Preparation and Distribution Measurements for Polyethylene Single Crystals for Various Type of Sizes

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Summary: The size and size distribution measurements were carried out for single crystals of poly ethylene by an optical microscope. The single crystals were obtained from the dilute solutions (0.1 %) of polyethylene in *p*-xylene in the temperature range 74-94°C. It was observed that the mean size of the crystals increase from 15.11 to 32.98 μm at magnification 320 (47.22 mμ- 103.66 mμ) with increase in crystallization temperature, which may be attributed to the uncoiling of the folds with the rise in temperature.

Introduction

Crystalline polymers like polyethylene, polypropylene etc. have the ability to form single crystals. The first single crystal of polyethylene was obtained in 1955 from its dilute solution [1]. It was observed that these crystals have lameller structure varying in habits from the regular lozenges to dentrites [2].

In single crystal the polymer chains are arranged in regular order. Keller [3,4] proposed a fold mechanism for the accomodation of long chains in these small regular structure. According to this mechanism the polymer chains are folded back upon themselves to produce a parallel chains perpendicular to the face of the crystal. Each fold contains approximately five carbon atoms [5]. Free energy plays an important role in the formation of such folds [6]. The habit of the crystals depends greatly on crystallization conditions like concentration [2], temperature [7,24] solvent [3,8,9,22,23] etc.

Since the development of single crystals of polyethylene various important aspects like kinetics, thermodynamics, morphology, irrdiation effects etc. have been studied extensively. For example Riande and Fatau [10] studied the kinetics of crystallization using dilatometric techniques and showed that crystallization process is dependent on the molecular weight. Noor and Sabz [11] conducted the light scattering and electro microscopic study on polyethylene crystals and showed that the molecular weight distribution the root mean square radius of gyration and the crystal size increased gradually with annealing temperature.

Voigt-Marin *et al.,* [12,21] measured the crystallite thickness distribution by Raman LAM and electron microscopic methods. They reported the formation of extended chain crystals at high crystallization temperature. Holfman [13] extended the nucleation theory approach to predict the under-cool-

Table 1: Number distribution data for polyethylene crystals (Magnification 320)

S.No.	Size range (X_1-X_2)Um	Mid value (X)Um	Freq (f)	% Freq. (dθ)	Cummu. % Freq (Cdθ)	Relative Freq. (d θ/dx)	xf
Tempt. 74°C							
1.	4.8-8.0	6.4	4	1.41	1.41	0.44	25.60 E0
2.	8.0-11.2	9.6	33	11.60	13.03	3.63	31.68 E1
3.	11.2-14.4	12.8	103	36.27	49.30	11.33	14.18 E2
4.	14.4-17.6	16.0	80	28.17	77.47	8.80	12.80 E2
5.	17.6-20.8	19.2	39	13.73	91.20	4.29	74.88 E1
6.	20.8-24.0	22.4	14	4.93	96.13	1.54	31.36 E1
7.	24.0-27.2	25.6	9	3.17	99.30	0.99	23.04 E1
8.	27.2-30.4	28.8	2	0.70	100.00	0.22	57.60 E0
Temp. 82°C							
1.	14.4-17.6	16.0	2	0.95	0.95	0.30	32.00 E0
2.	17.6-20.8	19.2	26	12.38	13.33	3.87	49.92 E1
3.	20.8-74.0	22.4	57	27.14	40.47	8.48	12.77 E2
4.	24.0-27.2	25.6	61	29.05	09.52	9.08	15.62 E2
5.	27.2-30.4	28.8	31	4.76	84.28	4.61	89.28 E1
6.	30.4-33.6	32.0	14	6.67	90.95	2.08	44.80 E1
7.	33.6-36.8	35.2	11	5.24	96.19	1.64	38.72 E1
8.	36.8-40.0	38.4	2	0.95	97.14	0.30	76.80 E0
9.	40.0-42.3	4.16	4	1.90	99.04	0.59	16.64 E1
10.	43.2-46.4	44.8	2	0.95	99.99	0.30	89.60 E0
Tepm. 90°C							
1.	24.0-27.2	25.6	9	4.0	4.0	1.25	23.04 E1
2.	27.2-30.4	28.8	37	16.44	20.4	5.14	10.66 E2
3.	30.4-33.6	32.0	95	42.22	62.66	13.19	30.40 E2
4.	33.6-36.8	35.2	54	24.00	86.66	7.50	19.01 E2
5.	36.8-40.0	38.4	22	9.78	96.44	3.06	84.48 E1
6.	40.0-43.2	41.6	6	2.67	99.10	0.83	24.96 E1
7.	43.2-46.4	44.8	2	0.89	99.99	0.28	89.60 E0

