

# INFLUENCE OF CRYSTALLIZATION CONDITIONS ON SINGLE CRYSTAL FORMATION

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## ABSTRACT

The effects of solvent, molecular weight of polymer and its distribution, and crystallization temperature on the formation and structure of single crystals from solution are discussed. With respect to the solvent effect, the intrinsic viscosity and lamellar thickness of crystals formed were investigated with various solvents as functions of temperature. It is pointed out that the solvent effect primarily reflects the equilibrium dissolution temperature and, moreover, affects the surface roughness or the conformation of fold portion which relates to the numerical value of the surface free energy. Concerning the effects of molecular weight and its distribution, measurements were carried out on the lamellar thickness, thickness of fold-containing surface, density, etc., with single crystals formed and taken out at constant temperatures. It is pointed out that, with sharp fractions of low molecular weights and at lower supercooling, we can obtain assembly of single crystals with higher density and larger thickness.

## INTRODUCTION

As is well known, there are two theoretical approaches to the formation of single crystals from solution. One, based on thermodynamic considerations developed by Peterlin, Fischer and Reinhold<sup>1</sup>, leads to the fold length of single crystals being directly related to the crystallization temperature  $T_c$ . The other theory, proposed independently by Price<sup>2</sup>, Lauritzen and Hoffman<sup>3</sup>, and Frank and Tosi<sup>4</sup>, is based on a kinetic approach, and predicts that the fold length of solution-grown single crystals depends on the degree of super-cooling,  $T_s - T_c$ , in which  $T_s$  denotes the melting temperature of single crystals with infinite fold length, and is alternatively called the equilibrium dissolution temperature.

Investigations into the effect of solvent on single crystal formation have been expected to help to differentiate between the kinetic and equilibrium theories. For several years, we have studied<sup>5-12</sup> the formation of single crystals from various solvents under different conditions, and pointed out that the fold length and the structure of fold surface are dependent on the crystallization condition.

Among the various crystallization conditions for solution-grown single crystals, nature of solvent is one of major importance, because thermodynamic values of the solvent, such as molar volume and solvent-polymer interactions, affect not only the dissolution temperature, but also the chain

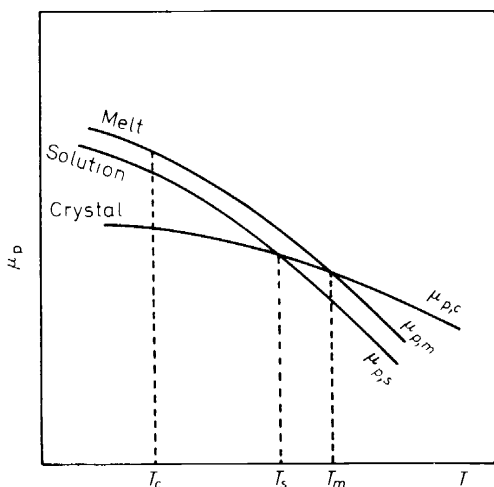
conformation at crystallization temperature, reflecting on the conformation of fold portions.

In connection with the structure of the fold surface, the effect of molecular weight and molecular weight distribution of the polymer solute being crystallized are also taken into account, because the solubility of polymer in solvent is a function of the molecular weight of the solute.

For these reasons, in this article, a discussion will be presented of the effects of solvent, and of the molecular weight of the solute and its distribution on the formation and structure of single crystals from solution.

### EFFECT OF SOLVENT ON SINGLE CRYSTAL FORMATION

In *Figure 1*, the chemical potentials  $\mu_p$  of polymer in the melt, dilute solution and crystal are schematically represented as functions of temperature. For chains with infinite chain length,  $T_m$  and  $T_s$  correspond to the equilibrium melting temperature and the equilibrium dissolution temperature, respectively. The former is unequivocally defined by the kinds of polymer, and the latter by the kinds of both polymer and solvent. Let us represent the crystallization temperature by  $T_c$ .



*Figure 1.* Temperature dependency of chemical potential of polymer.

Now we consider the formation of folded chain from dilute solution. The free energy of formation of a folded chain from a random chain,  $\Delta G$ , at  $T_c$  is given by

$$\Delta G = q + (\mu_{p,c} - \mu_{p,s})/N_A \quad (1)$$

where  $q$  is the free energy of fold formation per molecule,  $N_A$  is Avogadro's number, and  $\mu_{p,c}$  and  $\mu_{p,s}$ , respectively, denote the chemical potentials of polymer in crystal and in solution. The second term is a function of the sum of  $\Delta h_f$  heat of fusion of polymer and  $\Delta h_s$  heat of solution.  $\Delta h_f$  is always positive, but  $\Delta h_s$  is positive, zero, or negative in accordance with endothermic, athermal or exothermic solution process. With exothermic solution systems, the contribution of  $\Delta h_s$  ( $< 0$ ) is predominant and thus makes the quantity  $(\mu_{p,c} - \mu_{p,s})/N_A$  positive, therefore  $\Delta G > 0$ . With solvents forming endothermic solutions, the effect of  $\Delta h_s$  ( $> 0$ ) is superimposed on that of  $\Delta h_f$  ( $> 0$ ), so that  $(\mu_{p,c} - \mu_{p,s})/N_A$  is always negative below  $T_s$ . In such cases, if the free energy cost  $q$  ( $> 0$ ) in producing the fold is overcome by  $(\mu_{p,c} - \mu_{p,s})/N_A$ , then chain folding may occur. For these reasons, the solvent used for single crystal formation should not be exothermic in its solution process.

An analogous equation to that mentioned above is used to discuss the formation of a crystalline cluster with several faces and composed of  $N_A$  polymer molecules. In the case of single crystal formation,  $q$  is replaced by  $q = \sigma_e/2A$ , where  $\sigma_e$  is the free energy of the fold-containing surface in units of  $\text{erg cm}^{-2}$  and  $A$  is the cross-sectional area of a polymer chain in  $\text{cm}^2$ .  $q$  is expected to depend on the chain conformation at the crystallization temperature.

