Polymer Bulletin 10, 533-537 (1983)

Polymer Bulletin

# Average Molecular Weight and Viscosity of Acetone Solutions of Phenolic Resins

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## SUMMARY

The viscosity-diffusion method has been proposed as a technique for molecular weight determination of spherical polymers such as phenolic resins. When the average diffusion coefficient $D_A$ calculated from the area of diffusion curve is used in this technique, there exists the following relation between $D_a$ and the specific volume $\wp$ of solute in solution:

$$\wp \sqrt{D_A} = \text{const.}$$

therefore,

$$[\eta] = K M^{0.2}$$

is derived. Though the average molecular weight obtained from $D_A$ and $\wp$ generally falls between $M_n$ and $M_w$, there are some reports that the exponent of M rather increases when M is given as number average. We found that the exponent becomes larger than 0.2 when the polymolecularity of the sample becomes remarkable or it increases with molecular weight.

## INTRODUCTION

The specific volume calculated from solution viscosity data is important to study the formation mechanism of phenolic resins. But the relations between the specific volume and the molecular weight obtained by different investigators were not the same. For example, Wanscheidt et al.(1) proposed that the reduced viscosity of alcohol solution of novolak is proportional to the degree of polymerization, whereas, Tobiason et al.(2) determined Mark-Houwink-Sakurada equation (Eq.(1)) for novolak in several kinds of solvents and obtained $\alpha = 0.24$ in formamide and 0.47 in acetone. They concluded that chain coil compactness is differ with solvent.

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

We have proposed the viscosity-diffusion method for the molecular weight determination of spherical polymers such as phenolic resins and derived $\alpha = 0.2$, when the average diffusion coefficient $D_A$ is used(3~5).

In order to explain these differences in $\alpha$ value, the effects of polymolecularity is discussed in this paper.

## VISCOSITY-DIFFUSION AVERAGE MOLECULAR WEIGHT

The molecular weight of the spherical molecule is expressed as

$$M = \frac{4}{3} \pi r^3 N \wp^{-1} \tag{2}$$

where r is the radius of the molecule and N is Avogadro's number.

According to Einstein and Stokes, the diffusion coefficient at zero concentration $D_0$ is related to r by

$$D_0 = \frac{R\,T}{f} = \frac{R\,T}{6\,\pi\,\eta_0\,r\,N} \tag{3}$$

where f is the coefficient of friction and $\eta_0$ is the viscosity of solvent. From these equations, the viscosity-diffusion average molecular weight is obtained as follows:

$$M_{VD} = 0.9908\times10^{-27}\,\frac{T^3}{D_0^3\cdot\eta_0^3\cdot\varphi} \tag{4}$$

Two kinds of average diffusion coefficients are generally used.

$D_m = \Sigma\, c_i D_i \,/\, \Sigma c_i$ (calculated from moment of diffusion curve)

$D_A = (\,\Sigma\, c_i \,/\, \Sigma c_i D_i^{-0.5})^{\,2}$ (calculated from area of diffusion curve)

When $D_m$ or $D_A$ is used instead of $D_0$, the average molecular weight assigned $M_{VD_m}$ or $M_{VD_A}$ is obtained. They are defined as follows(6) :

$$M_{VD_m} = \frac{(\,\Sigma\, c_i)^4}{(\,\Sigma\, c_i M_i^{\alpha})\,(\,\Sigma c_i M_i^{(1+\alpha)/3})^3}$$

$$M_{VD_A} = \frac{(\,\Sigma\, c_i M_i^{(1+\alpha)/6})^6}{(\,\Sigma c_i M_i^{\alpha})\,(\,\Sigma\, c_i)^5}$$

Between these average molecular weights, there exists the following relation in phenolic resins.

$$M_w \geqq M_v \geqq M_{VD_A} \geqq M_{VD_m} \geqq M_n \tag{5}$$

$\varphi$ is determined by modification of Einstein's viscosity equation:

$$\eta_{sp} = a\left(\frac{c\,\varphi}{100 - c\,\varphi}\right) + b\left(\frac{c\,\varphi}{100 - c\,\varphi}\right)^2 \tag{6}$$

If the molecule is spherical, a and b are 2.5 and 4.4, respectively. This equation has sufficiently wide application range concerning the concentration of phenolic resins in acetone.

