Determination of Mark–Houwink–Sakurada Equation for Phenolic Resins and Estimation of their Molecular Conformation in Acetone Solution

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Synopsis

The effects of the molecular structure of phenolic resins on the Mark–Houwink–Sakurada (MHS) equation and the conformation in acetone solution were studied. The exponent in the MHS equation was remarkably less than that for linear polymers such as vinyl polymers, cellulose derivatives, and so on. As the cause, the branching and the hydrogen bonding between hydroxyl groups of the neighboring phenolic nuclei were considered. Several kinds of phenol-*p*-cresol and phenol-*p-tert*-butylphenol cocondensation resins whose composition differs from one another were synthesized. Despite the difference in the degree of branching, the exponent in the MHS equation for each was approximately equal. On the other hand, the exponent for *o*-cresol novolak, which was rich in ortho-para methylene linkages was larger than the all-ortho novolak and *p*-cresol novolak, which were rich in ortho–ortho methylene linkages. Methylation of the phenolic hydroxyl group increased the value of the exponent. From these results, it became obvious that while the hydrogen bonding lowered the exponent in the MHS equation due to molecular conformation compaction in acetone solution, the molecular branching had little effect on the exponent α.

INTRODUCTION

Phenol–formaldehyde resin is the oldest synthetic polymer, but these resins are being reevaluated because of their high functionality and performance. Their solution properties, however, were hardly studied because of their complex structure.

Tobiason et al.[1] determined the Mark–Houwink–Sakurada (MHS) equation [eq. (1)] for random novolak,

$$[\eta] = KM^{\alpha} \tag{1}$$

and obtained the value of $\alpha = 0.47$, 0.51, and 0.48 in acetone, tetrahydrofuran (THF) and $1N$ NaOH, respectively, and they estimated the molecular conformation corresponding to the linear polymer under θ condition. However, it was pointed out[2] that the wide molecular weight distribution resulting from successive precipitational fractionation (SPF) increased the exponent α.

Kamide and Miyakawa[2] reported that $\alpha = 0.5$ for high ortho novolak and $\alpha = 0.28$ for random novolak in acetone using the sample obtained by a

successive solutional fractionation (SSF) and explained that the former and
the latter may be taken as the linear polymer under θ conditions and the
branched polymer, respectively.

The following relation was proposed in a prior study for random novolak in
acetone at 25°C:[3]

$$[\eta] = 1.075\overline{M}_{VD}^{0.20} \tag{2}$$

where $\overline{M}_{VD}$ is the average molecular weight measured by the viscosity-diffu-
sion method.[4] The small α value suggests a compact and spherical conforma-
tion for novolak. Because $\overline{M}_{VD}$ was not generally used, the comparison with
the literature data based on $\overline{M}_n$ was impossible.

In this paper, several kinds of phenolic resins that differed in molecular
structure were synthesized, and the exponent α in the MHS equation based
on $\overline{M}_n$ were determined to estimate their molecular conformation in acetone
solution.

EXPERIMENTAL

Materials

Commercially available phenol, p-cresol, and o-cresol were distilled. Acid in
the formalin was removed by passage through an anion exchange column
(Amberlite XE168). The concentration of HCHO was determined by the
sodium sulfite method. Methyl iodide, sodium hydride, and p-$tert$-butylphenol
were of certified reagent grade and used without further purification. Acetone,
THF, dimethylformamide (DMF), and toluene were purified by the usual
methods.

Preparation of Resins

PC, OC, P–PC, and P–BP Resins. p-Cresol-formaldehyde resin (PC
resin), o-cresol-formaldehyde resin (OC resin), phenol–p-cresol-formalde-
hyde resin (P–PC resin), and phenol–p-$tert$-butylphenol-formaldehyde resin
(P–BP resin) were prepared under the conditions summarized in Table I. The
composition of P–PC and P–BP resins were determined by ^{1}H-NMR.

