

Asymmetric Oxidation of Poly(vinyl Sulfides) with Percamphoric Acid, *Aspergillus niger*, and *Penicillium notatum*

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Synopsis

The asymmetric oxidation of poly(phenylvinyl sulfide) (poly-PhVS) and poly(*t*-butylvinyl sulfide) (poly-*t*-BuVS) was carried out with optically active percamphoric acid, and the optically active polysulfoxides were obtained. The values of the specific rotation for the oxidation products of poly-PhVS and poly-*t*-BuVS were +1.0 (having 56% of sulfoxide unit contents) and +9.1 (49%), respectively. The specific rotation of the product increased with increasing the contents of sulfoxide units. The optical rotatory dispersion curves of the oxidation products of poly-PhVS and poly-*t*-BuVS were positive curves and were found to fit the simple Drude equation. The λ_c values of the oxidation products (poly-PhVS, 271 $m\mu$; poly-*t*-BuVS, 212 $m\mu$) suggested that the chromophore which caused optical activity was the sulfoxide group. Similarly, the asymmetric oxidation of *t*-BuVS-MMA copolymer, *t*-BuVS-styrene copolymer, and PhVS-MMA copolymer was carried out, and the optically active copolysulfoxides were obtained. Furthermore, the biosynthetic oxidation of poly-PhVS and PhVS-maleic anhydride copolymer treated with aqueous KOH was carried out using *Aspergillus niger* or *Penicillium notatum* in Czapek solution, and the optically active polymers were obtained.

INTRODUCTION

Recently, some attempts of asymmetric syntheses of polymers have been reported according to the reactions of optically inactive polymers containing functional groups. For example, the asymmetric reduction of poly(phenyl vinyl ketone) using chinine was carried out by Schultz.¹ We already reported the asymmetric reduction of poly(methyl vinyl ketone) with lithium borneoxylaluminumhydride in a previous paper,² and we presented the asymmetric hydroboration³ of polyisoprene with triisopinocampheyl-diborane.

The asymmetric syntheses of low molecular weight sulfoxides are well known. The oxidation⁴⁻⁶ of alkyl (or aryl) sulfide with percamphoric acid yielded optically active sulfoxide. The reaction of arylsulfonic acid menthyl ester with Grignard reagent yielded highly optically active sulfoxide.⁷ Furthermore, the biosynthetic oxidation⁸ of phenylbenzyl sulfide with *Aspergillus niger* was carried out to produce levorotatory

phenylbenzyl sulfoxide by Dodson et al.⁸ Auret et al.⁹ also carried out the asymmetric oxidation of sulfides with *Aspergillus niger*. The optical activity and configuration of optically active sulfoxide have been studied by many authors, especially Andersen et al.¹⁰ and Mislow et al.¹¹⁻¹³

It has been well known that compounds such as alkyl (or aryl) vinyl sulfoxides cannot be homopolymerized easily. Thus, up to now the behavior of optically active polyalkyl (or aryl) vinyl sulfoxide has not been studied. Recently, Mulvaney and Ottaviani¹⁴ carried out the copolymerization of vinyltosyl sulfoxide with styrene and investigated the optical activity of the copolysulfoxides.

In this paper, we attempted the asymmetric oxidation of poly(vinyl sulfides) according to the polymer reaction. The asymmetric oxidation of poly(phenylvinyl sulfide) (poly-PhVS), poly(*t*-butylvinyl sulfide) (poly-*t*-BuVS), PhVS-MMA copolymer *t*-BuVS-MMA copolymer, and *t*-BuVS-St copolymer using optically active percamphoric acid was carried out. The optically active oxidized polymers were obtained; the specific rotation of these oxidized polymers increased linearly with increase in the content of the sulfoxide group of the polymers. The optical rotatory dispersions of these polymers were found to fit the simple Drude equation. The value of λ_c for these polymers suggested that the chromophore which caused optical activity was the sulfoxide group.

