

Size and Shape Characteristics of Poly(vinylacetate) in Toluene by Light Scattering

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Summary: Light scattering measurements were performed for poly(vinylacetate), PVAc, sample in toluene at room temperature. The radius of gyration $\langle S^2 \rangle^{1/2}$ and second virial coefficient (A_2) for seven fractions and crude sample was determined by using the light scattering techniques such as turbidity, zimm plot method and dissymmetry. From the data it was concluded (i) that PVAc molecules have random coil conformation in toluene at 25°C (ii). The second virial coefficient depends strikingly on molecular weight for a given solvent (iii) there is also a good correlation between mean square radius of gyration and molecular weight.

Introduction

Stockmayer and Casassa [1] reached the conclusion from a light scattering and viscosity studies that in some solvents, such as methyl ethyl ketone the molecular chain of PVAc maintains the spherical shape. However, Shultz argued that their data of light scattering on PVAc in various solvents such as acetone, ethyl acetate did not support the spherical shape but rather favoured the coil conformation. Now the problem of main interest is to study toluene/PVAc system in order to see whether PVAc has a coil or sphere conformation.

Results and Discussion

Table 1 shows the second virial coefficient values for seven poly (vinylacetate) fractions in toluene at 25°C at 436 nm and 546 nm wavelength calculated from light scattering techniques (turbidity and zimm plot). It shows that second virial coefficient increases from higher to lower molecular weight fractions. The second virial coefficient is the parameter essentially determined the thermodynamic interactions between the polymer segments and the solvent molecules. So when the polymer has higher molecular weight the interaction between polymer-polymer is greater as compared to polymer-solvent, as in higher molecular weight there is entanglement, intra-molecular associations so solubility decreases and have small values of second virial coefficient while in low molecular weight polymer the polymer-solvent contacts are favoured and therefore the value of second virial coefficient increases with decrease of

Table 1: Values of second virial coefficient for different fractions by zimm plot and turbidity method at 436 nm and 546 nm wavelength.

Fraction No.	$A_2 \times 10^4$ (mol.ml/g ²)			
	436 nm		546 nm	
	Zimm plot	Turbidity	Zimm plot	Turbidity
I	5.28	5.25	5.15	5.13
II	5.45	5.40	5.25	5.21
III	5.61	5.55	5.32	5.30
IV	5.66	5.62	5.43	5.38
V	5.73	5.66	5.55	5.50
VI	5.78	5.71	5.62	5.55
VII	5.80	5.75	5.65	5.60

molecular weight and also quality of solvent increases. This can be shown from literature that for θ - solvent slope = 0, For good solvent slope >0 and for poor solvent slope <0 from plot of Hc/τ vs concentration [7,8]. The second virial coefficient values shows that toluene is good solvent for PVAc.

Table 2 shows the radius of gyration values for seven fractions at 436 nm and 546 nm wavelength calculated from Zimm plot and dissymmetry method. It is clear from table that the values of radius of gyration decrease from highest to lowest fraction this is as the radius of gyration is statistical average of the configurational distribution of segments around the center of mass. In high molecular weight fraction the polymer chain expands possesses high diameter and size while in lower molecular weight fractions the polymer chain contract because of segmental interactions, the

Table 2: Values of radius of gyration for different fractions by zimm plot and dissymmetry method at 436 nm and 546 nm wavelength.

Fraction No.	$2\theta/2$ ($^{\circ}$)		Zimm plot	Dissymmetry
	436 nm	546 nm		
I	232	230	287	284
II	227	223	265	260
III	220	218	253	251
IV	194	190	249	247
V	189	188	234	232
VI	184	184	236	233
VII	183	182	229	225

radius, of gyration decreases. The values of radius of gyration are found much coincident with coil like molecule when the result are compared with radius of gyration calculated with assumption that the molecules are coiled shape [9,10]. The relatively small difference between dissymmetry and zimm plot $\langle S^2 \rangle^{1/2}$ values are presumably due to incorporation of solvent with in the scattering particle and relatively minor deviation from coil shape.

Fig. 1 and 2 shows the molecular weight dependence of the radii of gyration and second virial coefficient determined from $\langle S^2 \rangle^{1/2}$ vs mol. wt. and $\log A_2$ vs \log Mol. wt. plot respectively is found to confirm the following equations obtained from least square fit.

$$\langle S^2 \rangle^{1/2} = 2 \times 10^{-6} + 1.03 \times 10^{-11} M$$

$$[\log A_2 = -2.83 - 0.09] 10 \text{ g M}$$

Experimental

PVAc was subjected to a number of refractionation to obtain narrow, more or less homogeneous fractions. Seven fractions were obtained. Dilute solution of these fractions were prepared by dissolving a preweighed quantity of the polymer in carefully filtered toluene. The concentration of these solutions was 0.2 - 1.0 gm/dl.

