Molecular Weight Estimation of Co-condensation Resin of Phenol-Urea-Formaldehyde System

by

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Synopsis

A method of molecular weight estimation for the co-condensation resins of phenol-urea-formaldehyde system was proposed. Samples were prepared by two steps reaction, that is, earlier condensation products of phenol with formaldehyde and urea with formaldehyde were prepared separately and then put together at 80°C. The co-condensation products were fractionated by fractional precipitation with acetone-methanol mixed solvent-water system.

Specific volume φ and diffusion coefficient D_A of each fraction were obtained from measurement of solution viscosity and diffusivity. The following relationship between φ and D_A was found to be valid regardless of their heterogeneity,

$$\varphi \sqrt{D_A} = K.$$

In DMF at 25°C, K is about 3.31×10^{-3} regardless of reaction condition.

Since the viscosity-diffusion average molecular weight M_{VD_A} is proprtional to $(\varphi \cdot D_A{}^3)^{-1}$, it is possible to estimate the molecular weight only from φ or D_A as follows :

$$M = 43.3\, \varphi^5$$
$$M = 0.17 \times 10^{-10}\ D_A{}^{-5/2}.$$

1. Introduction

In a previous paper[1], it was recognized from infrared and nuclear magnetic resonance spectrum that the co-condensation reaction takes place in phenol-urea-formaldehyde system and it became apparent that two steps reaction is suitable for the preparation of the co-condensation resins of high molecular weight in high yields than one step reaction.

Moreover, some informations about co-condensation reaction mechanisms were obtained from the standpoint of molecular weight change during the reaction by the viscosity-diffusion method[2]. In that paper, however, the average molecular weight of unfractionated sample was treated.

In this paper, the samples were fractionated and the specific volume and the diffusion coefficient of each fraction were measured. From the results, a method of molecular weight

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estimation was proposed.

2. Experimental

2.1. Materials

Phenol was distilled. Urea was recrystallized from water. Passing through a column of anion exchange resins, acid in formalin was removed. Acetone was refluxed with potassium permanganate and then dehydrated and distilled. Methanol and dimethylformamide (DMF) were distilled.

2.2. Preparation of resins

Phenol, formaldehyde and catalyst (aqueous ammonia or hydrochloric acid) were charged in a three-necked flask with a reflux condenser, a stirrer and a thermometer. The reaction was carried out at 100°C and was continued till emulsion appeared.

On the other hand, the mixture of urea and formaldehyde previously controlled pH value at 9 by NH$_4$OH was reacted for 20 minutes at 80°C. Into this reacted mixture, the reaction product of phenol and formaldehyde was poured. And then the co-condensation reaction began. We called this preparative method two steps reaction.

After 45 minutes the reaction solution was poured into water in order to stop reaction and to take off the water soluble fraction. It has been discribed that the co-condensation resins resolved in acetone-methanol mixed solvent. The reaction products were then reprecipitated wit hthe mixed solvent—water system and the co-condensation resins were obtained. The quantity of reagent used is shown in Table 1.

Table 1 Quantities of Reagents

Sample No.	1	2	3	4	5
[P] / [F]	0.5/0.5	0.5/0.5	0.5/0.5	.5/1.0	0.5/0.5
Catalyst (in P–F reaction)	NH$_4$OH	NH$_4$OH	NH$_4$OH	NH$_4$OH	NH$_4$OH
[U] / [F]	0.5/0.5	0.5/1.0	0.5/1.5	0.5/0.5	0.5/0.5
Sample No.	6	7	8	9	10
[P] / [F]	1.0/1.0	1.0/1.0	1.0/1.0	1.0/1.0	1.0/1.0
Catalyst (in P–F reaction)	NH$_4$OH	NH$_4$OH	NH$_4$OH	HCl	HCl
[U] / [F]	1.0/1.0	1.0/3.0	1.0/6.0	1.0/2.0	1.0/3.0

[P], [U] and [F] are the mole of phenol, urea and formaldehyde, respectively.

