A Research on Polymerization of *o*-, *m*-, and *p*-Vinylphenol

Masao Kato

Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Dependence of radical initiators on polymerizations of *o*-, *m*-, and *p*-vinylphenol (OVP, MVP, and PVP) was investigated. Initiator generating the carbon radical such as AIBN induced polymerizations of these monomers to give fine polymers. That is; MVP and PVP gave polymers with high molecular weight (21,000–53,000), while OVP gave polymers with relatively low molecular weight (7,600–9800). The results of the spectroscopic investigations of the polymers thus obtained suggested that all of the polymers consisted of the structure formed through the normal vinyl polymerization mechanism. Initiator generating the oxy radical such as BPO as well as the thio radical such as tetraethylthiuram disulfide did not induce appreciable polymerizability. A reasonable radical polymerization mechanisms for OVP, MVP, and PVP were considered from the results of the kinetic investigations of the polymerization reactions for these monomers. Copolymerizations of OVP, MVP, and PVP with styrene or methyl methacrylate by using AIBN as initiator were investigated. The monomer reactivity ratios and $Q-e$ values for OVP, MVP, and PVP were determined, respectively. The copolymerizations generally gave copolymers with relatively high intrinsic viscosity not only for MVP and PVP but also for OVP without distinction. Cationic polymerizations of OVP, MVP, and PVP with boron trifluoride etherate as initiator were investigated. As the result, it was of interest that on the cationic polymerization only PVP gave polymers with high molecular weight (66,000–192,000), whereas both OVP and MVP gave polymers with low molecular weight (~ 3950 for OVP and ~ 710 for MVP, respectively). The results of spectroscopic investigation for the polymers thus obtained indicated that PVP polymers consisted of the structures formed through the normal vinyl polymerization mechanism, while OVP and MVP polymers contain considerable portion of the structures due to the reaction of the vinyl group and the phenol nucleus. The rate of cationic polymerization and the molecular weight of the polymer decreased in the order $PVP \gg OVP > MVP$. Plausible polymerization mechanisms were considered.

Keywords: vinylphenols, radical polymerizations, radical copolymerizations, cationic polymerizations, polymer structures, polymerization mechanisms

1. Introduction

On the occasion of acceptance of the Photopolymer Science and Technology Award in 2008, I would like to describe here about a research on polymerization of *o*-, *m*-, and *p*-vinylphenol (OVP, MVP, and PVP), which is part of the achievement including in the award.

A challenge to synthesize polyvinylphenols via direct polymerizations of OVP, MVP, and PVP was started from 1965. Up to this time there was no information that these vinylphenols give high polymers by direct polymerizations, even though polymerization behavior for some of them has been studied by other groups [1–4]. In this research, radical and cationic polymerizations of OVP, MVP, and

PVP were investigated [5–9]. Furthermore, radical copolymerizations of the vinylphenols with styrene (St) or methyl methacrylate (MMA) were also investigated. Through the investigations, it was found that in the case of the radical polymerization every vinylphenol polymerizes to give a fine polymer only when initiator generating the carbon radical was used, although OVP polymer shows rather lower molecular weight, while in the case of the cationic polymerization only PVP gives a high polymer. From the results of the spectroscopic investigations for the polymers thus produced and the kinetic investigations for the polymerizations of the monomers, we could successfully obtain a clear understanding on the radical and

Table 1 Radical polymerization of *o*-vinylphenol

Polymerization condition							
Solvent ^{a)}	OVP concn. %	Initiator % / OVP	Temp °C	Time hr.	Conversion %	[η], dl/g	Avg. Mn ^{b)}
None	100	AIBN, 0.5	75	20	35.7	0.105	7950
None	100	BPO, 0.5	75	20	6.1	0.061	-
None	100	TETD, 0.5	75	20	-	-	-
None	100	AIBN, 0.5	50	20	11.8	0.133	9800
THF	61.1	AIBN, 1.0	75	20	77.5	0.090	7410
THF	61.1	AIBN, 1.0	50	20	27.2	0.114	8850

