

INVESTIGATION ON THE RELATIONSHIP BETWEEN INTRINSIC VISCOSITY AND MOLECULAR WEIGHT OF POLY (VINYL CHLORIDE-DIETHYL MALEATE)

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ABSTRACT

A poly (vinylchloride-diethyl maleate) copolymer has been fractionated by repeated precipitation method. All fractions and the unfractionated sample have been characterized by viscometry, dynamic osmometry, Zimm static osmometry, light scattering and gel permeation chromatography. After correction for polydispersity, a $[\eta] \sim M$ relationship for monodisperse polymer solutions has been obtained:

$$[\eta] = 1.99 \times 10^{-3} M^{0.87} \quad (\text{ml/g, at } 25^\circ\text{C, in cyclohexanone})$$

For the copolymer solution in THF, the second virial coefficient A_2 decreases as the molecular weight increases. The relationship is

$$A_2 = 2 \text{ slope } (\bar{M}_n RT)^{-1/2}.$$

Vinyl chloride-diethyl maleate copolymer (Chloro-Maleate Resin) is a kind of modified polyvinyl chloride resin. Its character is that plasticizer DBP may be replaced by cheaper paraffin wax chloride while the resin still retain its good end properties. In this work, a sample of chloro-maleic resin was first fractionated by successive reprecipitation for obtaining fractions with more homogeneous molecular weight distribution. The number average molecular weight of the fractions were determined by rapid dynamic osmometry^{[1][2][3]} and static osmometry; the weight average molecular weights were determined by light scattering and the intrinsic viscosities were determined by capillary viscometry. Thus we obtained the value of parameter K and α of Mark-Houwink relation $[\eta] = KM^\alpha$, and the second virial coefficients A_2 of the sample in tetrahydrofuran solution.

1. Polymer sample

Chloro-Maleate resin was provided by Changzhou Resin Factory. It was produced by suspension polymerization with IPP as initiator. It consists of seven percent diethyl maleate. The polymer samples were purified by extraction with methanol in a Soxhlet extractor.

2. Fractionation^[4]

THF and methanol were used as solvent and precipitant respectively for fractionating chloro-maleic resin by precipitation. The fractionation was carried out at $25^\circ \pm 0.01^\circ\text{C}$. Seven fractions were obtained as white gel-like precipitate. The fractionation data were listed in Table 1.

Table 1 The intrinsic viscosity, number and weight average molecular weights of chloro-maleic resin fraction

Fraction	Weight	Weight fraction w_i	Cumulative amount in I_i	$[\eta]$ (ml/g)	$\bar{M}_n \times 10^{-4}$		$\bar{M}_w \times 10^{-4}$ Light scattering	$\frac{\bar{M}_w}{\bar{M}_n}$
					Dynamic	Static		
1	1.6523	0.157	0.922	97.681	16.50	19.44	35.50	1.99
2	2.5417	0.241	0.723	99.918	19.40	21.64		
3	0.9464	0.090	0.558	97.402	12.40			
4	1.4316	0.136	0.445	88.585	11.43	10.70	17.80	2.12
5	1.4721	0.140	0.308	67.270	8.39	7.93		
6	1.2004	0.114	0.181	50.926				
7	1.3068	0.124	0.062	25.813	2.76	2.56		

sample weight 10.7940g

3. Osmotic pressure

A modified Bruss osmometer was used to determine the osmotic pressure of solution by extrapolating to zero flow rate with dynamic method^{[1][2][6]}. The osmotic pressure of the solution also had been determined by modified Zimm-Meyerson type glass osmometer^[4].

The experimental temperature was kept at $30 \pm 0.01^\circ\text{C}$ and THF was used as solvent. The semipermeable membrane was the regenerated cellulose cellophane produced by Fourth Tianjin Paper-Manufacturing Factory. It was treated first by soaking it in 20:80 alcohol-water for 20—30 days, and then the solvent was replaced successively by absolute alcohol, absolute alcohol-DMF (1:1) and DMF. It was soaked in each solvent at least for 5 hours. The DMF was replaced twice and the membrane was stored in it finally. Before using the membrane DMF was replaced by DMF-THF (1:1) for 5—7 hours and then twice by THF^[3].

