

## MOLECULAR WEIGHT DETERMINATION OF POLYETHYLENE BY LIGHT SCATTERING TECHNIQUES

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**Abstract.** The molecular weight determination of polyethylene crystals was carried out by the Zimm Plot method. These crystals were prepared from Marlex 6050 in dilute solutions using *p*-xylene as a solvent and the temperature range at 75-92°. The average molecular weights obtained at 436 mμ are 5.6 × 10<sup>6</sup> and 12.5 × 10<sup>6</sup> while at 546 mμ the average molecular weights are 5.8 × 10<sup>6</sup> and 12.6 × 10<sup>6</sup> at annealing temperatures of 75° and 92° respectively. An effort is made to compare these light scattering results with those obtained from electron micrographs. Also the values of molecular weights and particles sizes are given in the respective tables for both of these methods.

### Theoretical

The molecular weight of polymers can be determined by many methods, important of these being<sup>1</sup>: Functional End Group Analysis, measurement of the colligative properties by ultracentrifugation, measurements of dilute solution viscosity and light scattering measurements. With the exception of the viscosity measurement method, the rest are absolute. Due to the obvious advantages of the scattering measurements, light scattering methods have been used to determine molecular weights as low as those of sucrose and as high as those of proteins. In practice molecular weights in the range 10,000-10,000,000 can easily be measured with the possibility of extending the range in the earlier direction.

For unpolarized light the ratio of scattering to the incident beam from unit volume of particles in space is<sup>2</sup>:

$$\frac{i_{\theta}}{I_0} = \frac{2 \pi^2 (1 + \cos^2 \theta) \left( \frac{d\bar{n}}{dc} \right) Mc}{N \lambda^4 r^2} \quad \dots(1)$$

where  $\left( \frac{d\bar{n}}{dc} \right)$  = refractive index increment,

$N$  = Avogadro Number,

$\lambda$  = wave length of light in the medium,

$r$  = distance between the scattering centre and measuring device,

$i_{\theta}$  = intensity of the scattered light at angle  $\theta$ ,

$I_0$  = intensity of incident light.

For the intensity of light scattered by macromolecules in a two-components system, we have

$$\frac{i_{\theta}}{I_0} = \frac{2 \pi^2 (1 + \cos^2 \theta) \bar{n}_0^2 \left( \frac{d\bar{n}}{dc} \right)^2 Mc}{N \lambda^4 r^2} \quad \dots(2)$$

where  $\bar{n}_0$  is the refractive index of the solvent. As macromolecular solutions are not ideal,<sup>3, 4</sup> so in order to take into account non-ideality, Einstein and Debye introduced some factors in Eq. 2:

$$\frac{i_{\theta}}{I_0} = \frac{2 \pi^2 (1 + \cos^2 \theta) \bar{n}_0^2 \left( \frac{d\bar{n}}{dc} \right)^2 Mc}{N \lambda^4 r^2 (2Bc + 3Cc^2 + \dots)} \quad \dots(3)$$

Eq. 3 is the fundamental equation for the scattering of unpolarized light by particles much smaller than the wavelength of light.

To determine molecular parameter, we rewrite Eq. 3 as

$$R_{\theta} = \frac{i_{\theta}}{I_0} = \frac{2 \pi^2 (1 + \cos^2 \theta) \bar{n}_0^2 \left( \frac{d\bar{n}}{dc} \right)^2 Mc}{N \lambda^4 (2Bc + 3Cc^2 + \dots)} \quad \dots(4)$$

where  $R_{\theta}$  is the Rayleigh ratio and is independent of the scattering angle and is given by

$$R_{\theta} = \frac{KMc}{2Bc} \quad \dots(5)$$

$K$  being an optical constant given by

$$K = \frac{2 \pi^2 \bar{n}_0^2 \left( \frac{d\bar{n}}{dc} \right)^2}{N \lambda^4}$$