a) THF: Tetrahydrofuran

b) Measured by vapor pressure osmometer

Table 2 Radical polymerization of *m*-, and *p*-vinylphenol

AIBN, %							
Monomer	Monomer concn. % ^{a)}	based on monomer	Temp, °C	Time, hr	Conversion, %	[η], dl/g	Avg. Mn ^{b)}
MVP	100	0.5	70	45	46	0.295	47000
MVP	100	0.5	60	43	52	0.322	53000
MVP	66.7	1.0	50	20	49	0.237	35000
MVP	66.7	1.0	70	20	50	0.165	21000
PVP	55.6	1.0	70	20	66	0.176	22000
PVP	50.0	1.0	50	48	44	0.281	47000
PVP	50.0	0.5	50	48	32	0.245	37000

a) Tetrahydrofuran was used as solvent.

b) Measured by high-speed membrane osmometer

the cationic polymerization mechanisms of these vinylphenols. The detailed experimental results and the discussions about that will be described below.

In 1976, the industrialization of poly(PVP) resin was successfully achieved by Maruzen Oil Co. for the first time in the world. My fundamental research on the polymerization of the vinylphenols contributed to the success of the industrialization. It was very significant that the development of chemical amplification resist for eximer laser was accomplished by IBM researchers with the use of this resin [10, 11].

2. Radical polymerization of *o*-, *m*-, and *p*-vinylphenol

2-1 Polymerization

Initial polymerization experiment was conducted for OVP (bp 58-59 °C/1mmHg) because it is comparatively easier to synthesize [12, 5].

To estimate dependence of radical species on polymerization of OVP, azobisisobutyronitrile (AIBN) generating the carbon radical, benzoyl peroxide (BPO) generating mainly the oxy radical and tetraethylthiuram

disulfide (TETD) generating the thio radical were used as initiator, respectively. The results of the polymerizations are shown in Table 1. As indicated in Table 1, in the case of AIBN conversions increased with increasing temperature and conversely, the molecular weight decreased as seen in the usual radical polymerizations. In the case of BPO, BPO seems to hardly act as initiator for OVP since the rate of polymerization was much lower than the case of AIBN. In

Table 3 Absorption maxima of ultraviolet spectra for phenol derivatives in absolute ethanol

Compound	λ_{max} , nm
<i>o</i> -Cresol	275
<i>m</i> -Cresol	275
<i>p</i> -Cresol	280
<i>o</i> -(α -Phenylethyl)phenol	275
<i>p</i> -(α -Phenylethyl)phenol	279
2,6-Dimethyl phenol	273
2,4-Dimethyl phenol	281

the case of TETD, TETD exhibited no activity as initiator for OVP. These results might suggest that only the carbon radical has capability to initiate the polymerization to give a fine polymer not only for OVP but also for MVP as well as for PVP.

The radical polymerizations of MVP (bp 75-77 °C /1mmHg) and PVP (mp 69-70 °C) [13, 7] with AIBN as initiator were carried out and their results are shown in Table 2, together with the polymerization conditions. From these results, it can be seen that both of the monomers polymerized through the normal free-radical mechanism to give polymers having high molecular weight (21,000 - 53,000); generally the molecular weight increased with decreasing temperature and initiator concentration. A similar tendency was found in the case of OVP, however, the molecular weight of OVP polymer obtained by the polymerization under similar conditions to these were below 10,000 and is significantly lower than that of MVP and PVP polymers.

Estimations of the structures of polymers were performed by IR and UV spectrophotometries. Estimation by NMR was not made because the resolution of the apparatus in those days was fairly low (60Mc) for the polymer analysis. Model polymers of OVP, MVP, and PVP for the spectrophotometries were prepared by the radical polymerizations of respective acetoxystyrenes and subsequent saponifications [7].

