* would be consumed by addition of S_S monomer to the R_SSR_S-*pro-R* epimer, but there is no means of regenerating this pair of epimers. When optically pure monomer is used in this case, this pair of epimers may not be consumed and only the R_SSR_S-*pro-S* epimer may react, resulting in an isotactic polymer.

Some of the cases in which two of the four diastereomeric chain ends elect the same enantiomer of monomer are worthy of note. Cases 35 and 39 permit the formation of a syndiotactic polymer with optically pure monomer, although many triads are formed in the polymerization of racemic monomer. As seen in Scheme VI (case 35 of Table VII) for this to occur the chain end epimers R_SSR_S and R_SRR_S must generate each other, and due to stereoelection only the epimers R_SSR_S-*pro-R* and R_SRR_S-*pro-S* are reactive with only R_S monomer. Case 40 results in the simultaneous formation of two diastereomerically different polymers during the polymerization of racemic monomer

Table VII
Stereoisomeric Triads Formed by Three-Centered-Controlled Stereoelective Mechanisms

case	mechanism[a]	racemic[b]	opt active[c]	init[d]
1	$R_{\rm S}RR_{\rm S}{\rm proD}/R_{\rm S}$	1, 2, 4, 9, 10, 11, 12, 13, 14, 15, 16	(1)[e]	
2	$R_{\rm S}RR_{\rm S}{\rm proD}/S_{\rm S}$	5, 6, 7, 8	(1)[e]	(1),[f] 2, 3, 10, 12, 15, 16
3	$R_{\rm S}RS_{\rm S}{\rm proD}/R_{\rm S}$	5, 6, 8, 9, 10, 11, 12, 13, 14, 15, 16		
4	$R_{\rm S}RS_{\rm S}{\rm proD}/S_{\rm S}$	1, 2, 3, 4	1, 2, 3, 4	5, (6),[f] 7, 10, 12, 13, 14
5	$R_{\rm S}SR_{\rm S}{\rm proD}/R_{\rm S}$	1, 2, 3, 9, 10, 11, 12, 13, 14, 15, 16		
6	$R_{\rm S}SR_{\rm S}{\rm proD}/S_{\rm S}$	5, 6, 7, 8	(1)[e]	(1),[f] 2, 4, 9, 11, 13, 14
7	$R_{\rm S}SS_{\rm S}{\rm proD}/R_{\rm S}$	5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16		
8	$R_{\rm S}SS_{\rm S}{\rm proD}/S_{\rm S}$	1, 2, 3, 4	1, 2, 3, 4	5, (6),[f] 8, 9, 11, 15, 16
9	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-R}/R_{\rm S}$	1, 4, 5, 8, 9, 11, 12, 13, 14, 15, 16	1	
10	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 2, 3, 4, 6, 8, 10, 14, 15	1, 2, 3, 4	5, 7
11	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-S}/R_{\rm S}$	2, 4, 6, 8, 9, 10, 11, 13, 14, 15, 16		
12	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-S}/S_{\rm S}$	1, 4, 5, 6, 7, 8, 12, 13, 16	1	2, 3
13	$R_{\rm S}S{\rm C}_{\rm S}\textit{pro-R}/R_{\rm S}$	2, 3, 6, 7, 9, 10, 12, 13, 14, 15, 16	1	2, 3
14	$R_{\rm S}S{\rm C}_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 3, 5, 6, 7, 8, 11, 14, 15	1	2, 4
15	$R_{\rm S}S{\rm C}_{\rm S}\textit{pro-S}/R_{\rm S}$	1, 3, 5, 7, 10, 11, 12, 13, 14, 15, 16	1	
16	$R_{\rm S}S{\rm C}_{\rm S}\textit{pro-S}/S_{\rm S}$	1, 2, 3, 4, 6, 7, 9, 13, 16	1, 2, 3, 4	5, 8
17	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-R}/R_{\rm S}$	1, 2, 3, 4, 9, 11, 12, 13, 15, 16	1	10, 14
18	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-R}/S_{\rm S}$	5, 6, 7, 8	1	(1),[f] 2, 3, 4, 10, 11, 14, 15 9, 16
19	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-S}/R_{\rm S}$	1, 2, 3, 4, 10, 11, 12, 13, 14, 15	1	
20	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-S}/S_{\rm S}$	5, 6, 7, 8	1	(1),[f] 2, 3, 4, 9, 12, 13, 16 11, 14
21	$R_{\rm S}{\rm B}S_{\rm S}\textit{pro-R}/R_{\rm S}$	5, 6, 7, 8, 9, 10, 12, 13, 15, 16		
22	$R_{\rm S}{\rm B}S_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 2, 3, 4	1, 2, 3, 4	5, (6),[f] 7, 8, 10, 11, 14, 15 12, 16
23	$R_{\rm S}{\rm B}S_{\rm S}\textit{pro-S}/R_{\rm S}$	5, 6, 7, 8, 9, 10, 11, 13, 14, 15		
24	$R_{\rm S}{\rm B}S_{\rm S}\textit{pro-S}/S_{\rm S}$	1, 2, 3, 4	1, 2, 3, 4	5, 6, 7, 8, 9, 12, 13, 16
25	${\rm A_S}RR_{\rm S}\textit{pro-R}/R_{\rm S}$	1, 4, 6, 7, 9, 12, 16	1	2, 3, 10, 13, 14
26	${\rm A_S}RR_{\rm S}\textit{pro-R}/S_{\rm S}$	5, 6, 7, 8, 9, 11, 13, 14, 15		2, 4, 10
27	${\rm A_S}RR_{\rm S}\textit{pro-S}/R_{\rm S}$	1, 2, 3, 4, 10, 12, 13, 14, 15	1, 2, 3, 4	5, 7, 11
28	${\rm A_S}RR_{\rm S}\textit{pro-S}/S_{\rm S}$	1, 4, 6, 7, 9, 12, 16	1	5, 8, 11, 13, 14
29	${\rm A_S}RS_{\rm S}\textit{pro-R}/R_{\rm S}$	5, 6, 7, 8, 10, 12, 13, 15, 16		2, 3, 9
30	${\rm A_S}RS_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 3, 6, , 10, 11, 14	1	2, 4, 9, 15, 16
31	${\rm A_S}RS_{\rm S}\textit{pro-S}/R_{\rm S}$	1, 3, 6, 8, 10, 11, 14	1	5, 7, 12, 15, 16
32	${\rm A_S}RS_{\rm S}\textit{pro-S}/S_{\rm S}$	1, 2, 3, 4, 9, 11, 13, 15, 16	1, 2, 3, 4	5, 8, 12
33	$R_{\rm S}RS_{\rm S}{\rm proD}/R_{\rm S}$ $R_{\rm S}SR_{\rm S}{\rm proD}/R_{\rm S}$	1, 2, 3, 5, 6, 8, 9, 10, 11, 12, 15, 16	(1)[e]	
34	$R_{\rm S}RS_{\rm S}{\rm proD}/S_{\rm S}$ $R_{\rm S}SR_{\rm S}{\rm proD}/S_{\rm S}$	1, 2, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14	(1)[e]	
35	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-S}/R_{\rm S}$ $R_{\rm S}S{\rm C}_{\rm S}\textit{pro-R}/R_{\rm S}$	2, 3, 4, 6, 7, 8, 9, 10, 13, 14, 15, 16	2	
36	$R_{\rm S}R{\rm C}_{\rm S}\textit{pro-S}/S_{\rm S}$ $R_{\rm S}S{\rm C}_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 3, 4, 5, 7, 8, 11, 12, 13, 14, 15, 16	1	
37	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-S}/R_{\rm S}$ $R_{\rm S}{\rm B}S_{\rm S}\textit{pro-R}/R_{\rm S}$	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16	1	
38	$R_{\rm S}{\rm B}R_{\rm S}\textit{pro-S}/S_{\rm S}$ $R_{\rm S}{\rm B}S_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16	1	
39	${\rm A_S}RR_{\rm S}\textit{pro-S}/R_{\rm S}$ ${\rm A_S}RS_{\rm S}\textit{pro-R}/R_{\rm S}$	2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 1k	2	
40	${\rm A_S}RR_{\rm S}\textit{pro-S}/S_{\rm S}$ ${\rm A_S}RS_{\rm S}\textit{pro-R}/S_{\rm S}$	1, 4, 6, 7, 9, 12, 16[g] 1, 3, 6, 8, 10, 11, 14	1	