BP Resin. p-$tert$-Butylphenol-formaldehyde resin (BP resin) was prepared
through two steps. At first, a mixture of 1.0 mol of p-$tert$-butylphenol, 2.0 mol
of formaldehyde (using 35 wt % formalin), and 0.5 mol of HCl was stirred at
70°C for 10 min to give an emulsion. Then the reaction mixture was trans-
ferred into an evaporating dish and it was heated at 130–140°C on a sand
bath with stirring for 6 h.

AO Resin. Forty grams of BP resin was dissolved in 500 mL of toluene and
then 48 g of anhydrous AlCl$_3$ was added. The mixture was allowed to stand at
10–15°C for 10 h. ^{1}H-NMR analysis showed that 90% of the $tert$-butyl groups
in the BP resin were eliminated. This resin was treated as an all-ortho novolak
resin (AO resin).

TABLE I
Reaction Conditions[a]

Sample	Molar ratio						Temp (°C)	Time (h)
	P	PC	BP	OC	F	HCl		
P–PC-1 resin	3	1	—	—	4	0.20	80	3.0
P–PC-2 resin	3	2	—	—	5	0.25	85	8.0
P–PC-3 resin	1	1	—	—	2	0.10	90	8.0
P–PC-4 resin	2	3	—	—	5	0.25	90	8.0
P–BP-1 resin	3	—	2	—	5	0.25	110	4.5
P–BP-2 resin	1	—	1	—	2	0.10	110	5.5
P–BP-3 resin	2	—	3	—	5	0.25	110	6.0
PC resin	—	1	—	—	1	0.05	120	10.0
OC resin	—	—	—	1	1	0.05	120	12.0

[a] P = phenol; PC = p-cresol; BP = p-tert-butylphenol; OC = o-cresol; F = formaldehyde (35 wt % formalin).

Methylation of Phenolic Hydroxyl Group

The fractionated P–PC and P–BP resins were methylated according to the literature,[5] that is, 2 g of the sample resin was dissolved in 30 mL of THF/DMF mixed solvent (10/1 volume ratio) containing 0.33 g of sodium hydride. After the addition of 2 mL of methyl iodide, the solution was refluxed for 2 h.

Fractionation

All resins purified by reprecipitation were fractionated by a successive solutional fractionation with acetone or THF as a solvent and water as a nonsolvent.

Measurements

The gel permeation chromatography (GPC) was carried out on a JASCO 880-PU equipped with two 50 cm polystyrene gel packed columns (Shodex A803 × 2) and a UV detector (JASCO UVIDEC 100). THF was used as an eluent at room temperature and the flow rate was 1.0 mL/min. The number average molecular weights ($\overline{M}_n$) were determined by vapor pressure osmometry using Hitachi Perkin-Elmer Model 115 molecular weight apparatus. ^{1}H-NMR spectra were obtained from a Jeol NMR spectrometer (JNM FX-100S). IR spectra were taken on a Jasco Fourier transform infrared spectrophotometer (FT/IR-3) in a KBr disk. The viscosity of acetone solutions were measured using a Ubbelohde type viscometer at 25°C.

