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Preparation and characterization of high molecular weight novolak resins

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Summary

High molecular weight novolak resins were prepared from phenol and paraformaldehyde in organic solvents, e.g., 2-propanol, ethyl propionate, 2-methoxyethanol, 4-methyl-2-pentanone, dioxane and acetic acid. The molecular weights were estimated by gel permeation chromatography (GPC) and solution viscosity measurement and it was confirmed that high molecular weight resins were formed in organic solvents. The structure was determined by ^{13}C-NMR measurements, and it was found that the resin obtained in organic solvent was a random novolak with higher molecular weight than a conventional novolak.

Introduction

Phenol-formaldehyde resins are readily prepared from phenol and formaldehyde by an acid and/or a base catalysis, but the number-average molecular weight (Mn) in soluble parts is never over several thousands because of the gelation in the condensation (1).

The preparation of linear and high molecular weight phenolic resins has been reported (2). However, the lack of reproducibility was pointed out (3) and a resin with high molecular weight has not been recognized yet.

By considering the mechanism of formation of phenolic resins, the homogeneous reaction system and the high molar ratio of formaldehyde component (F) to phenolic unit (P) ($F/P > 0.8$) should be necessary to obtain high molecular weight resins without gelation. In this paper, high molecular weight phenol resins of the novolak type are prepared from phenol and paraformaldehyde in organic solvents, and the molecular weight are estimated by gel permeation chromatography (GPC) and solution viscosity measurement. Furthermore, the structure is determined by ^{13}C-NMR measurements and is compared with that of a conventional novolak resin.

Experimental

Reagents : Tetrahydrofuran (THF) and acetone were distilled and then were used. Phenol, paraformaldehyde and other chemicals were commercially obtained and were used without further purification.

Synthesis : Phenol (18.8 g, 0.2 mol) and a 95 % paraformaldehyde (6.3 g, 0.2 mol as a formaldehyde component) were dissolved in 50 mL of organic solvent (e.g., 2-propanol, ethyl propionate, 2-methoxyethanol, 4-methyl-2-pentanone, dioxane and acetic acid). Conc. HCl (0.83 mL, 0.01 mol) was added dropwise and the reaction mixture was stirred at 80 ℃ (40 ℃ for acetic acid) for the prescribed period. The reaction mixture was poured into a large amount of water to obtain the resin.

Measurements : ^{13}C-NMR spectra were obtained on a Bruker AC-300P spectrometer operating at 75 MHz. Approximately 1.5 g of resin was dissolved in 5 mL of dioxane-d_8 and spectra were recorded in 10 mm diameter sample tubes. Gel permeation chromatography (GPC) experiments were carried out on a Shimadzu high-performance liquid chromatography LC-6A with two TSKgel GMHXL columns (30 cm × 7.8 mmID). THF was used as an eluent and a Jasco UVIDEC-100 spectrophotometer as a detector. The flow rate was 1.0 mL・min.$^{-1}$ The chromatograms were analyzed with a Shimadzu C-R4A data processing apparatus. Solution viscosity measurements were carried out with an Ubbelohde type viscometer in acetone at 25 ℃.

GPC calibration : GPC calibration curve was obtained from ten standard polystyrene samples (the weight-average molecular weight (Mw) = 500, 2,980, 5,570, 9,100, 19,600, 37,900, 96,400, 190,000, 355,000 and 1,090,000 ; Mw/Mn : 1.01 - 1.14), purchased from TOSOH Co. Ltd.

Results and discussion

GPC measurements

The novolak resins were prepared by HCl catalysis in several organic solvents. The typical chromatogram of novolak resin obtained in each solvent before gelation was shown in Figure 1. The number- and weight-average molecular weights calculated by GPC analyses of the chromatograms were listed in Table 1. The molecular weight distribution (MWD) of the resin prepared in dioxane at 80 ℃ for 22 h is very wide, and it is obvious that high molecular weight molecules were formed, whose molecular size in THF is equivalent to that of the polystyrene with Mw = 1,000,000. On the other hand, the MWD of the resin prepared in acetic acid at 40 ℃ was bimodal, and was narrower rather than that in dioxane as shown in Figure 2. Of these organic solvents, the rate of reaction in acetic acid was most rapid and the yield reached more than 90 % in only 1 h. This seems to be due to the formation of active intermediates such as $ClCH_2OCH_2Cl$ (4,5) and/or $ClCH_2OCOCH_3$ (5,6), which are formed by the reaction of formaldehyde component with acetic acid by HCl catalysis. The Mn of