Eq. 5 may be written as

$$\frac{Kc}{R_{\theta}} = \frac{1}{M} + 2Bc + \dots \quad \dots(6)$$

Eq. 6 is for particles much smaller than the wavelength. If the linear dimension of the particles approaches 1/20th of the wavelength of light or greater than this, then the particles is no longer considered to be point source and internal interference



rence occurs. In order to allow the augmentation of internal interference. Debye introduced a new factor  $P_\theta$ . So Eq. 6 becomes :

$$\frac{Kc}{R_\theta} = \frac{1}{M P(\theta)} + 2 Bc \dots \quad \dots(7)$$

where  $P_\theta = 1 - \mu^2 \overline{R_G^2}/3$  ... (8)

$$\lim_{\theta \rightarrow 0} \frac{1}{R_G^2} = \text{Mean-square-radius of gyration.}$$

$$\text{Also } \mu = \frac{4\pi}{\lambda} \sin \theta/2$$

Putting the value of  $\mu$  in Eq. 8,

$$P_\theta = 1 - \frac{16\pi^2}{3\lambda^2} \frac{\overline{R_G^2}}{R_G^2} \sin^2 \theta/2$$

$\lim_{\theta \rightarrow 0} P_\theta = 1$

Introducing the value of  $P_\theta$  in Eq 7, we get the final equation :

$$\frac{Kc}{R_\theta} = \frac{1}{M} \left[ 1 + \frac{16\pi^2}{3\lambda^2} \frac{\overline{R_G^2}}{R_G^2} \sin^2 \theta/2 \right] + 2 Bc \dots \quad \dots(8)$$

Plot of  $\frac{Kc}{R_\theta}$  vs  $\sin^2 \theta/2 + kc$  gives the famous

Zimm plot<sup>5</sup> which achieves both the objectives of: (i) extrapolation of the data at each angle to zero concentration and (ii) at each concentration to zero angle.  $k$  is an arbitrary constant chosen so as to provide a convenient spread of the data on a piece of graph paper.

The intercept at  $c=0$  and  $\theta=0$  line is equal to  $\frac{1}{M}$ . The mean square radius of gyration,  $\overline{R_G^2}$ , is given by;

$$\overline{R_G^2} = \left( \frac{3\lambda^2}{16\pi^2} \right) \left[ \frac{\text{Initial slope at } c=0 \text{ line}}{\text{Intercept at } \theta=0 \text{ line}} \right]$$

The initial gradient of the graph at  $\theta=0$  line gives a measure of the second virial coefficient.

$$\text{Thus } B = \frac{k}{2} (\text{Initial slope of } \theta=0 \text{ line}).$$

Experimental values for the radius of gyration provides a good tool for the determination of molecular structure.

$$\text{For sphere of diameter } D, \overline{R_G^2} = \frac{3}{20} D^2$$

$$\text{For rod of length } L, \overline{R_G^2} = \frac{L^2}{12}.$$

### Experimental

**Materials and Solvents.** The sample used in this work is a linear polyethylene called by the trade name Marlex 6050, manufactured by Phillips Petroleum Company, USA. All crystallization<sup>6,7</sup> has

been conducted in dilute solution, *i.e.* 0.1% in solvent *p*-xylene in temperature range 75-92°.

**Refractive Index Increment.** The refractive index increment,  $\left( \frac{d\bar{n}}{dc} \right)$  was measured by the Brice-Phoenix

Differential refractometer, model BP-2000-V. Measurements were carried out using unpolarized light from a mercury vapour lamp, type AH-3 with spectrum filters whose wavelengths are 436 and 546 m $\mu$ . The instrument constant was obtained by standard solution of KCl<sup>8</sup> and NH<sub>4</sub>NO<sub>3</sub> reagent grade and dried in even at 80-100°.

**Light Scattering Measurement.** The photometer used is the universal light scattering photometer, type DM 2000. All the measurements were carried out over the range of scattering angles between 15-135°.

### Results

**Zimm Plot Method.** The results of angular measurements of light scattering were analyzed according to the Eq. 9:

$$\frac{Kc}{R_\theta} = \frac{1}{M} \left[ 1 + \frac{16\pi^2}{3\lambda^2} \frac{\overline{R_G^2}}{R_G^2} \sin^2 \theta/2 \right] + 2 Bc \dots \quad \dots(9)$$

$\frac{Kc}{R_\theta}$  vs  $\sin^2 \theta/2 + kc$  was plotted according to the Zimm method as shown in Fig. 1 and 2 at 436 m $\mu$  and in Figs. 3 and 4 at 546 m $\mu$ .

Tables 1 and 2 list the average molecular weight,  $\overline{M_w}$ , root-mean-square-radius of gyration,

$\sqrt{\overline{R_G^2}}$ , and the second virial coefficient,  $B$ , at the wave-lengths of 436 and 546 m $\mu$  respectively at the two extreme annealing temperatures of 75 and 92°.