There was observed perfect correspondence between the IR pattern of the resulted polymer and that of the corresponding model polymer in each case. Accordingly, it is suggested that OVP, MVP, and PVP polymers obtained by the radical polymerizations with AIBN consist mainly of the structures formed through the normal vinyl polymerization mechanism.

The UV spectra of OVP, MVP, and PVP polymers in absolute ethanol were also compared with those of the corresponding model polymers. For the purpose of interpreting the spectra of the polymers, the UV spectra of some phenol derivatives in ethanol were investigated. The results obtained are shown in Table 3. It can be found that the absorption maxima of the monosubstituted phenols show essentially the same values regardless of the substituent (methyl or the α -phenyl ethyl) if the substituted position is the same. It is also known [14] that methyl-, ethyl-, and cyclohexyl-phenols reveal the same absorption maxima if the substituted position is the same. In the case of disubstituted phenol, the absorption maximum is also considered to be shifted toward higher wavelength when a

substituted group (such as shown in Table 3) is located in the *para* position with respect to the hydroxyl group of phenol than when no *p*-substituent is present. These data may be helpful in interpreting the polymer structures, especially for OVP and PVP polymers. If a vinylphenol polymer contains some element of structure due to the reaction between the vinyl group and the phenol nuclei, the shape of the UV absorption curve and the absorption maximum of polymer are expected to differ from that of the corresponding model polymer.

It was of interesting that the absorption maxima of OVP, MVP, and PVP model polymer were at 275, 274, and 279 nm respectively, which agreed with those of *o*-, *m*- and *p*-cresols (275, 275, and 280 nm, respectively). Moreover, the shapes of the absorption curved of the model polymers were very similar to those of the corresponding cresols. The spectrum of the polymer obtained by the polymerization with AIBN showed a perfect agreement with that of the corresponding model polymer. This suggests that all of the polymers formed by the radical polymerization consist mainly of the structures of vinyl type polymer. A different spectrum was observed in the case of polymerization with cationic initiator, as described later.

2-2 Kinetics of polymerization

The rates of polymerizations of OVP, MVP, and PVP, as dependence on initiator and monomer concentrations in THF at 70 °C were investigated. The results are summarized in Table 4, together with the apparent activation energies of polymerizations [6, 7, 8]. As seen in Table 4, comparison of the rate equations suggests that only OVP shows anomalous polymerization behavior; i.e., the fact that R_p is proportional to $[I]^{0.72}$ implies that the growing chain radicals are terminated not only by the mutual termination but also to a considerable extent by a chain-transfer mechanism. Therefore, the results in Table 4 correspond to those indicated in Table 1 and Table 2. The apparent activation energies decreases slightly in the order PVP > MVP > OVP.

Table 4 Experimental equations of the rate of polymerization and apparent activation energies of polymerization for *o*-, *m*-, and *p*-vinylphenol

Monomer	Rate of polymerization R_p , mole/l. sec	Apparent activation energy, kcal/mole
OVP	$K_o[M][I]^{0.72}$	21.5
MVP	$K_m[M][I]^{0.52}$	20.1
PVP	$K_p[M][I]^{0.50}$	18.0

The reaction of initiation and propagation might follow the usual free-radical mechanism in each case. However, the termination reactions are very complicated. It is possible to give some explanations for the reactions. Minoura et al [15] have shown that phenol and cresol act as weak chain-transfer agents in polymerization of styrene under oxygen-free conditions. Similar transfer reactions are considered to occur in these monomers as illustrated in eq. (1). The growing radical $p \cdot$ attacks the hydroxyl group

of the monomer molecule to terminate by hydrogen abstraction. Of course, chain transfer to polymer seems to occur, but is quite limited at the initial reaction step because of low polymer concentration. The contribution of such termination reactions as attack of $p \cdot$ on the phenol nucleus might be present to a very small extent.