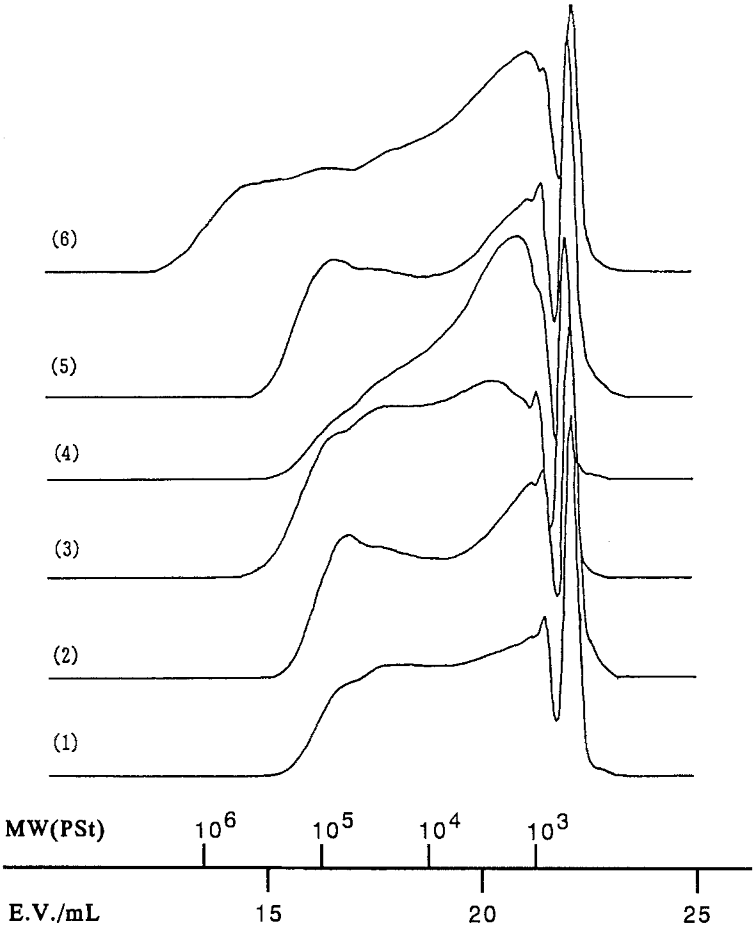

Figure 1. GPC curves of novolak resins prepared in organic solvents at 80 ℃. (1) in 2-propanol for 4 h; (2) in ethyl propionate for 2.5 h; (3) in 2-methoxyethanol for 8 h; (4) in H_2O for 5 h; (5) in 4-methyl-2-pentanone for 5 h; (6) in dioxane for 22 h

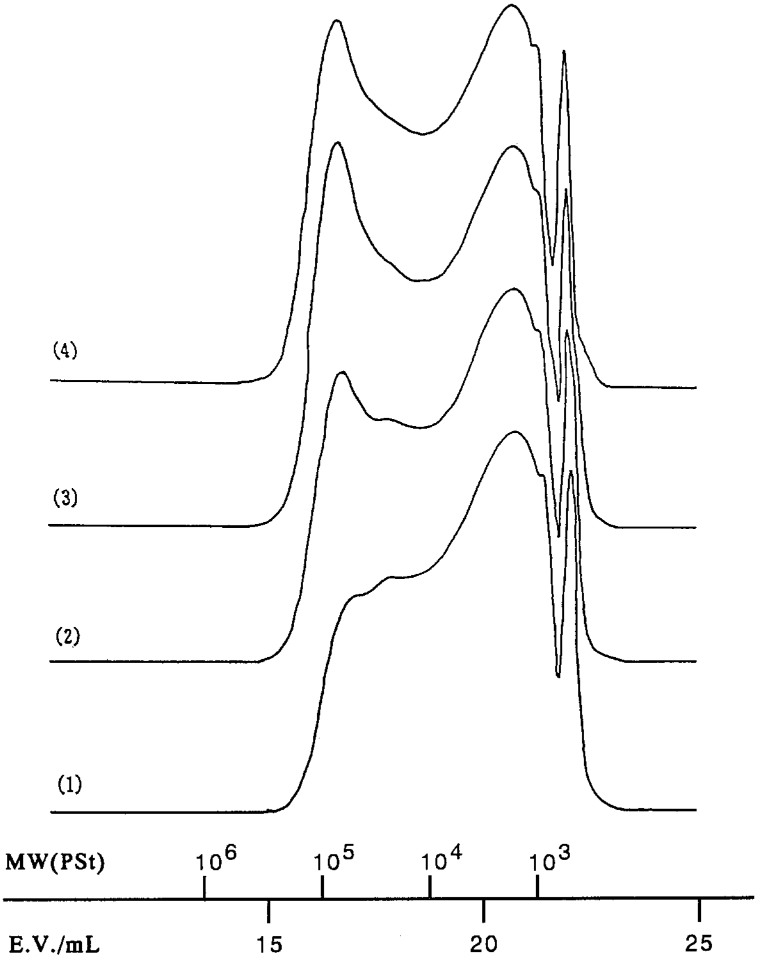

Figure 2. GPC curves of novolak resins prepared in acetic acid at 40 ℃. (1) for 1 h; (2) for 3 h; (3) for 5 h; (4) for 7 h

resins prepared in some organic solvents are over 3,000, and it is found that the use of homogeneous reaction system in organic solvent and paraformaldehyde as a formaldehyde component is adequate to obtain high molecular weight novolak resins.

