

## POLYMERIZATION OF o-VINYLPHENOL

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### SYNOPSIS

The structure of the polymer of o-vinylphenol was studied. o-Vinylphenol(o-VP) was prepared by thermal decarbonization of o-cumaric acid which was obtained by hydrolysis of coumarin with sodium ethylate. Free radical and cationic polymerization of o-VP were carried out in bulk or in  $\text{CH}_2\text{Cl}_2$  solution by using BPO, AIBN,  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{AlCl}_3$ , and  $\text{TiCl}_4$  as initiator. The polymers were reprecipitated by water from methanol solution and residual monomer was removed with dilute aqueous alkaline solution. The resulting polymers were white powder or viscous materials.

The structure of the polymers were investigated by UV, IR, and NMR spectral measurement. UV spectra showed that the polymers have similar structures except for the one prepared by using  $\text{BF}_3 \cdot \text{OEt}_2$ . IR spectra showed the presence of methyl group and 1,2,4-trisubstituted benzene structure which are not expected from ordinary vinyl polymerization mechanism. The relative intensities of  $-\text{CH}_3$  and  $-\text{CH}_2$  group differ among polymers and suggested only the polymer prepared by using AIBN had relatively few  $-\text{CH}_3$  group. NMR spectral study supported the results obtained from IR spectra. The presence of  $-\text{CH}_3$  group was confirmed by C-methyl determination method (chromic acid oxidizing method) and the amounts of C- $\text{CH}_3$  groups were determined.

From these results it was concluded that o-VP polymerizes through two different propagation steps, one is ordinary vinyl polymerization mechanism and the other the addition of vinyl group to phenolic nuclei.

### INTRODUCTION

o-Vinylphenol seems to be an interesting monomer for its high reactivity based on phenolic hydroxyl group. Polymer of o-vinylphenol is expected to be sufficiently reactive to a wide variety of reactions including hydroxymethylation, sulfonation, diazo coupling, complex forming ability, and so on. Thus, poly-o-vinylphenol can be expected as one of the most reactive polymers in the synthetic trial of functional materials.

The polymerization of o-vinylphenol and the structure of the polymer had been investigated previously<sup>1)</sup> by one of the authors in

this study, and the polymer was found to have the structure of the addition of vinyl group to phenolic nuclei resulting in the formation of methyl groups in addition to the ordinary vinyl polymer structure. Later, this was confirmed by Kato and Kamogawa<sup>2,3,4)</sup> in their more detailed study of the polymerization of vinylphenols. However, the relative extent of the two polymerization mechanisms, the position of the addition of vinyl group to phenolic nuclei and the substitution patterns of aromatic ring, and the reliable reaction mechanisms have not been determined yet.

This study intends to clarify the detailed

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structure of the polymer of *o*-vinylphenol and to have a basis for the chemical modifications of the polymer.

## EXPERIMENTAL

### 1. Reagents in polymerization

#### 1.1 Preparation of *o*-vinylphenol<sup>1)</sup>

*o*-Cumaric acid was prepared by the hydrolysis of cumarin with sodium ethylate. Crude product was purified by recrystallization from aqueous solution. *o*-Vinylphenol was obtained by pyrolysis of *o*-cumaric acid. *o*-Vinylphenol was purified by distillation under reduced pressure.

#### 1.2 Initiators

Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol solution. Benzoylperoxide (BPO) was purified by reprecipitation with methanol from chloroform solution. Boron trifluoride etherate (BF<sub>3</sub>·OEt<sub>2</sub>) was purified by distillation under reduced pressure. Aluminum chloride (AlCl<sub>3</sub>) was purified by sublimation. Commercial titanium tetrachloride (TiCl<sub>4</sub>) was used without further purification.

#### 1.3 Solvents

Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) and methanol were purified by distillation.

### 2. Polymerization

The reaction condition of polymerization is shown in Table 1.

