

Acrolein 과 Phenol 류의 중합

沈 貞 變* · 全 榮 升*

Polymerization of Acrolein with Phenols

*Jyong Sup Shim · *Young Sung Jun

Dept of Chem. Eng., Seoul National Univ.

Abstract

The polymerization of acrolein with phenol was studied in acidic and basic conditions for various reaction times. The initial reaction products were separated by thin layer chromatography and analyzed by infrared spectra, and then the polymer obtained by further reaction was also analyzed. The polymerization mechanism was discussed from the analytical results of the initial products and final cured polymers. According to the nearly related mechanism of polymerization of acrolein with phenol, the reactions of acrolein with phenols also yielded condensation polymers like phenol-formaldehyde polymers.

Introduction

It has been reported that Alder and Tingstam¹⁾ synthesized a derivative of coumarone from 1 mole of acrolein with 2 moles of phenol in acetic acid solution, and also Farnham²⁾ synthesized triphenylol by the reaction of acrolein with excess of phenol in hydrochloric acid solution. But there have not been any reports on the mechanisms of the polymerization of acrolein with phenols except a few patents.^{3), 4), 5)}

In this paper, in order to investigate the mechanism of the polymerization of acrolein with phenol, the reactions of acrolein with phenol were carried out under acidic and basic conditions, and the obtained polymers by further reaction were confirmed by various analytical methods and the basic properties of the polymers were measured. Thus, the initial reaction products formed under acidic and basic conditions were separated by thin layer chromatography

and confirmed by infrared spectroscopy and molecular weight determinations. And then the polymerizations were carried out in various conditions of PH, temperature and mole ratio of acrolein to phenol, and the yields, the molecular weights and the infrared spectra of the obtained polymers were determined. From the analytical results, the mechanism of the polymerization was proposed.

Experimental

Acrolein was washed with aqueous sodium chloride solution and distilled water, then dried with anhydrous sodium sulfate, and distilled at 27-28°C under reduced pressure. It was kept at -10°C before use. Phenol, m-cresol and hydroquinone (HQ) were reagent grades and were used without further purification.

Reaction procedure of acrolein with phenol for analysis of thin layer chromatography

In Acidic Solution. In a 4-necked round bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser were charged 50%

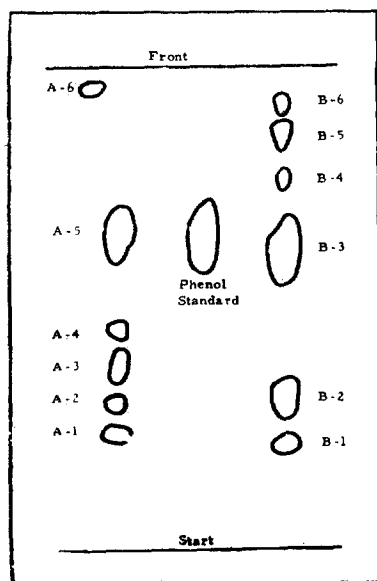
*서울工大 化學工學科

aqueous solution of $\frac{1}{2}$ mole of phenol and 50% aqueous solution of $\frac{1}{2}$ mole of acrolein, and then the pH of the mixture was adjusted to 1.6 by 1N HCl solution. After the mixture was reacted at 70–75°C for 8 hrs., the red brown oily liquid was obtained as a prepolymer, which was concentrated by evaporation of water and unreacted acrolein by vacuum oven, but still it contained intermediate products, little water and phenol (Sample A)

In Basic Solution. The reaction was carried out in the same procedure as in an acidic solution except that the pH of mixture was adjusted to 12.4 by 1N NaOH solution. The yellow brown oily liquid was obtained as a prepolymer. (Sample B)

Separation of the initial products by thin layer Chromatography (TLC)

The glass plates were coated by a spreader with a



(A)-: the products formed under acidic condition;

(B)-: the products formed under basic condition.