The biosynthetic asymmetric oxidation of poly-PhVS and PhVS-maleic anhydride (PhVS-MAn) copolymer treated with aqueous KOH was carried out using *Aspergillus niger* and *Penicillium notatum*, which was used recently on the oxidative degradation of poly(vinyl alcohol),¹⁵ and the optically active oxidized polymers were obtained.

EXPERIMENTAL

Materials

Phenylvinyl sulfide (PhVS) was prepared from 2-chloroethylphenyl sulfide according to Montanari's¹⁶ modified method and was purified by distillation under reduced pressure, bp 84°-85°C/15 mm Hg (lit.¹⁷ 85.0°C/15 mm Hg). *t*-Butylvinyl sulfide (*t*-BuVS) was prepared by the dehydration of 2-hydroxyethyl-*t*-butyl sulfide, bp 115°C (lit.¹⁸ 114°C).

Maleic anhydride (MAn) was purified by recrystallization from chloroform. Styrene (St) and methyl methacrylate (MMA) were distilled over calcium hydride at reduced pressure in a stream of nitrogen just before use.

α, α' -Azobisisobutyronitrile (AIBN) used as radical initiator was recrystallized twice from ethanol.

The bulk polymerization of PhVS and *t*-BuVS and the copolymerization of PhVS with MMA and of *t*-BuVS with St and MMA was carried out with AIBN as a initiator by the sealed-tube method at 60°C. In order to obtain water-soluble polymers, the alternating copolymerization¹⁹ of PhVS with MAn was also done with AIBN at 60°C.

The obtained poly-PhVS and poly-*t*-BuVS and copolymers were purified by precipitation from tetrahydrofuran (THF) with ethanol.

The compositions of the copolymers obtained were determined by elemental analysis.

The percamphoric acid used was prepared by the method of Milas, and McAlevy,²⁰ washed with ice-cold low-boiling petroleum ether, and dried under vacuum. The peracid was finally dried in a vacuum desiccator over concentrated sulfuric acid having a melting point of 135–142°C (in a sealed tube); $[\alpha]_D^{25} + 60.0$ (in THF).

ANAL. Calcd for C₁₀H₁₆O₅: C, 55.6%; H, 7.4%. Found: C, 54.6%; H, 7.4%; active O, 81%.

Benzene and THF were purified by the usual method, dried with sodium metal, and distilled before use.

Oxidation with Percamphoric Acid

A benzene solution of poly(vinyl sulfide) in a three-necked flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer was added dropwise to a benzene solution of percamphoric acid with vigorous stirring. The reaction was carried out on an ice bath for 4 hr. After the reaction period, the reaction mixture was evaporated to remove benzene, and the residue was dissolved in THF and the polymer solution was precipitated into a large amount of alkaline solution. The precipitation was carried out until the optical rotation of the polymer showed a constant value.

Oxidation with *Aspergillus niger* (NRRL, 337)

To 150 ml of Czapeck solution (saccharose, 30.0 g; NaNO₃, 2.0 g; K₂HPO₄, 1.0 g; MgSO₄·7H₂O, 0.5 g; KCl, 0.5 g; and FeSO₄, 0.01 g dissolved in 1000 ml water, pH 7) was added 1 g poly-PhVS powder in a Sakaguchi flask. After heating at 80°C for 1/2 hr, *Aspergillus niger* was added. The flask was shaken at 25°C over a period of five days (run 21). The reaction mixture was extracted with THF to recover the oxidized poly-PhVS. In the case of oxidation of hydroxylated PhVS–MAN copolymer treated with aqueous KOH solution, 1 g hydroxylated PhVS–MAN copolymer was dissolved in 150 ml Czapeck solution in a Sakaguchi flask (pH 7). After heating at 80°C for 1/2 hr, *Aspergillus niger* was added. The flask was shaken at 25°C over a period of seven days. The polymer solution was filtered and the filtrate was evaporated to recover the oxidized polymer (run 22).

Oxidation with *Penicillium notatum* (NRRL, 1978)

To 150 ml Czapeck solution was added 1 g of the hydrolyzed poly-PhVS–MAN copolymer in a Sakaguchi flask. After heating at 80°C over a period of 1/2 hr, *Penicillium notatum* was added. The flask was shaken on a shaker at 25°C over a period of seven days. The polymer solution was filtered and the filtrate was evaporated to recover the oxidized polymer (run 24).

