

Surface Free Energy of Poly(oxymethylene) Single Crystals Grown in Various Solvents

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ABSTRACT: Single crystals of poly(oxymethylene) were prepared isothermally from dilute solution in various solvents such as phenol, *m*-cresol, fulfuryl alcohol, benzyl alcohol, and acetophenone, and the surface free energies of the single crystals were estimated from the relation between the folded length and crystallization temperature using the modified Lauritzen and Hoffman equation. It is pointed out that more regularly folded single crystals may be formed with solvent having a larger thermodynamic interaction parameter and larger molar volume. This result is compared with that of polyethylene single crystals previously reported.

KEY WORDS Single Crystal / Poly(oxymethylene) / Lamellar Thickness / Crystallization Temperature / Solvent Effect on Crystallization /

Since the discovery of folded-chain polymer single crystals,¹ a number of suggestions have been advanced as to the cause of regularity of folding. At present two theoretical treatments have been developed which can be compared with experimental results. One, developed by Peterlin, Fischer, and Reinhold,² suggests that the fold period is determined thermodynamically corresponding to a minimum in the free energy density of the crystals at the crystallization temperature. The other, suggested independently by Price,³ Lauritzen and Hoffman,⁴ and Frank and Tosi⁵ on the basis of a kinetic approach, was subsequently developed and applied to crystallization from both solution and melt. According to the kinetic theories, the observed chain-folded crystals correspond to the structure with maximum probability. Both theories succeeded in accounting for the observed temperature dependency of fold length, but equilibrium theory failed in the explanation of solvent dependency of lamellar thickness, since fold length of solution-grown single crystals depends on the degree of supercooling but not on the crystallization temperature.^{6,7} One may conclude that chain-folded polymer crystallization, therefore, normally proceeds by means of the kinetic mechanism.

According to Lauritzen and Hoffman,⁴ the lamellar thickness of polymer single crystals grown at T_c is given by the following equation:

$$\bar{l} = \frac{kT_c}{d_0\sigma_s} + \frac{2\sigma_e}{\Delta f} \quad (1)$$

where \bar{l} is the average lamellar thickness of the crystals, T_c the crystallization temperature, σ_e and σ_s the free energy of the fold-containing surface and the lateral surface, respectively; d_0 the effective width of a polymer chain in the crystal lattice, and Δf the free energy difference between the supercooled liquid and the crystal phase. The term Δf is approximated by the expression⁸

$$\Delta f_1 = \frac{\Delta h_f(T_s - T_c)T_c}{T_s^2} \quad (2)$$

where Δh_f (erg/cm³) is the heat of fusion per unit volume of perfect crystal at the melting temperature, and T_s is the melting temperature of single crystal of infinite fold length in the presence of a large quantity of solvent, and often called the dissolution temperature.

Combining eq 1 and 2, we obtain the following equation

$$\bar{l} = \frac{kT_c}{d_0\sigma_s} + \frac{2\sigma_e T_s^2}{\Delta h_f(T_s - T_c)T_c} \quad (3)$$

If we assume that the surface free energies, σ_e and σ_s , are nearly constant in a narrow range of crystallization temperatures, the plot of \bar{l}/T_c against the quantity $1/(T_s - T_c)T_c^2$ gives a straight line, from whose slope the value σ_e will be obtained.⁷ In a previous paper⁷ we found that the value of σ_e of a single crystal of polyethylene from various solvents is dependent on the quantity $(1 - \chi_1)/V_1$, where χ_1 is the thermodynamic interaction parameter and V_1 is the molar volume of solvent.

In this paper we report the effect of solvent on the surface free energy of single crystals of poly(oxymethylene) (POM) from solution and compare this result with the result on the single crystals of polyethylene. In the previous paper,⁷ we evaluated σ_e using eq 3 but eq 2 is not strictly accurate. The term Δf is given more accurately, as shown in Figure 1, as follows

$$\begin{aligned} \Delta f_2 &= \Delta f_0 - \Delta f' \\ &= \frac{\Delta h_f(T_m - T_c)T_c^*}{T_m^2} - \Delta h_f T_c \left(\frac{1}{T_s} - \frac{1}{T_m} \right)^{**} \\ &= \frac{\Delta h_f(2T_m - T_m^2/T_s - T_c)T_c}{T_m^2} \quad (4) \end{aligned}$$

Combining eq 4 with eq 1, we obtain the following equation***

* ref 8.