2.3. Fractionation

The resins prepared were fractionated into several fractions by fractional precipitation using the mixed solvent as solvent and water as precipitant. The mixture was warmed to about 50°C and then cooled slowly to room temperature in order to ensure the establishment of equilibrium. Then the precipitate was separated by centrifugation at 4,000 r. p. m. and dried under reduced pressure.

2.4. Viscosity and diffusivity measurement

Since the mixed solvent resolved the co-condensation resins selectively and evaporated easily, it was used in extraction of the co-condensation resins from the reaction products and in fractionation. However, in viscosity and diffusivity measurement, DMF was used as the solvent, because some of the dried samples of high molecular weight fractions became insoluble in the mixed solvent but soluble in DMF. Solution viscosity was measured by the Ostwald type viscometer. The determination of the diffusion coefficient was performed by a Hitachi Tiselius Electrophoretic Apparatus HTB–2 equipped with a Schlieren optical system and a U–shaped glass cell. Measurements were carried out at 25° C.

There are several kinds of average diffusion coefficients for example, D_m and D_A as defined below,

$$D_m = m_2/2t, \qquad (1)$$

$$D_A = A^2/4\pi H^2 t, \qquad (2)$$

where m_2, A and H are the second moment, the area and the maximum hight of the diffusion curve, respectively, t is the diffusion time.

D_A is also defined by eq. (3),

$$D_A = (\sum c_i/\sum c_i D_i^{-\frac{1}{2}})^2, \qquad (3)$$

where c_i and D_i are weight fraction and diffusion coefficient of i–th component, respectively.

2.5. Viscosity−diffusion average molecular weight

The specific volume of polymer molecule, φ, is obtained from

$$\eta_{sp} = 2.5\left(\frac{c\varphi}{100-c\varphi}\right) + 4.4\left(\frac{c\varphi}{100-c\varphi}\right)^2, \qquad (4)$$

where η_{sp} and c are specific viscosity and concentration (g/100ml), respectively[3].

The molecular weight of a spherical molecule is given by

$$M = \frac{4}{3}\pi r^3 \frac{N}{\varphi} \qquad (5)$$

where r is the radius of the molecule and N is Avogadro's number. The relationship between r and D is represented by eq. (6), proposed by Einstein :

$$r = \frac{RT}{N} \cdot \frac{1}{6\pi\eta_0 D}. \qquad (6)$$

From these equations, the viscosity−diffusion average molecular weight, M_{VD}, is obtained by

$$M_{VD} = \frac{R^3}{162\pi^2 N^2} \cdot \frac{T^3}{\eta_0^3 D^3 \varphi}. \qquad (7)$$

3．Results and discussion

The results of the molecular weight determination are shown in Table 2

Table 2 Results of Viscosity and Diffusivity Measurement

Sample 1				Sample 2			
Fraction No.	φ (cc/g)	$D_A \times 10^6$ (cm²/sec)	M_{VD_A}	Fraction No.	φ (cc/g)	$D_A \times 10^6$ (cm²/sec)	M_{VD_A}
1	4.64	0.64	47820	1	4.56	0.80	24780
2	3.01	0.95	22430	2	2.99	1.14	13080
3	2.36	1.35	9970	3	2.36	1.76	4490
4	2.29	1.81	4260	4	2.23	1.96	3450
5	1.92	2.84	1320	5	1.87	3.22	930
unfractd.	2.13	2.56	1570	unfractd.	2.52	2.08	2460
Sample 3				**Sample 4**			
1	4.83	0.74	29610	1	4.55	0.79	23060
2	3.02	1.18	11660	2	4.57	0.72	30000
3	2.64	1.60	5350	3	2.97	1.23	9490
4	2.30	2.11	2680	4	2.28	1.80	3960
5	1.87	3.23	920	5	1.80	3.00	1080
unfractd.	3.38	1.64	3750	unfractd.	2.03	2.26	2240
Sample 5				**Sample 6**			
1	3.49	0.88	21540	1	2.82	1.56	5160
2	2.25	1.56	5990	2	2.39	1.93	3220
3	1.88	2.04	3220	3	1.98	2.94	1100
4	1.74	2.63	1620	4	1.72	4.63	320
5	1.62	3.57	690				
unfractd.	1.88	2.62	1510	unfractd.	2.13	2.52	1620
Sample 7				**Sample 8**			
1	3.91	1.03	13320	1	4.70	0.82	21420
2	2.68	1.54	5800	2	3.59	1.11	11310
3	2.17	2.19	2500	3	2.53	1.71	4390
4	1.84	2.93	1250	4	1.88	2.98	1120
5	1.68	4.29	440	5	1.53	4.78	330
unfractd.	2.32	2.58	1430	unfractd.	2.82	2.03	2350
Sample 9				**Sample 10**			
1	2.66	1.89	3060	1	4.05	0.98	14300
2	2.50	2.12	2320	2	3.22	1.18	10300
3	2.09	2.58	1530	3	2.30	1.99	3000
4	1.85	3.34	800	4	1.86	3.19	900
5	1.65	4.35	410	5	1.48	4.49	410
unfractd.	2.14	3.00	950	unfractd.	2.51	2.29	1810

