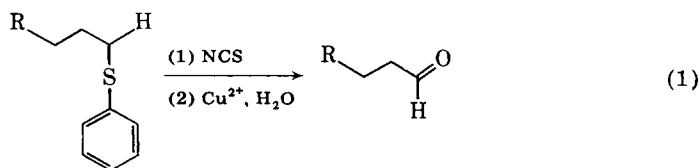


Introduction of Carbonyl Group to the Main Chain of Poly(phenyl Vinyl Sulfide)

Recently, much attention has been focused on the degradation of polymers. The representative photodegradation polymer is the material containing carbonyl group which absorbs the light of ultraviolet region. The degradation mechanisms of these polymers have been studied in detail.¹⁻⁵ The methods of the preparation of such polymers have been widely investigated, but most of them were prepared from the copolymerization of vinyl ketones,¹⁻³ methyl methacrylate,⁴ and carbon monoxide⁵ with other vinyl monomers. As a series of the reaction of sulfide polymer,⁶⁻⁸ we report here one of the examples for preparing ketone polymer by the use of poly(phenyl vinyl sulfide) (PPVS) as a starting material.

There are many reports on the conversion of organic sulfur compounds to carbonyl compounds.⁹ Several years ago, Bakuzis et al.¹⁰ succeeded in preparing aldehydes by the chlorination of phenyl alkylsulfides followed by oxidation:



If an α -proton of alkyl phenyl sulfide in eq. (1) is replaced with an alkyl group, the structure of the resulting sulfide is the same as the structure of PPVS. From this viewpoint, we expected that PPVS could be converted to the polymer containing carbonyl group to the main chain of the polymer.

EXPERIMENTAL

Preparation of PPVS (I)

PPVS was prepared by the same procedure as described previously.¹¹

Chlorination of PPVS (I)

Method A: A solution of PPVS (10.88 g) and *N*-chlorosuccinimide (10.86 g) in 400 mL of benzene was refluxed under nitrogen for 6 h. After cooling, the mixture was filtered, and the solvent was removed under reduced pressure. The crude polymer was purified by the reprecipitation with benzene-methanol and was dried. The yield was 10.16 g.

ANAL: Cl, 28.18%.

Method B: A solution of PPVS (1.36 g) and *t*-butyl hypochlorite (1.09 g) in 30 mL of benzene was irradiated by 60-W tungsten lamp with a 10-cm path length for 2 h under nitrogen. After evaporation of the solvent, the crude polymer was purified by reprecipitation with benzene-methanol. The yield was 1.15 g.

Oxidation of Chlorinated PPVS (II)

Chlorinated PPVS (4.6 g), acetone (140 mL), CuCl_2 (9.3 g), CuO (9.3 g), and water (3 mL) were placed in a three-necked flask. The mixture was refluxed with stirring for 6 h. After cooling, the product was extracted with benzene and dried. Evaporation of the solvent gave crude oxidized polymer. This polymer was purified by reprecipitation with benzene and petroleum ether. The yield was 1.73 g.

ANAL: C, 60.81%; H, 4.99%; S, 18.09%; Cl, 14.04%.

Photolysis of Polymers

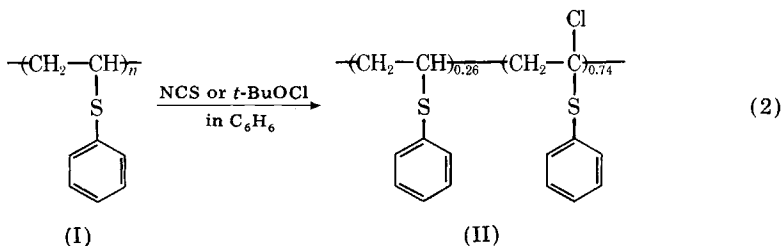
A solution of polymer (1.0 g) in 50 mL of benzene was placed in a flask and irradiated with RIKO 100-W high pressure mercury lamp by the use of Pyrex filter for a given time. After evaporation of the solvent, the residue was dried under vacuum overnight, and then the viscosity was measured in benzene at 30°C.

Instrument

IR spectra were recorded on a JASCO IRA-2 spectrometer.