### Electron Microscopy

Many single crystals of essentially linear polyethylene show secondary structural features, including corrugation which results from the fact that many single crystals grow in the form of hollow pyramid<sup>10,12</sup>. Fig. 5 and 6 show typical electron micrographs\* polyethylene (Marlex 6650) single crystals, annealed at 75° and 92° respectively.

The molecular weight of polyethylene can be determined by the direct counting method in the electron microscope. The solution is sufficiently diluted to allow its particles to be counted in a known volume. If the total amount of the polyethylene in a certain volume of the solution is known, its density is determined, then the molecular weight and the volume of a single particle and hence the size of the particle can be calculated easily.

\*These electron micrographs were obtained by Dr. Noor Ahmad at the Electron Microscopic Institute of Karlsruhe University, West Germany, during his visit to the University as a UNESCO research fellow.



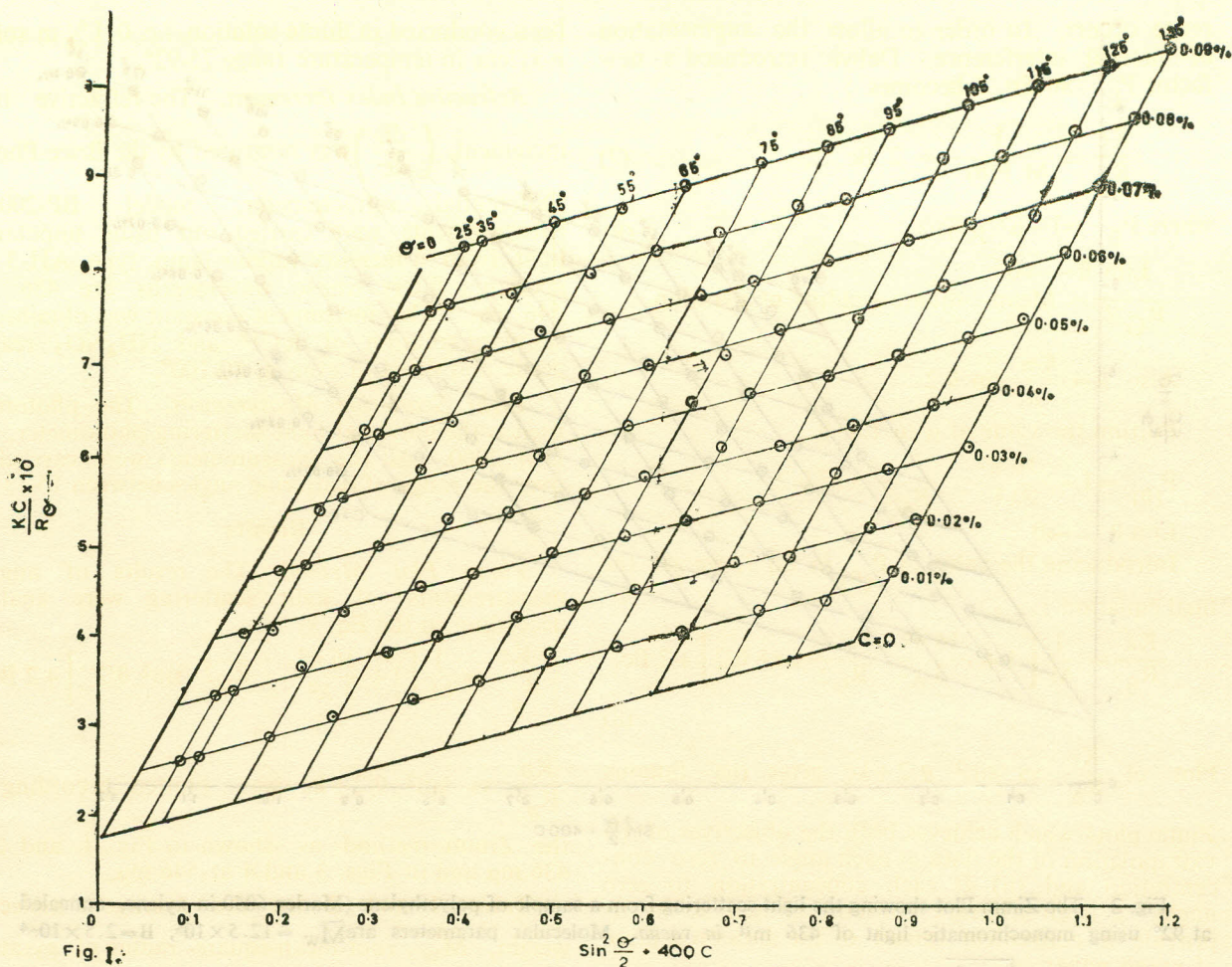


Fig. 1.