A cathetometer and a stop watch were used to determine the time elapsed for the distance travelling up or down 1 mm. Simultaneously the liquid bead difference Δh between the solution and solvent was also determined. The flow rate was calculated by the formula

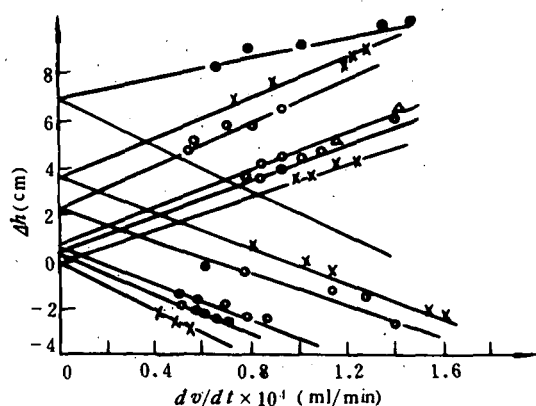
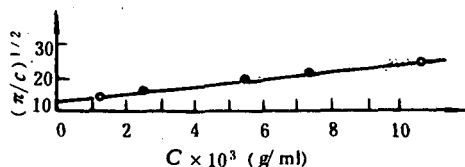
$$\frac{dv}{dt} = 60\pi r^2 h / t \quad (\text{ml/min}) \quad (1)$$

in which r is the radius of the capillary (cm), t is the time elapsed for the liquid meniscus in the capillary moved a distance of h , in the present case it is 0.1cm. Plot of the liquid bead Δh versus dv/dt is shown in Fig 1. The product of multiplying Δh_0 by solution density ρ represented the osmotic pressure value π , $\pi = \Delta h_0 \cdot \rho$. Usually the density values at all concentrations could be obtained from the density-concentration curve determined previously. The density data was listed in Table 2.

Five solutions with difference concentrations were prepared for each sample and the osmotic pressure π was determined. From the plot (Fig.2), the number average molecular weights were obtained by the formula

Table 2 Concentration density and osmotic pressure of the fraction I-1

No	$C(\text{g/ml})$	$\rho(\text{g/cm}^3)$	ρ/C	$\Delta h_0(\text{cm})$	π/C	$(\pi/C)^{1/2}$
1	0.001221	0.87928	720.1	0.27	194.4	13.94
2	0.002442	0.87975	360.3	0.62	223.4	14.95
3	0.005495	0.88100	160.3	2.32	368.7	19.20
4	0.007325	0.88172	120.4	3.70	445.5	21.11
5	0.01099	0.88319	80.36	6.90	544.5	23.55

**Fig. 1** Flow rate-applied pressure extrapolation for chloro-maleate resin**Fig. 2** $\left(\frac{\pi}{C}\right)^{1/2}$ vs. C plot for fractions sample I-1

$$\left[\left(\frac{\pi}{C}\right)_{C \rightarrow 0}^{1/2}\right]^2 = \frac{RT}{\bar{M}_n} \quad (2)$$

The second virial coefficients were calculated from the slopes of the plot according to formula^[7]

$$\left(\frac{\pi}{C}\right)^{1/2} = \left(\frac{RT}{\bar{M}_n}\right)^{1/2} + \frac{1}{2}A_2(\bar{M}_n RT)^{1/2} \cdot C \quad (3)$$

$$A_2 = 2(\bar{M}_n RT)^{1/2} \times \text{slope}$$

The A_2 data are listed in Table 3.

Table 3 A_2 Values of the fractions

Fraction	1	2	3	4	5	6	7
$A_2 \times 10^3$	1.09	1.02	1.73	1.95	2.01		3.56

The second virial coefficient decreases as the molecular weight increases.