Fig. 1 Thin layer chromatogram of the initial products of acrolein-phenol

mixture of 25g of Kieselgel HF₂₅₄ (E. Merck, Germany) and 50 ml of distilled water. After drying they were activated at 105°C for 40 minutes in a drying oven. After a few drops of the sample (A), (B)

and pure phenol were dropped on the starting line of the glass plate, they were developed in a tank filled with the solvent of 25 : 2 benzene-methanol. The separated spots on the plate by developing were detected in a box with a fluorescent light. The sample (A) and (B) were separated into six spots respectively. The spots were taken off and extracted in the solvent of 1 : 1 benzene-methanol.

Preparation of Acrolein-Phenol Polymer

After 50% aqueous solution of phenol and 50% aqueous solution of acrolein were charged in a flask, the pH of the mixture was adjusted by 1N HCl or 1N NaOH solution. The mixture was reacted at 67–74°C for a given time to yield black brown resin, which was purified by dissolving it in a solvent of 1 : 1 benzene-methanol and precipitating it in hexane. After a reprecipitation, it was dried in vacuo. The reaction conditions, molecular weights and yields in the polymerization were summarized in Table II.

Preparation of Acrolein-m-Cresol and Acrolein-Hydroquinone Polymers.

After 50% aqueous solution of $\frac{1}{2}$ mole of m-cresol and 50% aqueous solution of $\frac{1}{2}$ mole of acrolein were charged in a flask, the pH of the mixture was adjusted to 1.4 by 1N HCl solution. When it was reacted at 70–75°C for 26 hours, it gave black brown resin insoluble in solvent. It was washed with distilled water and was dried in vacuo.

The polymerization of acrolein with hydroquinone was carried out to give black brown resin insoluble, in the same experimental procedure as in the polymerization of acrolein with m-cresol except that the pH of the mixture was adjusted to 1.5 and it was reacted for 38 hours.

Analytical Methods

Molecular Weight Determinations. Molecular weights of acrolein-phenol polymers were determined with Hewlett-Packard 302B Vapor Pressure Osmometer by using ethyl alcohol as solvent. Those of the polymers of acrolein-m-cresol and acrolein-hydroquinone were not determined due to their insolubility.

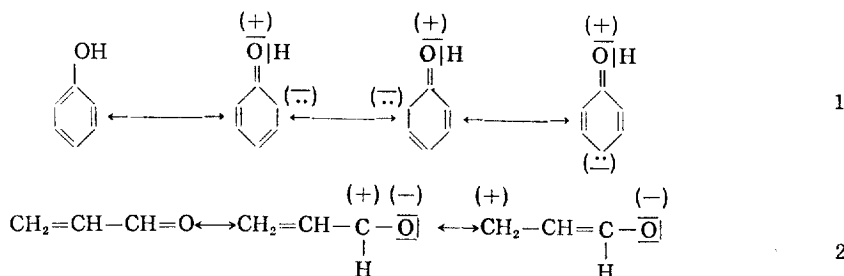
Infrared Spectra. The infrared spectra of acrolein-phenol polymers were recorded through film on KBr

plate and the cured acrolein-m-cresol and acrolein-hydroquinone polymers were recorded through by Beckman IR-12.

Elementary Analyses. The polymers formed by the reactions of the acrolein with phenol, m-cresol and hydroquinone were analyzed by Coleman Carbon and Hydrogen Analyzer, and Coleman Nitrogen Analyzer.

Results and Discussion

In the acid catalyzed and the base-catalyzed reactions between phenol and acrolein, there are many possibilities to react on the ortho and para positions of the phenol, and on the vinyl and aldehyde groups of the acrolein. The ortho and para positions of the phenol are indicated negatively by resonance hybrid symbolism, eq. 1.



The conjugated molecule of the acrolein also presents resonance form eq. 2.

Accordingly, from the view point of the possible reaction between the nucleophilic ortho and para positions of phenol and the electrophilic carbon atoms of acrolein molecule, it is suggested that the formation of alcoholic form-compounds by the addition reaction of aldehyde group to phenol, and the formation of the aldehyde form-compounds by the addition reaction of the double bond to phenol occur concurrently but predominantly.