** $\Delta f'$, the difference between the chemical potential of polymer unit in melt and the unit in the solution is expressed as follows¹¹

$$\Delta f' = RT_c(V_u/V_1)(v_1 - \chi_1 v_1^2)$$

Flory derived melting temperature depression as follows¹¹

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

If V_u/V_1 , χ_1 , and v_1 at melting temperature are assumed to be the same as those at dissolution temperature and on changing $\Delta f'$ to represent quantity per unit volume of perfect crystal at the melting temperature, we can obtain the following equation from the above two equations.

$$\Delta f' = \Delta h_f T_c (1/T_s - 1/T_m)$$

*** Usually the term Δf_0 is approximated by the expression⁴ $\Delta f_0 = \Delta h_f(T_m - T_c)/T_m$. In this case we obtain the following expression for \bar{l} instead of eq 5:

$$\bar{l} = kT_c/d_0\sigma_s + 2\sigma_e T_s/\Delta h_f(T_s - T_c) \quad (5')$$

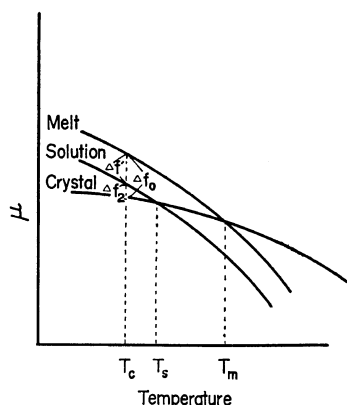


Figure 1. Temperature dependency of the chemical potential of polymer in solid state, solution, and melt.

$$\bar{l} = \frac{kT_c}{d_0\sigma_s} + \frac{2\sigma_e T_m^2}{\Delta h_f(2T_m - T_m^2/T_s - T_c)T_c} \quad (5)$$

In this paper, we evaluate σ_e using eq 5.

On the other hand, the simple thermodynamic consideration leads to the following equation,⁹

$$T_s(l) = T_s(1 - 2\sigma_e/\Delta h_f \cdot \bar{l}) \quad (6)$$

where $T_s(l)$ and T_s are the dissolution temperature of the single crystal of fold length \bar{l} and infinite fold length in solvent, respectively. The plot of $T_s(l)$ against $1/\bar{l}$ gives a straight line, from whose slope the value σ_e can be obtained.⁹

EXPERIMENTAL

Polymer Sample

Delrin 500 was used as the sample of POM for single crystal formation. The sample was extracted for 24 hr at 110°C by a mixture of phenol and ethyl cellosolve (95.5) using a Soxlet extractor; then the residue was dissolved in phenol and the resulting solution poured into methanol. The precipitate was dried for 48 hr at 50°C *in vacuo*. For determination of T_m of POM, and T_s in the POM—solvent system, POM obtained by radiation-induced solid state polymerization of trioxane was also used. The melting temperature T_m of this sample determined by polarized light microscope equipped with hot stage, was 187°C. The sample seemed to consist of extended crystals of POM.¹⁰

Estimation of Thermodynamic Interaction Parameter χ_1

Thermodynamic interaction parameter χ_1 for POM—solvent systems was estimated from Flory's melting temperature depression equation¹¹

$$1/T_s - 1/T_m = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (7)$$

where T_m is the melting temperature of POM crystal of infinite fold length, T_s the melting temperature of the single crystal in the presence of solvent at the volume fraction of solvent v_1 , ΔH_u the enthalpy of fusion per repeating unit, and V_u and V_1 the molar volume of polymer repeating unit and of solvent, respectively. Interaction parameter χ_1 was given by the following equation, where B is the interaction energy density:

$$\chi_1 = BV_1/RT_s \quad (8)$$

Substituting eq 8 into χ_1 of eq 7 we have the following equation

$$(1/T_s - 1/T_m)/v_1 = (R/\Delta H_u)(V_u/V_1)[1 - (BV_1/R)(v_1/T_s)] \quad (9)$$

From the plot of the quantity $(1/T_s - 1/T_m)/v_1$ against v_1/T_s , we can calculate ΔH_u and B . Dissolution temperature was measured by the visual method.

Preparation of Single Crystals from Dilute Solution

The single crystal was prepared by isothermal crystallization from 0.1-% solutions of POM in phenol, *m*-cresol, fulfuryl alcohol, benzyl alcohol, and acetophenone. The details of the



Figure 2. Electron micrograph of single crystal of POM grown from *m*-cresol at 90°C.

