

Temperature Dependence of Chain Conformation in the Vicinity of Crystallization Temperature for Single Crystals

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To discuss the change of polymer chain conformation with temperature in connection with the single crystal formation, the viscosity number of fractionated linear polyethylene was measured in decalin and tetralin (both are "good" solvent), and diphenyl ether ("bad" solvent), in temperature range down to a temperature as near as possible to the crystallization temperature. According to the results, change in chain conformation in "good" and "bad" solvent was schematically illustrated. In addition, it was pointed out that the modified-Flory equation for excluded volume effect is applicable even to the system below the theta-temperature in some temperature range.

INTRODUCTION

Preparation of single crystals of crystalline polymers is usually carried out from dilute solution of about 0.1% polymer concentration. We have discussed¹⁻³⁾ effects of solvent during crystal formation, on linear polyethylene, especially with regard to "goodness" (or "badness") and size of the solvents in which the single crystals were formed. However, little has been known about the temperature variation of chain conformation in the vicinity of crystallization temperature. Ueyama measured intrinsic viscosities of unfractionated linear polyethylenes in xylene⁴⁾ and tetralin,⁵⁾ which are known as "good" solvent for polyethylene, in temperature range 95-120°C and 100-140°C, respectively, and discussed the temperature variation of the intrinsic viscosities as a compensatory effect of solvation and flexibility of chains. However, the lowest temperature of his measurements seems to be high for discussion for single crystal formation.

The purpose of this work is to discuss the change in polymer chain conformation with temperature in connection with the single crystal formation, by measuring the viscosity number of fractionated linear polyethylene in "good" and "bad" solvent, in temperature range from higher temperature down to a temperature as near as possible to the crystallization temperature.

EXPERIMENTAL RESULTS

A linear polyethylene Sholex 6009 was fractionated into about 20 fractions in a column designed by us,⁶⁾ among which three fractions were used for the experiment.

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Table 1. Equilibrium Melting Temperature T_m° , highest Crystallization Temperature $T_{c(\text{highest})}$, and Critical Consolute Temperature T_{crit} for Sample FIII.

Solvent	T_m° (°C)	$T_{c(\text{highest})}$ (°C)	T_{crit} (°C)
Decalin	108.7	83.9	
Tetralin	112.6	89.8	
Diphenyl ether	122.0	109.1	151.5(FIII)