Free radical polymerization: To 5 g. of *o*-vinylphenol contained in a glass wall polymerization tube was added an 0.025 g. of initiator (BPO or AIBN) by weight. The tube was alternately evacuated and flushed with nitrogen three times, sealed, and then heated at 75°C.

Cationic polymerization: To a mixture of 5 g. of *o*-vinylphenol and 10 ml. of methylene chloride contained in a polymerization tube at 0°C was added an appropriate amount of cationic catalyst (BF<sub>3</sub>·OEt<sub>2</sub> 0.222 g., AlCl<sub>3</sub> 0.0125 g., TiCl<sub>4</sub> 1.73 g.). The tube was alternately evacuated and flushed with nitrogen

three times, sealed, and then allowed to stand at 0°C.

After 20 hr., polymerization tube was opened and the content was dissolved in methanol. Polymer was precipitated by using water as a precipitant. Residual monomer was removed by extracting with dilute aqueous alkaline. The obtained polymers will be abbreviated as P-A, P-B, P-BF, P-Al, and P-Ti according to the used initiators.

### 3. Preparation of model compounds

#### 3.1 4,4'-Ethylidenediphenol<sup>5)</sup>

In a three-necked round bottomed flask equipped with a stirrer and a dropping funnel was placed 25g. of phenol. The flask was cooled externally with crushed ice. Ten grams of acetaldehyde was added slowly during agitation. Then, 0.5ml. of hydrochloric acid was added and the reaction mixture was stirred at a temperature below 5°C for 3hr.. Then, the flask was placed in a refrigerator overnight. The white crystalline product was collected by filtration and washed with cold benzene. Unreacted phenol was removed from the product by steam distillation. The resulting product was recrystallized with a mixture of benzene and petroleum ether. This compound will be abbreviated as EDP.

#### 3.2 *o*-( $\alpha$ -Phenylethyl) phenol<sup>6)</sup>

To a mixture of 94 g. of phenol and 10 g. of sulfuric acid heated to 100°C, 52 g. of styrene dissolved in 100 ml. of toluene was added in small portions. After refluxing for 6 hr., the reaction mixture was washed with dilute aqueous sodium bicarbonate and dried over sodium sulfate. Solvent was removed and the residue was fractionated to give *o*-( $\alpha$ -phenylethyl)phenol. This compound will be abbreviated as EMP.

### 4. Analysis (Polymer characterization)

#### 4.1 Inherent viscosity

Inherent viscosities of the polymers were measured for the dilute solution in tetrahydrofuran (0.5g./100ml.) by using Ubbelohde type viscometer immersed in a constant

temperature bath regulated at 30°C.

#### 4.2 Cryoscopy

Molecular weights of model compounds were determined by cryoscopy with Thermo-electric cooling unit for cryoscopy of Knauer Co.. Purified benzene was used for cryoscopy solvent.

#### 4.3 UV spectra

Ultraviolet absorption spectra of polymers and monomer in dilute solution (0.21 mg./ml.) of absolute ethanol were measured by using a Hitachi UV-VS spectrometer model 323.

#### 4.4 IR spectra

Hitachi infrared spectrometer model 285 was used for the measurement of infrared spectra. Monomer, model compound, P-B, P-AI, and P-Ti polymers were measured by liquid film, P-A and P-BF by KBr disk method.

#### 4.5 NMR spectra

Measurement of nuclear magnetic resonance spectra in DMSO-d<sub>6</sub> solution (10 wt/v %) at 50°C was made with Nihon Denshi NMR spectrometer, model JNM-MH-100 (100 MHz).

#### 4.6 C-Methyl determination

The content of C-methyl group (methyl group attached to carbon atom) was determined by the method previously reported by Kuhn-Roth.<sup>7)</sup> Five ml. of chromic acid oxidizing solution (prepared by mixing 250 ml. sulfuric acid, 168 g. of chromic acid anhydride, and 1000 ml. of distilled water) was added to the sample and the reaction mixture was refluxed at 130°C. After 1.5 hr. the reaction mixture was cooled slightly, 7g. of anhydrous magnesium sulfate added, and the mixture steam distilled until 50 ml. distillate collected. The distillate was titrated with 0.05 N sodium hydroxide by using a microburet and phenolphthalein as indicator. The C-methyl number was determined by calculation from the titre.