In the case of run 23, 150 ml of Czapeck solution was placed in a Sakaguchi flask. After treating at 80°C for 1/2 hr, *Penicillium notatum* was added. The flask was shaken on a shaker at 25°C over a period of two days. The reaction mixture was filtered and the solid phase was collected and washed with NaCl aqueous solution after washing with acidic aqueous solution (pH 6). This solid phase was added to the flask of aqueous solution of hydrolyzed poly-PhVS-MAn copolymer. The flask was shaken on a shaker at 25°C for seven days. The solution was filtered and the filtrate was evaporated to recover the oxidized polymer.

Measurements

The intrinsic viscosity of the polymers was measured in THF at 30°C ± 0.1°C with an Ubbelohde viscometer.

The infrared spectra of the polymers were measured by the use of film on NaCl plate on a photospectrometer (Japan Spectroscopic Co., Ltd., Model IR-E).

The D-line optical rotation and the optical rotatory dispersion were measured with a Shimadzu Model QV-50 polarimeter equipped with a xenon source.

RESULTS AND DISCUSSION

Asymmetric Oxidation of Poly(phenylvinyl Sulfide) (poly-PhVS)

The asymmetric oxidation of poly-PhVS was carried out with percamphoric acid in benzene at 0°C. The oxidized polymer was optically active in spite of four precipitations.

The oxidation conditions and results are shown in Table I. The infrared spectra of the obtained polymers are shown in Figure 1. The absorp-

TABLE I
Asymmetric Oxidation^a of Poly(phenylvinyl Sulfide)
with Percamphoric Acid^b

Run no.	Mole ratio PCA/poly- PhVS	Oxidized polymer			
		Yield, g	$[\eta]_{\text{THF}}^{30}$	Sulfoxide unit molar fraction	$[\alpha]_{\text{D}}^c$
1	0.50	0.50	0.122	0.29 ^d	+0.3
2	0.75	0.49	0.177	0.42 ^d	+0.6
3	1.00	0.50	0.104	0.49 ^e	+1.0
4	1.50	0.42	0.089	0.56 ^e	+1.0

^a Oxidation reactions were carried out in benzene at 0°C using 0.80 g of poly-PhVS, $[\eta]_{\text{THF}}^{30} = 0.119$. Calcd for C₈H₈S: C, 70.6%; H, 5.9%. Found: C, 69.8%; H, 5.9%.

^b $[\alpha]_{\text{D}}^{25} = +60.0$ in benzene.

^c Measured in THF at 25°C.

^d Calculated by elemental analysis.

^e Estimated by IR analysis.

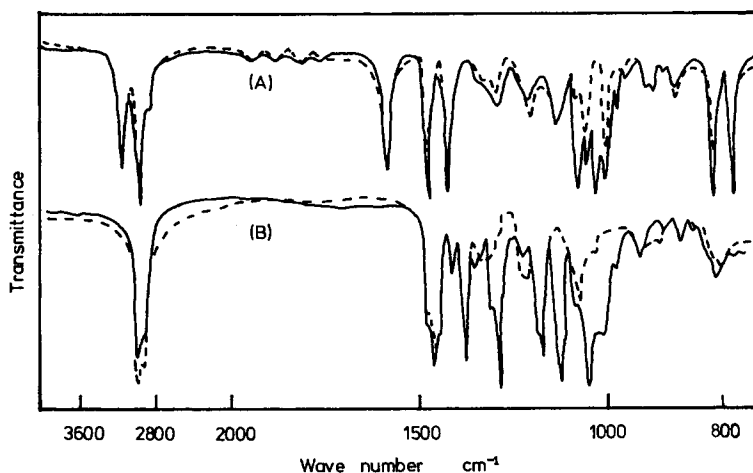


Fig. 1. Infrared spectra of (A): (---) poly(phenylvinyl sulfide); (—) oxidized polymer; (B): (---) poly(*t*-butylvinyl sulfide); (—) oxidized polymer.

tion due to the sulfoxide group appeared at 1040 cm^{-1} ; the absorption due to the carbonyl group of optically active impurity at 1700 cm^{-1} was not observed.