RESULTS AND DISCUSSION

Effects of Branching

In our previous paper,[6] it was proposed that the most probable number of branches in a molecule of 10- and 15-phenolic nuclei novolaks are two and three, respectively, using the computer simulation technique. In addition,
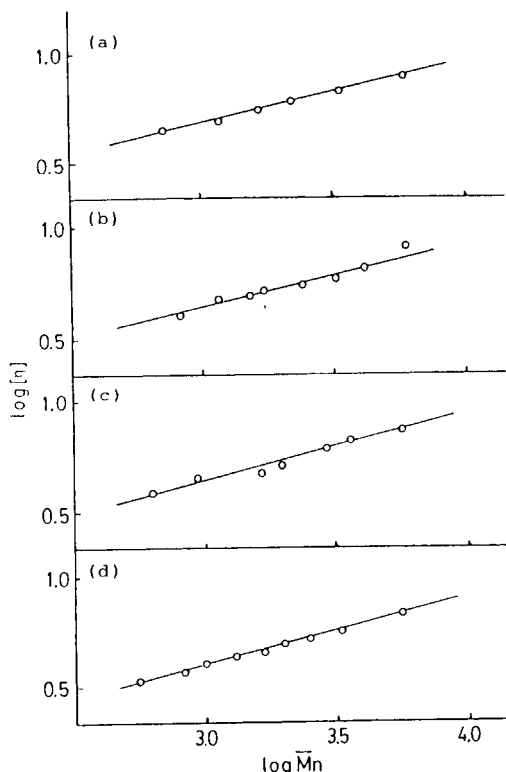
Fig. 1.   Relation between log[η] and log $\overline{M}_n$ for P–PC resins in acetone at 25°C ([η] in cm^3/g): (a) P–PC-1 resin; (b) P–PC-2 resin; (c) P–PC-3 resin; (d) P–PC-4 resin.

Kamide et al.[2] showed two branches in a novolak molecule with 11-phenolic nuclei by ^{13}C-NMR spectroscopy. Thus, the molecule of phenolic resin has in general some branches.

It is important to discuss the effect of branching on the molecular behavior in solution. In order to obtain the sample resins whose degree of branching differ from one another, the cocondensation reactions among phenol, p-cresol, formaldehyde and phenol, p-tert-butylphenol, formaldehyde were made under several molar ratios shown in Table I.

Since phenol is a three-functional monomer and p-cresol and p-tert-butylphenol are two-functional monomers, the difference in the composition of the resin results in the difference in the degree of branching. The parameters in the MHS equation of P–PC-1, -2, and -3 resins and PC resin, which were obtained from the relation between [η] and $\overline{M}_n$ shown in Figure 1, are listed in Table II with the composition of each resin. From the result, it is known that the exponent α is independent of the degree of branching.

In the case of P–BP resins, however, the composition of each fraction was somewhat different (i.e., BP content varies 31–49% in P–BP-1 resin) and [η] vs. $\overline{M}_n$ plot shows some scatter as shown in Figure 2, but the trend that the branching had little effect on the exponent α described above is probably real also for P–BP resins.

TABLE II
Effects of the Degree of Branching on the MHS Equation

Sample	Composition of resin (%)		α	K
	P	PC		
P–PC-1 resin	72	28	0.27	0.72
P–PC-2 resin	58	42	0.26	0.73
P–PC-3 resin	45	55	0.29	0.59
P–PC-4 resin	34	66	0.30	0.49
PC resin	0	100	0.28	0.54
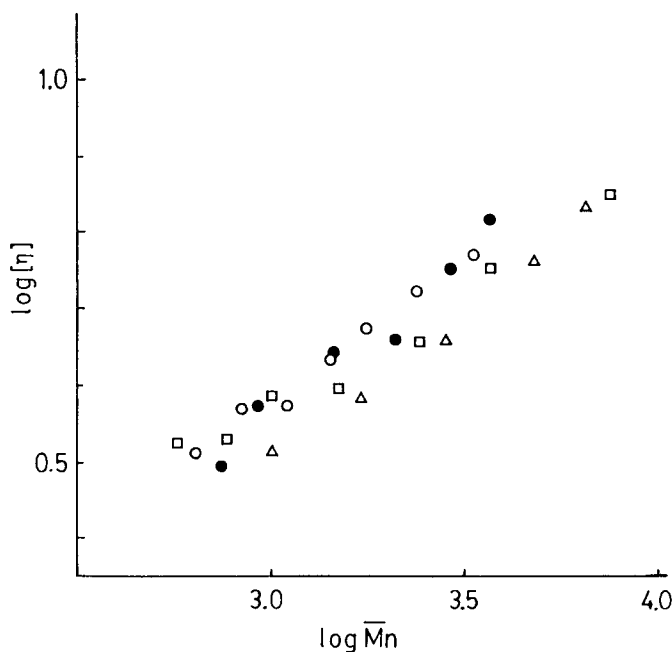
Fig. 2.   Relation between $\log[\eta]$ and $\log \overline{M}_n$ for P–BP-1 resin (○), P–BP-2 resin (●), P–BP-3 resin (□), and BP resin (△) in acetone at 25°C ($[\eta]$ in cm^3/g).