The Zimm Plot showing the light scattering from a sample of polyethylene (Marlex 6050 in xylene, annealed at 75°, using monochromatic light of wavelength 436 mμ in vacuo. Molecular parameters are  $\overline{M}_W = 5.6 \times 10^6$ ,  $B = 3.5 \times 10^{-4}$  ml-mole-g<sup>-2</sup> and  $\sqrt{R_G^{-2}} = 80.25$  m μ

TABLE 1. MOLECULAR PARAMETERS OF POLYETHYLENE (MARLEX 6050) CALCULATED BY THE ZIMM PLOT METHOD, USING MONOCHROMATIC LIGHT OF 436 Mμ IN VACUO.

Annealing temperature (°C)	Molecular weight $\overline{M}_W$	Root-mean-square radius of gyration, $\sqrt{R_G^2}$ (mμ)	Size (when approximated to sphere) (mμ)	Second virial coefficient (ml-mole-g <sup>-2</sup> )
75	$5.6 \times 10^6$	80.25	207	$3.5 \times 10^{-4}$
92	$12.5 \times 10^6$	133.00	343	$2.5 \times 10^{-4}$

TABLE 2. MOLECULAR PARAMETERS OF POLYETHYLENE (MARLEX 6050) CALCULATED BY THE ZIMM PLOT METHOD, USING MONOCHROMATIC LIGHT OF 546 Mμ IN VACUO.

Annealing temperature (°C)	Molecular weight $\overline{M}_W$	Root-mean-square radius of gyration $\sqrt{R_G^2}$ (mμ)	Size (when approximated to sphere) (mμ)	Second virial coefficient (ml-mole-g <sup>-2</sup> )
75	$5.8 \times 10^6$	81.5	211	$3.5 \times 10^{-4}$
92	$12.6 \times 10^6$	136.0	352	$2.8 \times 10^{-4}$