Now, denoting the free energy difference with respect to polymer component between the supercooled solution and the crystal phase by  $\Delta f$  (in  $\text{erg cm}^{-3}$ ) which is equal to  $-(\mu_{p,c} - \mu_{p,s})$  when we reduce the unit of  $\mu$  ( $\text{erg mol}^{-1}$ ) to  $\text{erg cm}^{-3}$ , we obtain the following equations (see also Figure 1)

$$\begin{aligned}\Delta f &= \Delta f_{m-c} - \Delta f_{m-s} & (2) \\ &= \{\Delta h_f(T_m - T_c)T_c\}/T_m^2 - \Delta h_f T_c(1/T_s - 1/T_m) \\ &= [\Delta h_f\{2T_m - (T_m^2/T_s) - T_c\}T_c]/T_m^2 & (3)\end{aligned}$$

where  $\Delta f_{m-c}$  is the free energy difference between the melt and the crystal phase,  $\Delta f_{m-s}$  is that between the melt and the solution phase, and  $\Delta h_f$  is the heat of fusion of polymer in  $\text{erg cm}^{-3}$  unit.

In the above equations, the contribution of the heat of solution is reflected through  $T_s$  according to Flory's equation<sup>13</sup>

$$1/T_s - 1/T_m = [R V_u (v_1 - \chi_1 v_1^2)]/(\Delta H_u V_1) \quad (4)$$

where  $\Delta H_u$  ( $\text{cal mol}^{-1}$ ) is the heat of fusion per repeating unit,  $V_u$  and  $V_1$  the molar volume of polymer repeating unit and of solvent respectively,  $v_1$  the volume fraction of solvent and  $\chi_1$  the interaction parameter. In equation 4,  $T_s$  and  $T_m$  are defined for polymer in a perfect crystal<sup>14</sup>. We found<sup>15</sup> that equation (4) holds in the whole concentration range for such systems as polyethylene-*n*-alkanes which give the crystal-liquid phase equilibrium.

Equation (4) tells us that the effect of solvent is reflected by the ratio  $V_u/V_1$  and parameter  $\chi_1$ . Increasing either or both of  $\chi_1$  and  $V_1$ ,  $T_s$  becomes large. We estimated  $\chi_1$  from equation (4).

Polymers used to investigate the solvent effect were polyethylene, polyoxymethylene and poly-4-methylpentene-1. To determine  $T_m$  and  $T_s$ ,

Table 1. Samples used for determination of  $T_m$  and  $T_g$ 

Preparation	$T_m$ (°C)	$\Delta H_u$ (cal mol <sup>-1</sup> )	$\Delta h_f$ (erg cm <sup>-3</sup> )
	Polymethylene		
High pressure crystallization at 4760 atm and 227°C for 20 h (Dr. Wunderlich)	141.4	980 (per mol CH <sub>2</sub> )	$2.9 \times 10^9$
	Polyoxymethylene		
Radiation-induced solid state polymerization of trioxane (Dr. Nishi)	187.0	1796	$3.78 \times 10^9$
	Poly-4-methylpentene-1		
Fractionated sample was crystallized at 232°C for 4.5 h	244.1	2850	$1.2 \times 10^9$

samples with satisfactorily long fold length are necessary. Sample preparations and thermodynamic quantities obtained with those polymers are given in *Tables 1* and *2*.

Now we shall refer to chain conformation and its temperature dependency. Inherent chain flexibility may be estimated from the characteristic ratio  $\langle R_0^2 \rangle / n b^2$ , in which  $\langle R_0^2 \rangle$  is the unperturbed chain dimension, and  $n$  and  $b$  are the number and length of bonds in the chain respectively, and from the steric factor  $s$  defined by  $[\langle R_0^2 \rangle / \langle R_0^2 \rangle_f]^{\frac{1}{2}}$  (subscript  $f$  refers to free rotation chain). As examples, experimental results obtained by us for polyethylene<sup>16</sup> and poly-4-methylpentene-1<sup>17</sup> are given together with Nagai's theoretical

Table 2. Thermodynamic quantities obtained from polymer-solvent systems

Solvent	$T_g$ (°C)	$\chi_1$ (at $T_g$ )	$V_1$ (at $T_g$ )
	Polyethylene		
Decalin	111.3	0.0097	177.7
Toluene	112.5	0.44	116.5
<i>p</i> -Xylene	114.2	0.38	134.8
Tetralin	115.1	0.37	145.7
<i>n</i> -Octane	121.9	0.29	181.0
<i>n</i> -Hexadecane	127.8	0.15	322.8
	Polyoxymethylene		
<i>m</i> -Cresol	132.7	0.05	115.1
Furfuryl alcohol	146.5	0.26	96.1
Benzyl alcohol	153.2	0.25	116.0
Acetophenone	161.3	0.30	137.4
	Poly-4-methylpentene-1		
Decalin	123.0	-0.40	176
<i>p</i> -Xylene	127.5	-0.04	138
Tetralin	145.8	0.11	149

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Table 3. Characteristic ratio and its temperature dependency

$T(^{\circ}\text{C})$	$\langle R_0^2 \rangle / nb^2$	$s$	$d \ln \langle R_0^2 \rangle / dT$	$f_T^{18}$
Polyethylene <sup>16</sup>				
163.9	6.80	1.84	$-1.21 \times 10^{-3}$	
127.5	7.10	1.88		
140				0.67
70				0.71
Polyoxymethylene <sup>48</sup>				
25	10.5	2.3		
Poly-4-methylpentene-1 <sup>17</sup>				
210.0	13.2	2.55	0	
176.6	13.1	2.56		

result<sup>18</sup>, in Table 3. We point out that these polymers are not tightly coiled even in the unperturbed state and increase or almost do not change the characteristic ratio with decreasing temperature. According to Nagai, the fraction  $f_T$  of *trans* bonds in polyethylene chain is expected to be 67% at 140°C and 71% at 70°C. In solvent better than the  $\Theta$ -solvent, the chain conformation is more extended and richer in *trans* fraction. At temperatures above  $T_s$ , a molecular chain with any chain length exists in a random chain conformation.