[a] Stereoelection by three of the last four chiral centers of the growing chain for monomer: ${\rm A_SBC_SproD/E_S}$ where Cahn–Ingold–Prelog notation is substituted for the controlling centers and the enantiomer of monomer it elects. For the first 32 cases the three diastereomeric combinations of controlling centers to the one listed elect the other enantiomer of monomer. These were generated with the first controlling center listed being common to all four diastereomers (for examples see Schemes IV and V). For the last eight cases the two chains ends diastereomeric to the two listed elect the other enantiomer of monomer (for example, see Schemes VI and VII). [b] Triads of Figure 3 that may be formed throughout the chain upon polymerization of racemic monomer. [c] Triads of Figure 3 that may form by using optically pure monomer. [d] Additional triads of Figure 3 that may form as the initial triad of the chain using racemic monomer. [e] Although high polymer would not form, isotactic oligomers may be formed in a small amount with triads of structure 1 of Figure 3. [f] Two diastereomeric polymers would form, one that contains the triads listed in the first row and one that contains the triads listed in the second. [g] Two diastereomeric polymers would form.

(Scheme VII). Using optically pure monomer again would result in an isotactic polymer.

Finally there are two cases (cases 37 and 38) that permit the formation of all 16 different diastereomeric triads with racemic monomer, yet an isotactic polymer results upon polymerization of optically pure monomer. In these cases the analysis of triad tacticity leads one to conclude that there is little order in this polymer where racemic monomer is used. However there are only 32 tetrads that may be formed in these cases. In contrast, a polymerization that occurs with no stereocontrol could generate 72 diastereomerically different tetrads. Therefore if an analysis of the tetrads could be made, one would conclude that some stereoregulation has occurred.