The sulfoxide content of the oxidized polymers was determined with infrared spectra and elemental (C and H) analysis. The sulfoxide content of polymer products which did not have the sulfone group was determined by elemental analysis. The relationship between the sulfoxide content determined by elemental analysis and the value of $D_{1040}\text{ cm}^{-1}/D_{1460}\text{ cm}^{-1}$ obtained by infrared analysis was found to be linear. On the other hand, the sulfoxide content of oxidized polymers having a sulfone group was estimated by infrared analysis using the values of $D_{1040}\text{ cm}^{-1}/D_{1460}\text{ cm}^{-1}$ according to the above relationship.

The asymmetric oxidation of poly-PhVS was carried out by changing the molar ratio of percamphoric acid to poly-PhVS, and the optically active polymers were obtained. The intrinsic viscosity of the obtained optically active polymers decreased with increase in the induced sulfoxide group content. The maximum value of the specific rotation of the oxidized poly-PhVS was $+1.0^\circ$, having a sulfoxide content of 56%. The specific rotations of the oxidized polymers increased linearly with increase in sulfoxide contents, as shown in Figure 2. The specific rotation of the completely oxidized polymer was estimated to be $+1.7^\circ$ by extrapolation. Folli et al.²¹ obtained optically active Ph-S-Me ($[\alpha]_D +6.5^\circ$, optical purity 3.6%)



and Ph-S-*t*-Bu ($[\alpha]_D +2.4^\circ$, optical purity 1.4%) by oxidation with per-



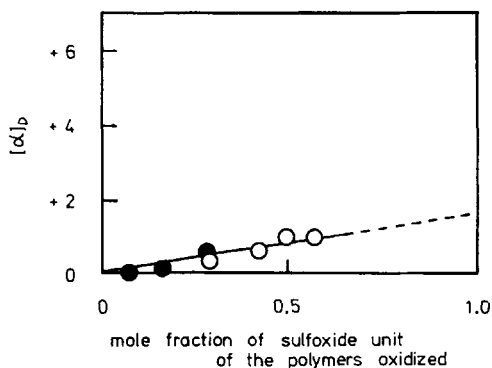


Fig. 2. Relationship between absolute value of specific rotation and mole fraction of sulfoxide units for oxidized polymers: (O) poly(phenylvinyl sulfide); (●) phenylvinyl sulfide-MMA copolymer.

camphoric acid. These values are similar to the value of $+1.7^\circ$ obtained in this paper.

The optical rotatory dispersions were measured and the positive curves were obtained (Fig. 3). The curves were found to fit the simple Drude

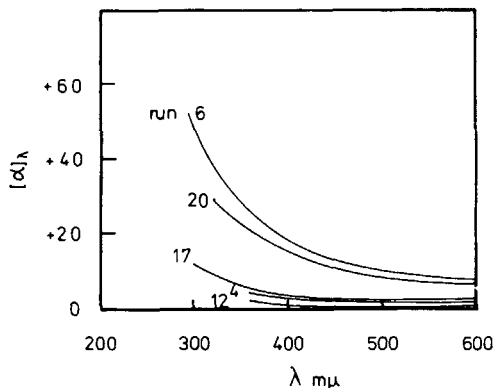


Fig. 3. Optical rotatory dispersion curves of oxidized polymers: run 4 (Table I), run 6 (Table II), and runs 12, 17 and 20 (Table III).

equation; the average λ_c value was $271 \text{ m}\mu$. The λ_c ($271 \text{ m}\mu$) suggested that the chromophore that caused the optical activity was the $-\text{S}-$ group.



The λ_c value ($271 \text{ m}\mu$) was different from the $200 \text{ m}\mu$ for percamphoric acid. It is thought that the λ_c value is a reasonable value for the transition of sulfoxide compared with the λ_c value ($250\text{--}260 \text{ m}\mu$) of isopropyltolyl sulfoxide¹² considered as a model compound.

