

## Molecular Weight Distribution of Cellulose Acetate and its Relations to Different Parameters

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**Summary:** Cellulose acetate obtained from Ravi Rayon Ltd. was fractionated into nine different fractions by fractional precipitation using acetone as a solvent and water as a precipitant. For fractional precipitation, an apparatus is designed which gave better results. Using light scattering and viscometry methods, the relationship between molecular weight and refractive index increment, second virial coefficient, radius of gyration and viscosity is developed. The integral and differential molecular weight distribution curves are also plotted.

### Introduction

The properties of polymers depend not only on molecular weight, its distribution but also on irregularities of chain structure etc. These are related to polymer molecular weight by a general equation [1]

$$P = KM^a$$

where  $P$  is the property of polymer having molecular weight  $M$ , related through the constants  $K$  and  $a$ . For multivariables this equation can be written as:

$$P = A \prod_{i=1}^n V_i^{a_i}$$

where  $\pi$  is the sign of product;  $a$  is constant  $V_i$  is the  $i$ th variable and  $a_i$  the exponent of  $i$ th variable.

The most frequent method for experimental determination of the distribution of molecular weight in a high polymer sample requires fractionation as nearly homogeneous as possible with respect to their molecular weight. The sample should be separated into completely homogeneous fractions by which

weights and molecular weight distribution curves could be constructed. In practice, it is difficult to achieve this degree of separation. As a result it becomes necessary to reconstruct distribution curves from weights and average molecular weights from more or less homogeneous fractions. To effect this reconstruction, it is common practice to make use of the "integral weight distribution curve". Nonetheless, the frequency distribution curve is a discontinuous function, that is defined only for integral values of degree of polymerization  $P$ . It can be written as a continuous function  $n_p(p)$ , if the average degree of polymerization is large. Under this condition  $P$  is for fractional purpose, a continuous variable. the  $n_p(p)$  should be equal to the number of moles of polymer whose degree of polymerization lies between  $p$  and  $p+dp$ , thus

$$dn = n_p(p) dp \quad (1)$$

A similar equation can be written for

$$\omega_p(p) = M_p n_p(p) \quad (2)$$

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where  $M_p = pM$ ,  $n_p$  and  $\omega_p$  are known as the differential frequency and weight distribution curves. If we define  $\Omega(p)$  as the "integral weight distribution curve"  $\Omega(p)$  represents the total weight of polymer whose degree of polymerization is less than or equal to  $p$ . Clearly,

$$\Omega(p) = \int_0^p \omega_p(t) dt.$$

where  $t$  is a dummy variable;  $\Omega(p)$  and  $\omega_p(p)$  are related by  $d\Omega(p)/dp = \omega_p(p)$  ----- (3)

Thus, if  $\Omega(p)$  is known as a function of  $p$ ,  $\omega_p(p)$  and  $n_p(p)$  can be determined [2,3] from equation (2) and (3).

As fractional precipitation method gives reliable results and does not require any sophisticated instrument [2], so we have used this method to get different fractions of polymers with respect to molecular weight. Though a number of research workers [4-8] have already used this method, to find the molecular weight viscosity relationship, but they have used osmometry to find the molecular weight of the fractions, moreover the molecular weight distribution curve is not constructed. Therefore in this work, we are going to draw molecular weight distribution curve and develop the relation between molecular weight, refractive index increment, second virial coefficient, radius of gyration and viscosity, using light scattering technique and viscometry.

### Experimental

The apparatus designed for fractional precipitation is schematically shown in figure 1. It is a double walled glass vessel (A,B) closed to air by water seal (D). (J) is the holder of the

stainless steel stirrer (C), by the rotation of which the contents of the vessel are stirred. The solution of the polymer can be put in the vessel through stopcock (E). The temperature of the contents of the vessel can be controlled by circulating water from a thermostat through the jacket. The precipitant was added through stopcock (F). The precipitated or separated material was taken out through another stopcock (G). All the stopcock used were of glass. The capacity of the inner vessel was 4.5 litres.