In conclusion, the polymerization of racemic vinyl phenyl sulfoxide results in the formation of an apparently atactic polymer. In contrast, the polymerization of highly optically enriched monomer yields an apparently stereoregular polymer. This can be explained by a series of stereospecific and stereoelective vinyl additions to the diastereomeric ion pair chain ends, where the ion pair epimers may interconvert freely. Such a polymerization allows one to control the structure of the polymer backbone by control of the optical purity of the monomer.

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Registry No. **2**, 96614-05-0; **3**, 20451-53-0; **3** (homopolymer), 87500-51-4; **3** (dimer), 102848-46-4; **3** (trimer), 102848-47-5.

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(7) Stereochemical nomenclature conforms with that used in organic chemistry. Therefore the stereoselective reaction of **3** with **2** refers to the preferential formation of a chiral methine carbon. It does not indicate whether stereoselectivity results from the reaction of one-face of an achiral carbanion preferentially or if one of two interconverting diastereomeric ion pairs react only syn or anti to the counterion. The latter is a stereospecific reaction. The stereoelective addition of **3** to **2** indicates that one enantiomer of **2** reacts with one enantiomer of **3** preferentially. Thus a reaction may occur with stereoselection and stereoelection.

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(9) The Cahn–Ingold–Prelog convention is used, with subscript S denoting sulfur chirality. The configuration of any oligomer or chain end is listed starting with the initiator fragment. Polymeric triads are listed as if the next sequential pair of chiral centers were that which contain the chiral ion pair. When optically active reagents are used the notation is for the major enantiomer formed. When racemic reagents are used it should be understood that the notation stands for relative configurations with both enantiomers present in equal quantities. In all other cases the notation refers to relative configurations.

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(11) The ion pair α to the sulfinyl group is chiral. These two diastereomeric ion pairs can epimerize to an equilibrium mixture of the two forms. The ion pair chain ends that may interconvert are referred to as a pair of epimers throughout this paper.

(12) The relative integration of ^{1}H NMR signals for the methyl and aromatic protons was used to determine the degree of polymerization of the various oligomers.

(13) For example, the symmetric methylated dimers $R_{\mathrm{S}}SR_{\mathrm{S}}S$-**7b** and $R_{\mathrm{S}}SS_{\mathrm{S}}R$-**7b** cleanly separated from the asymetric dimers $R_{\mathrm{S}}SR_{\mathrm{S}}R$-**7b** and $R_{\mathrm{S}}SS_{\mathrm{S}}S$-**7b**.

(14) The area under the LC trace for trimers was very small relative to that for tetramer, pentamer, and higher oligomers under all conditions.

(15) The poorest signal-to-noise ratio observed was a factor of 20.

(16) In contrast to the intense yellow color of the THF solution of **2**, which diminished in intensity upon addition of an equivalent of **3**, the THF solution of **10** at the same concentration is almost colorless and becomes intensely yellow upon mixing with **3**.

(17) For longer chain lengths the chain should be able to catalyze the interconversion of the epimers also. This is indicated in lithium binding studies with the four diastereomers of **7b** and with **3**: Buese, M. A.; Hogen-Esch, T. E.; Xu, W. Y.; J. Smid, J. *Makromol. Chem.*, in press.

(18) Recent GPC studies of the anionic polymerization of **3** indicate that a high molecular weight polymer with a narrow molecular weight distribution can be formed: Kanga, R.; Hogen-Esch, T. E., unpublished results.

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Macroporous Gels. 2. Polymerization of Trimethylolpropane Trimethacrylate in Various Solvents

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ABSTRACT: Free-radical polymerization of trimethylolpropane trimethacrylate (TRIM) was performed in various solvents. Several of the resulting polymers were found to be macroporous. The BET surface area as well as the amount of unreacted carbon–carbon double bonds of the resulting polymers varied with the solubility parameter of the solvent used as the pore-forming agent. The pore size distribution of poly(TRIM) made in ethyl acetate was found to vary with the polymerization conditions. It differed appreciably from that of poly(TRIM) made in toluene. The small pores showed three maxima, one pronounced at 20 Å and two less pronounced at about 26 and 36 Å, instead of the single one observed from poly(TRIM) made in toluene.

Introduction

Polymeric macroporous systems have different structural properties dependent upon the polymerization conditions.[1]

In a previous paper,[2] the preparation and structure of trimethylolpropane trimethacrylate (TRIM) polymers made with toluene as the pore-forming agent were described. In this paper we shall describe the influence of the solvent's solubility parameter on the pore size distribution and the morphology of poly(TRIM). The solvents used had solubility parameters in the range of 15.1×10^3 $(\mathrm{J/m^3})^{1/2}$ (heptane) to 24.8×10^3 $(\mathrm{J/m^3})^{1/2}$ (benzyl alcohol).

A detailed study was performed of the pore size distributions of poly(TRIM) made in ethyl acetate. The polymers were studied with covered nitrogen adsorption–desorption isotherms (BET and BJH), mercury porosimetry, shrinkage experiments, solid-state ^{13}C NMR spectroscopy, and scanning electron microscopy.

Experimental Section

Polymerization. Trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck

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