Table 1. Reaction conditions and molecular weights of novolak resins estimated by GPC analysis.

run	solvent	reaction time (h)	*Mn*	*Mw*
1	2-propanol	4	2,990	16,700
2	ethyl propionate	2.5	2,830	18,600
3	2-methoxyethanol	8	3,870	22,900
4	H_2O	5	2,550	12,100
5	4-methyl-2-pentanone	5	3,030	24,100
6	dioxane	22	3,580	75,700

Molar ratio : Phenol / Formaldehyde component / HCl = 1 / 1 / 0.05
Reaction temperature : 80 ℃

Solution viscosity

The following Mark-Houwink-Sakurada equation has been reported for novolak resins with relatively broad MWD in acetone at 25 ℃ ([η] in mL • g^{-1}) : (7)

$$[\eta] = 0.190\,Mn^{0.47} \qquad (1)$$

The solution viscosity of resin obtained in organic solvent was measured and the molecular weight was estimated from Eq.(1). The viscosity-concentration curves for an unfractionated resin prepared in acetic acid at 40 ℃ for 5 h were shown in Figure 3. The values of intrinsic viscosity and molecular weight estimated were given to be 16.1 mL • g^{-1} and 13,000 g • mol^{-1}, respectively. Such a high molecular weight of unfractionated novolak resin in soluble parts has never been reported. However, it is known that the intrinsic viscosity of unfractionated sample is estimated to be higher than that of a fraction from which monomer has been removed, even though with the same molecular weight (7). Accordingly, we will fractionate the resin instantly and the molecular weights and the MWD should be exactly determined.

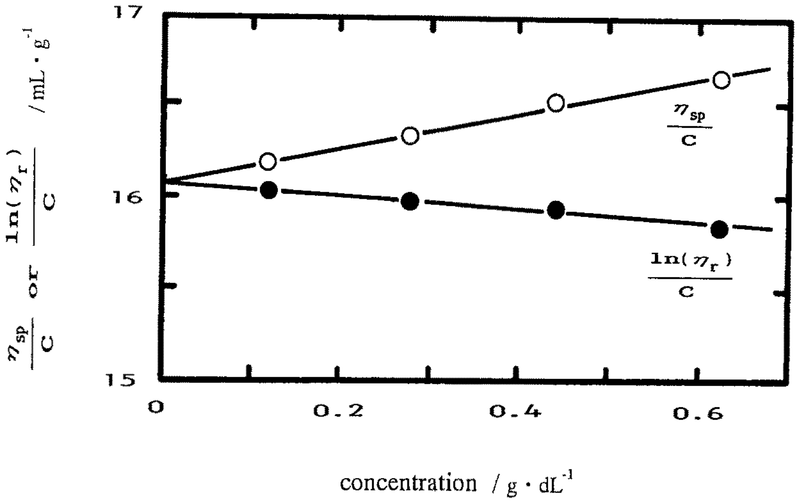

Figure 3. Reduced and inherent viscosity-concentration curves in acetone at 25 ℃ for a novolak resin prepared in acetic acid at 40 ℃ for 5 h.

Structure

The fractions of *o-o'*, *o-p'* and *p-p'* methylene linkage, and of terminal, linear and branch phenolic component, and the molar ratio of methylene linkage to phenolic unit that is a parameter indicating the degree of polymerization, of novolak resins obtained in organic solvents were determined by ^{13}C-NMR measurements (8, 9) and were compared with those of a conventional random novolak. The typical results were listed in Table 2. The each fraction of *o-o'*, *o-p'* and *p-p'* methylene linkage of resins obtained in organic solvents is the same as that of a conventional resin and the resins prepared in this work are considered to be a random novolak type. However, the fraction of terminal, linear and branch phenolic component and the ratio of methylene linkage to phenolic unit are different from those of a conventional resin. In resins obtained in organic solvents, the fraction of terminal component was decreasing and that of branch one increasing. And the molar ratio of methylene linkage to phenolic unit is larger and is given to be unity. These structural results indicate that the molecular weight of novolak obtained in organic solvent is higher, as described above.

Table 2. ^{13}C-NMR analysis of novolak resins

novolak	methylene linkage (%)			phenolic component (%)			methylene linkage / phenolic unit
	o-o'	*o-p'*	*p-p'*	terminal	linear	branch	
conventional	32	43	25	47	44	9	0.81
in acetic acid	33	45	22	26	47	27	1.00
in dioxane	37	45	18	29	45	26	1.00

Conclusions

High molecular weight novolak resins were prepared from phenol and paraformaldehyde in organic solvents. The molecular weights were estimated by GPC and solution viscosity measurements and the structure was determined by ^{13}C-NMR spectra. It was found that high molecular weight molecules that have never been reported were formed. The resins prepared in this work were random novolaks with higher molecular weight.

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