Figures 2 and 3 show the temperature dependency of the intrinsic viscosities in temperature ranges related to single crystal formation for polyethylene. Diphenyl ether is a  $\Theta$ -solvent at 163.9°C and the broken line shown in Figure 2 shows the relation between the intrinsic viscosity in  $\Theta$ -solvent and temperature, calculated from the data given in Table 3. Decalin and

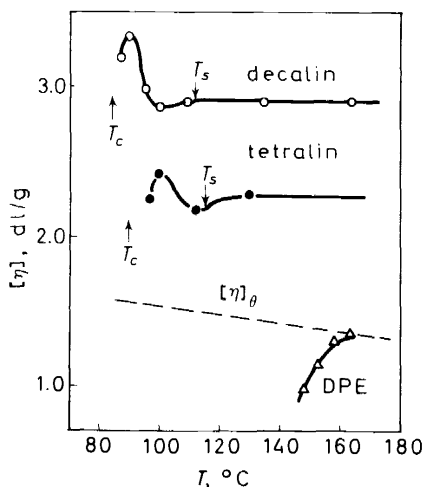


Figure 2. Intrinsic viscosity vs temperature for polyethylene in decalin, tetralin and diphenyl ether ( $\Theta$ -solvent at 163.0°C).

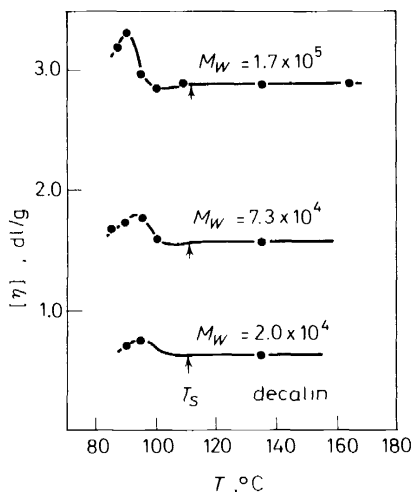


Figure 3. Intrinsic viscosity in decalin vs temperature for polyethylene with different molecular weights.

tetralin are 'good' solvents, and the expansion factors  $\alpha = ([\eta]/[\eta]_{\theta})^3$  of the polymer ( $M_w = 1.7 \times 10^5$ ) are  $\alpha = 1.27$  (135°C) in decalin and  $\alpha = 1.16$  (130°C) in tetralin. As known from Table 2, the equilibrium dissolution temperatures  $T_s$  are 111.3°C and 115.1°C for decalin and tetralin, respectively. The highest crystallization temperatures  $T_c$  practically used for single crystal formation are 83.9°C (decalin) and 89.8°C (tetralin). With decalin and tetralin, a crystal-liquid phase equilibrium occurred at  $T_c$ , but with diphenyl ether ( $\Theta$ -solvent), a liquid-liquid phase equilibrium first took place and then the single crystals were formed from the concentrated liquid phase at  $T_c (= 109.1^\circ\text{C})$ . The course of the curve for diphenyl ether in Figure 2 is quite different from those for decalin and tetralin. That is, the intrinsic viscosities in diphenyl ether decrease steadily with decreasing temperature below the  $\Theta$ -temperature. For these reasons, so-called  $\Theta$ -solvents are not suited to obtain 'good' single crystals. In decalin and tetralin, on the other hand, intrinsic viscosities, with decreasing temperature, first slightly decrease below  $T_s$ , increase rather sharply, and then again decrease through a maximum. Such changes in intrinsic viscosity may be related to the formation of primary nuclei. Presumably, at the temperature corresponding to the maximum point, more than one chain may come together, which leads to primary nuclei with lowering temperature. With decalin, the maximum point is located at 90°C, the lowest temperature at which viscosity measurements were possible was 87°C, and the highest crystallization temperature was 83.9°C (Figure 2). It is pointed out that with better solvents the relative height of the maximum becomes larger and the temperature corresponding to the maximum becomes lower. In Figure 3, intrinsic viscosities of polyethylene with different molecular weights in decalin were plotted against temperature. Marked differences with respect to the temperature where the

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curve exhibits abrupt changes were not found within the range of molecular weight used here.

Perhaps the primary nuclei include loose loops and may not be composed of sharp folds. On such primary nuclei, single crystals may grow. At higher crystallization temperatures, with solvents giving higher  $T_s$  but excepting  $\Theta$ -solvents, we may obtain 'good' single crystals, because chains tend to rearrange at higher temperatures.

According to the kinetic theory proposed by Lauritzen and Hoffman<sup>3</sup> the average fold length (lamellar thickness)  $l$  of polymer single crystals formed at  $T_c$  is given by the following equation

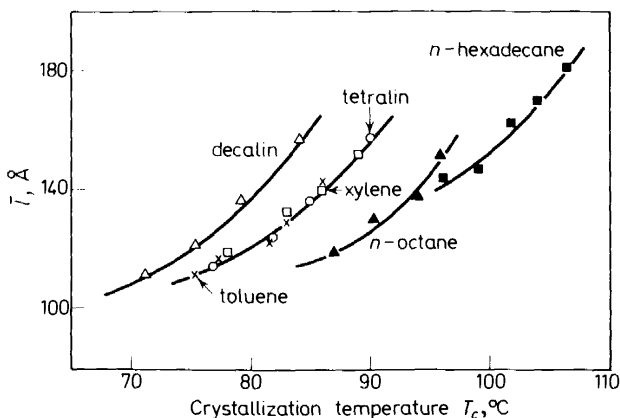
$$l = k T_c / (d_0 \sigma_s) + 2 \sigma_e / \Delta f \quad (5)$$

where  $\sigma_e$  and  $\sigma_s$  are the surface free energies of the fold-containing surface and the lateral surface, respectively,  $d_0$  the effective width of a polymer chain in the crystal lattice, and  $\Delta f$  the free energy difference between the supercooled liquid and crystal phase. Introducing an approximate expression for  $\Delta f$ , Hoffman and co-workers arrived at the following equation

$$l = \frac{k T_c}{d_0 \sigma_s} + \frac{2 \sigma_e T_s}{\Delta h_f (T_s - T_c)} \quad (6)$$

Thus the kinetic theory requires that the fold length is approximately proportional to the reciprocal of the supercooling  $T_s - T_c$ . This is contrary to the prediction from the thermodynamic equilibrium theory<sup>1</sup>, that the fold length is directly related to the crystallization temperature  $T_c$ .