In the previous paper[4], it was shown that eq. (8) was valid for fractionated samples of alkali catalized phenolic resin.

$$\varphi \sqrt{D} = K. \tag{8}$$

In the case of a heterogeneous system, it is reasonable to use D_A as defined in eq. (3) instead of D as in eq. (8).

If the next equation for a homogeneous system is applicable to a heterogeneous system,

$$\varphi_i = KD_i{}^k, \tag{9}$$

since φ is weight average value, the following equation are valid

$$\varphi = \Sigma c_i \varphi_i / \Sigma c_i$$

$$= K \Sigma c_i D_i{}^k / \Sigma c_i$$

$$= K D_A{}^k$$

$$= K \Big(\Sigma c_i / \Sigma c_i D_i{}^{-\frac{1}{2}} \Big)^{2k}. \tag{10}$$

If $k = -\frac{1}{2}$ in eq. (11), eq. (12) is obtained.

$$\Sigma c_i D_i{}^k / \Sigma c_i = \Big(\Sigma c_i / \Sigma c_i D_i{}^{-\frac{1}{2}} \Big)^{2k}, \tag{11}$$

$$\varphi \sqrt{D_A} = K. \tag{12}$$

Subsequently the application of these equations to the co-condensation resins and the estimation of the molecular weight from φ or D_A is shown.

From a plot of log φ vs. log D_A as shown in Fig. 1, K is found to be about 3.31×10^{-3}.

If D_A is used, the viscosity diffusion average molecular weight defined in eq. (7) is calculated by the next equation.

$$M_{VD_A} = K'/D_A{}^3 \varphi \tag{13}$$

Fig. 1. Plots of log φ vs. log D_A for all samples
(Solid line is obtained from eq. (12))

From eq. (12) and (13), the following equations are obtained.

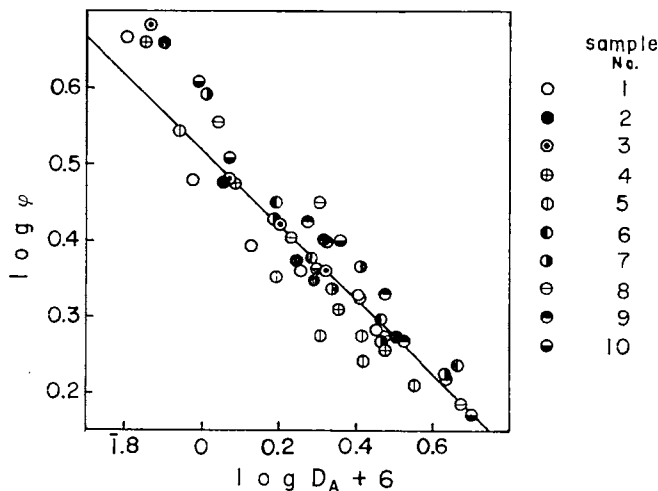$$M_{VD_A} = (K'/K^6) \, \varphi^5 \tag{14}$$

$$M_{VD_A} = (K'/K) \, D_A{}^{-\frac{5}{2}} . \tag{15}$$

Where $K' = R^3 T^3 / 162\pi^2 N^2 \eta_0{}^3$.