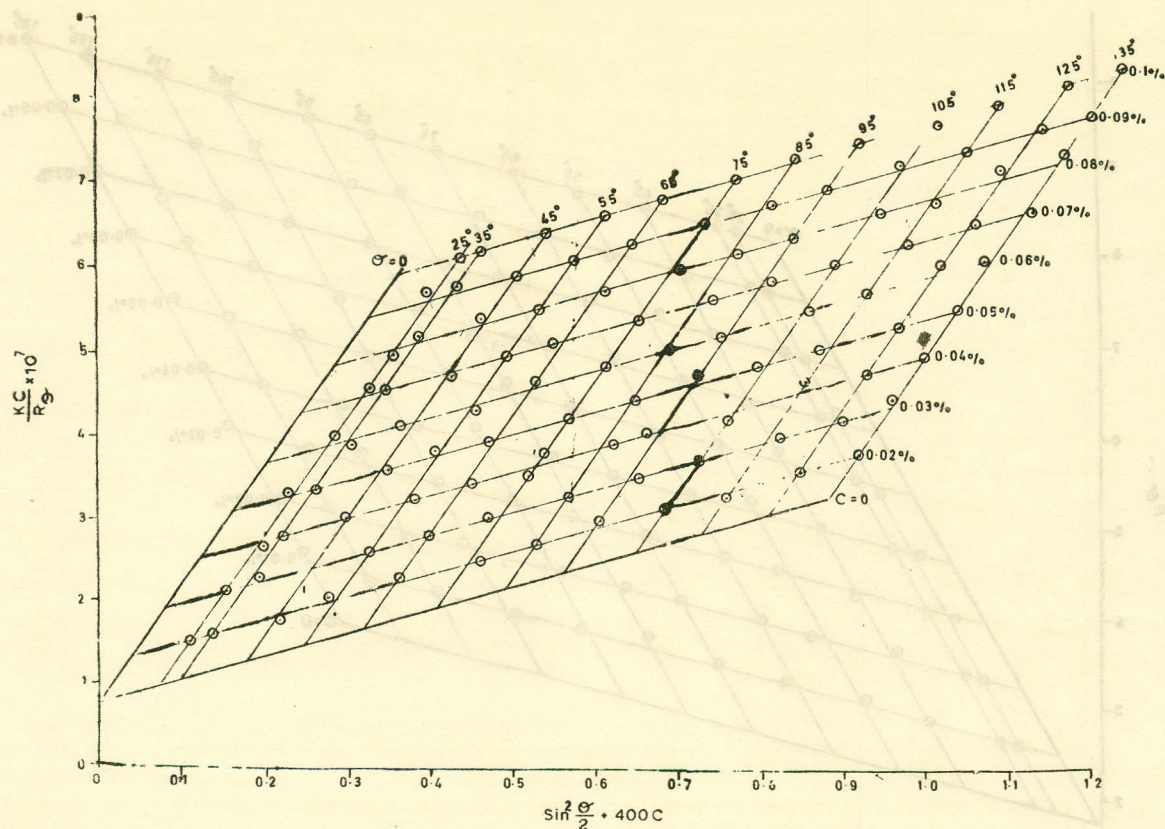


Fig. 2. The Zimm Plot showing the light scattering from a sample of polyethylene (Marlex 6050 in xylene, annealed at 92° using monochromatic light of 436 mμ in vacuo. Molecular parameters are  $\bar{M}_W = 12.5 \times 10^6$ ,  $B = 2.5 \times 10^{-4}$  ml-mole-g<sup>-2</sup> and  $\sqrt{R_G^{-2}} = 133.00$  mμ

TABLE 3. MOLECULAR WEIGHT AND PARTICLE SIZE OF POLYETHYLENE (MARLEX 6050) SINGLE CRYSTALS, ANNEALED AT 75° AND 92°, AS CALCULATED FROM ELECTRON MICROSCOPIC MEASUREMENTS.

Annealing temperature (°C)	No. of particles per ml. (n)	Mass of a single particle in g. (m)	Vol. of a single particle in cc. (v)	Molecular weight $\bar{M}_W$	Size (mμ)
75	$10.0 \times 10^{13}$	$.99 \times 10^{-17}$	$1.03 \times 10^{-18}$	$6.0 \times 10^6$	208
92	$4.7 \times 10^{12}$	$2.10 \times 10^{-17}$	$2.18 \times 10^{-17}$	$12.7 \times 10^6$	356

Denoting by g, the total weight of the particles in one ml, by V, its volume, and by p, their density,  $V = g/p$ . If v be the volume of a single particle, m is the mass of a single particle and their total number in one ml be n, then  $V = Vn$  or  $v = g/np$ .

As the particles of polyethylene are bipyramidal in shape as shown by electron micrographs in Fig. 5

and 6, the volume of a particle is given by  $V = \frac{2}{3}Bh$ ,

where B is the areas of the base and h is the length of a bipyramid. The area of the base can be calculated from electron micrographs (Fig. 5 and 6). Having determined the volume, V, and the area of the base, B, the length of the bipyramid, h, can be easily calculated. Table 3 shows the molecular