To check the applicability of these two theories, the fold length  $l$ , determined by low-angle x-ray diffraction with the incident x-ray beam parallel to the surface of the crystal mat, is plotted against the crystallization temperature  $T_c$  for polyethylene and polyoxymethylene in *Figures 4 and 5*.



*Figure 4.* Relation between lamellar thickness  $l$  and crystallization temperature  $T_c$  for polyethylene grown from various solvents.

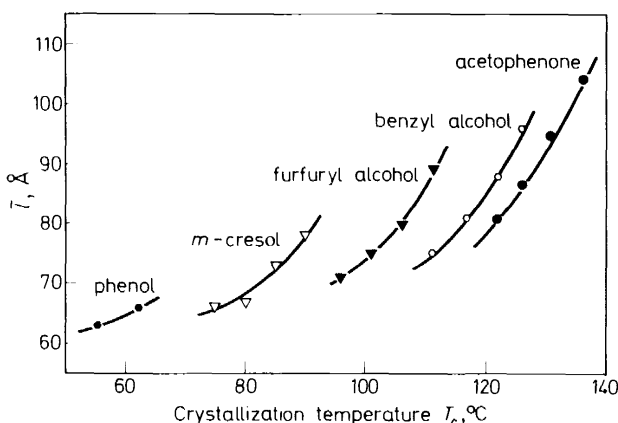


Figure 5. Relation between lamellar thickness  $\bar{l}$  and crystallization temperature  $T_c$  for polyoxymethylene grown from various solvents.

respectively. Further, in Figure 6 the fold length  $l$  is plotted against the supercooling,  $T_s - T_c$ , for polyethylene<sup>5</sup>, polyoxymethylene<sup>12</sup> and poly-4-methylpentene-1<sup>8</sup>. From these plots, it is seen that the fold length is not a function of  $T_c$  but is approximately proportional to the reciprocal of  $T_s - T_c$ . This is the same result pointed out by Kawai and Keller<sup>41</sup>. Thus the comparison of theories with experimental results may incline to support the kinetic theory.

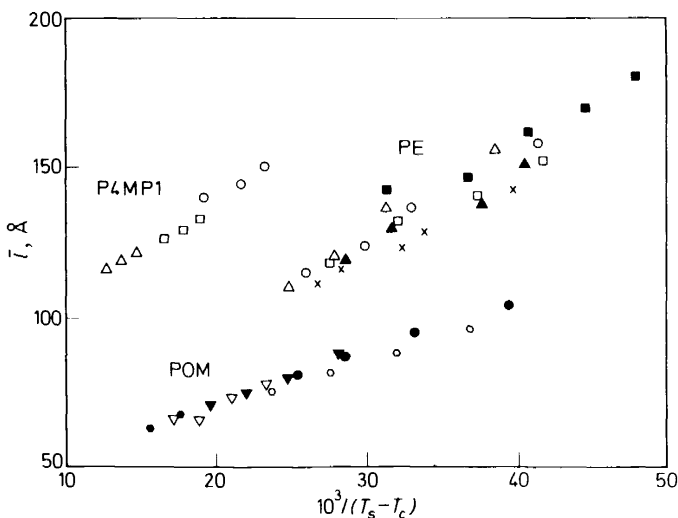


Figure 6. Relation between lamellar thickness  $\bar{l}$  and reciprocal of degree of supercooling.

$\Delta$ : decalin,  $\times$ : toluene,  $\square$ : *p*-xylene,  $\circ$ : tetralin.  
 $\blacktriangle$ : *n*-octane,  $\blacksquare$ : *n*-hexadecane,  $\bullet$ : phenol,  $\bullet$ : acetophenone.  
 $\nabla$ : *m*-cresol,  $\blacktriangledown$ : furfuryl alcohol,  $\circ$ : benzyl alcohol.



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More accurately the term  $\Delta f$  is given by equation (3) above. Combination of equation (5) with (3) yields the following equation

$$l = \frac{kT_c}{d_0\sigma_s} + \frac{2\sigma_e T_m^2}{\Delta h_f \{2T_m - (T_m^2/T_s) - T_c\} T_c} \quad (7)$$

If we assume that the surface free energy is constant in a narrow range of crystallization temperature, the plot of  $l/T_c$  against the quantity  $1/\{2T_m - (T_m^2/T_s) - T_c\} T_c$  gives a straight line, from whose slope the value  $\sigma_e$  will be obtained. Thus we evaluated  $\sigma_e$  from equation (7).

The value of  $\sigma_e$  is also from the following equation<sup>19</sup> derived from simple thermodynamic considerations

$$T_s(l) = T_s \{1 - (2\sigma_e/\Delta h_f l)\} \quad (8)$$

where  $T_s(l)$  and  $T_s$  are the dissolution temperature of polymer in solvent for the single crystals of fold length  $l$  and of infinite fold length, respectively. The plot of  $1/T_s(l)$  against  $1/l$  gives a straight line, from whose slope the value  $\sigma_e$  will be obtained<sup>19</sup>.

Table 4. Surface free energy calculated from equations (7) and (8).

Solvent	$\sigma_e$ (erg cm <sup>-3</sup> ) from eq(7)	$\sigma_e^*$ (erg cm <sup>-3</sup> ) from eq(8)	$q$ (kcal mole <sup>-1</sup> ) from eq(7)
Polyethylene			
Decalin	113	114	5.94
Toluene	97	97	5.10
<i>p</i> -Xylene	88	99	4.63
Tetralin	94	102	4.94
<i>n</i> -Octane	90	98	4.73
<i>n</i> -Hexadecane	83	88	4.36
Polyoxymethylene			
<i>m</i> -Cresol	61	63	1.29
Furfuryl alcohol	57	56	1.21
Benzyl alcohol	51	56	1.08
Acetophenone	55	56	1.16
Poly-4-methylpentene-1			
Decalin	24	36	6.01
<i>p</i> -Xylene	25	28	6.26
Tetralin	27	20	6.76

The experimental values of  $\sigma_e$  obtained by equations (7) and (8) were summarized in Table 4, together with  $q$ , the free energy to form one mole fold, which is related to  $\sigma_e$  and the cross-sectional area  $A$  by  $q = 2A\sigma_e$ . In Table 4,  $\sigma_e$  obtained from equation (8) was designated as  $\sigma_e^*$  to distinguish it from  $\sigma_e$  obtained from equation (7). As a first approximation, as indicated also in Figure 6,  $\sigma_e$  is almost the same for different solvents, but closer examination of Table 4 shows that  $\sigma_e$  also depends on the kinds of solvent.  $\sigma_e^*$ s obtained from equation (8) are almost equal to  $\sigma_e$ .