Thus, it was attempted to confirm the initial reaction products obtained from the reaction of acrolein phenol under acidic or basic condition. Fig. 2 and Table I are the results obtained from TLC separation, IR absorption spectra analyses, and molecular weight determinations of the initial reaction

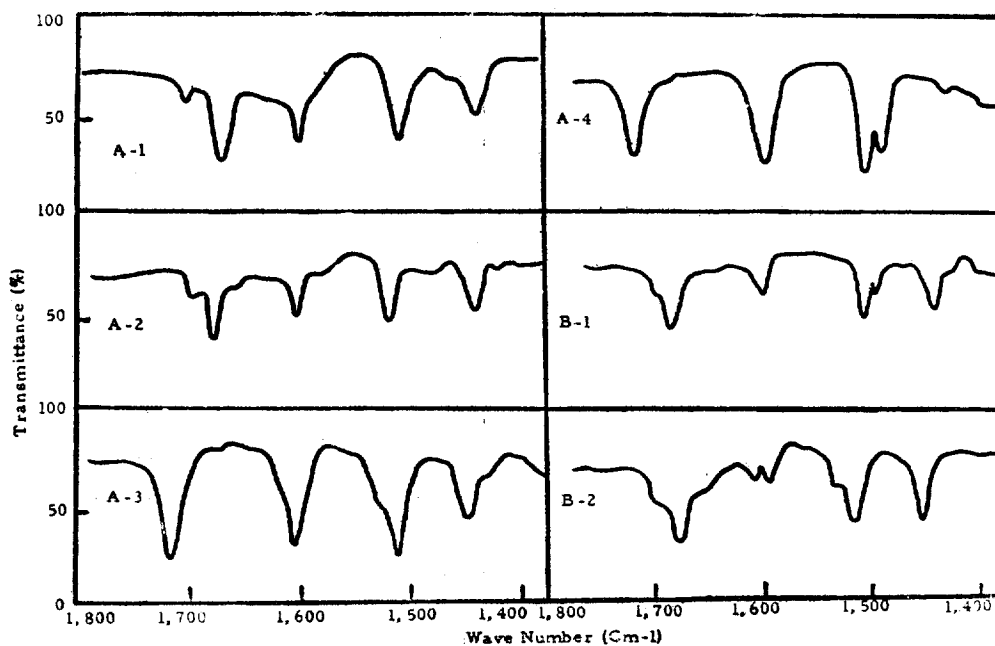
products.

Since the absorption bands of C=C at 1670 cm^{-1} and secondary —OH group at 1120 cm^{-1} in IR absorption spectra of Spot No. A-1, A-2, B-1 and B-2, and their molecular weights of 158 to 161 in Table I confirm the formation of the compounds with a double bond and a OH group in structure, they must be alcoholic form-compounds. Similarly, since the absorption bands of —CHO at 1720 cm^{-1} of Spot No. A-3 and A-4 and their molecular weights of 151 to 153 confirm the formation of compounds with a aldehyde group in their structure, they must be aldehyde form-compounds.

But as shown in Fig. 1, there are two isomers of Spot No. A-1 and A-2 or Spot No. B-1 and B-2 in alcoholic form-compounds, and also there are two isomers of Spot No. A-3 and A-4 in the aldehyde form compounds.

On the other hand, substituents ortho⁶⁾ to the hydroxyl group of the phenol tend to increase the values of rate of flow (Rf) because they reduce the adsorption affinity to the adsorbent, hence the Rf of the ortho compound produced in this experiment is greater than that of the para-compound. In the earlier papers,^{7),8),9)} it has been reported that the formation of the ortho compound under alkaline sodium hydroxide solution and the formation of the para compound under strongly acidic condition respectively, occur predominantly in the initial reaction products of phenol and formaldehyde.