4. Determination of intrinsic viscosity

A ID-4-0.7(mm) Ubbelohde viscometer was used to determine the solution viscosities by successive dilution for 5 concentrations. The flow rate was measured with a stop watch read to 0.1 sec. at $30 \pm 0.01^\circ\text{C}$ and taking cyclohexanone as solvent. The intrinsic viscosities were calculated

by extrapolation according to Huggins Equation.

$$\eta_{sp}/C = [\eta] + K[\eta]^2 c \quad (4)$$

$$\ln \eta_r / C = [\eta] - \beta [\eta]^2 C. \quad (5)$$

The results obtained were listed in Table 1.

5. Determination of light scattering^[4]

A Shimazu PG 21 light scattering photometer was used to determine the intensity of the scattered light of THF solution. The weight average molecular weight was calculated according to Debye equation. The results obtained are listed in Table 1.

6. Gel permeation chromatography analysis.

A SN-ON GPC instrument was used. The columns were packed with beads and tetrahydrofuran was used as solvent. The chromatogram obtained was nearly a normal distribution.

7. The relationship between intrinsic viscosity and molecular weight

The Mark-Houwink equation relating intrinsic viscosity and molecular weight usually should be determined from narrow molecular weight distribution samples with $\bar{M}_w/\bar{M}_n \leq 1.25$. If the number average molecular weight of polydispersed sample is used to evaluate the parameters of $[\eta] \sim M$ relation a large error may be introduced.

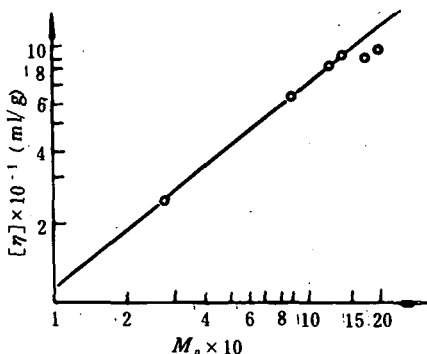


Fig. 3 The experimentally determined $[\eta]$ and $\bar{M}_n$ values of the fractions are plotted on double logarithmic coordinate system

Since the effect of polydispersity is much more pronounced for parameter K , so a correction for it is necessary. For this purpose, a $\log [\eta]$ versus $\log \bar{M}_n$ plot was first drawn for all fractions as shown in Fig. 3. From the slope and intercept of straight line obtained, We have

$$K_n = 3.5 \times 10^{-3}$$

$$\alpha = 0.87$$

$$[\eta] = 3.50 \times 10^{-3} \bar{M}_n^{0.87}. \quad (6)$$

For samples with log normal distribution^[5], the relationship between the apparent parameter K_n and the monodispersed parameter K may be written as:

$$K_n = K \left(\frac{\bar{M}_w}{\bar{M}_n} \right)^{(\alpha^2 + \alpha)/2} \quad (7)$$

in which

$$q_n = \left(\frac{\bar{M}_w}{\bar{M}_n} \right)^{(\alpha^2 + \alpha)/2} \quad (8)$$

is the polydispersity correction factor when the heterogeneity index $\bar{M}_w/\bar{M}_n$ equal to 2. From the average data of all fractions, the corrected parameter K according to equation 8 is summarized in Table 4.

Table 4 The corrected Mark-Houwink parameter

$\bar{M}_w/\bar{M}_n$	α	q_n	$K_n \times 10^3$	$K \times 10^3$
2	0.87	1.757	3.50	1.99

The monodispersed Mark-Houwink relation of chloromaleate resin in cyclohexanones at 30°C is

$$[\eta] = 1.99 \times 10^{-3} M^{0.87} \quad (9)$$

Keywords:

Intrinsic viscosity; Molecular Weight; Poly(vinyl chloride-diethyl maleate); Chloro-Maleate Resin; Osmotic pressure, Mark-Houwink parameter.

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