Hoffman and co-workers<sup>20</sup> have pointed out that the surface free energy of fold-containing surface is decreased towards an equilibrium value by annealing without thickening. The fact that  $\sigma_e$  does not differ significantly from  $\sigma_e^*$  may mean that such an annealing effect has not occurred during the heating process to determine  $T_s(l)$ .

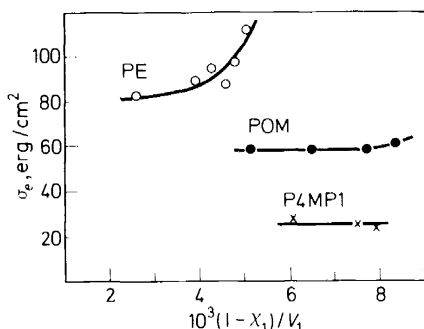


Figure 7. Surface free energies  $\sigma_e$  of single crystals of polyethylene, polyoxymethylene, and poly-4-methylpentene-1 as functions of  $(1-\chi_1)V_1$ .

In Figure 7,  $\sigma_e$  was plotted against  $(1-\chi_1)V_1$ . It is pointed out that  $\sigma_e$  is not independent of  $(1-\chi_1)/V_1$  for polyethylene, but is almost constant for polyoxymethylene and poly-4-methylpentene-1.

We may conclude that the solvent effect primarily reflects in the equilibrium dissolution temperature, and moreover affects the surface roughness or the conformation of fold portion which relates to the amount of the surface free energy. With larger  $\chi_1$  and  $V_1$ ,  $T_s$  becomes higher and  $\sigma_e$  becomes smaller, which leads to sharply folded, 'good' single crystals.

Recently, Jackson and Mandelkern<sup>21</sup> estimated  $\sigma_e$  of polyethylene single crystals grown from various solvents, by plotting  $1/T_c$  against  $1/lT_c$ , and pointed out that  $\sigma_e$  is independent of the kind of solvent. The equation used by them concerns the size  $l^*$  of critical nucleus and they assumed  $l^*$  is equal to  $l$ . But  $l^*$  is probably not equal to  $l$ . In such a case<sup>12</sup>, the plot of  $1/T_c$  against  $1/lT_c$  may not be a straight line but a curve concave upwards for  $T_c > T_s/2$ . Therefore, if the slopes of the plots for various solvents are the same, then it follows that the value of  $\sigma_e$  is dependent on the solvents. At any rate, however, differences in the numerical values of  $\sigma_e$  may not be large.

The smallest values of  $q$  (kcal mole<sup>-1</sup>) in Table 4 are 4.36, 1.08 and 6.01 for polyethylene, polyoxymethylene and poly-4-methylpentene-1, respectively. These values are not inconsistent when taking into account the mode of chain packing in the lattice.

### EFFECT OF MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF POLYMER, AND CRYSTALLIZATION TEMPERATURE

In addition to the effect of solvent, the molecular weight and molecular weight distribution and the crystallization temperature are also important

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factors affecting single crystal formation from solution. The effect of molecular weight on the morphology of single crystals has been discussed by Holland<sup>22</sup>, Keller<sup>23</sup>, and Wunderlich<sup>24</sup>. Generally, single crystals are apt to become more dendritic as the molecular weight of polymer is increased sufficiently. According to Holland<sup>22</sup>, polyethylene single crystals crystallized at 80°C from xylene solution were diamond-shaped both for samples with molecular weight of 10000 and 120000, but crystallization at 40°C gives diamond-shaped single crystals for a sample with molecular weight of 10000, but dendritic crystals with molecular weight of 120000. The highest (critical) crystallization temperatures were 84°C and 92.2°C for the former and latter, respectively. Wunderlich<sup>24</sup> has derived the relation between the critical crystallization temperature  $T_c^*$  and the molecular weight  $M$  for polyethylene crystals grown from 0.1% xylene solution:  $T_c^* = M \times 10^3 / (2.747M + 170.6)$ .

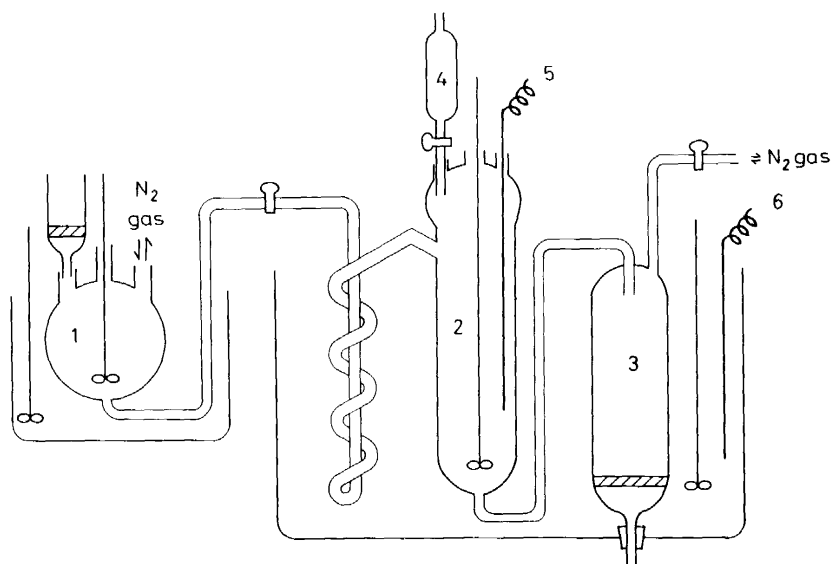


Figure 8. Apparatus for single crystals preparation: (1) dissolution flask; (2) crystallization vessel; (3) precipitation and filtration vessel; (4) dropping funnel; (5) thermistor thermometer; (6) thermistor temperature controller.