Therefore, comparing the sizes and the Rf's of the spots in Fig. 1 and Table 1, Spot No. A-2 and B-2 are believed to be ortho compounds of alcoholic form and Spot No. A-4 to be ortho compound of aldehyde form. Also Spot No. A-1 and B-1 are believed to



A-1, B-1 : p-aldol-
 A-2, B-2 : o-aldol-
 A-3 : p-aldehyde-
 A-4 : o-aldehyde-form compound

Fig. 2 Infrared Spectra of the Separated Spots by TLC

Table 1. Analytical Data of Initial Products

Spot No.	Rf	Mol. wt.	Detected Group by IR Spectra	Formula
A-1	0.23	159	—C=C	<chem>Oc1ccc(cc1)C=C</chem> <chem>Oc1ccc(cc1)C(O)C=C</chem>
A-2	0.31	158	—C=C	<chem>Oc1ccc(cc1)C(O)C=C</chem> <chem>Oc1ccccc1C(O)C=C</chem>
A-3	0.38	153	—CHO	<chem>Oc1ccc(cc1)CC=O</chem> <chem>Oc1ccc(cc1)CC=O</chem>
A-4	0.46	151	—CHO	<chem>Oc1ccc(cc1)CC=O</chem> <chem>Oc1ccc(cc1)CC=O</chem>
A-5	0.65	94	a	<chem>Oc1ccccc1</chem>

A-6	0.96	—	—	—
B-1	0.23	161	—C=C	<chem>Oc1ccc(cc1)C=C</chem> <chem>Oc1ccc(cc1)C(O)C=C</chem>
B-2	0.33	160	—C=C	<chem>Oc1ccc(cc1)C(O)C=C</chem> <chem>Oc1ccccc1C(O)C=C</chem>
B-3	0.61	94	a	<chem>Oc1ccccc1</chem>
B-4	0.78	—	—	—
B-5	0.86	—	—	—
B-6	0.93	—	—	—

a pure phenol, standard.

be para compounds of alcoholic form, and Spot No. A-3 to be para compound of aldehyde form. Since the Rfs of the Spot No. A-5 and B-3 are consistent with that of the standard phenol in Fig. 1, they seem to be phenol. Although Spot No. A-6, B-4, B-5, and B-6 can not be identified with infrared

spectra, but they seem to be derivatives of acrolein itself because their Rfs are greater than that of phenol.

Accordingly, summarizing the analytical results of the initial reaction products in Table I, the reaction under acidic condition yielded two isomers of alcoholic form compounds α -(o-hydroxy phenyl)- and α -(p-hydroxy phenyl) allyl alcohols and two isomers of aldehyde form-compounds 3-(o-hydroxy phenyl)- and 3-(p-hydroxy phenyl) propionaldehydes of ortho and para substituents, and the reaction under basic condition yielded two isomers of alcoholic form-compounds α -(o-hydroxy phenyl)- and α -(p-hydroxy phenyl) allyl alcohols of ortho and para substituents.

After initial addition reaction aforementioned, further reaction proceeded to form viscous liquid, resinous brittle material and finally crosslinked resin stepwise. As shown in Table II, the yields and the molecular weights of the polymers formed under strongly acidic condition are greater than under basic condition. Under acidic condition the reaction of 1:1 acrolein-phenol proceeded to form a crosslinked polymer finally, however, under basic condition the only reaction in which the mole ratio of acrolein to phenol was greater than 1:1, formed a crosslinked polymer finally.

In order to clarify the polymerization mechanism, the IR absorption analyses of the intermediate products and the finally crosslinked polymers (Table II) gave the following Fig. 3.

The absorption bands of $C=C$ at 1670 cm^{-1} , $-CHO$ at 1720 cm^{-1} , secondary $-OH$ at 1120 cm^{-1} appeared in the infrared spectrum of the intermediate product (Run No. 2) formed under acidic condition as in (A) of Fig. 3, but on the other hand, the absorption bands of $-CHO$, and secondary $-OH$, disappeared and those of $-OH$ and $C=C$ was decreased in the spectrum of the final product (Run No. 4) formed under acidic condition as in (B) of Fig. 3.