RESULTS AND DISCUSSION

PPVS (I) was chlorinated by *N*-chlorosuccinimide (NCS) to give a polymer (II). The IR spectrum of (II) was in good agreement with that of the product obtained from the reaction with *t*-butyl hypochlorite under irradiation. Considering the previous report,¹⁰ this chlorination would occur on α -position of the sulfur atom. From the elementary analysis for chlorine, it was shown that 74% of α -proton was substituted with chlorine:



Next, the chlorinated PPVS (II) was treated with cupric chloride, cupric oxide, acetone, and water to give (III). As can be seen in Figure 1, the IR spectrum of (III) shows a characteristic absorption band of carbonyl group at 1720 cm^{-1} , and the absorption band based on sulfoxide or sulfone is not observed. UV absorption caused by carbonyl group was not detected clearly. This result is probably attributed to the overlap of large absorption band of phenylthio group with that of carbonyl group.

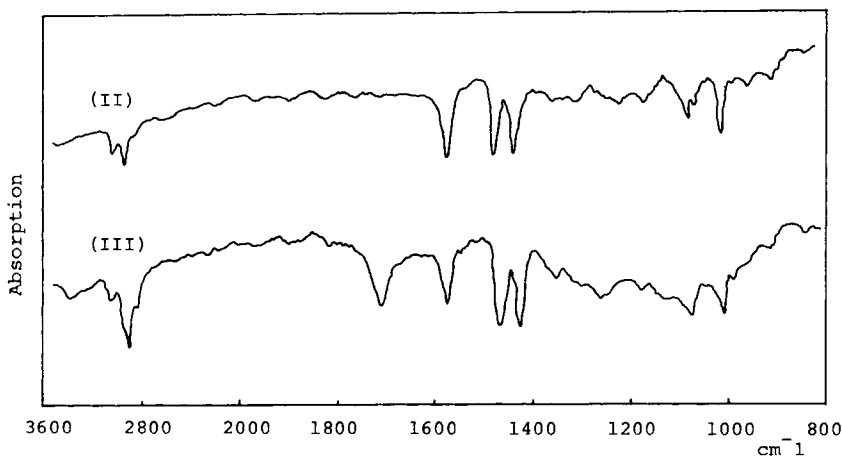
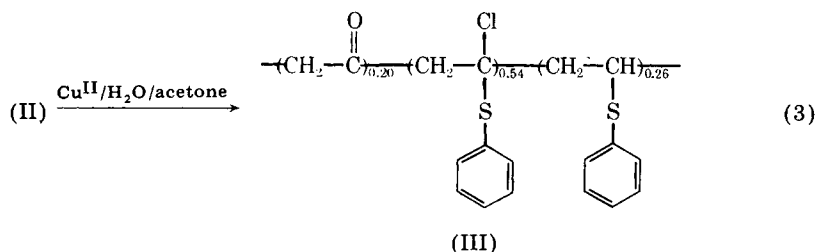


Fig. 1. IR spectra of chlorinated PPVS (II) and oxidized PPVS (III).

TABLE I
Change of Viscosity for Irradiation Time

Time (h)	Intrinsic viscosity (cm ³ /g)		
	Polymer (I)	Polymer (II)	Polymer (III)
0	14.6	12.0	10.4
12	13.8	11.5	9.7
24	13.6	11.5	7.8
48	13.8	11.6	4.9

These facts indicate that the next reaction occurred:



The ratio of structure unit in oxidized polymer (III) was calculated from the result of elementary analysis, as is shown in eq. (3). Interestingly, the percentage of the unit of phenyl vinyl sulfide (III) is the same as that for (II). This means that only the unit of 1-chloro-1-phenylthioethylene was oxidized under this condition. It has been shown by Hartly and Guillet⁵ that ethylene-carbon monoxide copolymer decomposes by the irradiation of medium mercury arc in quartz cell. Therefore, we tried to decompose the polymer (III) by photochemical conditions and measured the intrinsic viscosity to estimate the molecular weight. As shown in Table I, the viscosity of oxidized polymer (III) was significantly decreased as the irradiation time proceeded, but that of polymer (I) and (II) did not change. This result indicates that the oxidized polymer (III) absorbs the light of ultraviolet region to cause the cleavage of main chain of (III) and the decrease of molecular weight. Although we did not study the decomposition mechanism, the decomposition of (III) would occur as Norrish type II because of the similarity of the structure of (III) with the copolymer of ethylene and carbon monoxide.⁵

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