We<sup>25</sup> have paid attention to the effect of molecular weight on single crystal structure, and reported that the density and the heat of fusion become larger with samples of smaller molecular weight. On the contrary, Mandelkern<sup>26-28</sup>, Bair<sup>29</sup>, and Takamizawa<sup>30</sup> have reported that the density and the heat of fusion are independent of the molecular weight. In particular, Mandelkern has criticized that our data are too high. Polyethylene samples used in that experiment were obtained by fractional solution with a large-scale column apparatus designed by us<sup>31</sup>. We have since noticed that small amounts of

Celite and silicone grease were included in that polyethylene sample, and thus the value for the density is feared to be somewhat high. For this reason, we have obtained further sharp polyethylene fractions by using the usual fractional precipitation together with fractional crystallization<sup>32, 33</sup>, and prepared single crystals isothermally from 0.1% xylene solution at various temperatures. With the use of the apparatus<sup>5</sup> shown in *Figure 8*, we can form and, at the same time, take out single crystals isothermally at given temperatures, and can avoid mixing single crystals formed at different temperatures. In *Table 5*, the density and lamellar thickness of single crystals formed with these sharp fractions are summarized<sup>34</sup> together with the data on an unfractionated sample.

*Table 5.* Density and lamellar thickness of polyethylene single crystals grown from 0.1% xylene solution.

Molecular weight <i>M</i>	Cryst. temp. <i>T<sub>c</sub></i> (°C)	<i>l</i>	Density (g cm <sup>-3</sup> )	
			Dry	Wet
6000 (sharp fraction)	70	118	0.976	—
	80	146	0.980	0.988
8000 (sharp fraction)	85	152	0.985	0.991
	70	112	0.975	—
56000 (fraction)	80	120	0.977	0.984
	85	132	0.980	—
	70	114	0.969	—
480000 (fraction)	80	120	0.971	0.978
	85	128	0.974	0.980
	70	112	0.967	0.975
60000 (unfractionated)	80	118	0.971	—
	85	130	0.977	0.981

As is obvious from *Table 5*, for great supercooling the molecular weight scarcely affects the density or lamellar thickness, but for slight supercooling both quantities become larger with decreasing molecular weight. However, for such discrimination the molecular weight distribution of samples should be as sharp as possible. We may point out that most work on single crystal formation has been carried out with unfractionated or insufficiently fractionated polymer samples. For the present experiment, about 600 mg sharp fractions were obtained from 120 g original material by careful fractionation. Though values in *Table 5* are somewhat lower than those reported previously<sup>25</sup>, the tendencies are the same as those of the previous paper. The density of dried mats are approximately in accord with the values of Mandelkern<sup>26</sup>. Numerical values of density (wet) measured with suspensions are somewhat larger than those with dried mats. This difference may be due to the presence of voids in dried mats. In the course of crystal formation, these voids are filled with solvent, but by the drying process the solvent is removed from the voids. Such voids are difficult to perfectly refill with the liquid in

the course of density measurement even though the system is sufficiently evacuated. Thus, the density measured with dried mats may be estimated as smaller than that measured with suspensions.

To verify the presence of voids between lamellae in dried mats, the x-ray small angle scattering intensities were compared with undried and dried polyethylene mats (whose crystallization temperatures are both 80°C), and we found that the intensity of diffuse scattering was considerably increased by drying<sup>35</sup>. This fact may be due to the presence of voids in dried mats.

Fischer<sup>36</sup>, assuming a simplified structure model consisting of two phases only, that is, of crystalline and amorphous phases, has derived the following relation between the mean square fluctuation of electron density,  $\langle \eta^2 \rangle$ , which is calculated from the invariant of x-ray small angle scattering intensity, and the degree of crystallinity,  $w_c$ .

$$\langle \eta^2 \rangle = (\rho_c - \rho_a)^2 w_c (1 - w_c) \quad (9)$$

where  $\rho_c$  and  $\rho_a$  denote the densities of crystalline and amorphous phase, respectively. From experimental results,  $\langle \eta^2 \rangle = 3.37 \times 10^{-3} (\text{g cm}^{-3})^2$  and  $w_c = 0.82$  determined from heat of fusion, Fischer<sup>37</sup> obtained  $\rho_c - \rho_a = 0.159 \text{ g cm}^{-3}$ . He further obtained  $\rho_c - \rho_a = 0.160 \text{ g cm}^{-3}$  from the measurement of density on dried mats of this sample. From the mutual agreement of these values, he concluded that no detectable amount of voids existed in his sample\*.

Fischer and co-workers<sup>38</sup> have opposed our suggestion that the low density of the dried mats is due to voids. Our experimental result<sup>35</sup> on the intensity of diffuse scattering mentioned above strongly suggests that some dried mats of single crystals may contain a small amount of voids, which corresponds to the density difference between wet and dried samples. These voids may be located between aggregates of lamellae.

Generally, however, correct determination of densities of single crystals is very difficult. To confirm our density values, we have calculated<sup>34, 35</sup> densities from x-ray scattering intensities on polyethylene samples reacted with iodine, according to the method proposed by Fischer<sup>39</sup>. In *Figure 9*, the meridional intensity of an iodine-reacted polyethylene relative to that of an unreacted one,  $J_k/J_u$ , was plotted against the iodine content,  $c_k$ . The relative intensity first decreases, then increases through a minimum. The plot was replotted in *Figure 10*, from which we obtain the average density  $\bar{\rho}$  of the single crystals, if the density value  $\rho_c$  for perfect crystals is known. Using the density value  $\rho_c = 0.993$  obtained by Kitamaru and Mandelkern<sup>40</sup>, we arrived at  $\bar{\rho} = 0.978$  for polyethylene single crystals grown from xylene solution at 70°C with unfractionated sample. This value agrees well with the density (wet) value for corresponding single crystals shown in *Table 5*.

In the next place, we shall refer to the effect of molecular weights of polymer on lamellar thickness. In general, the lamellar thickness, as given by equation (6), does not depend on the molecular weight, but takes definite values according to the degrees of supercooling. However, with respect to

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\* If we assume the scattering is due to voids, scattering power should be seven- or ten-fold higher than the measured value. But in reality, it seems that single crystal dried mats consist of crystalline core, intercrystalline surface layer and a small amount of voids.