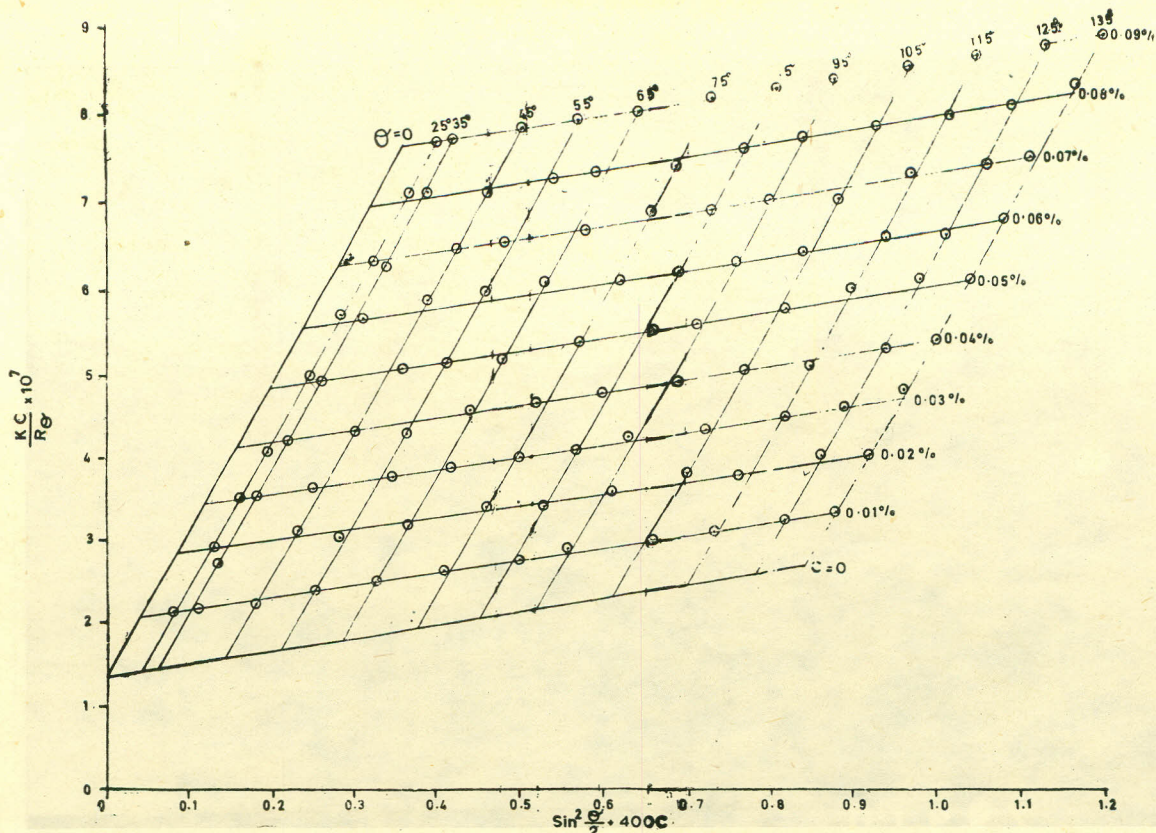


Fig. 3. The Zimm Plot showing the light scattering from a sample of polyethylene (Marlex 6050) in xylene, annealed at 75°, using monochromatic light of 546 m $\mu$  *in vacuo*. Molecular parameters are  $\bar{M}_W = 5.8 \times 10^6$ ,  $B = 3.5 \times 10^{-4}$  ml-mole-g $^{-2}$  and  $\sqrt{R_G^2} = 81.5$  m $\mu$