If the transfer reaction proceeds through a mechanism of the type shown in eq. (1), transfer should take place very frequently only in the case of OVP, and whereas to a limited extent with MVP and PVP. However, there is no plausible reason why OVP shows such a peculiarity. Accordingly, other mechanisms may be concerned in addition to the mechanism as shown in eq. (1). One of them may be of the

type shown in eq. (2). Here the growing radical abstracts a hydrogen atom from the adjacent hydroxyl group located in the same nucleus to deactivate the radical. This intramolecular self-deactivating reaction, therefore, can be regarded as an *ortho* effect.

Owing to resonance, the radicals formed in eqs. (1) and (2) should be relatively stable and not likely to regenerate active chain radicals by adding monomers. If such radicals are incapable of carrying on the polymerization chains, they eventually disappear through combination with other growing free radicals or with each other. Accordingly, polymer formed through the free-radical mechanism contains linkages due to the substitution of the phenol nucleus and the etherification of the hydroxyl group, although these must be in the minority.

2-3 Copolymerization

Copolymerizations of OVP, MVP, and PVP with St or MMA by using AIBN as initiator in THF at 60 °C were investigated. The monomer reactivity ratios r_1 , r_2 and $Q-e$ values for each pair thus obtained are listed in Table 5. The alternating tendency in each case is greater in MMA than in St. Values of Q_1 and e_1 for each vinylphenol monomer with

Table 5 Monomer reactivity ratios r_1, r_2 and $Q-e$ values for *o*-, *m*-, and *p*-vinylphenol at 60°C

Monomer (M ₁)	Comonomer (M ₂)	r_1	r_2	$r_1 r_2$	Q_1	e_1
OVP	St	1.32±0.25	0.72±0.10	0.950	1.66	-1.03
OVP	MMA	0.21±0.06	0.33±0.08	0.069	1.15	-1.23
MVP	St	1.21	0.91	1.10	1.10	-0.80
MVP	MMA	0.40±0.02	0.43±0.06	0.172	1.02	-0.93
PVP	St	1.20±0.13	0.79±0.08	0.948	1.52	-1.03
PVP	MMA	0.25±0.04	0.34±0.06	0.085	1.14	-1.16

Table 6 Copolymerizations of *o*-, *m*-, and *p*-vinylphenol with methyl methacrylate or styrene

Monomer molar ratio	Monomer concn, %	AIBN, % based on monomer	Temp °C	Time hr	Conversion, %	$[\eta]$, dl/g
OVP/St = 1	75.0	1.0	65	45	97	0.321
OVP/MMA = 1	75.0	1.0	65	39	100	0.432
MVP/MMA = 1	50.0	1.0	70	24	89	0.341
PVP/MMA = 1	50.0	1.0	60	45	100	0.438

Table 7 Cationic polymerizations of *o*-, *m*-, and *p*-vinylphenol

Monomer	Solvent ^{a)}	BTE, % based		Temp, °C	Time, min	Conversion, %	[η], dl/g	Avg. Mw
		Monomer concn, %	on monomer					
OVP	EC	33.3	2.9	-30	120	98	0.061	-
OVP	MC	33.3	8.5	-15	900	94	0.066	3900 ^{b)}
OVP	MC	22.2	0.2	-22	120	29	0.043	-
MVP	MC	20.0	3.0	-20	120	20	-	-
MVP	MC	20.0	3.0	-20	1140	54	0.040	-
MVP	MC	20.0	3.0	3	120	18	0.037	710 ^{b)}
MVP	MC	20.0	0.3	-40	120	trace	-	-
PVP	MC	25.0	3.0	10	10	96	0.345	66000 ^{c)}
PVP	MC	20.0	3.0	12	5	93	0.330	62000 ^{c)}
PVP	MC	16.7	0.2	12	5	95	0.505	126000 ^{c)}
PVP	MC	3.2	0.2	-22	60	93	0.545	142000 ^{c)}

a) EC = ethylene chloride; MC = methylene chloride

b) Measured by vapor pressure osmometer

c) Measured by high-speed membrane osmometer

MMA and with St differ somewhat between pairs; the Q_1 and e_1 values are lower in MMA than in St. Even though different $Q-e$ values were obtained, OVP and PVP can be considered to be monomers having similar negative polarities, the negativities being larger than that for MVP. This result agree with the interpretation derived from the resonance theory.