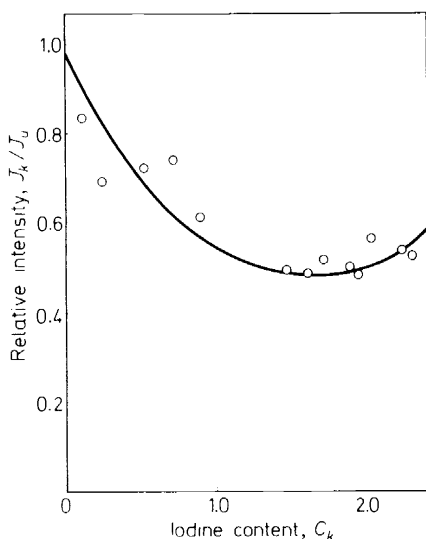


Figure 9. Relative change  $J_k/J_0$  of maximum intensity of x-ray small angle scattering plotted against iodine content  $c_k$  for single crystals grown from xylene solution at 70°C with unfractionated polyethylene.

single crystals formed from homogeneous fractions. the lamellar thickness of single crystals prepared from low molecular weight fractions becomes larger (see also *Table 6* below). Such result will be discussed later.

To make clear the structure of a fold portion, we<sup>34, 35</sup> estimated the thickness of fold-containing surface,  $l_u/2$ , and the thickness of crystallite,  $l_c$  (see *Figure 11*), according to the method proposed by Tsvankin<sup>41</sup>. Tsvankin has proposed a method of interpreting small-angle x-ray long period measurements which utilizes both the position of the long period maximum

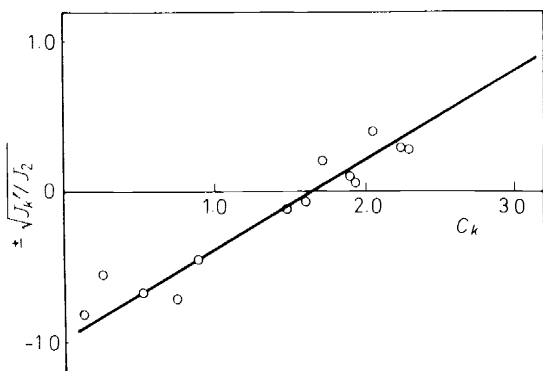


Figure 10.  $\pm \sqrt{J_k/J_0}$  plotted against  $c_k$  for the same sample as shown in *Figure 9*. For designations, see ref. 39.

## SINGLE CRYSTAL FORMATION

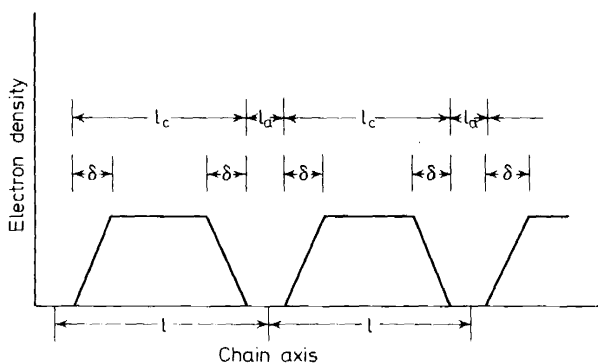


Figure 11. Tsvankin's model adapted to single crystal.

and its half-width to obtain values  $l_a$  and  $l_c$ . His treatment is based on a model of polymer structure in which regions of alternating higher and lower electron densities are projected onto a fibre axis. The scattering curves were calculated for various values of the parameters,  $\beta/\alpha$  (where,  $\alpha = l_c/l_a$  and  $\beta = \Delta/l_c$ ;  $\Delta$  is the deviation of  $l_c$ ), and  $\epsilon = \delta/l_c$  ( $\delta$  is the thickness of intermediate region traversing from perfect crystal to amorphous phase, and included in  $l_c$ ). The position and half-width of the computed maxima can be related to those of experimentally observed maxima through the construction of sets of calibration curves. Two examples of analyses of long period by Tsvankin's method are illustrated in Figure 12.  $l_a$  and  $l_c$  estimated from such curves are listed in Table 6, together with the lamellar thickness  $l$ . As seen in Table 6, the value of  $l_a$  is smaller with lower molecular weight of the

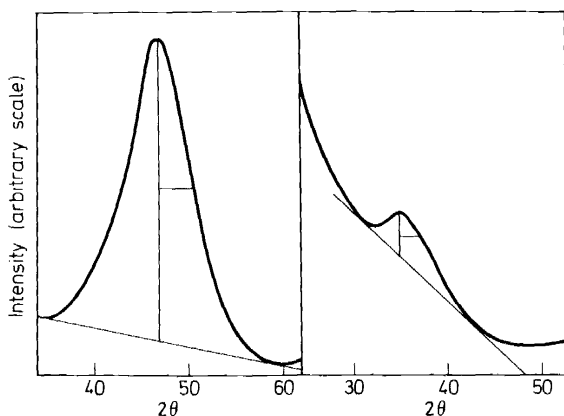


Figure 12. Small angle scattering curves for solution-grown polyethylene single crystals: (a) unfractionated sample grown at 70°C; (b) fractionated sample of  $M = 3700$ , grown at 85°C. Analyses of  $l_a$ ,  $l_c$ , and  $l$  were performed with  $\beta/\alpha = 0.2$  and  $\epsilon = 0.01$  by Tsvankin's method.

Table 6. Lamellar thickness  $l$  and  $l_c$  and  $l_a$  calculated by Tsvankin's method for polyethylene single crystals crystallized at 85°C from sharp fractions with various molecular weights.

Molecular weight $M$	Lamellar thickness $l(\text{Å})$	$l_c(\text{Å})$	$l_a(\text{Å})$
3 700	151	ca. 136	ca. 10
42 000	132	114	14
440 000	126	102	20

sample. This fact may mean that more regularly folded crystals are formed with lower molecular weight samples. When we use our density value for single crystals measured in suspension, we have  $\rho_a = \text{ca. } 0.90 \text{ g cm}^{-3}$  for the density of the fold portion, on the basis of the results shown in Table 6. This density value, 0.90, is considerably higher than the value  $\rho_a = 0.841 \text{ g cm}^{-3}$  obtained by Fischer<sup>38</sup> for the amorphous region from the two-phase model mentioned above.