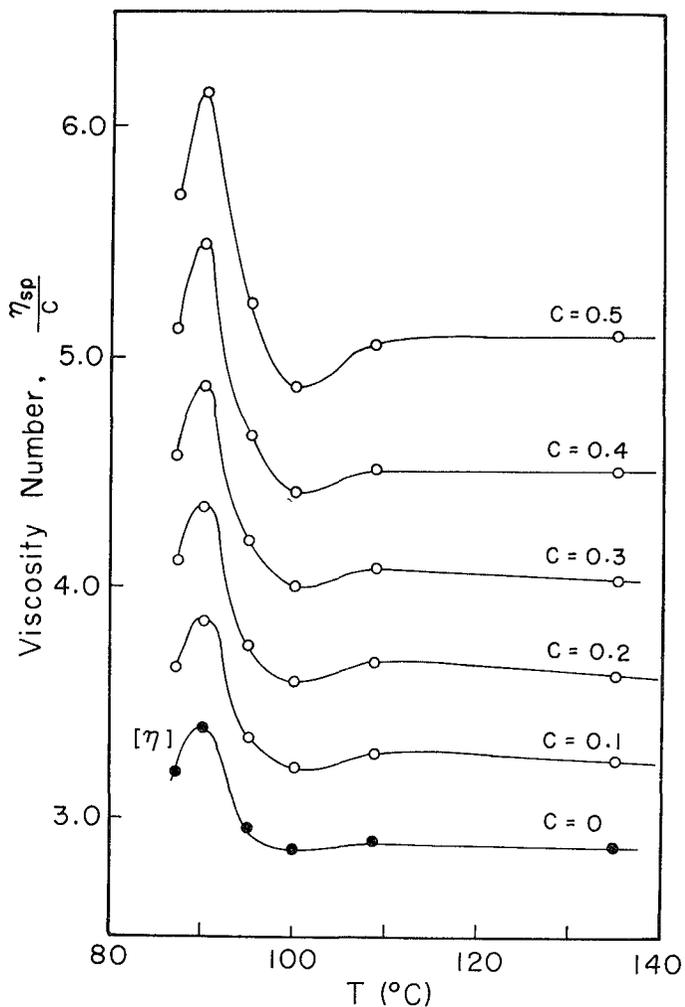


Fig. 1. Plots of viscosity number *vs.* temperature for polyethylene FIII ($M_w=1.7 \times 10^5$) in Decalin. *c* in g/dl.

These are designated as FI, FII, and FIII. Their molecular weights were determined from the intrinsic viscosity in decalin $[\eta]_{\text{decalin}}$, according to the equation:

$$[\eta]_{\text{decalin}, 135^\circ\text{C}} = 6.2 \times 10^{-4} M_w^{0.70}$$

$$\text{FI}; \quad M_w = 2.0 \times 10^4$$

FII; $M_w = 7.3 \times 10^4$ FIII; $M_w = 1.7 \times 10^5$

Decalin and tetralin were used as "good" solvent for the polymer and diphenyl ether was used as "bad" solvent. The latter is known to behave as a θ -solvent at 163.9°C.

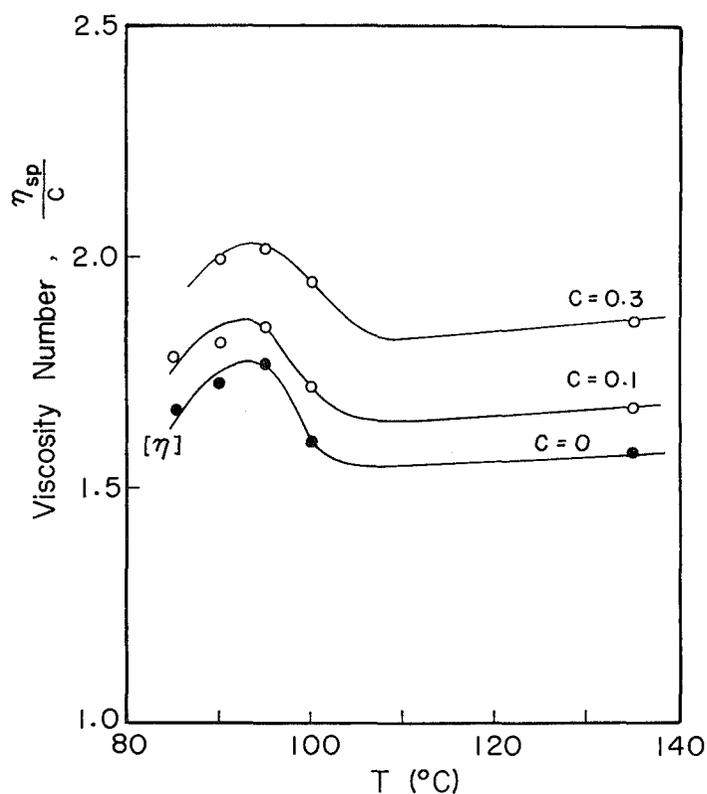


Fig. 2. Plots of viscosity number *vs.* temperature for polyethylene FII ($M_w = 7.3 \times 10^4$) in Decalin. *c* in g/dl.

Table 2. Temperature Variation of Intrinsic Viscosity $[\eta]$ and Huggins Constant k' in Decalin for Polyethylene Fractions with Different Molecular Weight.