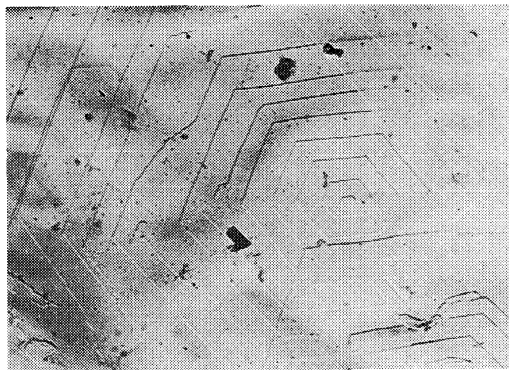


Figure 3. Electron micrograph of single crystal of POM grown from fulfuryl alcohol at 111°C.



Figure 4. Electron micrograph of single crystal of POM grown from benzyl alcohol at 131°C.

method have been described in the previous paper.⁷ The single crystal suspension thus grown isothermally was separated from solvent by filtration at the crystallization temperature and the single crystal mat thus formed was dried *in vacuo* at 60°C for 24 hr. The lamellar thickness of the single crystal was determined by means of small-angle X-ray scattering. Dissolution temperatures T_s and $T_s(l)$ were measured by visual methods in 0.1-% solution. In Figures 2—4 electron micrographs of single crystals formed from *m*-cresol, fulfuryl alcohol, and benzyl alcohol are shown.

RESULTS AND DISCUSSION

Thermodynamic Properties of the Solvents Used in Preparation of Single Crystal of POM

Plots of the quantities $(1/T_s - 1/T_m)/v_1$ against v_1/T_s are shown in Figure 5. The enthalpy of

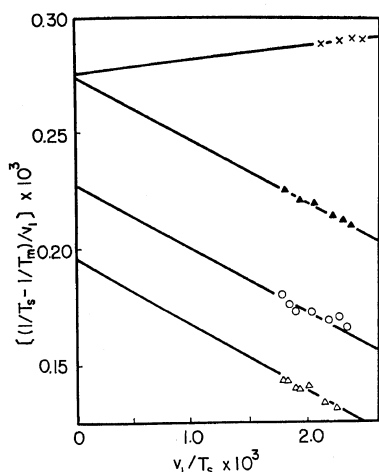


Figure 5. $(1/T_s - 1/T_m)/v_1$ plotted against v_1/T_s for mixtures of POM with *m*-cresol (×), fulfuryl alcohol (▲), benzyl alcohol (○), and acetophenone (△).

Table I. Thermodynamic parameters from POM—solvent systems

Solvent	ΔH_u , cal/mol	χ_1 (at T_s)	V_1 (at T_s)	$(1-\chi_1)/V_1$ (at T_s) $\times 10^3$, cm^{-2}
<i>m</i> -Cresol	1614	-0.05	115.06	9.12
Fulfuryl alcohol	1589	0.26	96.05	7.70
Benzyl alcohol	1978	0.25	115.97	6.47
Acetophenone	1935	0.30	137.37	5.10
av 1796				

fusion per repeating unit of POM, ΔH_u , and the interaction parameter, χ_1 , calculated respectively from the intercept and the slope of straight line obtained are shown in Table I together with the molar volume of solvent and the quantity $(1-\chi_1)/V_1$. Average value of ΔH_u of POM, 1796 cal/mol, agrees with the value reported by Starkweather and Boyd,¹² but is a little larger than the value by Inoue.¹³

Surface Free Energy of Single Crystal of POM

The fold lengths of solution-grown single crystals were plotted against the crystallization temperatures, T_c , at which the crystals were formed, in Figure 6. With these data, \bar{l}/T_c was plotted against $1/(2T_m - T_m^2/T_s - T_c)T_c^2$ according to eq 5. These plots give straight lines

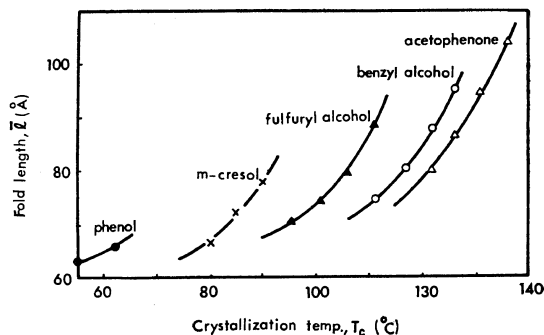


Figure 6. Plots of fold length against crystallization temperature for POM single crystals crystallized from dilute solutions.