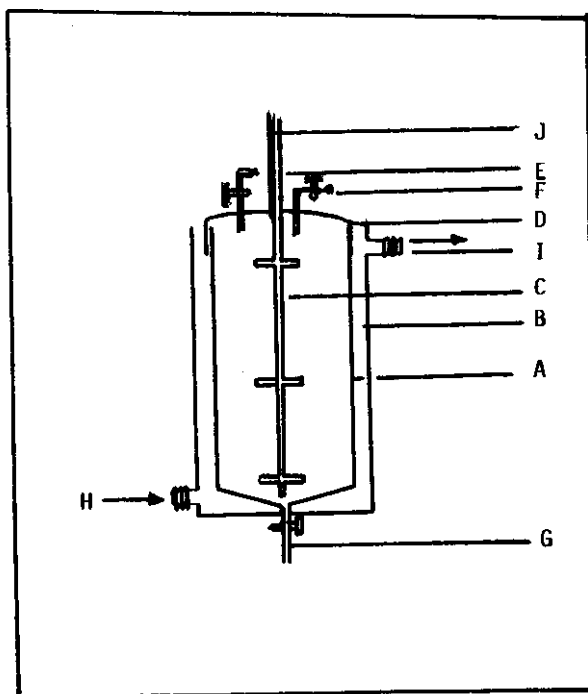


Fig.1: Schematic representation of the apparatus used for the fractional precipitation.

### Fractionation

For this purpose, granules of cellulose acetate\* (supplied by Ravi Rayon Ltd. Lahore, Pakistan) was used as a solute, acetone as a solvent and water as a precipitant. To determine suitable concentration of cellulose

\* Degree of substitution is 2.4

acetate for fractionation, three different concentrations (0.5, 0.75 and 1.0%) were employed. The solid granules were dissolved in acetone. That solution was further diluted to the required concentration. From preliminary screening, only 0.75% proved to be more suitable for fractional precipitation.

#### *Procedure*

Firstly 0.75% solution of cellulose acetate in acetone was introduced in the fractionating vessel (Fig.1) through stopcock (E) then the temperature of the system was brought at 31°C by water circulation. The precipitant was added drop by drop through the inlet (F) and vigorous stirring was carried out simultaneously. The precipitant was added until the mixture appeared to be densely cloudy. The temperature of the contents of the vessel was then raised to such a degree that the cloudiness of the solution disappeared. Normally 10-15°C above the bath temperature was sufficient. The solution was slowly cooled down at 31°C  $\pm$  0.01° to allow the polymer for precipitation; the stirring was stopped and reprecipitated polymer was allowed to settle for 24 hours. In this case the precipitate was a moderately viscous solution that could be drained in the receiver by opening the stopcock (G). The stopcock was closed after the last portion of the fraction had passed through it. Thus preventing the supernatant liquid from draining through. This liquid was again subjected to the same procedure until no precipitation occurred. The fractionated material was again subjected to the same fractionating procedure to obtain more homogeneous fractions. The different fractions obtained in this way were dried under vacuum at room

temperature to avoid change in the structure and molecular weight during drying. After complete drying of samples (by drying upto constant weight), the weight of the samples was noted and redissolved in acetone for further studies.

#### *Refractometry*

A Brice Phoenix Differential Refractometer, supplied by Phoenix Precision Inc. Co. was used to measure refractive index increment ( $dn/dc$ ) of every fraction. The apparatus employed a partitioned, stoppered cell and a precision of  $\pm 2.10^{-6}$  refractive index units. The cell is housed in a thermostat with  $\pm 0.02^\circ\text{C}$  fluctuations in temperature. The instrument is equipped for measurements with light of wave lengths 436 nm and 546 nm. 1% solution was normally employed to determine  $dn/dc$  at the temperature of 25°C.