Temp(°C)	FI $M_w = 2.0 \times 10^4$		FII $M_w = 7.3 \times 10^4$		FIII $M_w = 1.7 \times 10^5$	
	$[\eta]$ (dl/g)	k'	$[\eta]$ (dl/g)	k'	$[\eta]$ (dl/g)	k'
85			1.67	0.44		
87					3.20	0.40
90	0.70	0.35	1.73	0.33	3.34	0.39
95	0.74	0.32	1.77	0.35	2.98	0.41
100			1.60	0.47	2.86	0.41
108.7					2.90	0.41
135	0.63	0.49	1.58	0.39	2.90	0.41
163.9					2.90	0.44

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The solution viscosity measurements were carried out in a modified Ubbelohde-type dilution viscometer designed by us,⁷⁾ in temperature range from higher temperature down to a temperature as near as possible to the crystallization temperature: for decalin system, 87-163.9°C; tetralin, 97-130°C; and diphenyl ether, 148-163.9°C.

Data on single crystal formation, *i.e.*, the equilibrium melting temperature in the solvent T_m° , the highest crystallization temperature $T_{c(\text{highest})}$, and the critical

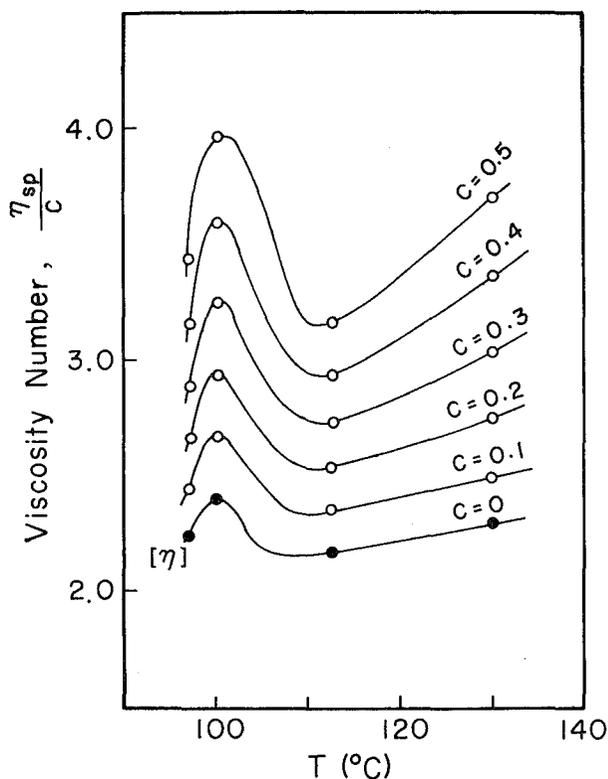


Fig. 3. Plots of viscosity number *vs.* temperature for polyethylene FIII ($M_w=1.7 \times 10^5$) in tetralin. *c* in g/dl.

Table 3. Temperature Variation of Intrinsic Viscosity $[\eta]$ and Huggins Constant k' in tetralin and diphenyl ether Polyethylene for Fraction FIII ($M_w=1.7 \times 10^5$).

Temp (°C)	Tetralin		Diphenyl ether	
	$[\eta](\text{dl/g})$	k'	$[\eta](\text{dl/g})$	k'
97	2.24	0.40		
100	2.41	0.42		
112.6	2.17	0.40		
130	2.28	0.49		
148			0.97	1.22
153			1.14	0.81
158			1.30	0.74
163.9			1.35	0.74

consolute temperature T_{crit} , which were cited from the preceding paper,²⁾ were shown in Table 1.

The experimental results on solution viscosities for "good" and "bad" solvent systems are shown in Figs. 1 - 3, and Fig. 4, respectively. The numerical values of the intrinsic viscosity $[\eta]$ and the Huggins constant k' are listed in Tables 2 and 3.

