Formaldehyde Resins. LXXV. Novolak Resin from p-Chlorophenol and Formaldehyde*

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In 1956, Burke et al. obtained some novolak resins of a high molecular weight by the reaction of *p*- or *o*-chlorophenol with *s*-trioxane at 150°C in a sealed tube1). They reported that, after fractionation and acetylation of the resin, a fraction of a lower molecular weight showed the molecular weight of 2090, which was determined by the cryoscopic method using benzil as the solvent. This result attracted our attention, as it had previously been believed that the molecular weight of novolak was below 1000. In a foregoing paper of this series, Imoto and Tanigaki2) repeated Burke's experiments, using *p*-chlorophenol and α-polyoxymethylene, but the molecular weight of the resin obtained was below 1000.

In the present study, we followed Burke's experiment accurately and determined the molecular weight distribution of the resin. The molecular weight of the resin obtained here was 400 to 1000. No novolak resin of a high molecular weight, such as those described by Burke, could be obtained. The molecular weight distribution of the resins obtained at the early stage of the reaction showed rather a good agreement with the theoretical equation submitted by one of the present authors (M. I.)3), but as a general rule, they did not agree. This lack of agreement was due to a reaction of the "reformation" of the novolak-molecules4). Therefore, it was considered that the distribution should be ruled by Poisson's distribution equation, as was proved to be true.

Experimental

Materials.—*p*-Chlorophenol was of a commercial grade and was used after distillation (b. p., 79∼80°C/5 mmHg). *p*-Toluenesulfonic acid was refined by recrystallization from water; m. p., 103∼104°C. *s*-Trioxane was of a purity of over 99%. The solvent, bis(2-ethoxyethyl) ether, was synthesized according to the method given in the literature5); b. p., 77∼80°C/11 mmHg.

The Formation of the Resin.—A solution composed of 12.86 g. (0.1 mol.) of *p*-chlorophenol, 3.03 g. (corresponding to 0.101 mol. of formaldehyde) of *s*-trioxane, 0.200 g. of *p*-toluenesulfonic acid and 15 ml. of bis(2-ethoxyethyl) ether was placed in a sealed tube and heated at 150°C for 2∼24 hr. in an oil bath. After cooling the reaction mixture, it was added slowly with vigorous stirring into about 500 ml. of water containing a small amount of hydrochloric acid. The resin precipitated here was dissolved in about 50 ml. of acetone to purify it. When the reaction was carried out at 150°C over for 11 hr., a small amount of the insoluble resin in acetone was obtained. The acetone solution was poured into one liter of water to precipitate the novolak resin. After the resin had been filtered, it was dried at about 60°C under reduced pressure (1 mmHg).

The Acetylation of the Resin.—After 1 g. of the resin had been dissolved in 10 ml. of pyridine, 2∼3 ml. of acetic anhydride was added and left standing for several days at room temperature. The reaction mixture was poured into water to yield an acetylated resin. The purification was carried out by the reprecipitation method, using acetone and water. The completion of the acetylation was comfirmed by the disappearance of the OH bands in the infrared absorption spectra.

The Saponification of the Acetylated Resin.—One gram of caustic potassium was dissolved in 15 ml. of methanol, and the solution was maintained at 5°C, Then, 1 g. of acetylated resin was dissolved in 25 ml. of acetone, and the afore-mentioned solution was added and cooled at 5°C for 24 hr. The reaction mixture was poured into water to yield a saponified resin. The completion of the saponification reaction was comfirmed by the disappearance of the CO absorption bands in the infrared spectra.

The Fractionation of the Resin.—Fractionational precipitation was carried out by the successive addition of a poor solvent to the resin solution or by removing the solvent from the resin solution. Acetone, tetrahydrofuran or dimethylformamide was used as the solvent, and water or 33% ethanol-water as the poor solvent. Five to seven fractions were obtained from an about 5% resin solution by the successive addition of the poor solvent at 30.0 ±0.1°C and by removing the solvent.

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* LXXIV: M. Imoto, T. Tanigaki and A. Fukui, *Memoirs of the Faculty of Engineering, Osaka City University*, **4**, 181 (1962).

1) a) W. J. Burke et al., *J. Polymer Sci.*, **20**, 75 (1955). b) W. J. Burke et al., ibid., **32**, 221 (1958).

2) M. Imoto and T. Tanigaki, *Memoirs of the Faculty of Engineering, Osaka City University*, **1**, 1 (1959).