While the absorption bands of $C=C$ at 1670 cm^{-1} , secondary OH at 1120 cm^{-1} , and $-OH$ at 3400 cm^{-1} appeared in the infrared spectrum of the intermediate

Table II. Polymerization of Acrolein with Phenol

Run No.	React ants Acr. Phen. mole	Conditions			Products	
		Temp °C	Time hr.	pH	Yield %	Mol. wt.
1	1 1	70-75	30	1.3	41.5	289
2	1 1	67-74	50	1.3	78.5	737
3	2 1	73-78	81	1.3	92.2	b
4	1 1	67-74	96	1.3	90.2	c
5	1 1	68-73	30	12.4	29.3	294
6	1 1	69-74	50	12.4	36.8	465
7	1 1	69-74	82	12.4	68.7	623
8	3 1	70-75	108	12.4	93.4	a
9	1 1	71-76	40	1.5	56.2	—
10	1 1	71-76	40	1.2	81.6	986
11	1 1	70-75	40	12.6	37.2	—
12	1 1	69-74	40	12.7	42.4	—

a Percentage of the amount of the obtained polymer to the total amount of the acrolein and phenol after a reprecipitation.

b, c, d, Insoluble in solvent.

product (Run No. 6) formed under basic condition as in (C) of Fig. 3, the band of $C=C$ remained

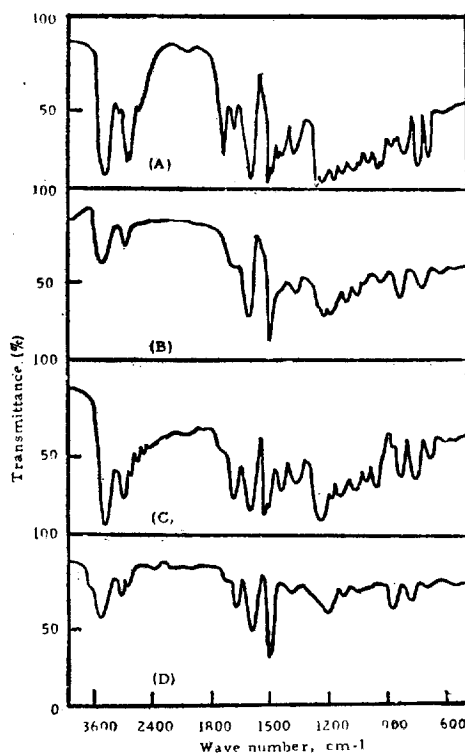


Fig. 3 Infrared spectra of acrolein-phenol polymers
(A) Run No. 2; (B) Run No. 4;
(C) Run No. 6; (D) Run No. 7.

and that of $-\text{OH}$ was decreased in the spectrum of the final product (Run No. 7) formed under basic condition as in (D) of Fig. 3.