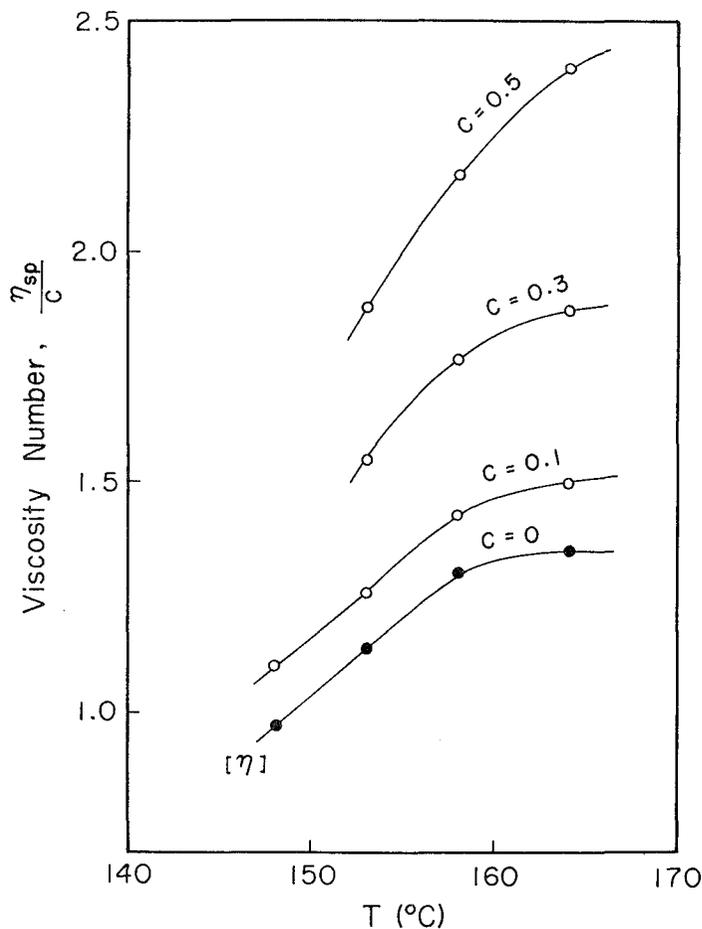


Fig. 4. Plots of viscosity number *vs.* temperature for polyethylene FIII ($M_w=1.7 \times 10^6$) in diphenyl ether. c in g/dl.

DISCUSSION

As obvious from Figs. 5 and 6, summarized for sample FIII, behavior of $[\eta]$ and k' in "good" and "bad" solvent are remarkably different in each other. In good solvent, $[\eta]$ slightly decreased then increased markedly, passed through a maximum, and again decreased with decreasing temperature, but k' was almost constant in the temperature range examined here. On the other hand, in bad solvent, $[\eta]$ decreased and k' increased with decreasing temperature below theta temperature. These results will be discussed in detail with regard to chain conformation, in the following.

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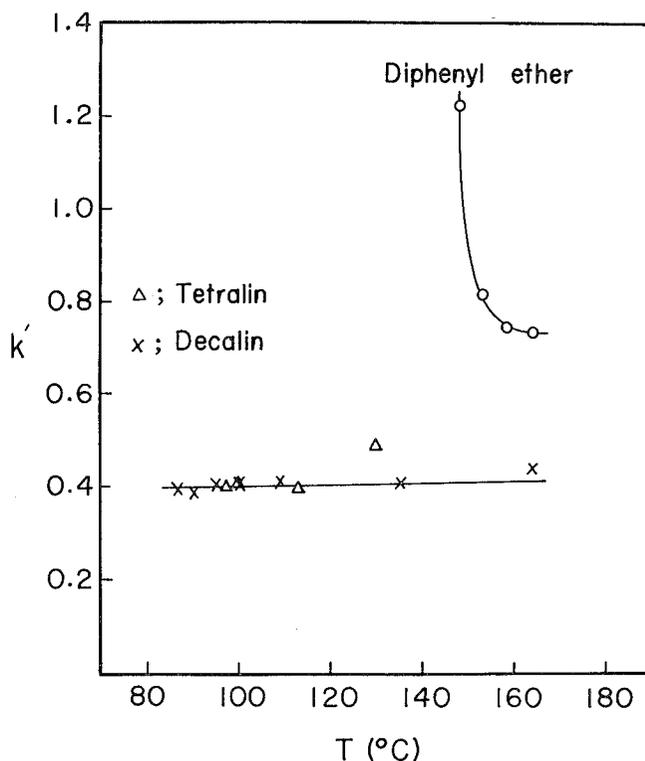


Fig. 5. Variation of the Huggins constant k' with temperature in "good" solvents (decalin and tetralin) and in "bad" solvent (diphenyl ether).