3) M. Imoto, *Textile World (Japan)*, **35**, 589, 634 (1944).

4) a) M. Imoto, H. Kakiuchi and T. Otsu, *Chem. High Polymers, Japan*, **8**, 497 (1951); b) H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1651 (1960); c) cf. also Ref. 2.

5) L. H. Cretcher and W. H. Pittenger, *J. Am. Chem. Soc.*, **47**, 164 (1925).

The Molecular Weight Determination of the Resin.—The molecular weight of the resin was determined by the cryoscopic method, using camphor as solvents. It was shown by Imoto and Tanigaki²⁾ in the previous paper that camphor was suitable for the molecular weight determination of the novolak resin. When the molecular weight reached over 1000, however, the determination of molecular weight became difficult, because of the coloring of the camphor solution. Moreover, the acetylated resin is only with difficulty soluble in camphor. Therefore, we used benzil for the resin which could not be determined with camphor, as was described in Burke's papers.

Results

The Yield and Molecular Weight of the Resin. — The yield of the resin reached about 90% at 150°C for 2 hr. The maximum of the yield was seen at 8 hr. With the reduction in yield after that time, a small quantity of the insoluble resin was observed. The molecular weight of the soluble resin became larger with an increase in the yield at the initial stage, but it had the tendency to drop once when the formation of the insoluble resin had taken place and then to increase again (Fig. 1). The yields and the molecular weights of the resins obtained at 120°C increased with the reaction time (Fig. 2).

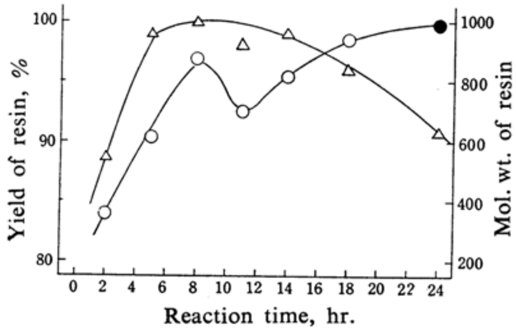


Fig. 1. The process of the formation of resin at 150°C.
△ Yield of resin ○ Mol. wt. of resin
● Mol. wt. calculated from mol. wt. of acetate

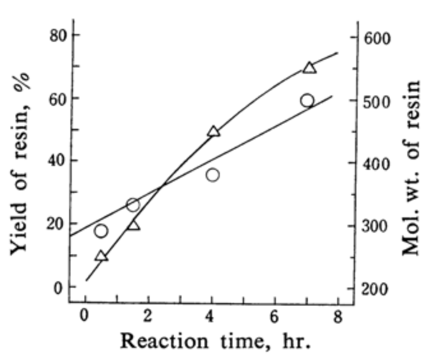


Fig. 2. The process of the formation of resin at 120°C.
△ Yield of resin ○ Mol. wt. of resin

The Viscosity of the Resin. — The viscosity of the resin was determined at 25°C in a solution of 10 ml. of *N, N*-dimethylformamide containing 0.05 g. of the sample. Changes of the solution viscosity with reaction time showed the same tendency as that of the molecular weight (Fig. 3). No definite relationship between the molecular weight and the viscosity could be obtained.

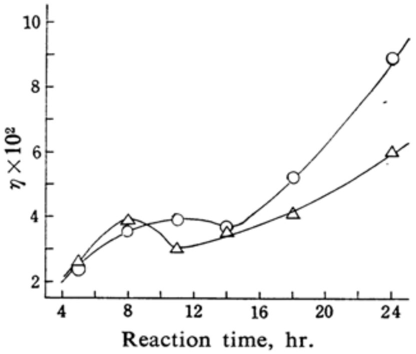


Fig. 3. The changes of specific viscosity of resins with reaction time.
△ Viscosity of acetate
○ Viscosity of resin

TABLE I. FRACTIONATION OF THE RESIN OBTAINED BY THE REACTION AT 120°C FOR 4 hr.

Fraction	Yield*, g.	Differential weight, %	Mol. wt.
1	0.762	15.72	910
2	1.078	22.25	600
3	0.652	13.45	510
4	0.750	15.48	340
5	1.604	33.18	280
Total	4.846	100.0	

* Sample weight: 5.02 g.