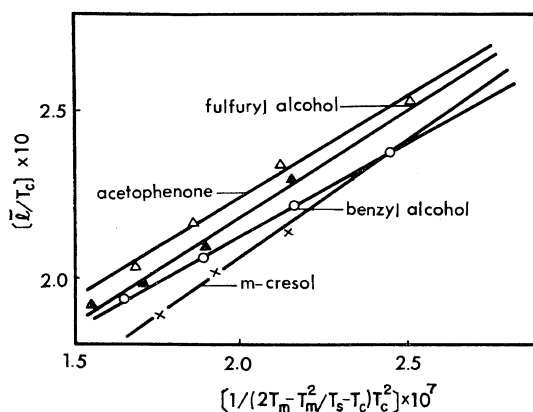


Figure 7. \bar{l}/T_c plotted against $1/(2T_m - T_m^2/T_s - T_c)T_c^2$.

as shown in Figure 7, from whose slopes we obtain the end surface free energies σ_e . The results are shown in Table II. The value of Δh_f , 3.78×10^9 erg/cm³, was calculated from $\Delta H_u = 1796$ cal/mol. In Table II, σ_e obtained from eq 6 is also shown.

Effect of Solvent on the Surface Free Energy of Solution-Grown Single Crystals

From Tables I and II, it is shown that the surface free energy of POM single crystals is dependent on the quantity $(1-\chi_1)/V_1$ as well as the case of polyethylene in a previous paper.⁷ Single crystals with smaller values of σ_e are formed from solvents with larger values of χ_1 and of the molar volume V_1 . The effect of solvent on σ_e of the POM single crystal, however, is not so great compared with the case of the polyethylene single crystal.

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Table II. Surface free energies calculated from eq 5 or 6 for POM single crystal grown from various solvents

Solvent	T_c , °C	\bar{l} , Å	T_s , °C	σ_e , erg/cm ² (from eq 5)	$T_s(l)$, °C	σ_e , erg/cm ² (from eq 6)
Phenol	62.2	66	119.4	—	93.7	77
	55.2	63			93.1	
<i>m</i> -Cresol	90.0	78	132.7	61±3	115.9	63
	85.0	73			114.2	
	80.0	67				
	74.5	66				
Fulfulyl alcohol	111.0	89	146.5	57±3	—	56
	106.0	80			131.0	
	101.0	75			130.2	
	95.5	71			129.4	
Benzyl alcohol	126.0	96	153.2	51±3	—	56
	122.0	88			138.6	
	117.0	81			137.8	
	111.0	75			136.6	
Acetophenone	136.0	104	161.3	55±3	147.9	56
	131.0	95			148.0	
	126.0	87			146.0	
	122.0	81			145.2	

Table III. Surface free energy of polyethylene single crystal from various solvents

Solvent	T_s , °C	σ_e , erg/cm ² (from eq 5)	$[(1-\chi_1)/V_1] \times 10^3$ (at T_s)
Decalin	111.3(108.7) ^a	113(121) ^a	±5 5.08
Toluene	112.5(109.9)	97(93)	±5 4.81
Xylene	114.2(111.1)	88(82)	±5 4.59
Tetralin	115.1(112.6)	94(97)	±5 4.32
<i>n</i> -Octane	121.9(119.2)	90(93)	±5 3.92
<i>n</i> -Hexadecane	127.8(125.0)	83(69)	±5 2.63

^a Figures in parentheses represent data appearing in a previous paper⁷.

In the case of polyethylene single crystals, the values of σ_e were calculated using eq 3. In this paper we recalculate them by means of eq 5. In Figure 8, the value of \bar{l}/T_c of polyethylene single crystal grown in various solvents was plotted against the quantity $1/(2T_m - T_m^2/T_s - T_c)T_c^2$ according to eq 5. The σ_e values calculated from the slopes of the straight lines are shown in Table III together with the values of dissolution temperature T_s and of $(1-\chi_1)/V_1$. Dissolution temperature T_s of polyethylene crystals with infinite fold length was measured with the extended-chain crystal of polymethylene prepared from diazomethane, crystallized under high pressure of 4760 atm at 227°C for 20 hr.¹⁴ The melting temperature of this crystal is 141.4°C,