ing (ΔT) at which a chain of specified length will have 'f' folds per molecule, where f= 1,2,3.... for polyethylene oxide fractions. Leung *et al.*, [14,18] measured the melting points, dissolution temperature and heat of fusion (ΔH) for solution grown crystals of polyethylene (mol. wt. 1000-11600) as a function of crystallization temperature. The enthalpy of fusion of crystals of various fractions generally increases with crystallization temperature (Tc) in parallel with their thickness. For example with molecular weight 3100 and 4050 sigmoidal curves are obtained when ΔH is plotted against Tc. This behaviour is explained on the basis of transition in number of folds per molecule as Tc increases.

In the present investigation we have considered the effect of temperature on the satistical distribution of the size of polyethylene single crystal measured by an optical microscope. The statistical mean, median and modal values of the solution grown single crystal of polyethylene in the temperature range of 74-94°C are reported.

Results and Discussion

The polyethylene single crystal was obtained from its dilute solution in *p*-xylene in the temperature range 74-94°C. The size and the corresponding number of crystals determined microscopically are presented in column 3 and 4 Table 1. The data in table are plotted in the form of histograms as shown in Figures 1-3. In order to make an easy comparison of the histograms at different temperatures we have used the percent frequency (dτ=dN x 100/N) (column 5 in Table 1) instead of the actual number of the crystals.

Figure 4 is a representation of cummulative percent frequency and relative percent frequency curves [17,20]. The cummulative percent frequency (c.d.) (column 6 Table 1) at a particular size represents the number of crystals greater or smaller than that particular size. Median size of the crystal corresponds to 50% value along the c.d. exis of a commulative frequency curve. Modal size of the crystal

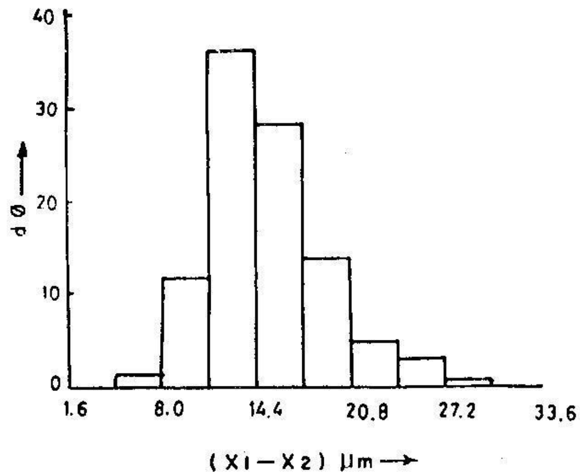

Fig. 1: Histogram representing number distribution for polyethylene crystals at 74°C. dθ is % frequency and (X_1-X_2) is size range of the crystals.

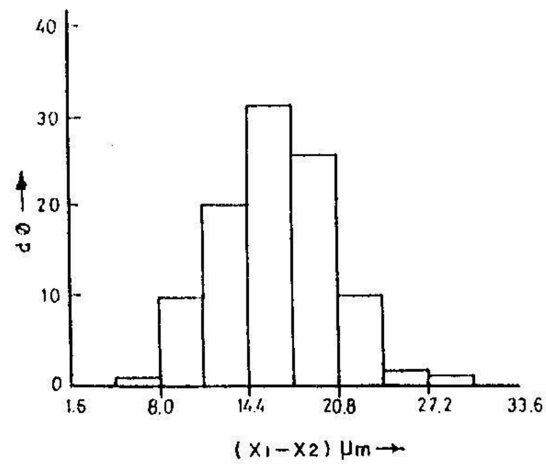

Fig.2: Histogram representing number distribution for polyethylene crystals at 78°C .dθ is % frequency and (X_1-X_2) is size range of the crystals.

corresponds to the highest point along (d dx) axis (column 7) of a relative percent frequency curve.