The results for the copolymerizations of OVP, MVP, and PVP with MMA or St (1:1 molar ratio) with the use of AIBN are shown in Table 6. A relatively higher intrinsic viscosity was obtained in each case. In the case of OVP, the mechanism of eq. (2) seems to be reduced significantly by exchanging some portion of OVP with these comonomers.

3. Cationic polymerization of *o*-, *m*-, and *p*-vinylphenol

Cationic polymerizations of OVP, MVP, and PVP in methylene chloride or ethylene chloride with boron trifluoride etherate (BTE) as cationic initiator were conducted. Polymerization conditions and the results of the polymerizations are listed in Table 7. Most of the polymers were isolated from solution after polymerization, except when conversion was low (all MVP polymers and an OVP polymer). The polymerizations of PVP went to completion very rapidly. The rate of polymerization for OVP appeared to be significantly slower than that for PVP but considerably faster than that for MVP. Dependence of the molecular weight was independent on the polymerization conditions in the case of OVP and MVP. The molecular weight for the

MVP polymers seems to be considerably lower. It is remarkable that only PVP gave a polymer having a very high molecular weight which could not be reached by the radical polymerization. Furthermore, Table 7 shows that only PVP follows the normal vinyl polymerization mechanism. If polymerization of PVP was to be conducted in suitable solvents capable of dissolving the resulting polymers (recently, acetonitrile has been used), polymers of higher molecular weight might be produced.

The IR spectra of OVP, MVP, and PVP polymers and the corresponding model polymers were compared. The IR spectrum of PVP polymer corresponded perfectly with that of PVP model polymer and indicated that the polymerization of PVP by the cationic mechanism as well as the radical one gives polymer consisting mainly of normal vinyl-type polymer. On the contrary, some differences were observed among the spectra of OVP and MVP polymers and those of OVP and MVP model polymers. The absorption bands with medium intensity at 890 cm^{-1} in the spectrum of OVP polymer and at 820 cm^{-1} in that of MVP polymer, which are absent in the corresponding model polymers and monomers, might be attributable to the 1, 2, 4-trisubstituted aromatics [16].

The UV spectra of OVP, MVP, and PVP polymer and the model polymers were also compared. Again, the spectrum of PVP polymer corresponded perfectly with that of PVP model polymer. On the other hand, the spectra of OVP and MVP polymer were considerably different from

Table 8 Absorption maxima of ultraviolet spectra for cationically obtained *o*-, *m*-, and *p*-vinylphenol polymers and model polymers in absolute ethanol

	λ_{max} nm	
	Model polymer	Polymer
OVP	275	280
MVP	274	281
PVP	279	279

those of the corresponding model polymers: the absorption maxima of these cationically obtained polymers were shifted toward higher wavelength as shown in Table 8; in addition, shapes of the absorption curves of the polymers changed considerably. With reference to the results shown Table 3, these results appear to suggest that OVP and MVP polymers contain considerable portions of structure caused by the substitution of the phenol nucleus, especially by the substitution of the *para* position with respect to the hydroxyl group.

These IR and UV spectroscopic investigations indicate that the polymerization of PVP takes place almost exclusively through the normal vinyl polymerization mechanism. On the other hand, the polymerization of OVP and MVP proceeds through the reaction between the vinyl group and the phenyl nucleus, in addition to the one between the vinyl groups.

The structures due to the substitution of the phenol nucleus in OVP and MVP polymers obtained by the cationic polymerization with BTE, might be shown as I-VI.

The structure VI in MVP polymer seems to be formed by the result of an intramolecular self-deactivation reaction of the growing cation. It might be presumed that these structures cause formation of highly branched polymers.