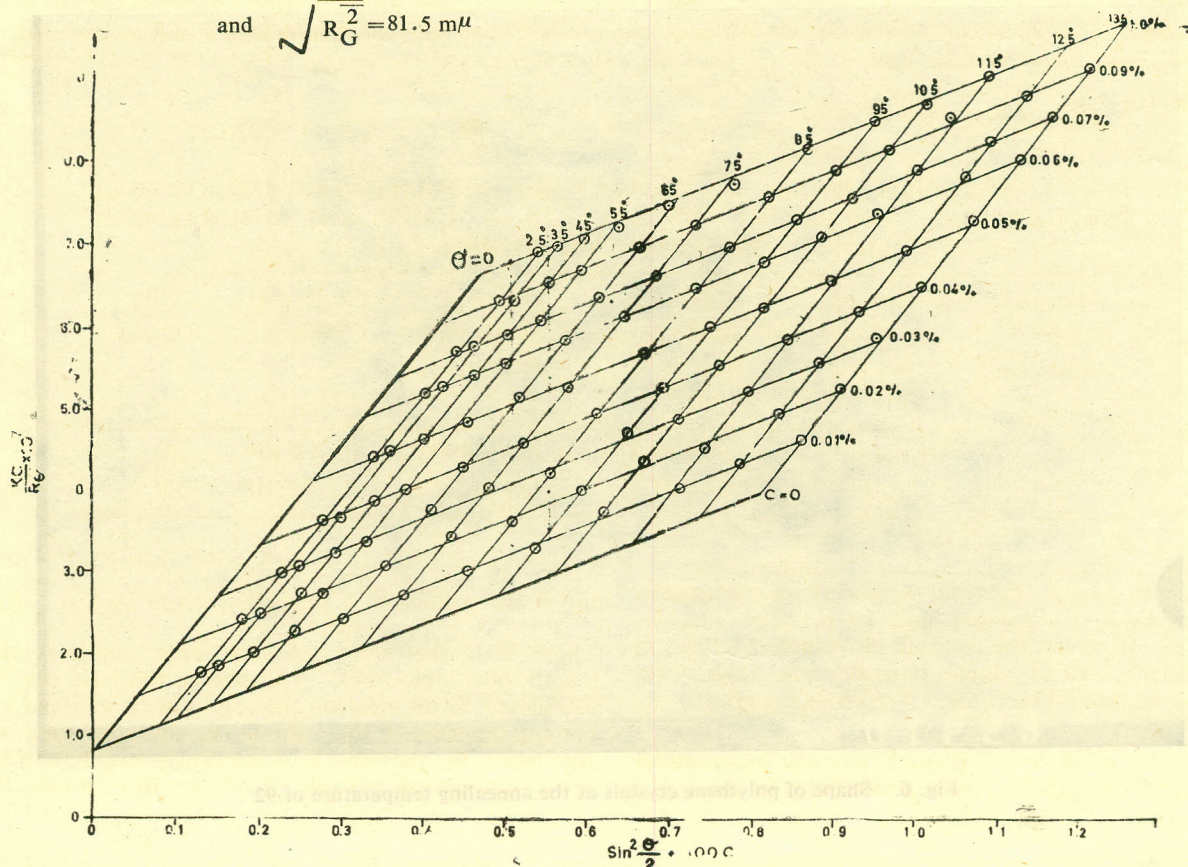


Fig. 4. The Zimm Plot showing the light scattering from a sample of polyethylene (Marlex 6050) in xylene, annealed at 92°, using monochromatic light of wavelength 546 m $\mu$  *in vacuo*. Molecular parameters are  $\bar{M}_W = 12.6 \times 10^6$ ,  $B = 2.8 \times 10^{-4}$  ml-mole-g $^{-2}$  and  $\sqrt{R_G^2} = 136$  m $\mu$



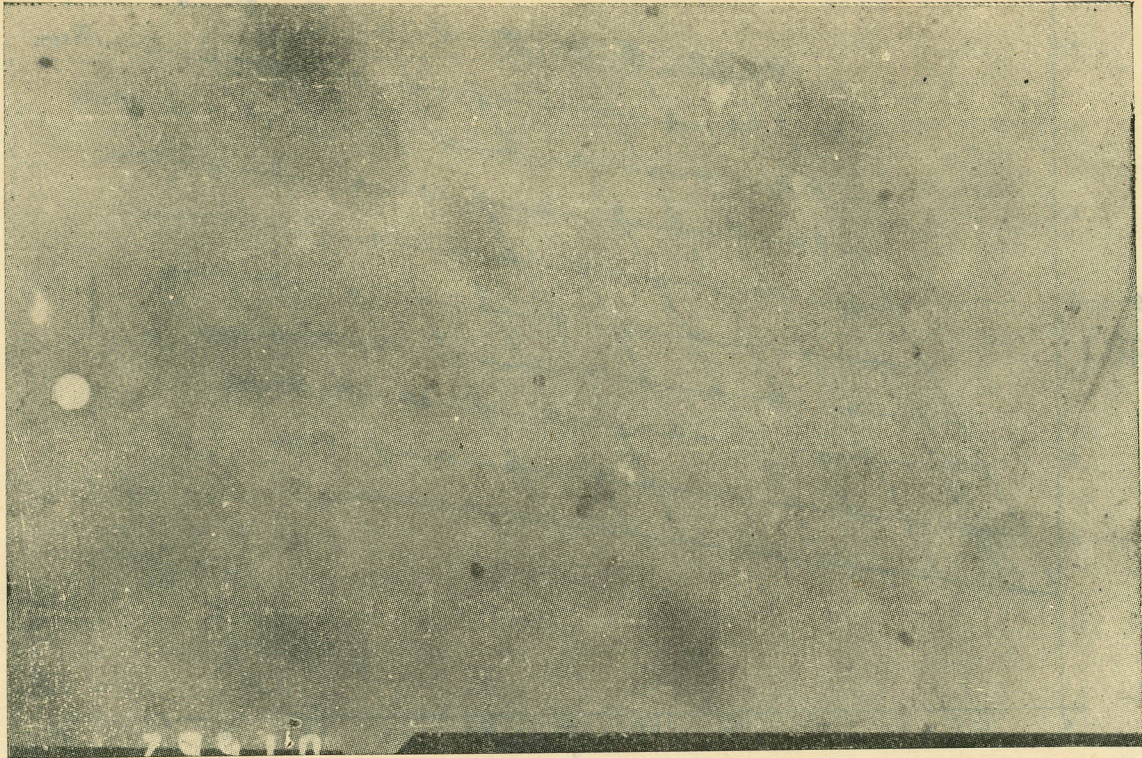


Fig. 5. Shape of polythene crystals at the annealing temperature of 75°.