The mean, median and modal size [15,16] of the crystals calculated using equations 1-3 are listed in Table 2. As can be seen from the table, the crystal size increases with increase in crystallization temperature. These results are shown graphically in Figure 5 which shows that the crystal size increases slowly with increase in the crystallization temperature 74-78°C. However, a singificant increase in the crystal size occurs in the temperature range 78-86°C, after which any signifcant change was not observed.

Table 2: Mean, median and modal sizes of polyethylene crystals at various temperatures (magnification, 320)

Temp. (°C)	Mean size (Ʊm)	Median size (Ʊm)	Model sinze (Ʊm)
74	15.11	14.46	13.61
78	16.34	16.36	16.53
82	25.86	25.05	24.38
86	28.95	29.01	29.02
90	29.72	29.48	29.66
94	32.98	32.64	32.27

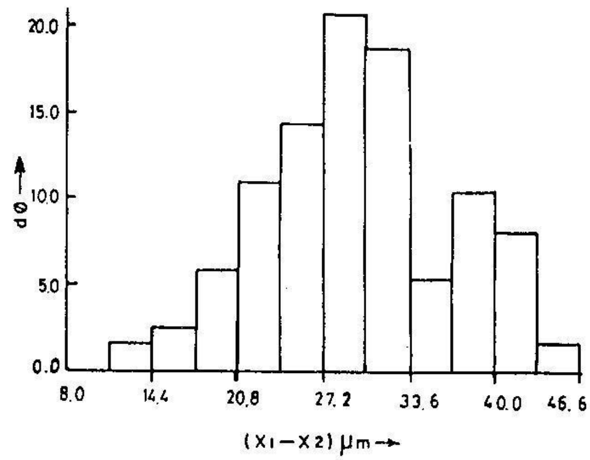

Fig.3: Histogram representing number distribution for polyethylene crystals at 90°C. dθ is % frequency and (X_1-X_2) is size range of the crystals.

Increase in the crystal size can be due to the fact that extended chain crystals are formed [18] in this temperature range (78-86°C). Further increase in temperature upto 94°C did not significantly change the size of crystals, which means that the chains have attained their extended chain conformation.

Experimental

The materials used in this investigation were high density polyethylene supplied by Philips Petroleium Co. USA and *p*-xylene (solvent) obtained from Merck, West Germany.

Dilute solutions (0.1% w/w) of unfractionated polyethylene were prepared in *p*-xylene. For complete and rapid dissolution of polyethlene granules, the system was heated to 138°C and then transferred to a thermostate present at the crystallization temperature. The temperature of the bath was controlled by a thermoregulator to ± 1°C. For annealing purpose, the polyethylene solutions were kept in the bath for