## RESULTS AND DISCUSSION

### 1. Property of polymerized o-vinylphenol

The polymerization product of o-vinylphenol was white powder for P-A and P-BF. Other products were viscous materials. Yields were 58% for P-A, 38% for P-B, 69% for P-BF, 8% for P-Ti, 10% for P-AI, respectively. Inherent viscosities of the products are shown in Table 1.

Table 1. Polymerization of o-vinylphenol.

	Solvent	Initiator	Temp. °C	Time hr	( $\eta$ ) (dl/g)	State
P-A	None	AlBN	75	20	0.13	Solid
P-B	None	BPO	75	20	—	Viscous
P-BF	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> O(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0	20	0.03	Solid
P-AI	CH <sub>2</sub> Cl <sub>2</sub>	AlCl <sub>3</sub>	0	20	—	Viscous
P-Ti	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	0	20	—	Viscous

( $\eta$ ) of polymers were measured for the tetrahydrofuran solution (0.5g./100ml.) at 30°C by single point method.

### 2. Model compounds

The identification of EDP and EMP were done by cryoscopic molecular weight determination (EDP: Calc. 214, Obs. 213; EMP: Calc. 198, Obs. 206), IR spectra, and NMR spectra (shown in Fig. 4).

### 3. UV spectra

Ultraviolet absorption spectra of monomer and polymers are shown in Fig. 1. As

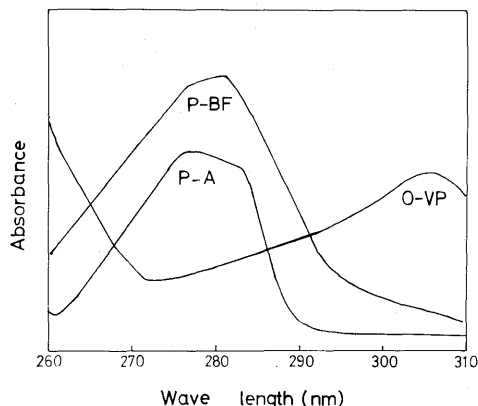


Fig. 1. Ultraviolet spectra of the monomer and the polymers of o-vinylphenol.

seen in the Fig. 1, spectra of polymers are similar with each other except for P-BF. The absorption at 305 nm observed for *o*-vinylphenol, originating from unsaturated C=C double bond, disappeared by polymerization, and a new absorption maximum at 276.5 nm and a bulge at 283 nm appeared except for P-BF polymer. On the other hand, P-BF shows an absorption maximum at 281 nm and a bulge at 276.5 nm. The shape of the spectra strongly suggests that the polymers do not consist of simple sequence of repeating unit but of different unit more than two. By considering the position of absorption maximum, it can be expected that the polymers except P-BF include mainly vinyl polymer type structure in the backbone.

#### 4. IR spectra

Infrared spectra of monomer and polymers are shown in Fig. 2. All polymers have absorptions at  $2950\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}\text{CH}_3$  stretching vibration of  $-\text{CH}_3$ ,  $2920\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}\text{CH}_2$  stretching vibration of  $-\text{CH}_2-$ , and  $1375\text{ cm}^{-1}$  assigned to  $\delta_{\text{s}}\text{CH}_3$  deformation vibration of  $-\text{CH}_3$ . However the intensity ratio of methyl and methylene are

different among polymers, suggesting that only P-A polymer has fewer methyl groups as compared with others. The existence of methyl group indicates that the polymerization of *o*-vinylphenol does not proceed according to the simple vinyl polymerization