#### *Light Scattering*

For light scattering measurements, Brice Phoenix light scattering photometer model DM 2000 was used, in which the light detectors and measuring system were replaced by Photovolt Corporation, New York. This alteration made the calculations easily. The instrument is equipped for use with incident radiations for 436 nm and 456 nm but only 546 nm wave length of light was used for all the measurements. The scattering cell which fitted with air tight cap was thermostated by circulating the water at required temperature through the jacket.

To determined the molecular weight, second virial coefficient and radius of gyration by light scattering, the following usual equations were used:

$$\lim_{\theta \rightarrow 0} \frac{Kc}{R(\theta, c)} = \frac{Kc}{R(\theta, c)} = 1/M_w (1+2BC+ \dots) \text{----(4a)}$$

$$\lim_{c \rightarrow 0} \frac{Kc}{R(\theta, c)} = \frac{Kc}{R(\theta, c)} = 1/M_w (1+1/3(4\pi n/\lambda)^2 [S^2] \sin^2 \theta/2) \text{---- (4b)}$$

$$\lim_{\substack{\theta \rightarrow 0 \\ c \rightarrow 0}} \frac{Kc}{R(\theta, c)} = \frac{Kc}{R(0,0)} = 1/M_w \text{-----(4c)}$$

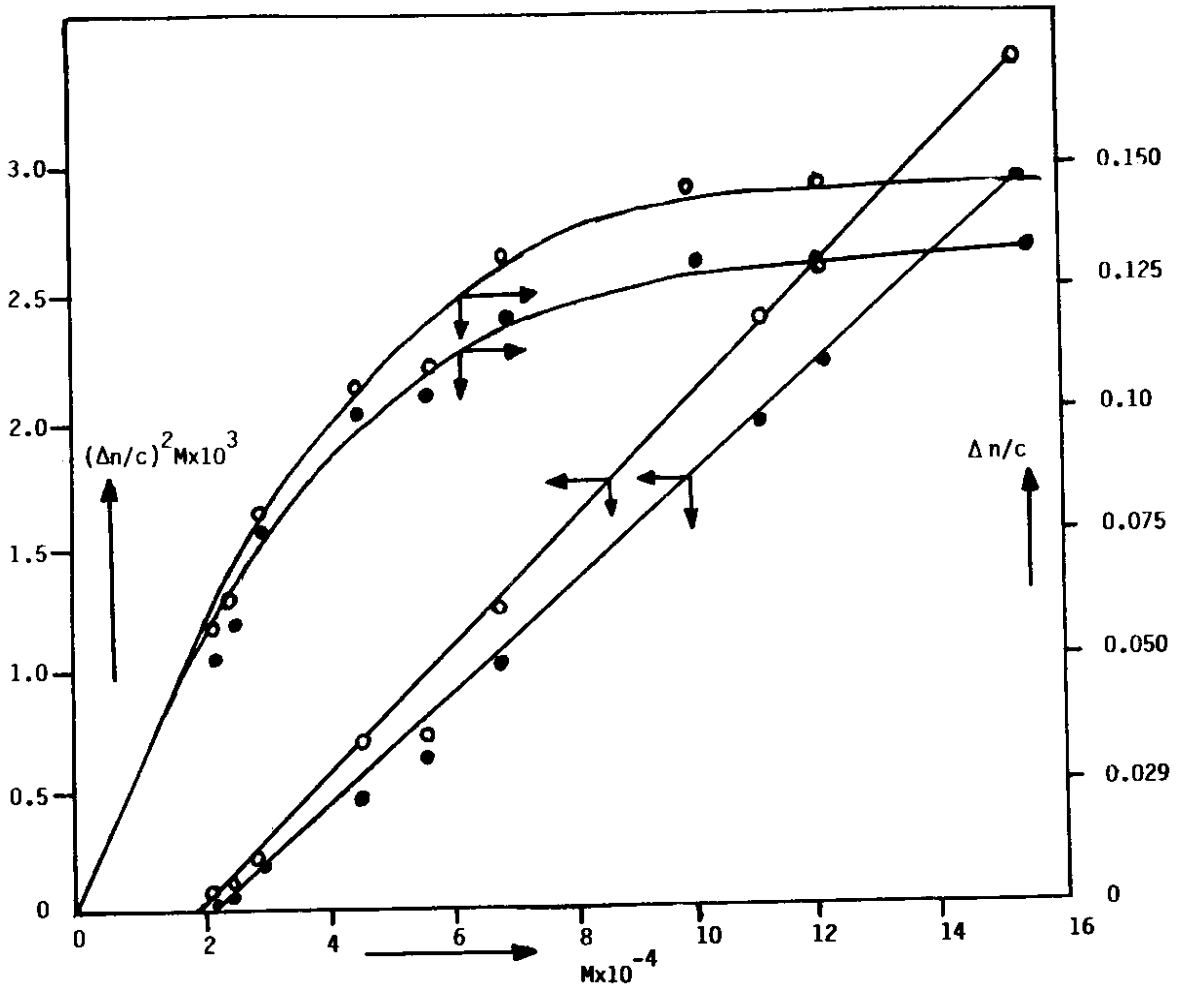


Fig.2: Dependence of refractive index increment on molecular weight of fractionated cellulose acetate measured by using light of (○) 436 nm and (●) 546 nm wave length.

Here  $K$  denotes  $K (dn/dc)^2$  and  $K$  is a numerical constant at a given wave length. For analysis, plots of  $Kc/R(\theta, c)$  against  $\sin^2 \theta/2$  at a given concentration were extrapolated to  $\theta \rightarrow 0$  to obtain  $Kc/R(\theta, c)$  were analysed

with equation (4a). Similarly the values of  $Kc/R(\theta, 0)$  were obtained by extrapolated to zero concentration at a given angle and analysis was made by equation (4b). The Raleigh ratios ( $R_\theta$ ) were calculated by using equation (5) given by Gruber et al. [9].

$$R_\theta = I_\theta R_{90}(\text{benzene}) (1 + \cos^2 \theta) \sin \theta / I_{90}(\text{benzene}) \text{----(5)}$$