"Good" Solvent System

The temperature variation of the intrinsic viscosities at theta temperatures $[\eta]_\theta$ is related to the unperturbed mean square end-to-end distance $\langle R_0^2 \rangle$ by the equation:

$$\frac{d \ln [\eta]_\theta}{dT} = \frac{3 d \ln \langle R_0^2 \rangle}{2 d T} \quad (1)$$

In our previous paper,⁷⁾ we reported

$$\frac{d \ln \langle R_0^2 \rangle}{dT} = -1.21 \times 10^{-3} \quad (2)$$

for linear polyethylene. Therefore, $[\eta]_\theta$ at given temperatures can be calculated by using the numerical value at 163.9°C (θ -temperature in diphenyl ether), $[\eta]_\theta = 1.35$, and Eqs.(1) and (2). Further, the hydrodynamic expansion factor denoted by α_η can be estimated by

$$\alpha_\eta^3 = [\eta] / [\eta]_\theta \quad (3)$$

In Table 4, $[\eta]$ and α_η at each temperature calculated by this way were shown.

On the basis of the change in α_η and the behavior of k' with decreasing temperature, we may propose Fig. 7 as a schematic representation on the change in chain conformation in the vicinity of crystallization temperature.

At point "a" in Fig. 6, polyethylene chain is dispersed monomolecularly in decalin

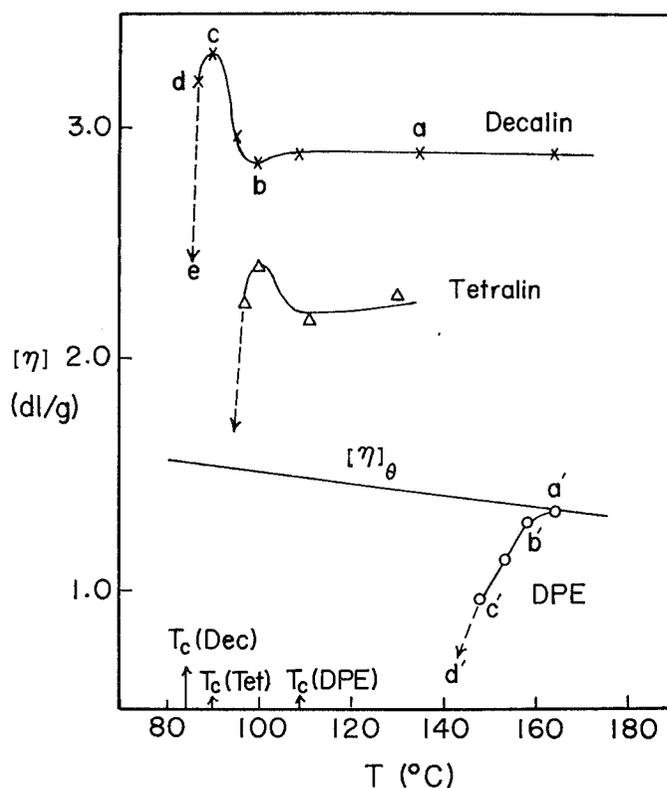


Fig. 6. Variation of the intrinsic viscosity $[\eta]$ with temperature in "good" solvents (decalin and tetralin) and in "bad" solvent (diphenyl ether). $T_c(\text{Dec})$, $T_c(\text{Tet})$, and $T_c(\text{DPE})$ denote the highest crystallization temperatures in decalin, tetralin, and diphenyl ether, respectively.