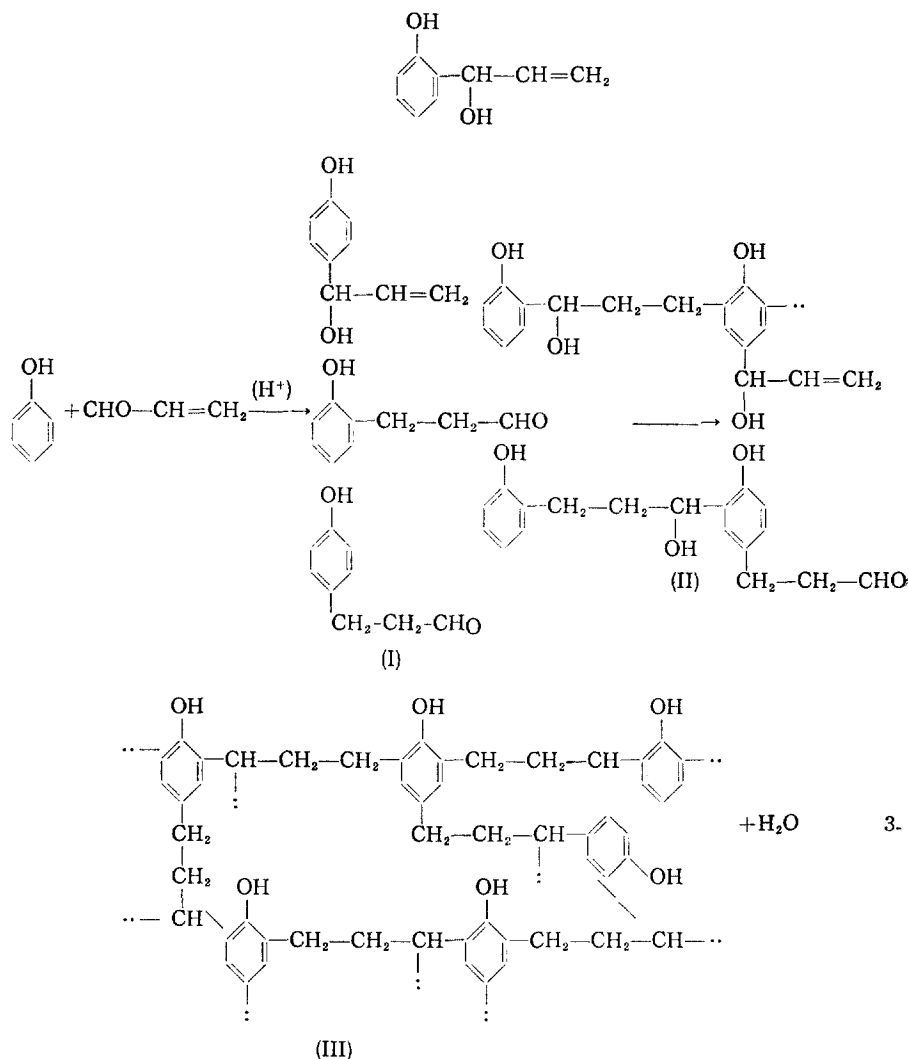
From the analytical results aforementioned, it is believed that the polymerization of phenol-acrolein, which is similar to that of phenol-formaldehyde, is carried out in 3 stages such as addition, condensation and crosslinking.

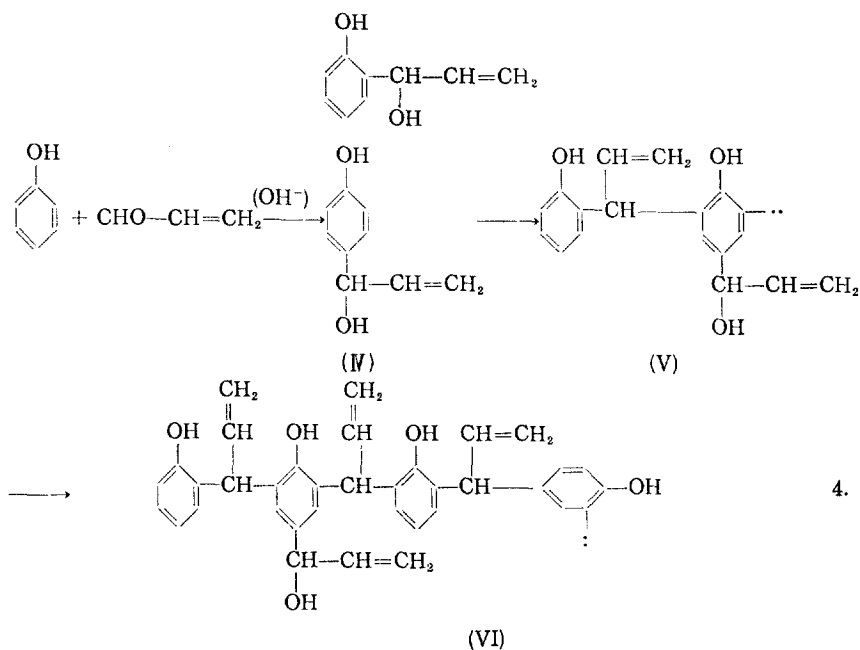
Therefore, the polymerization mechanism under acidic condition can be proposed as the following eq. 3 from the reactions e.g., the formation of initial reaction products of 4 isomers, the formation of intermediate products (oligomers) with $\text{C}=\text{C}$, $-\text{OH}$

group and $-\text{CHO}$ group in its structure, and the formation of the crosslinked polymer without $\text{C}=\text{C}$ bond and $-\text{CHO}$ group.