where  $I_{90}$  (benzene) and  $R_{90}$  (benzene) are the scattered light intensity at an angle; scattered light intensity by benzene at  $90^\circ$  angle and Raleigh ratio for benzene, measured at  $90^\circ$  angle respectively.

### Viscometry

The Ostwald viscometer supplied by Gallenkamp was used for all viscometrical measurements. Viscometer was immersed in a bath at constant temperature ( $25^\circ\text{C} \pm 0.02^\circ$ ). Data on five concentrations were plotted by using the relation [10] given below.

$$\frac{\eta}{c} = [\eta] + k [\eta]^2 c + \text{-----} \quad (6a)$$

to obtain  $[\eta]$  from the intercepts. Here  $\eta_{sp} = \eta_{rel} - 1$  and  $\eta_{rel} = \frac{t}{t_0} \frac{\rho_0}{\rho}$  where  $t$  and  $t_0$  are the flow times of solutions and solvent respectively;  $\rho$  and  $\rho_0$  are the density of solution and solvent respectively.

### Results and Discussion

We have tried to correlate the change in refractive index increment with the change in molecular weight. The results show that first the refractive index increment increases as the molecular weight of the polymer (Fig. 2). When the molecular weight is sufficiently high the curve starts bending towards the molecular weight axes and ultimately it becomes parallel. This shows that the refractive index increment is not only a function of molecular weight but also of other parameters like interactions, structure of the polymer, etc. [11]. Such type of dependence is also observed by other scientists [12], moreover the values of  $\Delta n/\Delta c$  obtained for a few fractions of the same system [13] also fall on these curves. To find more clear rela-

tion between  $\Delta n/\Delta c$  and molecular weight,  $M(\Delta n/c)^2$  is also plotted against  $M$ . in figure 2. This figure shows that in this way one gets a straight line and the refractive index increment can be related to the molecular weight of the polymer through a linear relation given below:

$$M(\Delta n/c)^2 = a + bM \text{-----} \quad (6)$$

$$(\Delta n/c)^2 = \frac{a}{M} + b \text{-----} \quad (7)$$

where  $a$  and  $b$  are constants depending upon solute, solvent, temperature and pressure of the system.