Asymmetric Oxidation of Poly(*t*-butylvinyl Sulfide) (Poly-*t*-BuVS)

The asymmetric oxidation of poly-*t*-BuVS was carried out by varying the molar ratio of percamphoric acid to poly-*t*-BuVS. The oxidized polymers were optically active as shown in Table II. Infrared spectrum of the obtained polymer is shown in Figure 1. The absorption due to the sulfoxide group appeared at 1040 cm^{-1} , and the absorption at 1700 cm^{-1} due to the carbonyl group of optically active impurity was not observed. The sulfoxide content of the oxidized polymers was determined with infrared spectra and elementary analysis as was described previously.

TABLE II
Asymmetric Oxidation^a of Poly(*t*-butylvinyl Sulfide)
with Percamphoric Acid^b

Run no.	Oxidation condition		Oxidized polymer			
	Mole ratio PCA/poly- BuVS	<i>T</i> , °C	Yield, g	$[\eta]_{\text{THF}}^{30}$	Sulfoxide	$[\alpha]_{\text{D}}^{\text{c}}$
					unit molar fraction	
5	0.25	0	0.25	0.133	19 ^d	+4.9
6	0.50	0	0.28	0.125	41 ^d	+8.6
7	0.75	0	0.24	0.120	49 ^e	+9.1
8	1.00	0	0.22	0.117	54 ^e	+8.0
9	1.00	20	0.25	0.120	50 ^e	+4.5
10	1.00	40	0.21	0.122	49 ^e	+4.1

^a Oxidation reaction were carried out in benzene using 0.50 g of poly-*t*-BuVS, $[\eta]_{\text{THF}}^{30} = 0.087$. Calcd for $\text{C}_6\text{H}_{12}\text{S}$: C, 62.1%; H, 10.3%. Found: C, 62.2%; H, 10.6%.

^b $[\alpha]_{\text{D}}^{25} = +60.0$ in benzene.

^c Measured in THF at 23°C.

^d Calculated by elemental analysis.

^e Estimated by IR analysis.

The oxidized polymers were optically active as shown in Table II. The intrinsic viscosity of the obtained optically active polymers decreased with increase in the induced sulfoxide groups content. The maximum value of the specific rotation for the oxidized polymer was $+9.1^\circ$, having a sulfoxide content of 49%. The specific rotation of the oxidized polymer increased with increase in the sulfoxide content, as shown in Figure 4. The specific rotation of the completely oxidized polymer was estimated to be $+19.2$ by extrapolation.

The optical rotatory dispersions were measured, and positive curves were obtained (Fig. 3). The curves were found to fit the simple Drude equation, and the average λ_c value was $210\text{ m}\mu$. The λ_c value ($210\text{ m}\mu$) was reasonable compared with λ_c value of $210\text{ m}\mu$ for optically active *n*-butyl methyl sulfoxide obtained by Mislrow et al.¹² It is thought that the λ_c value suggested that the chromophore that caused optical activity was the $n-\pi^*$ transition of the sulfoxide group.

Furthermore, the asymmetric oxidation of poly-*t*-BuVS was carried out at 20°C and 40°C. The oxidation conditions and results are shown in Table II. The specific rotations of the oxidized polymers decreased with increase in the reaction temperature. It appears that the asymmetrically induced efficiency decreased with increase in temperature.