Table 4. Temperature Variation of α_η for Sample FIII ($M_w=1.7 \times 10^5$) in Decalin and Tetralin.

Decalin							
Temp (°C)	87	90	95	100	108.7	135	163.9
$[\eta]$	3.20	3.34	2.98	2.86	2.90	2.90	2.90
$[\eta]_\theta$	1.55	1.54	1.53	1.51	1.49	1.42	1.35
α_η^3	2.06	2.17	1.95	1.89	1.95	2.04	2.15
α_η	1.27	1.29 _s	1.25	1.24	1.25	1.27	1.29
Tetralin							
Temp (°C)			97	100	112.6	130	
$[\eta]$			2.24	2.41	2.17	2.28	
$[\eta]_\theta$			1.52	1.51	1.48	1.44	
α_η^3			1.47	1.60	1.47	1.58	
α_η			1.14	1.17	1.14	1.16 _s	

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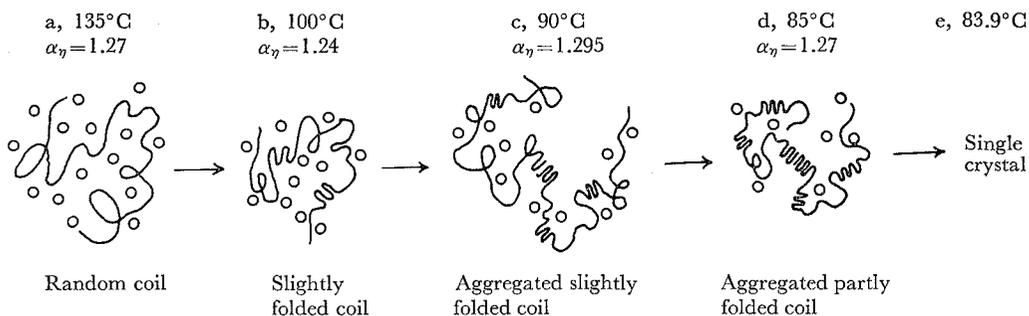


Fig. 7. Schematic representation of chain conformation of polyethylene FIII in decalin(good solvent) in the vicinity of crystallization temperature for single crystal formation.

with $\alpha_\eta=1.27$ as a random coil in good solvent. With decreasing temperature, solvation and at the same time chain flexibility are reduced (*i.e.*, “trans” conformation in the chain is increased), thus the chain tends to folded partially. Decrease in α_η at point “b” may reflect the existence of such folded conformation. But molecules as a whole may behave as random coils. Such tendency to fold up (in other words, interaction between polymer segments), may be increased not only intra-molecularly but also inter-molecularly, and may result in the aggregated slightly folded coil as shown in “c” of Fig. 7 at the maximum point of the curve in Fig. 6. With further decrease in temperature, folding are increased (point “d” in Fig. 6), and finally leads to the formation of single crystal (at 83.9°C).

It was observed that the appearance of dilute solutions down to 85°C (point “d”) was transparent, but it became abnormal at 83.9°C. Therefore, in a very small range of temperature as 1.1°C, an abrupt change in conformation should take place. Viscosity measurement was not able at 83.9°C, but one may expect large value for k' and small one for $[\eta]$. For such crystallizable polymer, θ -temperature can not be realized, because preferred conformation as “trans” may contribute to form intra-molecular folding and also inter-molecular aggregation, before reaching to a temperature at which the conditions for θ -solvent are fulfilled.

The effect of molecular weight of polymer on the $[\eta]$ *vs.* temperature curve is understood from Table 2, and Figs.1 and 2 as that the maximum position of higher molecular weight sample locates at lower temperature than the lower molecular weight sample.

Finally, comparison of the $[\eta]$ *vs.* temperature curves for decalin and tetralin systems (Fig. 6) concludes that with tetralin which is worse solvent than decalin, the maximum point of the curve locates at higher temperature and the height of the peak is less than that of decalin. These results are in accord with thermodynamic consideration.