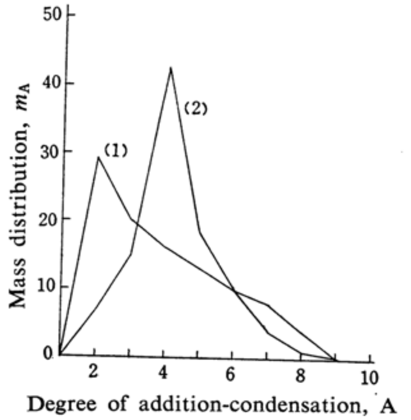


Fig. 4. Mass distribution curves of the resins reacted at 120°C.
(1) 120°C, 4 hr. (2) 120°C, 7 hr.

Fractionation.—Five fractions were obtained from a 100 ml. solution of acetone containing 5 g. of the resin, which was obtained by reacting for 4 hr. at 120°C, by removing the acetone, and by the addition of water. The yield was 96.5% (Table I).

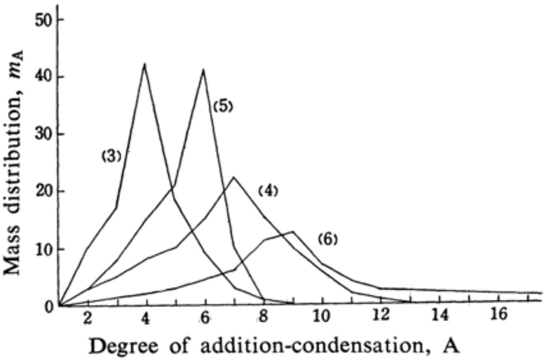


Fig. 5. Mass distribution curves of the resins reacted at 150°C.
(3) 150°C, 2 hr. (4) 150°C, 8 hr.
(5) 150°C, 14 hr. (6) 150°C, 24 hr.

TABLE II. REFORMATION OF THE RESIN

Original resin			Reformed resin		
Conditions of preparations		Mol. wt.	Conditions of reformation		Mol. wt.
hr.	°C		hr.	°C	
1.5	120	330	3	150	460
2	150	360	3	150	620
5	150	610	3	150	920*
8	150	870	3	150	840*
8	150	870	10	150	770*
11	150	700	3	150	930*

* The insoluble product was obtained in a small yield.

The distribution curves are shown in Figs. 4 and 5.

The Reformation of the Resin.—1.3 g. of the resin and 0.020 g. of *p*-toluenesulfonic acid were dissolved in 1.5 ml. of bis(2-ethoxyethyl) ether and then heated in a sealed tube for 3 hr. at 150°C. The reaction product was purified by reprecipitation from acetone with water. The results obtained may be seen in Table II. The yields in all runs were about 75%.

Discussion

A Comparison of Burke's and the Present Author's Results. — The results obtained by Burke and by us are shown in Tables III and IV.

As can be seen from these tables, our results agreed well with Burke's results with regard to the viscosity and elementary analysis. Also, the infrared spectra of the resins show a good agreement (Fig. 6). Consequently, it is believed that the resins obtained by both are the same; only the molecular weights are quite different.

The Molecular Weight Distribution of the Resin.—While the distribution curves of the resins obtained at 150°C did not agree at all with Imoto's equation, a tendency for agreement in Poisson's distribution was observed for the resin obtained by reaction for 8 hr. at 150°C (Fig. 7). It is believed that this was because the reaction was so violent that the yield reached 90% in only 2 hr. and that "a reformation reaction" had already occurred. We, therefore, carried out the reaction under milder conditions, at 120°C, and thus obtained a distribution curve of the resin at the early

TABLE III. COMPARISON OF ELEMENTARY ANALYSIS OF BURKE'S AND OUR RFSINS (150°C for 24 hr.)

	Burke et al.				Imoto and Nakade				
	[η]	C, %	H, %	Cl, %	[η]	C, %	H, %	Cl, %	Mol. wt.
Resin	0.095	60.55	3.96		0.088	60.85	4.49	20.88	—
Acetate	0.057	60.75	3.86	18.55	0.059	60.23	3.93	18.64	1250
Resin after saponification	0.097	61.00	3.80		0.080	60.38	4.03		—