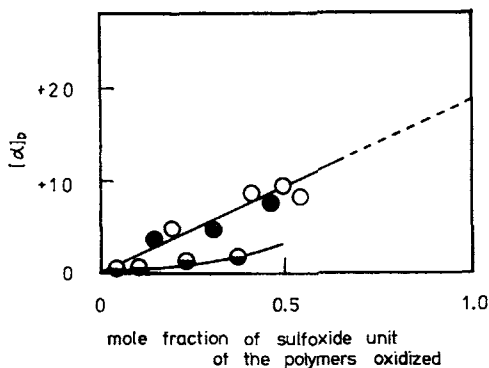
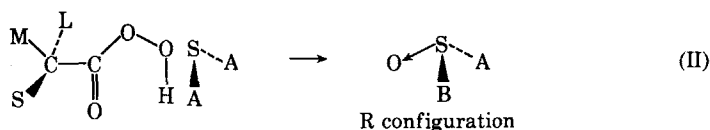
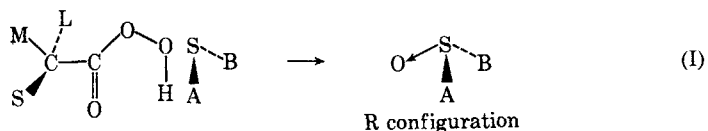


Fig. 4. Relationship between absolute value of specific rotation and mole fraction of sulfoxide units for oxidized polymers: (○) poly(*t*-butylvinyl sulfide); (●) *t*-butylvinyl sulfide-MMA copolymer; (◐) *t*-butylvinyl sulfide-styrene copolymer.

Montanari et al.^{5,6} proposed the structures for diastereomeric “transition states” of oxidation with (+)-*S*-percamphoric acid, which are depicted below:



(A is larger than B)

“Transition state (I)” was said to be lower in energy than “transition state (II)” since in the former the larger group A is placed in the less hindered position.^{5,6}

The oxidation of *n*-alkylphenyl sulfides with (+)-percamphoric acid yields (+)-*n*-alkyl phenyl sulfoxide, and since these compounds unquestionably have the R configuration, in analogy with the (+)-*n*-alkyl *p*-tolyl sulfoxides, I leads to R *n*-alkylphenyl sulfides, exactly as predicted by the arguments advanced by Montanari et al.^{5,6}

The configuration of poly(vinyl alkyl (aryl) sulfoxide) obtained in this paper suggests that Montanari's prediction is supported. The mechanism of oxidation would be illustrated by the Montanari's mechanism.

Asymmetric Oxidation of PhVS-MMA, *t*-BuVS-MMA and *t*-BuVS-St Copolymers

The asymmetric oxidation of PhVS-MMA, *t*-BuVS-MMA, and *t*-BuVS copolymers were carried out with percamphoric acid in benzene at 0°C. The oxidized polymers were optically active in spite of four precipitations. The conditions and results are shown in Table III. The relationship between the sulfoxide content of the oxidized polymer and the specific rotation is shown in Figure 2.

TABLE III
Asymmetric Oxidation^a of PhVS-MMA, *t*-BuVS-MMA, and *t*-BuVS-St Copolymers with Percamphoric Acid^b

Run no.	Copolymer	Mole fraction of sulfide unit	[η] ^c	Oxidized copolymer			
				Yield g	[η] ^c	Mole fraction ^d of sulfide unit	[α] _D ^e
11	PhVS-MMA	0.12	1.55	0.18	1.16	0.07	0.0
12	PhVS-MMA	0.37	0.86	0.16	1.11	0.14	+0.1
13	PhVS-MMA	0.67	0.18	0.15	1.13	0.28	+0.6
14	<i>t</i> -BuVS-MMA	0.04	0.63	0.47	0.57	0.04	+0.3
15	<i>t</i> -BuVS-MMA	0.11	0.30	0.45	0.28	0.10	+0.5
16	<i>t</i> -BuVS-MMA	0.33	0.15	0.47	0.13	0.23	+1.2
17	<i>t</i> -BuVS-MMA	0.62	0.14	0.48	0.10	0.37	+1.8
18	<i>t</i> -BuVS-St	0.28	0.23	0.43	0.97	0.15	+1.8
19	<i>t</i> -BuVS-St	0.49	0.77	0.47	0.31	0.30	+6.3
20	<i>t</i> -BuVS-St	0.73	0.44	0.44	0.12	0.46	+7.5

^a Oxidation reactions were carried out in benzene at 0°C. Polymer used: 0.40 g (runs 11-13); 0.80 g (runs 14-20).

^b [α]_D = +60.0 in THF.