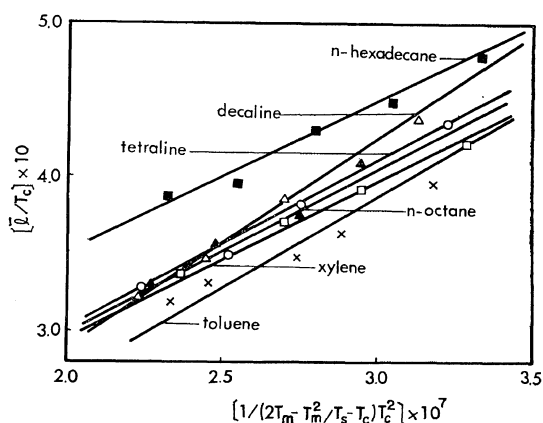


Figure 8. \bar{l}/T_c plotted against $1/(2T_m - T_m^2/T_s - T_c)T_c^2$.

while that of the extended-chain crystal of Marlex 50 polyethylene used in the previous paper was 138.7°C.¹⁴

As shown in Table III, effect of solvents on the value of σ_e is smaller than that of previous data but the value of σ_e is still dependent on the quantity $(1-\chi_1)/V_1$.

From the results described above, it may be concluded that the end surface free energy of the solution energy of the solution-grown polymer single crystals is dependent on thermodynamic properties of solvents used in preparation of single crystals and that the value of σ_e

is smaller as the polymer-solvent interaction parameter χ_1 and the molar volume V_1 of solvent are larger, that is, single crystals with more regular fold may be formed from solvent with larger χ_1 (poor solvent) and with larger molar volume.

Recently, Jackson, and Mandelkern¹⁵ estimated surface free energy of polyethylene single crystals grown from various solvents by plotting $1/T_c$ against $1/\bar{l}T_c$ and concluded that surface free energy is independent of the kind of solvent. According to nucleation theory,⁴ the size of critical nucleus in the chain direction is given by the following equation,

$$l^* = \frac{\kappa T_s}{\Delta h_f (T_s - T_c)} \quad (10)$$

where κ is proportional factor and depends on the surface free energy σ_e and the details of nucleation act. Eq 10 can be converted into the form

$$\frac{1}{T_c} = \frac{1}{T_s} + \frac{2\sigma_e}{\Delta h_f} \frac{1}{l^* T_c} \quad (11)$$

Assuming that l^* is equal to \bar{l} , they plotted $1/T_c$ against $1/\bar{l}T_c$ using crystallization data on polyethylene single crystals grown from various solvents.^{7,15,16} Then they obtained a group of parallel straight lines and concluded that the value of σ_e of polyethylene single crystals grown from various solvents is independent of the kind of solvent. They also obtained the dissolution temperatures T_s of polyethylene in various solvents from the intercepts of the straight lines. These are $118.6 \pm 2.0^\circ\text{C}$ for xylene, toluene, and tetralin; $127.7 \pm 2.0^\circ\text{C}$ for *n*-octane; $113.1 \pm 2.0^\circ\text{C}$ ⁷ (or $137.7 \pm 2.5^\circ\text{C}$)¹⁵ for *n*-hexadecane. These values of T_s are somewhat larger than our experimental data on corresponding systems. We believe, however, that l^* is not equal to \bar{l} . \bar{l} is better represented by eq 5 or 5'. If eq 5' is used instead of eq 10, then the following equation is obtained.

$$\frac{1}{T_c} = \frac{1}{T_s} + \frac{\{\kappa/\Delta h_f + \kappa/d_0\sigma_s(T_c - T_c^2/T_s)\}}{\bar{l}T_c}$$

If $1/T_c$ is plotted against $1/\bar{l}T_c$, the plot is represented by a curve concave upwards for $T_c > T_s/2$. Therefore if the slopes of the plots for various solvents are the same as each other, it

follows that the value of σ_e is dependent on solvents and their value of σ_e and T_s obtained respectively from the slope and the intercept of the plot may be overestimated. In addition, they plotted \bar{l} against $T_s/(T_s - T_c)$, and found that the experimental points for polyethylene single crystals grown from various solvents are on one straight line passing through the origin of the coordinate and gave evidence that l^* is equal to \bar{l} . This fact may suggest that σ_e is independent of solvent. However detailed observation of experimental points for individual solvent systems results in plots with different slopes.

In most cases of preparation of polymer single crystals from solution, however, solvents with similar thermodynamic properties are usually used. Thus the values of σ_e may not differ significantly.^{15,17-20}

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