The molecular weight, second virial coefficient and radius of gyration of every sample (fraction) is calculated from light scattering data using equation (4), that is Zimm plots method. The gradual change in the shape of the Zimm plots was observed by the change of fraction number that is molecular weight. This may be due to the change in shape of the polymer by the change in molecular weight. From these observations and from the results obtained for radius of gyration and molecular weight, it is easy to conclude that the shape of the polymer changes from rod-like to coil-like molecules (the rigidity of the molecules decreases) when molecular weight of the polymer increases. Such type of conclusions were also drawn by Stein and Doty [13]. The radius of gyration increases linearly as the molecular weight increases and it is plotted in fig.3.

This figure shows that the values for all fractions except few fall on the line. The log of second virial coefficient is also plotted against log of molecular weight in the same figure (fig. 3). From such type of dependence it can be concluded that the intramolecular interactions which effect

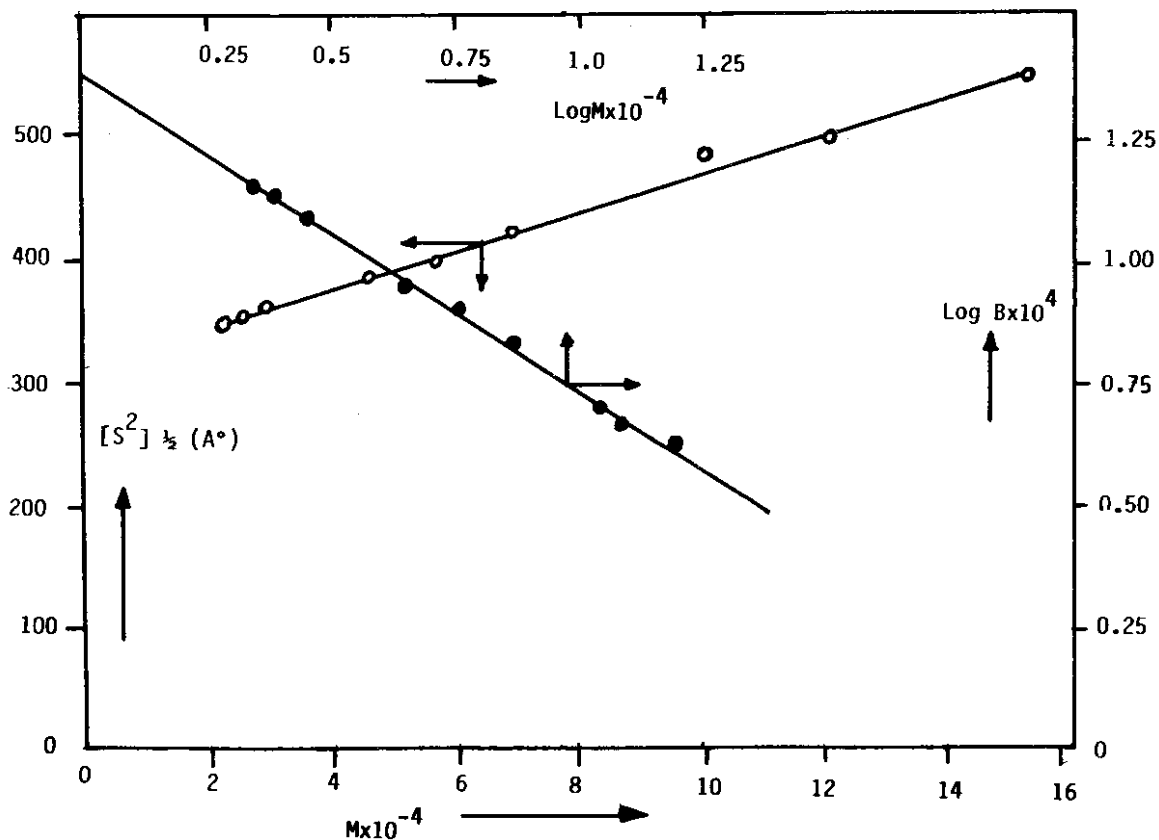


Fig.3: Dependence of radius of gyration and second virial coefficient on molecular weight of fractionated cellulose acetate.

chain dimensions are negligible in all cases, that is the excluded volume effect is small. Such type of dependence is usually observed in case of good solute solvent system [11]. The relation between radius of gyration and molecular weight as calculated from figure (3) is below:

$$[S^2]^{1/2} = 3.12 \times 10^{-6} + 1.45 \times 10^{-11} M \text{ ----- (8)}$$

As radius of gyration is dependent upon different parameters like temperature, pressure, inter and intramolecular interactions etc, so this equation is valid only for this system and under above mentioned conditions. The log of second virial coefficient decreases as the log of the molecular weight

(fig. 3). This dependence is as one expects from the equation (9) given by [11].

$$B = (2/3)^{5/2} \pi N_A \alpha \beta \gamma^3 / (M_0^{3/2} M^{1/2}) \text{ --- (9)}$$