TABLE IV. COMPARISON OF THE FRACTIONAL DATA

No. of fraction	Burke et al.			Imoto and Nakade		
	Wt. of resin recovered, g.	[η]	Mol. wt. of acetate	Wt. of resin recovered, g.	[η]	Mol. wt. of acetate
1	1.6	0.503	—	0.89	—	—
2	2.0	0.136	—	1.62	0.150	1250
3	1.7	0.089	—	0.52	0.068	1210
4	1.3	0.054	4260	0.85	0.035	1260
5	2.0	0.036	2090	0.76	0.035	720
6	1.0	0.017	—	0.30	0.023	380

TABLE V. ELEMENTARY ANALYSIS DATA OF RESIN

Reaction temp., °C	Reaction time, hr.	Mol. wt. of resin	Obs.			Formula	Calcd.		
			C, %	H, %	Cl[a], %		C, %	H, %	Cl, %
120	0.5	290	59.10	4.06	23.05, 23.01	$C_{13}H_{10}O_2Cl_2$	58.01	3.75	26.35
120	1.5	330	59.05	4.39	23.27, 23.00	$C_{20}H_{15}O_3Cl_3$	58.63	3.69	25.96
120	4.0	380	59.12	4.41	24.52	$C_{27}H_{20}O_4Cl_4$	58.93	3.66	25.76
120	7.0	500	59.42	3.59	24.36	$(C_7H_5OCl)_n$	58.81	3.59	25.22
150	2.0	360	59.64	4.65	24.21				
150	5.0	610	59.19	4.39	21.29, 21.21*				
150	8.0	870	59.90	4.35	21.04, 21.28, 22.57*				
150	11.0	700	61.21	4.41	22.64				
150	14.0	820	60.19	4.37	21.17, 21.36, 22.68*				
150	18.0	940	60.64	4.59	21.78*				
150	24.0	1250**	60.85	4.49	20.88*				

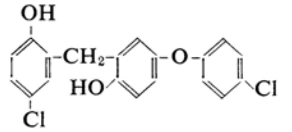
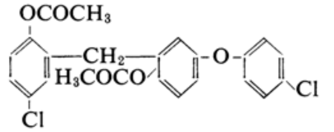
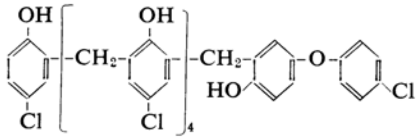
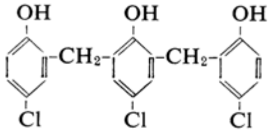
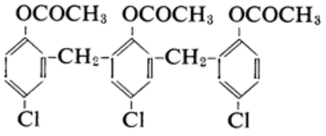
a) Determined by macro Carius method
* Observed values by micro analysis
** The mol. wt. of the acetate

TABLE VI. DEVIATIONS OF THE OBSERVED C1% FROM THE CALCULATED VALUES FOR THE LINEAR NOVOLAK STRUCTURE

Conditions of preparation	Novolak mol. wt.	Obs. Cl, %	Deviation, %	Acetylated resin	
				Obs. Cl, %	Deviation
150°C, 2 hr.	360	24.21	1.07[*1]	15.59	0.26[*3]
150°C, 14 hr.	820	21.36	4.23[*2]	17.68	1.97[*4]

[*1] Calcd. C1% for $C_{20}H_{15}O_3Cl_3$ (mol. wt. 410), 25.96
[*2] Calcd. C1% for $C_{41}H_{30}O_6Cl_6$ (mol. wt. 830), 25.59
[*3] Calcd. C1% for $C_{26}H_{21}O_6Cl_3$, 19.85
[*4] Calcd. C1% for $C_{53}H_{42}O_{12}Cl_6$, 19.65

TABLE VII. CALCULATED VALUES OF ELEMENTARY ANALYSIS OF THE RESIN CONTAINING THE STRUCTURE CAUSED BY DEHYDROCHLORINATION

Structure	Mol. wt.	C, %	H, %	Cl, %
	370	63.17	3.91	19.63
	450	62.60	3.20	16.07
	830	61.15	3.67	23.07
	410	58.63	3.69	25.96
	550	58.28	3.95	19.85