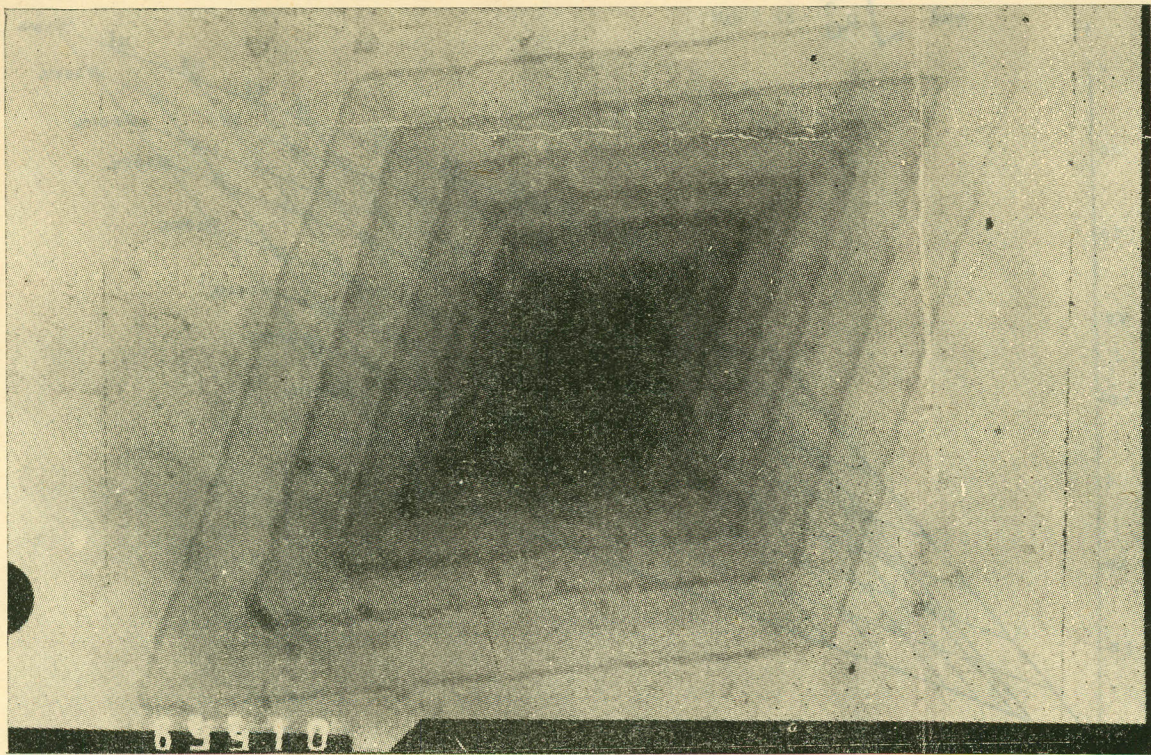


Fig. 6. Shape of polythene crystals at the annealing temperature of 92°.



weight distribution and sizes of polyethylene single crystals, annealed at 75° and 92°.

### Discussion

The results obtained for molecular weight and sizes of polyethylene single crystals, annealed at the two extreme temperatures of 75 and 92°, agree quite satisfactorily for the two wavelengths, the average molecular weight at 436 m $\mu$  being  $5.8 \times 10^6$  and  $12.5 \times 10^6$  while at 546 m $\mu$  the values are  $5.8 \times 10^6$  and  $12.6 \times 10^6$  at annealing temperatures of 75 and 92° respectively. Assuming the polyethylene particles to be spherical in shape, the diameters of the particles are calculated from the values of radius of gyration as shown in Tables 1 and 2 at 436 m $\mu$  and 546 m $\mu$  respectively.

The light scattering data in Tables 1 and 2 also indicate an influence of annealing temperature on the values of second virial coefficients, which is a measure of the interaction of the particles and the radius of gyration. Root-mean square radius of gyration increases with increasing annealing temperature.

These results have been compared with electron microscopic results, the molecular weights being  $6.0 \times 10^6$  and  $12.7 \times 10^6$  at the two annealing temperatures of 75 and 92° respectively as shown in Table 3. Approximating the bipyramidal shape of the particles (Fig. 5-6) to sphere, the size of the particles are obtained which are 208 m $\mu$  and 356 m $\mu$  at annealing temperature of 75 and 92° respectively (Table 3). These are in close agreement with the

values obtained by the Zimm Plot Method. However, the existing discrepancy can be narrowed if an exact theoretical equation could be applied for the actual model of polyethylene single crystal.

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