Also the polymerization mechanism under basic condition of NaOH aqueous solution (for complete dissociation) can be proposed as the following eq. 4 from the reactions, e.g., the formation of initial products of 2 isomers, the formation of intermediate products (oligomers) with $\text{C}=\text{C}$ bond and $-\text{OH}$ group, and the formation of the non-cured polymer with $\text{C}=\text{C}$ bond.

Polymerization of Acrolein with m-Cresol and Acrolein with HQ

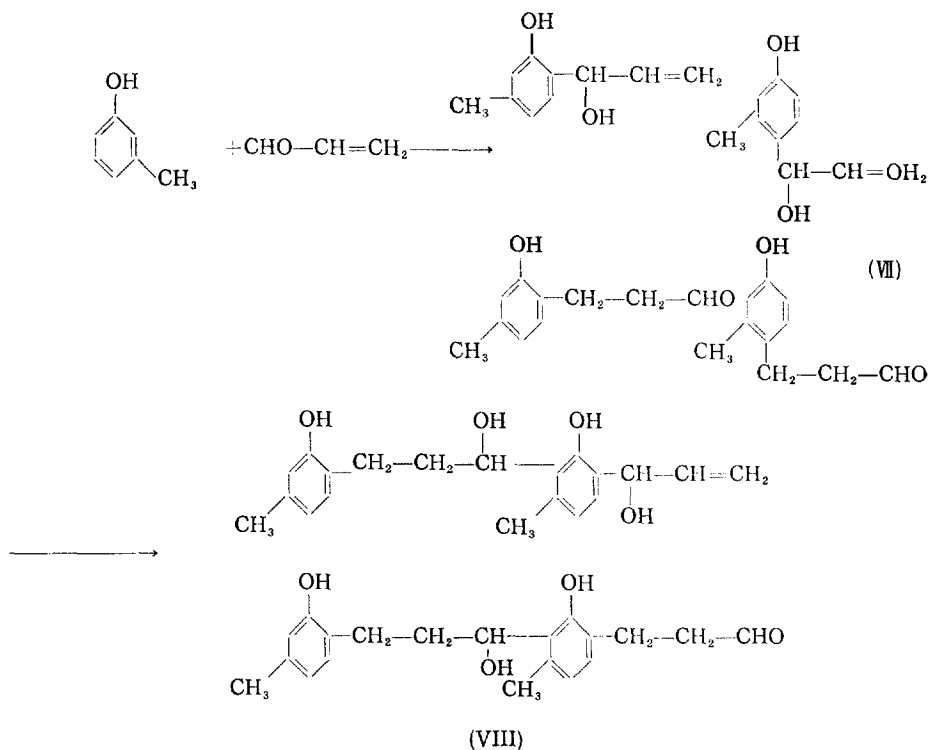


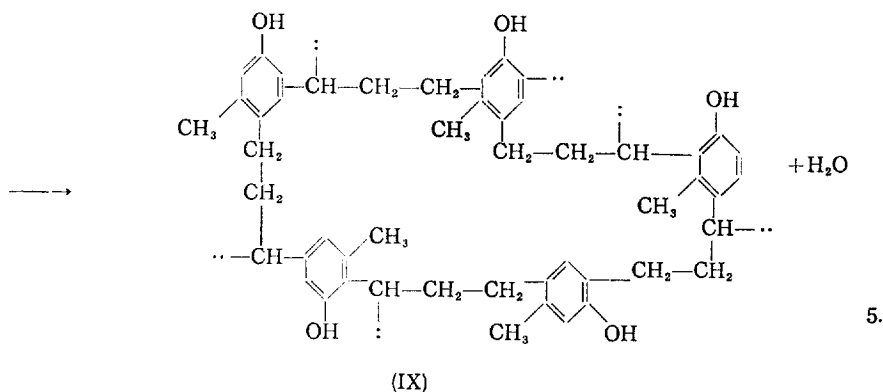


On the basis of the mechanism of phenol-acrolein, polymerization of the acrolein with m-cresol and with HQ was carried out to form polymers.

