

Determination of Mark-Houwink-Sakurada equation for phenolic resins containing alkylenediamine in the main chain and estimation of their molecular conformation in tetrahydrofuran solution

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Summary

Phenolic resins containing alkylenediamine in the main chain could be prepared by the co-condensation reaction of phenol, formaldehyde and alkylenediamines such as ethylenediamine and hexamethylenediamine. The molecular structures were determined by ¹H-NMR spectra, IR spectra and nitrogen content. The molecular conformation of these resins in THF solution were studied from the viscosity measurements, and it became clear that the molecules were considerably compact compared with linear vinyl polymers. To clarify the reason of this phenomenon, the resins whose degrees of branching were different from each other and the resins whose phenolic hydroxyl groups were acetylated were prepared. From viscosity data, it was pointed out that the intramolecular hydrogen bonding contributes to the compaction of the phenolic resins containing alkylenediamine in the main chain more strongly than the branching does.

Introduction

The phenolic resins are widely used because of their advantages such as heat resistance, electric insulation and so on. Their solution properties, however, were hardly studied because of their complex structure. Several investigators have discussed the molecular conformation of random novolak in solution from the exponent a in Mark-Houwink-Sakurada (MHS) equation (abbreviated as EX) and EX for random novolak was found to be

$$[\eta] = KM^a$$

remarkably smaller than those for linear polymers such as vinyl polymers, cellulose derivatives and so on. For example, $a=0.28$ by Kamide et al.(1) and $a=0.47$ by Tobiasson et al.(2). These results showed that the molecules of random novolak are relatively spherical and compact by the branching and the hydrogen bonding between hydroxyl groups of the neighboring phenolic nuclei.

On the other hand, it is well known that in the formation of the ammonia catalyzed phenolic resin, hexamethylenetetramine is initially formed by the reaction between formaldehyde and ammonia and then phenol attacks it to form amine compounds (3-5). If alkylenediamine such as ethylenediamine (ED) and hexamethylenediamine (HD) is made to react instead of ammonia, the phenolic resin containing alkylenediamine in the main chain may be prepared in a similar mechanism as the formation of the ammonia catalyzed phenolic resin.

We have recently reported that the hydrogen bonding contributed to lowering EX which correlated to the compaction of a molecule in solution (6). In this paper, several kinds of phenolic resins containing alkylen-

diamine in the main chain were synthesized, and EX were determined to estimate their molecular conformation in tetrahydrofran (THF) solution.

Experimental

Materials

Commercially available phenol and p-cresol were distilled. Acid in formalin was removed by passing through an anion exchange column (Amberlite XE168). The concentration of formalin was determined by the sodium sulfite method. ED, HD, acetic anhydride and pyridine were of certified reagent grade and used without further purification. Acetone and THF were purified by the usual method. N,N'-dimethylhexamethylenediamine (MHD) was synthesized according to the literature (7).

Preparation of resins

In the presence of various quantity of alkylenediamine, phenols were made to react with formaldehyde (35% formalin) under the conditions summarized in Table 1. In the cases of P-HD-1 and P-HD-3 Resins, a mixture of phenol, formaldehyde and HD was heated at 80°C or 95°C to give an emulsion and then the reaction mixture was transferred into a separatory funnel and the oily substance in the lower layer was heated in an evaporating dish at 100°C or 130°C on a sand bath with stirring. Ammonia resol was also prepared by two steps reaction.

Table 1 Reaction Conditions

sample	raw materials (molar ratio)	1st step		2nd step		N cont. (wt.%)
		temp. (°C)	time (min)	temp. (°C)	time (min)	
P-HD-1	P:F:HD = 1:1:0.1	80	15	100	45	3.1
P-HD-2	P:F:HD = 1:1:0.2	80	60			4.2
P-HD-3	P:F:HD = 1:1:0.3	95	5	130	60	9.2
P-ED	P:F:ED = 1:1:0.1	85	65			4.0
PC-HD	PC:F:HD = 1:1:0.1	120	300			2.5
P-MHD	P:F:MHD= 1:1:0.1	90	90			2.6
PC-MHD	PC:F:MHD= 1:1:0.1	90	1200			1.9
AR	P:F:NH ₃ = 1:1:0.1	80	40	100	60	
RN	P:F:HCl= 1:1:0.05	80	90			