Fractionation procedure of spherical polymer solution is rather troublesome because the solubility depends little on the molecular weight. But if it is needed to compare average molecular weight only, we can use a convenient relation for phenolic resin in acetone which is easily demonstrated to be independent of polymolecularity.

$$\varphi\,\sqrt{D_A} = \text{constant} \tag{7}$$

Substituting the above expression in eq.4, the following relation is obtained.

$$\varphi = K\,M^{0.2} \tag{8}$$

If the concentration of solute is represented by g/100 ml and the solute molecule is spherical, $[\eta]$ is related to $\varphi$ by

$$[\eta] = \varphi\,/\,40 \tag{9}$$

## RELATION BETWEEN VISCOSITY AND MOLECULAR WEIGHT

The sample resins were prepared as follows: 1 mole of phenol, 1 mole of formaldehyde (37% formaline) and 0.006 mole of HCl or 0.1 mole of $NH_4OH$ were charges in a three necked flask and the reaction was carried out at 70°C. When the reaction solution became turbid, the reaction was stopped. Then it was allowed to stand overnight in a separating funnel. The oily phase was transferred into an evaporating dish and hardening reaction was carried out at 100-105°C. Novolak and resol were prepared using HCl and $NH_4OH$ as catalyst, respectively.

These resins were fractionated by fractional dissolution using acetone as solvent and water as nonsolvent. GPC chromatograms of each fraction are shown in Fig.1 and 2. In these figures, GPC chromatograms of mixtures of two fractions which were used to compare the characteristics with fractionated samples as mention later are also shown. The characteristics of each fraction are listed in Table 1. All measurements were performed with acetone solution.

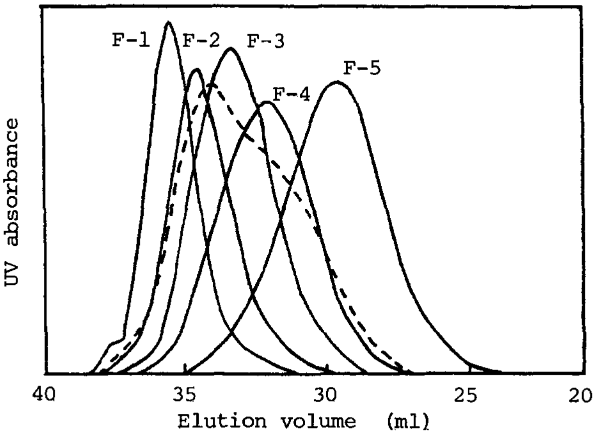

Fig.1 GPC chromatograms of fractionated and mixed sample for novolak

Solid line : fractionated sample

Dotted line : mixed sample (F-2 / F-4 = 1 / 1 in weight fraction)

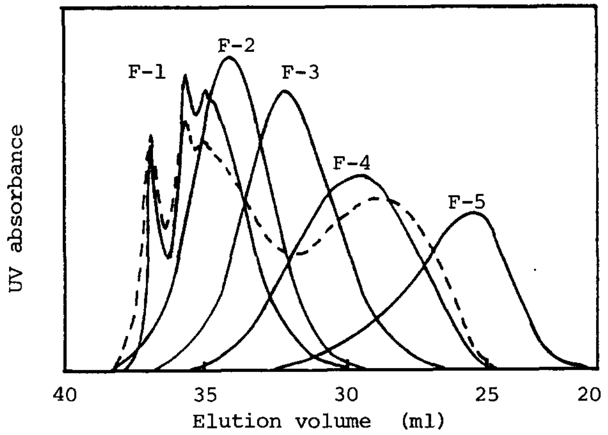

Fig.2 GPC chromatograms of fractionated and mixed sample for resol

Solid line : fractionated sample

Dotted line : mixed sample (F-1 / F-4 = 1 / 1 in weight fraction)

Table 1 Characteristics of fractions

| Resin | Fract.No. | $\varphi$ (ml/g) | $D_A \times 10^6$ ($cm^2$/sec) | $D_m \times 10^6$ ($cm^2$/sec) | $M_{VD_A}$ | $M_{VD_m}$ | $M_n^*$ |
|---|---|---|---|---|---|---|---|
| Novolak | F - 1 | 1.87 | 6.59 | 7.02 | 1680 | 1390 | 770 |
|  | F - 2 | 2.00 | 5.92 | 6.37 | 2170 | 1740 | 1300 |
|  | F - 3 | 2.17 | 4.88 | 5.34 | 3540 | 2710 | 1930 |
|  | F - 4 | 2.48 | 3.93 | 4.36 | 5930 | 4340 | 2280 |
|  | F - 5 | 2.95 | 2.96 | 3.42 | 11690 | 7580 | 4030 |
| Resol. | F - 1 | 1.58 | 9.58 | 10.68 | 650 | 470 | 370 |
|  | F - 2 | 1.68 | 7.95 | 8.83 | 1060 | 780 | 740 |
|  | F - 3 | 1.89 | 6.32 | 7.11 | 1880 | 1320 | 1500 |
|  | F - 4 | 2.27 | 3.93 | 4.60 | 6520 | 4060 | 2800 |
|  | F - 5 | 3.36 | 2.18 | 2.71 | 25900 | 13480 | 7530 |