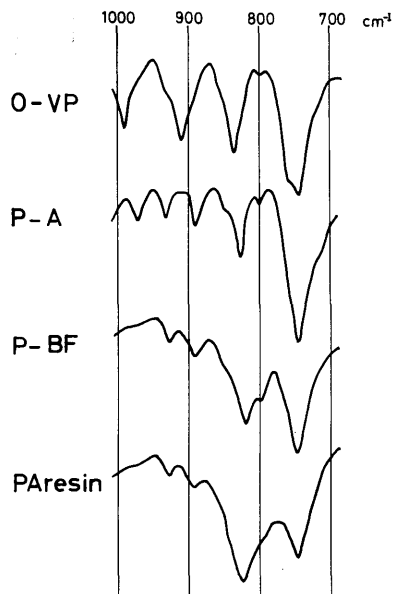


Fig. 3. Infrared spectra of the monomer and the polymers of *o*-vinylphenol and that of phenol-acetaldehyde resin in CH out-of-plane deformation region.

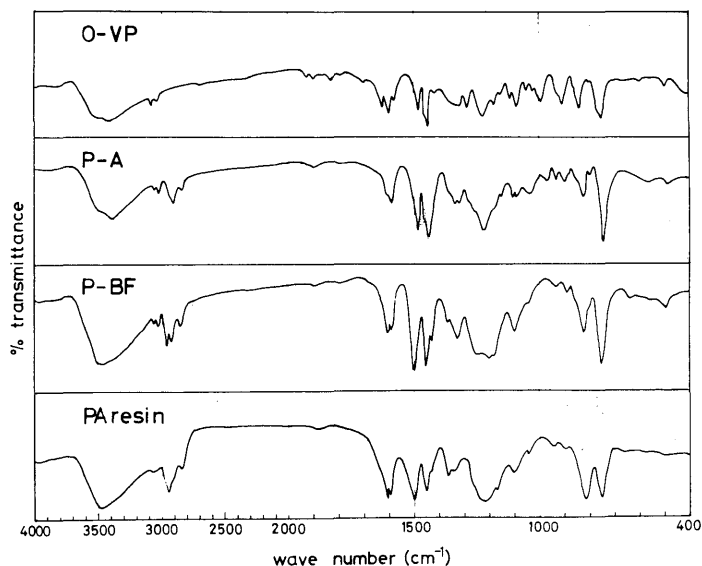


Fig. 2. Infrared spectra of the monomer and the polymers of *o*-vinylphenol and that of phenol-acetaldehyde resin.

mechanism alone. The C-H out-of-plane deformation absorptions reflecting the substitution patterns of benzene nuclei are shown in Fig. 3. The absorption at  $740\text{ cm}^{-1}$  is a characteristic band for 1,2-substituted benzene as seen for monomer. However, the appearance of absorptions at  $825$  and  $890\text{ cm}^{-1}$  suggest that polymers have 1,2,4-substituted structure. Furthermore, it appears that the ratio of 1,2- to 1,2,4-substituted structure differs among polymers.

In the spectrum of P-BF polymer, the absorption at  $1225\text{ cm}^{-1}$  which appeared in the

spectrum of monomer and assigned to C-O stretching vibration of phenolic OH, becomes broad and new bands appeared at  $1250$  and  $1190\text{ cm}^{-1}$ , which may safely be assigned to aromatic ether. The shape of O-H absorption near  $3500\text{ cm}^{-1}$  is also different from those of other polymers.

Fig. 2 includes the IR spectra of phenol-acetaldehyde resin (abbreviated as PA resin) for the comparison. It is obvious that the spectra of both poly-*o*-vinylphenol and phenol-acetaldehyde resin are quite similar.