Finally, we shall discuss the effect of crystallization temperature  $T_c$ . As mentioned above, the effect of  $T_c$  is to be discussed in connection with  $T_s$ . Table 5 shows that density becomes larger with smaller supercooling,  $T_s - T_c$ . This means that molecular movement becomes easier as  $T_c$  approaches  $T_s$ , thus resulting in the formation of more regularly folded crystals. A solvent exhibiting higher  $T_s$  is preferable to obtain regularly folded single crystals. In Figure 13 are shown the melting curves for polyethylene crystals grown at different crystallization temperatures. The melting curve of crystals grown at the higher temperature shows two peaks, while that at the lower temperature shows only the higher temperature peak.

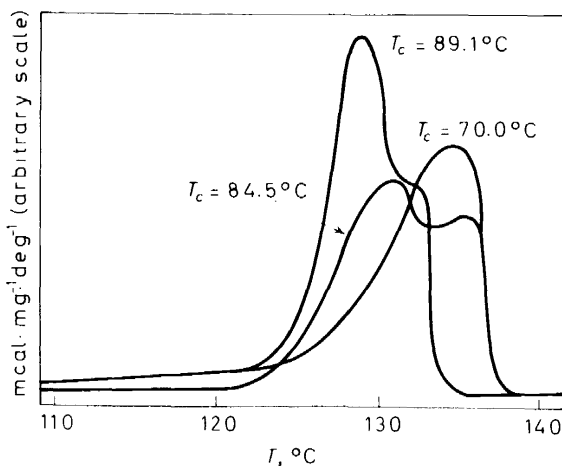


Figure 13. Melting curves for polyethylene (of  $M = 42\,000$ ) single crystals grown at 70°, 84.5°, and 89.1°C.



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Table 7. Effect of crystallization temperature  $T_c$  on  $l$ ,  $l_c$  and  $l_a$  of polyethylene single crystals, formed with a sharp fraction of molecular weight 42 000.

Cryst. temp. $T_c(^{\circ}\text{C})$	$l(\text{\AA})$	$l_c(\text{\AA})$	$l_a(\text{\AA})$
60	98	80	15
70	112	95	14
80	132	114	14
90	150	132	12

Crystals grown at lower temperatures are less stable thermally, but can recrystallize faster into crystals of greater lamellar thickness than the single crystals grown at higher temperatures, which are somewhat more stable but less mobile.

Table 7 shows the effect of crystallization temperature on  $l$ ,  $l_a$ , and  $l_c$ . It is shown that the lamellar thickness  $l$  increases with increasing crystallization temperature, but the thickness  $l_a$  of fold-containing surface is not greatly affected by the crystallization temperature.

Table 8 indicates the change in lamellar thickness at isothermal crystallization temperature during single crystal formation from tetralin solution. Series A and E are concerned with the effect of crystallization temperature for polyethylene sample with  $P = 1010$ , and series B, C and D with the effect

Table 8. Isothermal crystallization of polyethylene from 0.1% tetralin solution<sup>7</sup>.

Series	Degree of polymerization, $P$	Cryst. temp. $T_c(^{\circ}\text{C})$	Degree of super-cooling ( $^{\circ}\text{C}$ )	Cryst. time (h)	Lamellar thickness $l(\text{\AA})$
A	1010	77.2	35.4	2.17	114
				5.17	114
				17.17	116
				44.50	116
B	290	84.4	25.8	2.62	128
				6	131
				16	131
				23.75	131
C	3070	84.8	25.8	2	120
				5	126
				24	131
				145	130
D	5420	84.8	25.8	2.5	127
				6.75	127
				15	127
				25	127
E	1010	89.8	22.8	5.50	135
				10	140
				24	147
				95.33	146

of molecular weight of polymer at  $T_c = 84.8^\circ\text{C}$ . Comparison of series A with E indicates that at higher crystallization temperatures the lamellar thickness is larger and molecular rearrangement occurs more easily, that is, the lamellar thickness increases from 135 Å at 5.5 h to 147 Å at 24 h. The effect of molecular weight is not shown so markedly as in Table 5, but the tendency for the lamellar thickness to be greater with lower molecular weight sample can be recognized.

Why the density, heat of fusion and lamellar thickness of solution-grown polyethylene change as the molecular weight decreases is very difficult to explain. But taking into account the fact that these changes occur when we use very low molecular weight polyethylene with a very sharp molecular weight distribution, we may explain these changes according to the noteworthy observations reported by Arlie and co-workers<sup>42</sup>. Arlie studied the thickness of lamellae of melt-crystallized low molecular weight polyethyleneoxide with sharp molecular weight distribution, and found that the lamellar thickness increased only in a stepwise fashion with crystallization temperature and that each crystal thickness is a small integer submultiple of the average chain length. This evidence suggests that the chain ends are at the crystal surfaces, and that in this way short molecules promote crystal thickness to an integral submultiple of their length. Similar observations to those of Arlie were recently reported by Takamizawa<sup>43</sup> with respect to solution-grown polyethylene single crystals.

As mentioned above, it was found that, when single crystals are formed from solution with polyethylene of particularly sharp molecular weight distribution, the density, heat of fusion, lamellar thickness and thickness of fold-containing surface considerably change with decreasing molecular weight, and that the degree of supercooling,  $T_s - T_c$ , markedly affects the nature of single crystals.

In most cases, unfractionated polyethylene has been used for single crystal formation and, moreover, crystallization has not necessarily been conducted under constant temperature (e.g., even though crystallization is carried out at a specified temperature, filtration may be performed at room temperature). Such situations may result in a mixture of single crystals with different fold regularities ranging from regular to irregular fold. The evidence (staggering, sectoring, epitaxial growth, dislocation network) to verify the regular fold is obtained from observations with respect to regularly folded crystals chosen from the mixture, while the evidence (density, heat of fusion, ir, x-ray wide angle diffraction, nmr, nitric acid oxidation, etc.) for irregular folds is obtained from observation on crystal mats which yields average properties for such a mixture<sup>44, 45</sup>.

We suggest that polymers may crystallize more or less in the form of a mixture containing regularly folded lamellae and irregular folded ones. This figure is somewhat different from the so-called composite model<sup>46, 47</sup> which contains both regular and irregular folds in a lamella.

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