Therefore their polymerization mechanism will be proposed as in eq. 5.

In the spectra of the finally cured polymer obtained



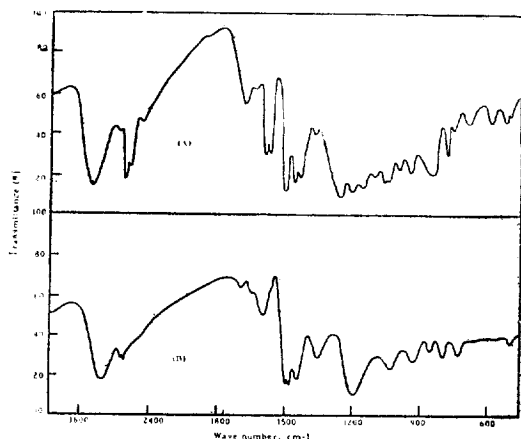


from the polymerization whose mechanism is shown in eq. 5, the absorption band of $-\text{OH}$ at 3400 cm^{-1} , the weak band of $-\text{CHO}$ at 1720 cm^{-1} and the

disappeared band of $\text{C}=\text{C}$ at 1670 cm^{-1} in (A) of Fig. 4 support the confirmation of acrolein-m-cresol polymer.

On the other hand, the analytical elementary analyses of the finally cured polymers of acrolein-m-cresol and acrolein-HQ in Table III have some deviation from the calculated values, which are believed to come from incomplete condensation.

Such results as infrared spectra, elementary analyses and infusibilities confirm the above proposed mechanism, eq. 5 of the polymerization of acrolein-cresol, like that of acrolein-phenol. On the basis of polymerization of acrolein-phenol, it was confirmed that the acrolein and other phenols, e.g., resorcinol, xylenol, catechol were reacted to form condensation polymers in preliminary experiment.



(A) Acrolein-m-Cresol, cured finally

(B) Acrolein-HQ, cured finally

Fig. 4 Infrared spectra of acrolein-phenols polymers

Table III. Characterization of Acrolein-m-Cresol and Acrolein-HQ Polymers

Polymer	Repeating unit	Color	MP, °C	Elemental analyses					
				Calculated (%)			Found (%)		
				C	H	O	C	H	O
Acrolein-m-Cresol	$ \begin{array}{c} \text{OH} \\ \\ \cdots - \text{C}_6\text{H}_3(\text{CH}_3) - \text{CH} - \text{CH}_2 - \text{CH}_2 - \cdots \\ \\ \text{CH}_3 \end{array} $	black brown opaque	infus.	82.19	6.85	10.96	81.88	6.91	11.21
Acrolein-HQ	$ \begin{array}{c} \text{OH} \\ \\ \cdots - \text{C}_6\text{H}_3(\text{OH}) - \text{CH} - \text{CH}_2 - \text{CH}_2 - \cdots \\ \\ \text{OH} \end{array} $	black brown opaque	infus.	72.97	5.41	21.62	72.42	5.44	22.14

References

1. Alder, Tingsteam, Arkiv Kemi Mineral Geol., B 16 No. 18, 1-7 (1943).
2. A.G. Farnham, Brit. Patent 787, 051 (1957).
3. Farbenfabriken Bayer Aktiengesellschaft (Ger.), Brit. Patent 747, 093 (1952).
4. J.S. Fry, J.L. Welch (U.S.A.), Brit. Patent 874, 245 (1962).
5. Bel. Patent 672, 190 (1966).
6. K.Randerath, Thin Layer Chromatography, Verlag Chemie, Darmstadt 3rd Edit., p.210 (1966).
7. J.H. Freeman and C.W. Lewis, *J. Am. Chem. Soc.*, 76, 2,080 (1954).
8. H.G. Peer, *Rec. Trav. Chem.*, 78, 851 (1959).
9. J.S. Rodia and J.H. Freeman; *J. Org. Chem.*, 24, 21 (1959).