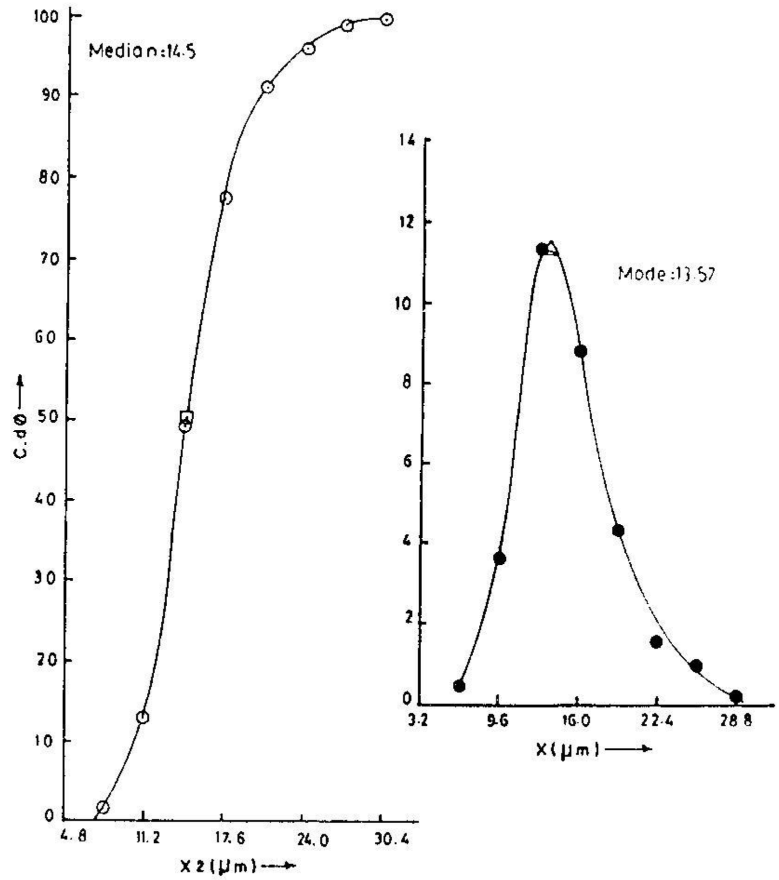

Fig.4: Cummulative frequency and relative frequency curves for polyethylene crystals at 74°C. θ = Cummulative % frequency (Cd θ) θ = Relative % frequency (d θ/dx)

50 hours. Prior to the size measurement, the suspension was allowed to cool down to room temperature.

For the measurement of size and number of crystals an optical microscope of Ogawa Seiki, Japan was used. The graduated eyepiece of the microscope was first calibrated with the stage micrometer. Two drops of suspension were put on the glass slide, the solvent was allowed to evaporate. The size of crystals were determined by counting the number of division of the eyepiece. The number of the crystals whose sizes have been measured were also determined.

The mean size of the crystals was calculated by the following expression [15]

$$\bar{x} = x.f./f \qquad (1)$$

Where $\bar{x}$ = mean size, x = mid size of the range = $(x_1+x_2)/2$, f = frequency or number of crystals having the size range $(x_1 - x_2)$.

The median and mode sizes were calculated by following formulae [15,16].

$$\text{Median size} = x_1 + \frac{n/2 - F_{(m-1)}}{f_m} C \text{ ....(2)}$$

$$\text{Mode size} = x_1 + \frac{f_1 - f_0}{2f_1 - f_0 - f_2} C \text{ ..... (3)}$$

Where

x_1 = lower limit of the size range.

n = Total number of crystals counted.

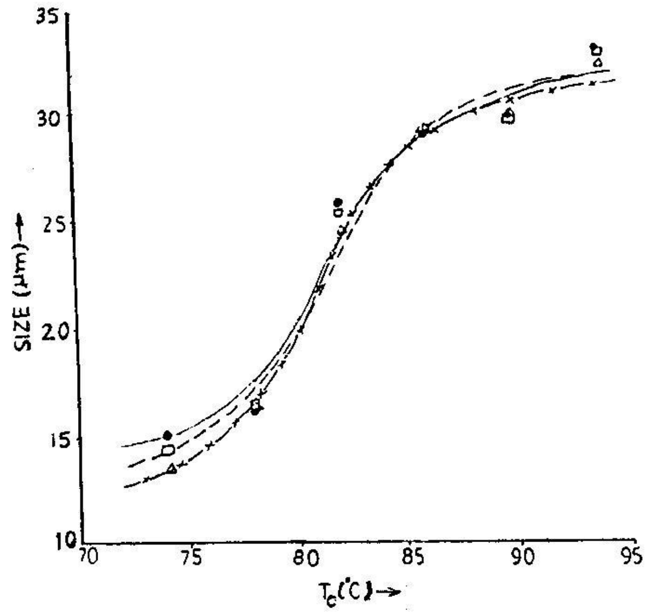

Fig.5: Graph showing variation in size of polyethylene crystals with crystallization temperatures. 0 = Mean size (solid line), =Medium size (--- line) and Δ=Model size (-x-x-line).

f_m = Frequency of the median class

$f_{(m-1)}$ Cummulative frequency of the class before the median class.

f_1 = Frequency of modal class

f_o = Frequency of the class before the modal class

f_2 = Frequency of the class after the modal class

C = Class range

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