Using $K = 3.31 \times 10^{-3}$, $\eta_0 = 0.7729$ c. p. (in DMF at 25°C), eq. (14) and (15) are transformed into eq. (16) and (17).

Table 3 Comparison of M_φ and M_{D_A} with $M_{V D_A}$

Sample 1				Sample 2			
Fraction No.	$M_{V D_A}$	M_φ	M_{D_A}	Fraction No.	$M_{V D_A}$	M_φ	M_{D_A}
1	47820	93230	52080	1	24780	85650	29700
2	22430	10720	19330	2	13080	10300	12250
3	9970	3170	8030	3	4490	3200	4140
4	4260	2750	3860	4	3450	2380	3160
5	1320	1130	1250	5	930	990	920
unfractd.	1570	1900	1620	unfractd.	2460	4440	2730
Sample 3				Sample 4			
1	29610	113350	36090	1	23060	84530	30260
2	11660	10930	11240	2	30000	86690	38650
3	5350	5570	5250	3	9490	10070	10130
4	2680	2780	2630	4	3960	2650	3910
5	920	980	900	5	1080	810	1090
unfractd.	3750	19130	4940	unfractd.	2240	1510	2210
Sample 5				Sample 6			
1	21540	22390	23400	1	5160	7710	5590
2	5990	2510	5590	2	3220	3360	3280
3	3220	1000	2860	3	1100	1310	1150
4	1620	690	1510	4	320	650	380
5	690	480	700				
unfractd.	1510	1020	1530	unfractd.	1620	1880	1680
Sample 7				Sample 8			
1	13320	39420	15790	1	21420	99100	27920
2	5800	6020	5780	2	11310	25890	13100
3	2500	2080	2400	3	4390	4490	4450
4	1250	920	1150	4	1120	1000	1120
5	440	580	450	5	330	360	340
unfractd.	1430	2930	1590	unfractd.	2350	7750	2900
Sample 9				Sample 10			
1	3060	5800	3460	1	14300	47060	17880
2	2320	4190	2590	2	10300	14970	11240
3	1530	1740	1590	3	3000	2810	3050
4	800	940	830	4	900	970	930
5	410	530	420	5	410	310	420
unfractd.	950	1940	1090	unfractd.	1810	4310	2140

$$M_{VD_A} \ (=M\varphi) \ = 43.3 \varphi^5 \tag{16}$$

$$M_{VD_A} \ (=M_{D_A}) \ = 0.17 \times 10^{-10} D_A^{-5/2} \ . \tag{17}$$

In order to distinguish these three kinds of M_{VD_A}, the molecular weights calculated by eq. (16) and (17) are symbolized $M\varphi$ and M_{D_A}, respectively.

The results are shown in Table 3, Fig. 2 and Fig. 3.

M_{D_A} shows a good agreement with M_{VD_A} regardless of reaction conditions. On the other hand, there is somewhat difference between $M\varphi$ and M_{VD_A}. It is because $M\varphi$ is proportional to φ^5 in eq. (14). However, the solution of the spherical molecule has no property which depends remarkably on the molecular weight and one can easily measure the solution viscosity, therefore, eq. (16) is useful for the estimation of the molecular weight of spherical molecules such as the co-condensation resin.