P=phenol; PC=p-cresol; F=formaldehyde; HD=hexamethylenediamine; ED=ethylenediamine; MHD=N,N'-dimethylhexamethylenediamine
AR=ammonia resol; RN=random novolak

Acetylation of phenolic hydroxyl groups

P-HD-2 and P-ED Resins were acetylated according to the literature (8), that is, 30 g of sample resin was dissolved in 200 ml of pyridine at 0°C. After the addition of 100 ml of acetic anhydride, the solution was kept at room temperature for 12 h.

Fractionation

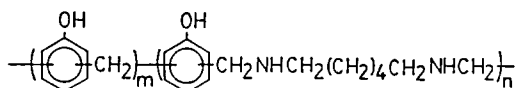
All sample resins purified by reprecipitation were fractionated by a successive solutional fractionation with acetone or THF as the solvent and water as the non-solvent.

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+A803) 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 weight (\bar{M}_n) was determined by vapor pressure osmometry using Hitachi Perkin-Elmer Model 115 molecular weight apparatus. Acetone was used as the solvent and the calibration curve was obtained with

P-HD-2 Resin

N cont. = 4.88 wt%
Kjeldahl = 4.60 wt%



P-ED Resin

N cont. = 3.77 wt%
Kjeldahl = 3.47 wt%

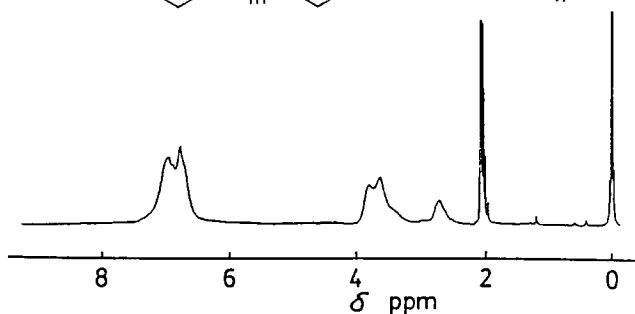
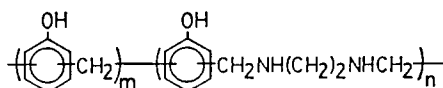


Figure 1. ^1H -NMR spectra of P-HD-2 Resin ($\bar{M}_n=5500$) and P-ED Resin ($\bar{M}_n=1700$) in acetone- d_6

benzyl-acetone solution. $^1\text{H-NMR}$ spectra were recorded on a JEOL FX-100S FT-NMR spectrometer (Japan Electron Optics Lab. Co. Ltd) using pyridine- d_5 and acetone- d_6 as the solvent and tetramethylsilane as the reference. IR spectra were obtained from KBr disk on a JASCO FT/IR-3 spectrophotometer (Japan Spectroscopic Co. Ltd). Nitrogen contents were determined from Kjeldahl method and the analysis of $^1\text{H-NMR}$ spectra. The viscosity of THF solution was measured using Ubbelohde type viscometer at 25°C.

Results and Discussion

Molecular structure of resins

$^1\text{H-NMR}$ spectra of the fractionated P-HD-2 and P-ED Resins are shown in Fig.1. The resonances at about 7.0 and 3.8 ppm are assigned to aromatic proton and methylene proton which is adjacent to aromatic ring, respectively. The resonances at 2.4, 1.5 and 1.1 ppm represent methylene proton in HD and at 2.7 ppm represents methylene proton in ED. The resonance of dimethylene-ether linkages ($-\text{CH}_2\text{OCH}_2-$) around 4.6 ppm can not be found. The nitrogen contents obtained from the analysis of $^1\text{H-NMR}$ spectra are in fair agreement with that obtained by Kjeldahl method. From these results, the molecular structures of each resin can be determined as shown in Fig.1.