Effects of Nuclear Position of Methylene Linkage

The MHS plots for AO, PC, and OC resins are shown in Figure 3 and the parameters are shown in Table III. Since all of these resins are absent of branching, the molecules should behave like a linear polymer. However, the α values of these resins are smaller than that for a linear polymer and change from 0.22 for an AO resin to 0.52 for an OC resin.

It has been known that the signals of o,o'-, o,p'-, and p,p'-methylene linkages in ^{1}H-NMR spirit into 4.3, 4.2, and 3.8 ppm, respectively, in a strong polar solvent such as pyridine.[7,8]

Unfortunately, two signals of o,o'- and o,p'-methylene linkages cannot be separated as shown in Figure 4. We calculated relative amounts of o,o'- plus o,p'-methylene linkages and p,p'-methylene linkage in OC resin to be 65 and
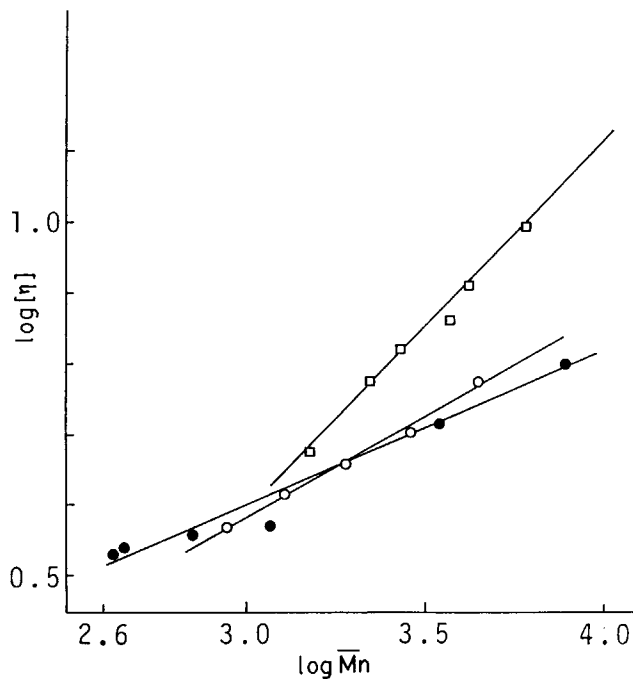
Fig. 3. Relation between $\log[\eta]$ and $\log \overline{M}_n$ for OC resin ($\square$), PC resin ($\bigcirc$), and AO resin ($\bullet$) in acetone at 25°C ($[\eta]$ in cm³/g).

TABLE III
Effects of Nuclear Position of Methylene Linkage and Substituent on the MHS Equation

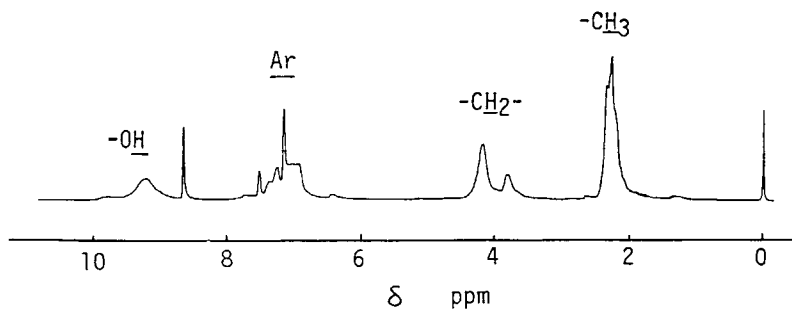| Sample	Methylene linkage (%)			α	K
	o,o'	o,p'	p,p'		
AO resin	100	0	0	0.22	0.89
PC resin	100	0	0	0.28	0.54
OC resin		65[a]	35	0.52	0.11
BP resin	100	0	0	0.40	0.22

[a] Total amounts of o,o' and o,p'.