^c Measured in THF at 30°C.

^d Calculated by elemental analysis.

^e Measured in THF at 25°C.

The specific rotations of oxidized PhVS-MMA and *t*-BuVS-MMA copolymers increased linearly with increase in the sulfoxide contents (Figs. 2 and 4). On the other hand, the specific rotation of the oxidized *t*-BuVS-St copolymer increased less with increase in the sulfoxide content compared with the oxidized (+)-BuVS-MMA copolymers (Fig. 4). It is thought that the relationships between the [α]_D and the sulfoxide content are caused by the difference of the structure of copolymers.

The optical rotatory dispersions of the oxidized copolymers were measured, and positive curves were obtained (Fig. 3). The curves were found

TABLE IV
Asymmetric Oxidation with *Aspergillus niger* and *Penicillium notatum*

No.	Copolymer	Oxidation condition		Oxidized polymer			
		Reaction time, days	$[\eta]_{\text{THF}}^{30}$	Elemental analysis		Mole fraction of sulfoxide ^a	$[\alpha]_{\text{D}}^{25}$ ^b
				C, %	H, %		
21	poly PhVS ^c	5	0.109	61.7	10.4	0.05	-0.1
22	PhVS-MAN copolymer ^d	7	0.301	58.2	4.5	0.02	-0.5
23	PhVS-MAN copolymer ^d	7	0.295	58.0	4.8	0.03	-0.6
24	PhVS-MAN copolymer ^d	7	0.290	58.2	4.8	0.02	-0.5

^a Estimated by elemental analysis.

^b Measured in THF at 25°C.

^c $[\eta]_{\text{THF}}^{30} = 0.119$. Found: C, 69.8%; H, 5.9%. Calcd for C₈H₈S: 70.6%; H, 5.9%.

^d $[\eta]_{\text{THF}}^{30} = 0.305$. Found: C, 57.6%; H, 4.8%.

to fit the simple Drude equation, the c values of oxidized PhVS-MMA, *t*-BuVS-MMA, and *t*-BuVS-St copolymers were 265, 208, and 205 $m\mu$, respectively. The λ_c value suggests that the chromophore that caused the optical activity is a $-\text{S}-$ group.



Asymmetric Oxidation of Poly(vinyl Sulfides) with *Aspergillus niger* and *Penicillium notatum*

The biosynthetic asymmetric oxidation of poly-PhVS and PhVS-MAN copolymer hydrolyzed with alkaline aqueous solution (2*N* KOH aqueous solution) was carried out. The oxidation conditions and results are summarized in Table IV.

The specific rotations of the polymers oxidized by *Aspergillus niger* were levorotatory, as was that for phenylbenzyl sulfoxide obtained by Dodson et al.⁸ They carried out the asymmetric oxidation of phenylbenzyl sulfide with *Aspergillus niger* and obtained optically active sulfoxide having $[\alpha]_D^{21} -20.2^\circ$. Other authors⁹ have tried the oxidation of sulfide with *Aspergillus niger* to obtain optically active sulfoxides. It is thought that one of the antipodes is produced preferentially because of the asymmetric structure of the reaction sites of the enzymes. The obtained polymer was not oxidized easily and had low optical purity. It was caused by the polymer-polymer reaction. However, even if a water-soluble polymer was used, the oxidation did not occur so easily and the specific rotation was low (run 22).

Furthermore, the asymmetric oxidation of hydrolyzed PhVS-MAN copolymers was carried out with *Penicillium notatum* and optically active polymers were obtained (runs 23 and 24), as shown in Table IV. The specific rotations of the oxidized polymers also were levorotatory. Compared with the optical yield of the polymers oxidized with percamphoric acid, the optical yield of the polymer oxidized in vivo (*Aspergillus niger* or *Penicillium notatum*) was larger in magnitude. The result shows that the oxidizing method in vivo has a highly asymmetric inducing power. The opposite sign of the latter polymer suggests that the sulfide group absorbed on the surface of the enzyme is attacked by oxygen from the opposite side of the enzyme.

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