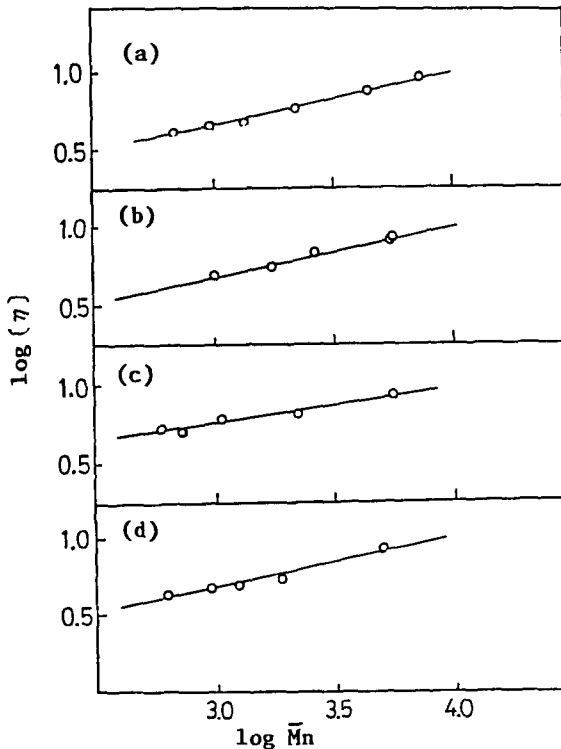


Figure 2. Relation between $\log(\eta)$ and $\log \bar{M}_n$ for (a) P-HD-1 Resin, (b) P-HD-2 Resin, (c) P-HD-3 Resin, and (d) P-ED Resin ((η) : cm^3/g)

Effects of molecular structure and content of diamines

The relations between (η) and \bar{M}_n for P-HD and P-ED Resins are shown in Fig.2 and the parameters of MHS equation are listed in Table 2 with their molecular composition (m/n). AR and RN Resins are also listed in Table 2 to compare with P-HD and P-ED Resins.

EX for phenolic resins containing alkylenediamine in the main chain are smaller than those for linear polymers such as vinyl polymers. It is assumed that the flexibility of the molecules increases as m/n decreases, that is, as the content of HD increases. But the opposite situation was obtained, that is, EX decreased from 0.34 to 0.23 as shown in Table 2. From these results, it is obvious that the molecular conformation is dependent on the content of alkylenediamine rather than the kind of alkylenediamine. It is estimated that the interaction between phenolic hydroxyl group and alkylenediamine makes the molecule compact.

Table 2 Parameters of MHS Equation for P-HD and P-ED Resins in THF at 25°C

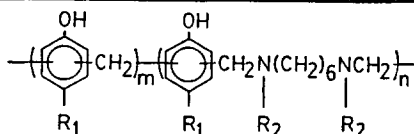
sample	composition m/n	a	K
P-HD-1	6.3	0.34	0.40
P-HD-2	4.1	0.32	0.55
P-HD-3	2.3	0.23	1.20
P-ED	4.8	0.34	0.45
AR		0.27	0.73
RN		0.28	0.80

Effects of branching

In order to discuss the influence of branching on the molecular dimensions, some resins were prepared using two functional compounds such as p-cresol and MHD. The MHS plots for PC-HD Resin, P-MHD Resin and PC-MHD Resin are shown in Fig.3 and the parameters of MHS equation are also shown in Table 3.

Table 3 Effect of Branching on the Parameters of the MHS Equation

sample	R ₁	R ₂	composition m/n	a	K
P-HD-1	H	H	6.3	0.34	0.40
PC-HD	CH ₃	H	7.4	0.32	0.39
P-MHD	H	CH ₃	6.7	0.32	0.57
PC-MHD	CH ₃	CH ₃	10.7	0.29	0.50