* $M_n$ is determined by VPO.

Mark-Houwink-Sakurada equation was determined using each average molecular weight in Table 1 and the results were shown in Table 2.

Table 2 Exponent $\alpha$ in Mark-Houwink-Sakurada equation

| Resin | Average Mol. Wt. | $\alpha$ | Resin | Average Mol. Wt. | $\alpha$ |
|---|---|---|---|---|---|
| Novolak | $M_{VD_A}$ | 0.233 | Resol | $M_{VD_A}$ | 0.201 |
|  | $M_{VD_m}$ | 0.252 |  | $M_{VD_m}$ | 0.221 |
|  | $M_n$ | 0.282 |  | $M_n$ | 0.250 |

When the solute molecules are compact and sphere, solution viscosity is independent of its molecular weight, that is, $\alpha = 0$ and is not affected by polymolecularity of solute. But for novolak generally, the viscosity changes slightly with dimension and conformation of solute molecule in solution and the effective fractionation is difficult, therefore, the effect of polymolecularity on $\alpha$ is not negligible. When $M_{VD_A}$ is used, however, $\alpha$ is not affected by polymolecularity as mentioned above. On the other hand, when $M_{VD_m}$ or $M_n$ is used, $\alpha$ is affected by polymolecularity and it becomes larger than that when $M_{VD_A}$ is used.

In order to make this effect clearer, heterogeneous samples were prepared by mixing several fractions in appropriate proportion. GPC chromatograms of typical mixed samples are shown in Fig.1 and 2. When $M_{VD_A}$ is used, $\alpha = 0.238$ for novolak and $\alpha = 0.203$ for resol and they are same as the value of fractionated samples, even though these samples are of polymolecularity. On the contrary, when $M_{VD_m}$ is used, $\alpha$ become larger, that is, 0.293 and 0.236 for novolak and resol, respectively.

During the hardening reaction, polymolecularity of resins prepared increases extremely. Results of viscosity and diffusion measurements of acetone solution are shown in Table 3. Even for such cases, we obtain $\alpha = 0.21$ from $M_{VD_A}$, but when $M_{VD_m}$ is used, $\alpha$ becomes large as 0.77.

As described above, the solution viscosity of phenolic resins is slightly dependent on the molecular weight and this relationship is influenced by polymolecularity.

Table 3 Characteristics of resins during the hardening reaction

| Reaction period (min) | $\varphi$ (ml / g) | $D_A \times 10^6$ ($cm^2$/sec) | $D_m \times 10^6$ ($cm^2$/sec) | $D_m/D_A$ | $M_{VD_A}$ | $M_{VD_m}$ |
|---|---|---|---|---|---|---|
| 35 | 1.52 | 10.85 | 15.70 | 1.45 | 530 | 180 |
| 60 | 1.75 | 8.35 | 13.45 | 1.61 | 1010 | 240 |
| 75 | 1.97 | 7.30 | 12.95 | 1.77 | 1350 | 240 |
| 90 | 2.03 | 6.00 | 12.20 | 2.03 | 2340 | 280 |
| 105 | 2.25 | 5.30 | 11.55 | 2.18 | 3060 | 300 |

## CONCLUSION

The corrected Einstein's viscosity equation has sufficiently wide application range concerning the concentration of phenolic resins in acetone and the values of the specific volume obtained are constant. Therefore, $[\eta]$ can be determined easily from any concentration. The relation between $[\eta]$ and M obeys Mark-Houwink-Sakurada equation $[\eta] = K M^{\alpha}$ and the influence of the extent of compactness and the polymolecularity on exponent $\alpha$ is not negligible. When $M_{VD_A}$ is used, however, $\alpha$ value is not affected by polymolecularity and becomes 0.2.

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*Accepted September 7, 1983* *S*