Here  $\gamma$  is the empirical parameter which relates the radius of gyration to the radius of equivalent solid sphere.  $\beta$  is a constant and independent of molecular weight;  $\alpha$  is also a constant,  $\alpha$  and  $\alpha$  both increase as the molecular weight increases.  $M_0$  is the molecular weight of unimer of the polymer having molecular weight  $M$ ;  $N_A$  is the Avogadro number; Moreover results obtained by [13] also fall on the same plot. The second virial coefficient is the parameter depending

upon the interactions of the system. The polymer having lower molecular weight will be easily soluble than with higher molecular weight. This means that the polymer with lower molecular weight will interact more with the solvent than the others and hence high second virial coefficient and vice versa. From such type of dependence, the equation obtained is given below:

$$\log B = -2.62 - 0.66 \log M \text{ ----- (10)}$$

As in other cases the constants are dependent upon different parameters like temperature, pressure, solvent and solute etc.

The viscosity of every fraction is measured at 25°C for five different concentrations. From this data the relative and specific viscosity is calculated and plotted against concentration

to find intrinsic viscosity of every fractionated sample. Log of intrinsic viscosity was plotted against log M, the M. Houwink constants ( $k, \alpha$ ) were determined from the slope and intercept of that curve. In this way the relation between molecular weight and intrinsic viscosity is established and is given below:

$$[\eta] = 1.42 \times 10^{-4} M^{0.826} \text{ -----(11)}$$

Results showed that  $\log [\eta]$  is linearly dependent upon  $\log M$ . This means that the samples are well fractionated and they are almost homogeneous [14] with respect to their molecular weight. To verify this equation, the molecular weight of the same unfractionated sample is determined by light scattering and viscosity, using equation obtained by us (equat.11) and relation already available in the literature [14]. The degree of dispersity

Table-I: Percentage of the fractionated samples as obtained by fractional precipitation and  $I(p_n)$  values for them.