### 5. NMR spectra

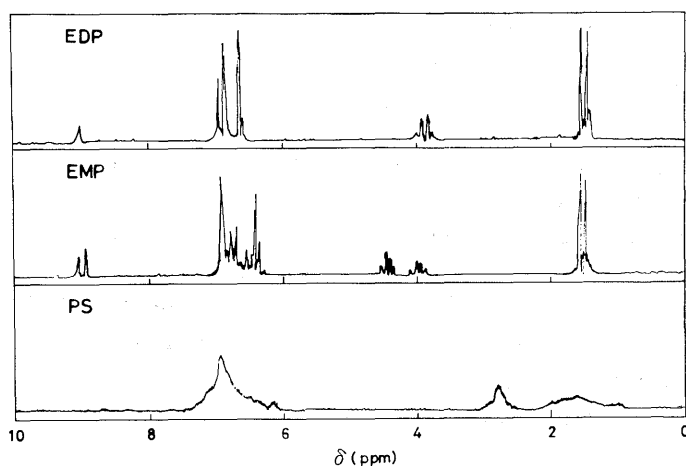


Fig. 4. Nuclear magnetic resonance spectra of the model compounds.

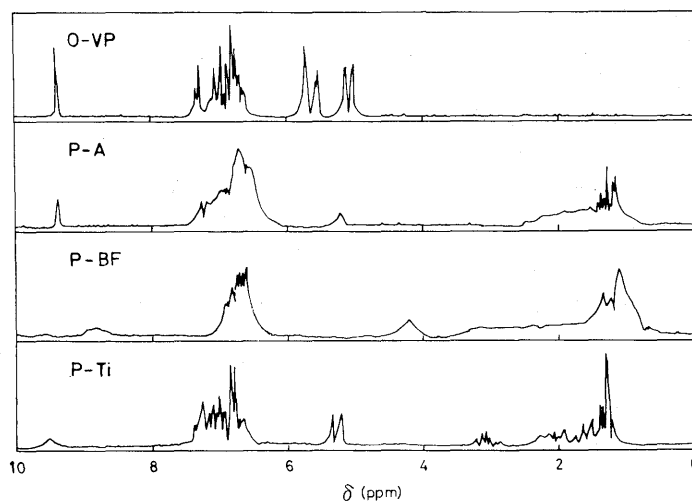


Fig. 5. Nuclear magnetic resonance spectra of the monomer and the polymers of *o*-vinylphenol.

Nuclear magnetic resonance spectra of model compounds and those of the polymers and the monomer are shown in Fig. 4 and 5, respectively.

Monomeric *o*-vinylphenol has absorptions at  $\delta=5.10$ , 5.70, and 6.69 assigned to vinyl proton, at  $\delta=7.0$  benzene nuclei proton, and at  $\delta=9.0$  OH proton.

EDP has absorptions at  $\delta=1.48$  assigned to methyl proton, at  $\delta=3.90$  methin proton, at  $\delta=7.0$  benzene nuclei proton, and at  $\delta=9.0$  OH proton.

EMP is a mixture of *o*- and *p*- isomer and shows absorptions at  $\delta=1.5$  assigned to methyl proton,  $\delta=4.0$  and 4.5 methin proton, and  $\delta=8.9$  and 9.8 OH proton. Polystyrene (abbreviated as PS resin), the model compound of vinyl polymer structure, shows absorption at  $\delta=1.28$  and  $\delta=2.5-3.0$  assigned to methylene proton and methin proton, respectively.

The assignment of the NMR absorptions of polymers were done by referring the chemical shifts of model compounds. In the NMR spectra of the polymers, in addition to the absorption at  $\delta=3.0-4.2$  assignable to methin proton, new absorption that was absent in the spectrum of monomer appeared near  $\delta=1.3$ , which is assignable to methyl proton. The absorption of OH proton is shifted and relatively weak only in P-BF polymer. Also, the absorption of terminal vinyl proton near  $\delta=5.5$  of P-BF is weak in comparison with others. It is conceivable that in the case of P-BF the polymerization proceeds more extensively and less terminal vinyl groups remain. This is in accordance with the observation of higher inherent viscosity of P-BF than the others.

From the results described above, it is considered that the polymers of *o*-vinylphenol contain methyl groups which was absent in monomer and was not expected from ordinary vinyl polymerization.