In these cases, the intrinsic viscosity $[\eta]$ is given as follows :

$$[\eta] = a\varphi/100 = \varphi/40. \tag{18}$$

From eq. (16) and (18). the next equation is valid.
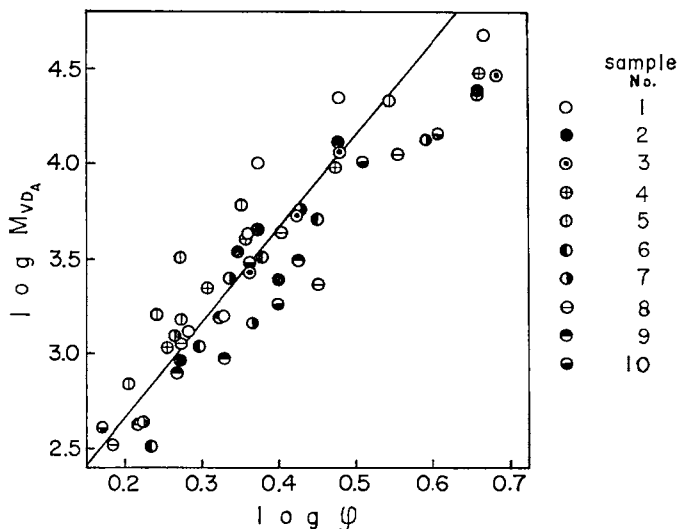
$$[\eta] = 1.28 \times 10^{-2} M\varphi^{1/5}. \tag{19}$$

Fig. 2. Plots of log M_{VD_A} vs. log φ for all samples
(Solid line is obtained from eq. (16))

Fig. 3. Plots of log M_{VD_A} vs. log D_A for all samples
(Solid line is obtained from eq. (17))

When the intrinsic viscosity is proportional to the α-th power of the molecular weight, the viscosity average molecular weight M_V is given by

$$M_V = \left(\sum c_i M_i^\alpha / \sum c_i \right)^{1/\alpha} . \tag{20}$$
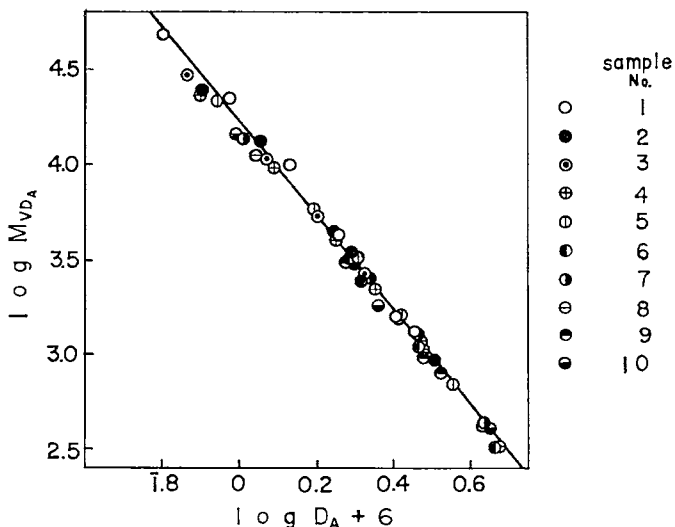
$M_{V D_A}$ was previously defined as follows[5] :

$$M_{V D_A} = \left(\sum c_i M_i^{(1+\alpha)/6} \right)^6 / \left(\sum c_i M_i^\alpha \right) \left(\sum c_i \right)^5 . \tag{21}$$

Since M_V and $M_{V D_A}$ have the same average when $\alpha = \frac{1}{5}$, it is reasonable to adopt D_A at the introduction of the relationship between viscosity and molecular weight.

4. Conclusion

In this paper, the fractionation of the co-condensation resins of phenol-urea-formaldehyde system by fractional precipitation and the determination of the viscosity-diffusion average molecular weight from the specific volume and the diffusion coefficient in DMF are performed.

From the results, the following conclusions are obtained.

1) The following equation is valid regardless of reaction conditions,

$$\varphi \sqrt{D_A} = K.$$

In DMF solvent at 25°C, K is 3.31×10^{-3}.

2) The relationship between φ and M or D_A and M are obtained as follows :

$$\varphi = 0.4707 \, M^{\frac{1}{5}}$$

$$D_A = 0.4915 \times 10^{-4} M^{-\frac{2}{5}} .$$

From these equations, the molecular weights can be estimated,

$$M = 43.3 \, \varphi^5 ,$$

$$M = 0.17 \times 10^{-10} D_A^{-\frac{5}{2}} .$$

Acknowledgement

Reference

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