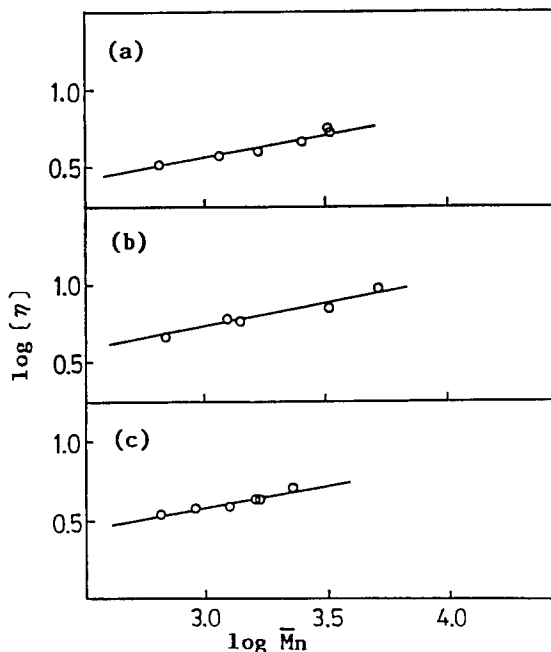


Figure 3. Relation between $\log(\eta)$ and $\log \bar{M}_n$ for (a) PC-HD Resin, (b) P-MHD Resin, and (c) PC-MHD Resin ($[\eta]$: cm^3/g)

It was expected that the molecules of these resins expand more than that of general phenolic resins because of their smaller degree of branching, but EX of these resins are approximately equal in each other. Therefore, it is known that the effect of the intramolecular hydrogen bonding on the molecular conformation is stronger than the effect of the branching.

We previously proposed 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 linkage, and therefore the former makes the molecules more compact. In this case acidity of phenolic hydroxyl groups and basicity of alkylenediamine lead to strong intramolecular hydrogen bonding in addition.

Effects of acetylation of hydroxyl groups

To establish the effect of hydrogen bonding on the molecular conformation of the phenolic resins containing alkylenediamine, the phenolic hydroxyl groups were acetylated.

The substitution was confirmed by the change of IR spectrum; the absorption of C=O stretching appeared at 1750 cm^{-1} and the absorption of O-H stretching disappeared. The degree of acetylation was estimated to be about 100%. The MHS plots for acetylated P-HD-2 Resin and P-ED Resin are shown in Fig.4 and the parameters of MHS equation are shown in Table 4 together with that before acetylation. It is obvious that the weakening of hydrogen bonding by acetylation expands the molecules and, therefore, EX becomes remarkably large.

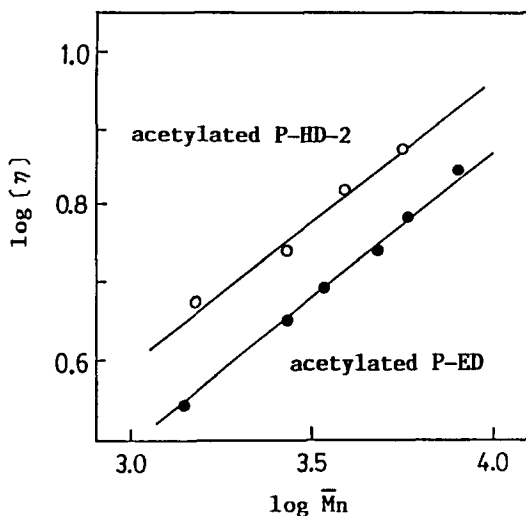


Figure 4. Relation between $\log (\eta)$ and $\log \bar{M}_n$ for acetylated P-HD-2 Resin \circ and acetylated P-ED Resin \bullet ((η) : cm^3/g)

Table 4 Effect of Acetylation of Hydroxyl Groups

sample	before-acetylation		after-acetylation	
	a	K	a	K
P-HD-2	0.32	0.55	0.43	0.19
P-ED	0.34	0.45	0.44	0.14
AR	0.27	0.73	0.57	0.04
RN	0.28	0.80	0.48	0.09

Conclusion

Phenolic resins containing alkylenediamine in the main chain could be prepared by the co-condensation reaction of phenol, formaldehyde and alkylenediamines such as HD or ED. The molecular conformation of these resins in THF solution was estimated from viscosity measurement. EX values for these resins are remarkably smaller than those for linear vinyl polymers, which shows that the molecules of these resins are compact. EX values for the resins whose degrees of branching are different from each other are approximately equal to those for the resins mentioned above. On the other hand, acetylation of phenolic hydroxyl groups makes EX large.

From these results, it becomes obvious that the hydrogen bonding between phenolic hydroxyl group and alkylenediamine makes the molecule compact rather than the effect of the branching.

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