Fraction No.	Degree of Polymerization	Percent weight of different fraction	$I(p_n) \times 10^2$
9	86	0.4	0.2
8	95	3.6	2.2
7	113	9.0	8.5
6	176	0.5	13.2
5	220	16.3	21.7
4	265	10.6	35.1
3	433	30.3	55.6
2	471	23.1	82.3
1	600	6.2	97.1

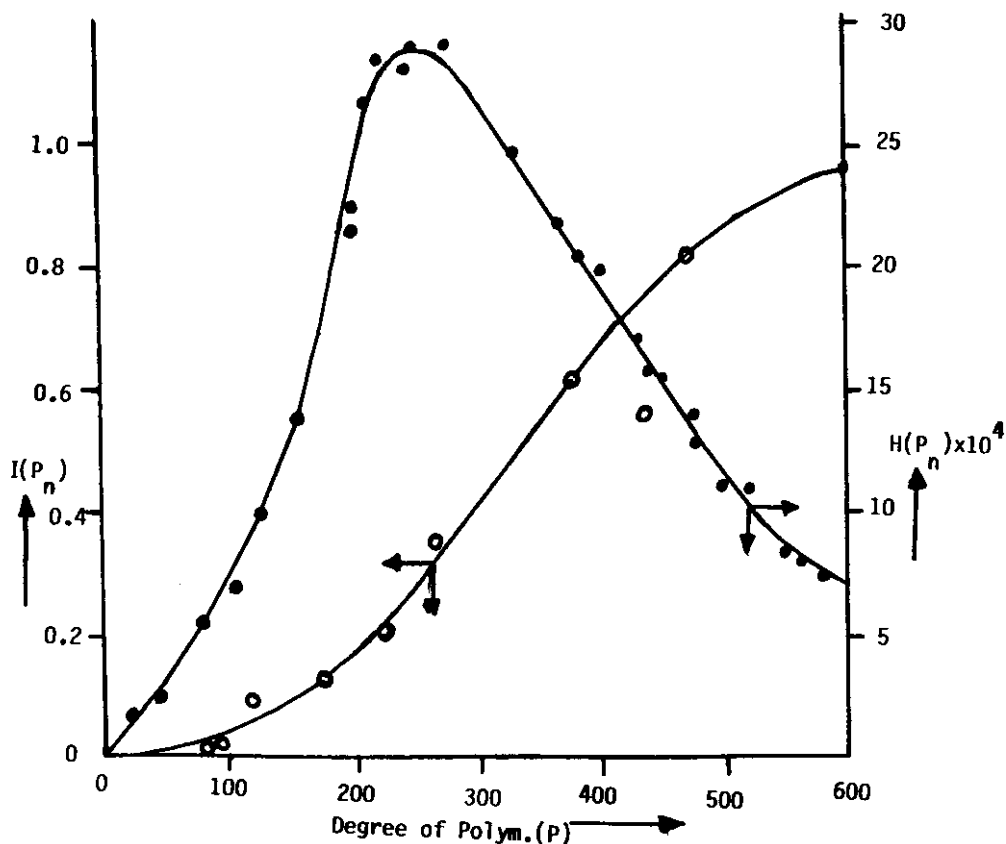


Fig.4: Integral and differential molecular weight distribution curves as obtained by fractional precipitation.

is calculated by using this data and the results obtained by using the equations [11,15] given below:

$$MW = \frac{\sum_{i=1}^n n_i M_i^2}{\sum_{i=1}^n n_i M_i} \quad M_n = \frac{\sum_{i=1}^n n_i M_i}{\sum_{i=1}^n n_i}$$

The results show, that the relation developed by us (equation (11)) gives more accurate and reliable results.

To draw integral and differential molecular weight distribution curves, the  $I(P_n)$  values are calculated from the primary data of different fractions

obtained. These values are given in Table-I and are plotted in figure 4, against degree of polymerization (p), and is called "integral curve". From this curve the  $H(p_n)$  values are calculated and plotted against degree of polymerization in the same figure. Both these curves shows that the polymer molecules having molecular weight higher or smaller have low probability. The polymer molecules with molecular weight equal to about  $250 \times M_0$  have maximum probability.

These curves also show that, though the probability of large molecules is very low, but it does not reach to a value of zero, moreover this distribu-



tion follows the pattern of linear polymers [16].

### Acknowledgement

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