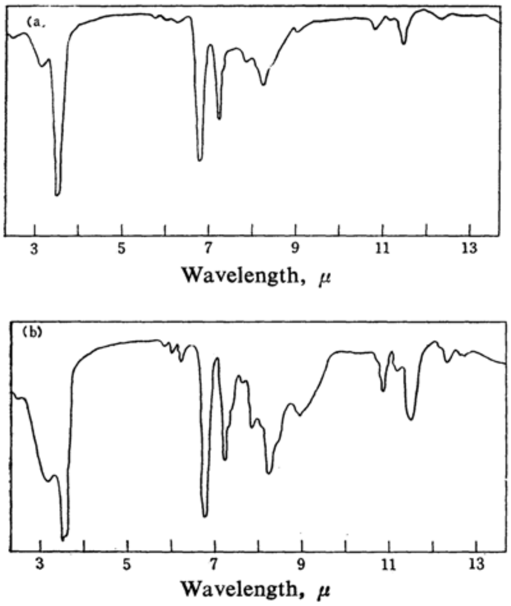


Fig. 6. Infrared absorption spectra of Burke's resin and the present author's resin in Nujol.
a) Burke's resin
b) The present author's resin

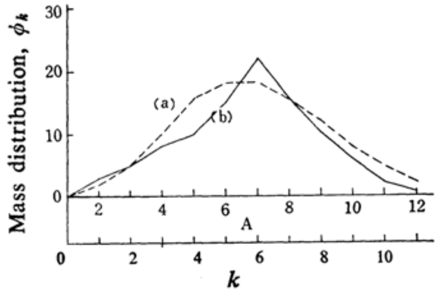


Fig. 7. Comparison between the experimental curve and Poisson's distribution curve.
(a) Theoretical curve calcurated from Poisson's equation $\left(\phi(k)=\dfrac{e^{-\lambda}\lambda^{k}}{k!},\ \lambda=6\right)$
(b) Experimental curve (150°C, 8 hr.)

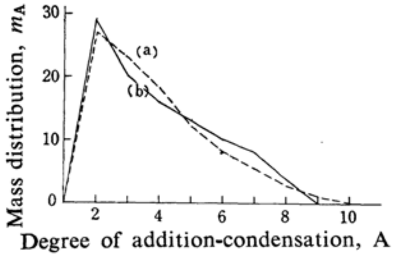


Fig. 8. Comparison between experimental curve and Imoto's theoretical curve.
(a) Theoretical curve ($\alpha=0.60-0.01$ A)
(b) Experimental curve (120°C, 4 hr.)

stage of the reaction. This curve, which agreed with Imoto's equation, is shown in Fig. 8.

Elementary Analysis of the Resin.—From the elementary analysis of the resins, it was made clear that another reaction, one differing from the usual novolak formation, took place. The results obtained are shown in Table V. The determined value of C% was larger than the calculated value, and the difference became lagrer as the reaction proceeded. Moreover, not only was the observed value of Cl% smaller than the calculated value, but the difference became larger with the reaction time and with the increase in the molecular weight, as is shown in Fig. 9. The values of Cl% of the acetylated resin, however, approached the theoretical values (Table VI).

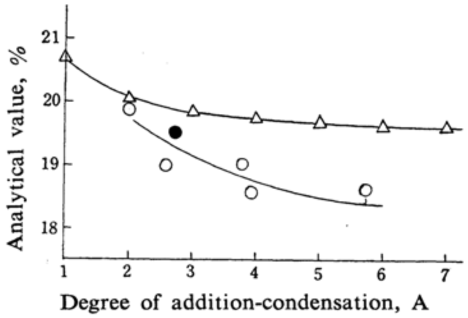


Fig. 9. Analytical values of Cl observed in the resin before and after fractionation. Acetate of the resin (150°C, 2 hr.) was used as sample.
△ Calculated values for acetate
● Observed value of acetate of resin
○ Observed values after fractionation on the acetate

From these facts it may be considered that the reaction of dehydrochlorination occurred, yielding the structure shown in Table VII.

Summary

A novolak resin of a higher molecular weight, as described by Burke et al., was not obtained. It was considered that the reaction of *p*-chlorophenol with *s*-trioxane proceeded as follows: (1) At first, a normal reaction of novolak formation proceeded. The molecular weight distribution was explained by Imoto's theoretical equation (120°C, 4 hr.). The analytical value of Cl% was rather close to the calculated value. (2) Then "reformation reaction" started (120°C, 7 hr. and 150°C, 2 hr.). (3) Reformation took place rather vigorously, and the molecular weight distribution became close to Poisson's distribution (150°C, 8 hr.). (4) A three-dimensional compound was formed, and the molecular weight of the soluble part was lowered (150°C, 11 hr.). (5)

The molecular weight of the soluble part increased by the decomposition of the three-dimensional compound and by the dehydrochlorination reaction (150°C, 24 hr.).

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