The vinyl groups in OVP and PVP are more negative than that in MVP since the hydroxyl group can exert an

influence to the vinyl group by conjugation only when it is in the *ortho* or *para* position. Hence, OVP and PVP should be more susceptible to cationic initiator than MVP. In the case of OVP, some steric hindrance may be induced because the hydroxyl group is located adjacent to the vinyl group. Accordingly, the reactivity between the vinyl groups decreases in the order PVP > OVP > MVP. On the other hand, the phenol nucleus itself is also susceptible toward electrophilic reagents. Such reactivity might decrease in the order MVP > OVP > PVP, because of the number of reaction sites and the fact that the reactivity of the *para* position with respect to the hydroxyl group is stronger than the *ortho* position. Thus competition between the reactions of two vinyl groups and the vinyl versus the nucleus may be induced, namely, the lower the reactivity, for the vinyl, the more the structure caused by the latter reaction increases. Thus, it is anticipated that the rate of polymerization, the molecular weight, and the contribution of structures formed through the vinyl polymerization mechanism decrease in the order PVP > OVP > MVP (actually, PVP >> OVP > MVP). This agrees well the experimental evidence.

Because of the uncertainty of the mechanism of catalytic action in these systems, no detailed explanation of the polymerization mechanism has been offered.

4. Conclusion

Direct polymerizations of *o*-, *m*-, and *p*-vinylphenol with radical and cationic initiators were investigated. As the results, it was clarified for the first time that in the case of radical polymerization, these monomers give polymers having a high molecular weight only when initiator generating the carbon radical is used, while in the case of cationic polymerization, only *p*-vinylphenol gives polymers having a high molecular weight. Through the spectroscopic investigations for the resulted polymers and the kinetic investigations of polymerizations for the monomers, a reasonable understanding for the polymerization mechanisms could be obtained.

It was very significant that this fundamental research contributed to the success of the industrialization of poly(*p*-vinylphenol) resin, which was achieved by Maruzen Oil Co. and the resin was used for the development of KrF excimer laser, which was accomplished by IBM.

5. References

1. C. S. Marvel, N.S. Rao, *J. Polym. Sci.* **4** (1949) 703.
2. E. P. Bonsoll, L. Vallentine, H. W. Melville, *Trans. Faraday Soc.* **48** (1952) 763.

3. T. Tanaka, T. Yamashita, T. Yokoyama, *Kogyo Kagaku Zasshi* **60** (1957) 1595.
4. J. Kumanotani et al, *paper presented at meeting of the Society of Polymer Science, Japan*, June 1964.
5. M. Kato, H. Kamogawa, *J. Polym. Sci. A-1* **4** (1966) 1773.
6. M. Kato, H. Kamogawa, *J. Polym. Sci. A-1* **4** (1966) 2771.
7. M. Kato, *J. Polym. Sci. A-1* **7** (1969) 2175.
8. M. Kato, *J. Polym. Sci. A-1* **7** (1969) 2405.
9. M. Kato, Y. Takemoto, Y. Nakano, M. Yamazaki, *J. Polym. Sci. Chem. Ed.* **13** (1975) 1901.
10. H. Ito, C. G. Willson, J. M. J. Frecht, *US Patent* 4,491,628 (1985).
11. H. Ito, C. G. Willson, *Polym. Eng. Sci.* **23** (1983) 1012.
12. K. Freis, G. Fickwirth, *Ber.* **41** (1908) 367.
13. B. B. Coorosan, W.J. Heitzelman, L. H. Schwartzman, H. E. Tiefenthal, R.J. Lokken, J. E. Nikers, G. R. Atwood, F. J. Pavlik, *J. Org. Chem.* **23** (1958) 544.
14. R. A. Freidel, M. Orchin, *"Ultraviolet Spectra of Aromatic Compounds"*, John Wiley, New York, N. Y. (1951).
15. Y. Minoura, N. Yamamoto, T. Ishiii, *Makromol. Chem.* **71** (1969) 159.
16. L. J. Bellamy, *"The Infra-red Spectra of Complex Molecules"*, John Wiley, New York, N. Y. (1954).