The specific refractive index increment was measured by using differential refractometer. For zimm plot, light scattering intensities of all the solutions of each sample were measured in the angular range 30° - 135° with an increment $\Delta\theta$ of 15° . The experimental data for the incident radiation of 436 nm and 546 nm wavelength, were used to calculate

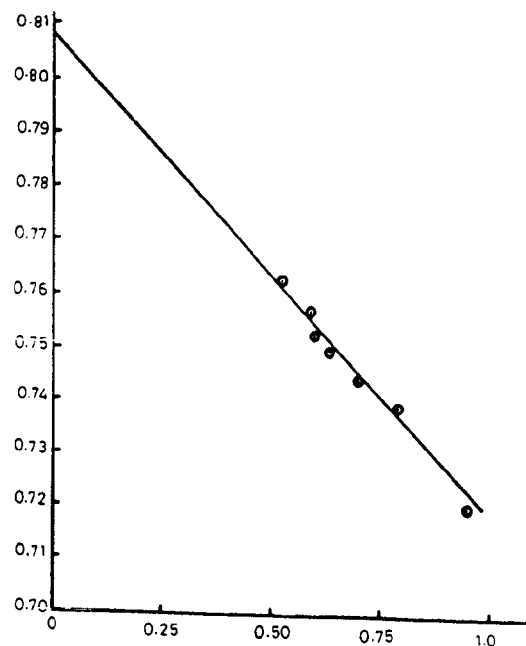


Fig.1: $\log A_2$ versus $\log M_w$ for different fractions at 30°C .

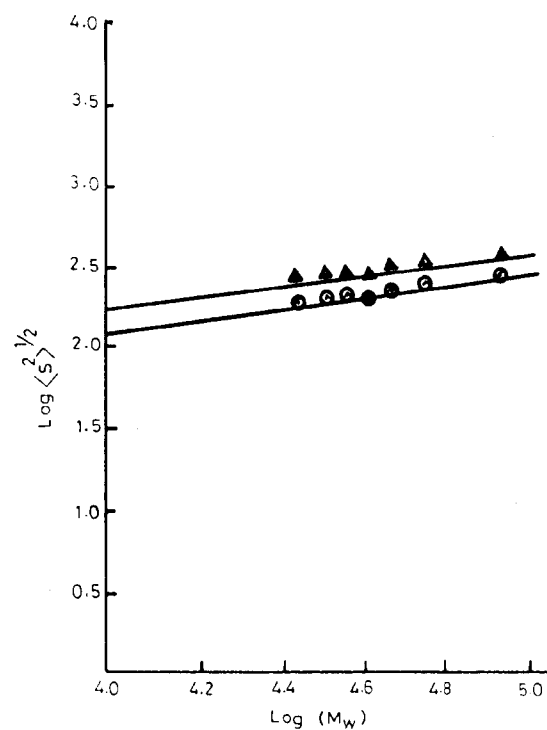


Fig. 2: Plot of radius of gyration versus M_w of fractions at different wavelength.

the rayleigh ratio using an equation given by Gruber and co-worker [3] as $R\theta = 10 R_{90}(\text{Benzene}) \sin \theta / 1 + \cos^2 \theta / 190(\text{Benzene})$

From Zimm equ : $Kc/R\theta = 1/MP\theta^{-1} + 2A_2C$

$$P\theta^{-1} = \frac{1 + 16\pi^2 \langle S^2 \rangle^{1/2} \sin^2 \theta / 2}{3\lambda^2}$$

values of $Kc/R\theta$ were plotted against $\sin^2 \theta / 2 + kc$ where k is an arbitrary constant, as suggested by zimm. Intercept was obtained by double extrapolation of the $kc/R\theta$ lines to zero angle and zero concentration. The intercept is inversely proportional to the weight average molecular weight. The mean square radius of gyration $\langle S^2 \rangle^{1/2}$ and second virial coefficient (A_2) were obtained by the relation.

$$\langle S^2 \rangle^{1/2} = \frac{3\lambda^2}{16\pi^2} \frac{(\text{Slope of the Line } C \rightarrow O)}{\text{Intercept}}$$

$$A_2 = \frac{2\pi n}{\lambda} (\text{Slope of Line } \theta \rightarrow O)$$

These results were also compared with the results obtained by turbidity and dissymmetry method.

To obtain dissymmetry ratio, Z , through the studies made on Brice Phoenix Light scattering photometers the following equation was used.

$$Z = \frac{(\text{FD45/DW}) \text{ solution} - (\text{FD45/DW}) \text{ Solvent}}{(\text{FD135/DW}) \text{ solution} - (\text{FD135/DW}) \text{ Solvent}}$$

Intrinsic dissymmetry [Z] was obtained from intercept of a plot of Z versus concentration [Z] is related with partial scattering function $P^{-1}(\theta)$ [4]. From the values of the $P^{-1}(\theta)$, thus obtained the shape of the PVAc molecules was estimated with the help of the theoretical prediction for various conformation [5,6] as for sphere

$$P^{-1}(\theta) \text{ sphere} = 1 + \frac{X^2}{5} + \frac{4X^4}{175}$$

$$\text{and } P^{-1}(\theta) = 1 + \frac{Z}{\text{coil } 3} + \frac{Z^2}{36} +$$

$$Z = \frac{8\pi^2 \langle S^2 \rangle^{1/2}}{3\lambda^2} \sin^2 \theta / 2$$

For turbidity measurements, the second virial coefficient is obtained from the slope of the Hc/τ versus concentration according to the equation

$$Hc/\tau = 1/M + 2A_2C$$

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