Fig. 4. ^{1}H-NMR spectrum of OC resin ($\overline{M}_n$ = 5000) in pyridine-d$_5$.
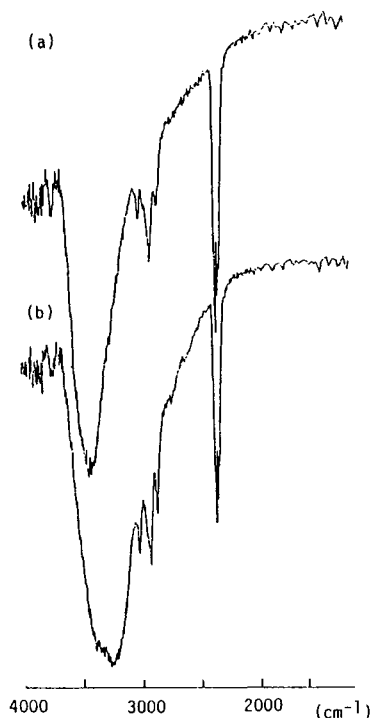
Fig. 5.   IR spectra of OC resin (a) and PC resin (b).

35%, respectively. IR spectra of PC resin and OC resin are shown in Figure 5. The absorption band of O—H stretching of PC resin shifts about 200 cm^{-1} towards a lower wavenumber from that of OC resin at 3435 cm^{-1}. This fact suggests that the hydrogen bonding between hydroxyl groups of neighboring phenolic nuclei bonded by o,o'-methylene linkage is stronger than that bonded by o,p'- or p,p'-methylene linkages.

From these results, it is assumed that the strength of the hydrogen bonding remarkably influences the molecular conformation of these resins making o,o'-linked resin more compact.

Effects of Substituent on Para Position

As shown in Table IV, the exponent α increases in order of the AO, PC, and BP resins, respectively, the bulkier is the substituent at the para position on the phenol.

Effects of Methylation of Hydroxy Group

To establish the effect of hydrogen bonding on the molecular conformation of the phenolic resins, the phenolic hydroxyl groups were methylated. The substitution was confirmed by the change of IR spectrum; the absorption of C—O stretching appeared at 1280 and 1020 cm^{-1} and the strength of absorption of O—H stretching decreased. The degree of methylation was estimated to be 40–50% by ^{1}H-NMR measurements.

SUE ET AL.

	Before methylation		After methylation	
Sample	α	K	α	K
P–PC-1 resin	0.27	0.72	0.54	0.09
P–PC-2 resin	0.26	0.73	0.33	0.41
P–BP-1 resin	0.35	0.33	0.47	0.14
P–BP-2 resin	0.41	0.21	0.56	0.07

The exponent α of methylated resins are shown in Table IV together with that of the unmodified resins. It is obvious that the exponent α for all the samples became remarkably larger with the methylation, which corresponds to molecular expansion with the reduction in hydrogen bonding.

CONCLUSION

In order to elucidate the contribution of the branching and the hydrogen bonding to the molecular conformation of phenolic resins, several kinds of model resins were synthesized and the Mark–Houwink–Sakurada equation for these resins in acetone solution were determined.

The following results were obtained. The exponent in the MHS equation for the resins which differ in the degree of branching were approximately equal. The exponent in the MHS equation for the resins which were rich in o,o'-methylene linkages were smaller than those of the others. The bulkiness of the substituent at the para position on phenol and the substitution of a phenolic hydroxyl group made the exponent in the MHS equation large.

From these results, it became obvious that the hydrogen bonding contributes to lowering the exponent in the MHS equation which correlates to molecular compaction in solution.

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