## 6. C-Methyl determination

The results of C-methyl determinations

are shown in Table 2. It is expected that the

Table 2. C-Methyl determinations of the model compounds and the polymers of *o*-vinylphenol by Kuhn-Roth's method.

	Sample mmole	C-CH <sub>3</sub> mmole	Content %
EDP	0.0933	0.0918	98
P-A	0.1880	0.0340	18
P-B	0.2668	0.1237	46
P-BF	0.1905	0.0850	45
P-AI	0.2229	0.0833	37
P-Ti	0.2642	0.1093	41

model compounds EDP will give the same amount of C-methyl group as the mole of sample. The result of determination, 0.0918 mmole, is in good agreement with 0.0933 mmole of sample and confirms the validity of this method.

From the results of the C-methyl determination for the polymers, it is clear that only P-A contains smaller amount of C-methyl group as compared with the others. This is in agreement with the estimation from the IR intensity ratio of methyl to methylene.

In conclusion, the polymers of *o*-vinylphenol have methyl group that is not expected from the simple vinyl polymerization scheme, and those amount of C-methyl group varies by the use of different initiators.

## 7. Reaction scheme

It is concluded that the polymers of *o*-vinylphenol have the structure of the addition of vinyl group to benzene nuclei in addition to the ordinary vinyl polymerization structure. Possible structures of the polymers and polymerization schemes are illustrated in Fig. 6.

In the case of cationic catalyst the polymerization is considered to proceed at least by the two mechanisms, one is cationic vinyl polymerization and the other the addition of vinyl group to benzene nuclei through proton transfer. For the latter mechanism the position against vinyl group in the aromatic

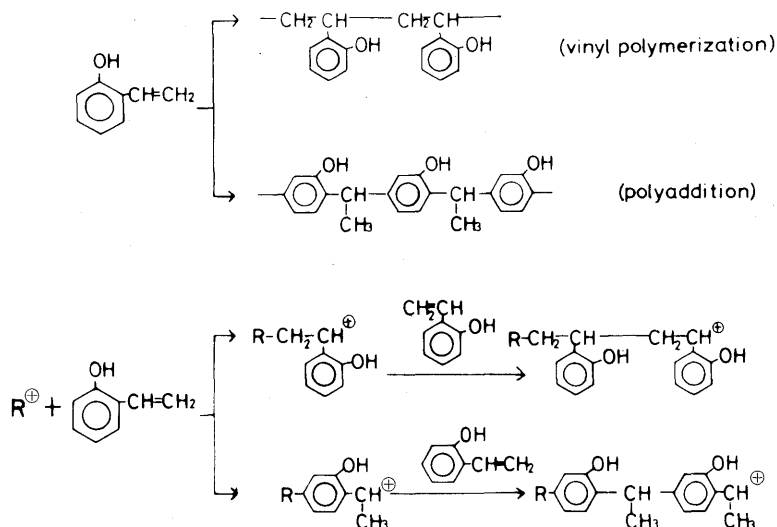


Fig. 6. Proposed polymer structures and polymerization schemes of o-vinylphenol.

nuclei is expected to be preferable from the literature value of electron density and steric requirement.

In the polymerization of o-vinylphenol with the use of radical initiator, it is conceivable that proton of phenolic OH group may work as cationic catalyst. From the observation of spectra, mechanisms other than those two described above may be conceivable, in which OH group participate in polymerization. The results of the determination of OH group, however, did not give any appreciable difference among polymers.

#### CONCLUDING REMARKS

o-Vinylphenol was polymerized with several initiators of different types and the structures of the resulting polymers were investigated. The relative amounts of methyl groups, that is the indices of the proportion of two different polymerization mechanism, one is ordinary vinyl polymerization and the other the addition of vinyl group to aromatic

nuclei, and the substitution patterns of phenolic nuclei could be determined. The ratio of the rates of the two polymerization mechanism, the length of the each polymeric sequence, and others should be studied in further investigation.

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