“Bad” Solvent System

Diphenyl ether is a bad solvent for polyethylene, and behaves as a θ -solvent at 163.9°C. In this work, solution viscosities of sample FIII were measured at 163.9°C down to 148°C. For this polymer sample, the critical consolute temperature T_{crit}

is 151.5°C. So the lowest temperature, 148°C, for measurement is said to be 3.5°C lower than T_{crit} . Owing to their low polymer concentrations, the solutions used for viscosity measurements were transparent within these temperature range even below T_{crit} (=151.5°C). However, below 148°C, the solution became turbid, which makes unable one to measure viscosity. In the temperature range between T_{crit} and θ , the polymer chain may be expected to disperse monomolecularly in solution.

With non-crystallizable polystyrene, Orofino⁸⁾ investigated variation of chain conformation in cyclohexane below its theta temperature (35°C), and discussed applicability of various theories on exclude volume effect, and the Huggins constant k' .

The present polymer, linear polyethylene, is different from Orofino's in that it is crystallizable and has much higher θ -temperature. Chain conformation of polyethylene below θ -temperature is, in this sense, significant to examine from the stand point of both exclude volume theory and single crystal formation.

In the first place, we shall refer to the change in k' shown in Fig. 5. Peterson and Fixman⁹⁾ derived an expression of k' as a function of polymer excluded volume, which predicts $k'=0.6912$ at the θ -temperature. Our result of $k'=0.74$ at the θ -temperature (163.9°C) is in accord fairly well with the value given by them. Also pointed out is that our experimental k' values at slightly below the θ -temperature are qualitatively acceptable by applying their expression to the region where the exclude volume effect is negative.

Secondary, we will discuss the temperature variation of the mean square end-to-end distance $\langle R^2 \rangle$ below θ -temperature. According to Flory,¹⁰⁾ the expansion factor α_R defined by

$$\alpha_R^2 = \langle R^2 \rangle / \langle R_0^2 \rangle \quad (4)$$

is related to the exclude volume parameter z by the equation

$$\alpha_R^5 - \alpha_R^3 = 2.60z \quad (5)$$

where,

$$z = (3/2\pi a^2)^{3/2} \beta n^{1/2}$$

in which n , a , and β are the number of segments in a chain, length of a segment, and segment exclude volume, respectively. Eq.(5) was later modified by Stockmayer,¹¹⁾ taking into account the result from the perturbation theory, to

$$\alpha_R^5 - \alpha_R^3 = 1.276z \quad (6)$$

which is often called the modified-Flory equation. Eq.(6) is alternatively represented, by parameters used by Flory, in the following way;

$$\alpha_R^5 - \alpha_R^3 = 1.276 \frac{6^{3/2}}{4^{3/2}\pi^{3/2}} \frac{2\bar{v}^2}{N_A V_1} \left(\frac{\langle R_0^2 \rangle}{M} \right)^{-3/2} \psi_1 \left(1 - \frac{\theta}{T} \right) M^{1/2} \quad (7)$$

where, ψ_1 , \bar{v} , V_1 , M , and N_A are the entropy parameter, specific volume of polymer, molar volume of solvent, molecular weight of polymer, and Avogadro's number, respectively. If one has numerical values for these parameters, one can estimate α_R at specified temperatures. This will be done later.

On the other hand, the ratio of intrinsic viscosities $[\eta]/[\eta]_\theta$ in the vicinity of the θ -temperature is known¹²⁾ to be expressed by

$$[\eta]/[\eta]_{\theta} = \alpha_{\eta}^3 = \alpha_R^p \quad (8)$$

Whose parameter p may be assumed to be 2.66 after Fixman.¹³⁾ Therefore, by the use of the experimental values of $[\eta]/[\eta]_{\theta}$, we can estimate α_R experimentally, as shown in Table 5 and Fig. 8.

Theoretical curve given by the modified-Flory equation [eq(7)] was obtained by using the numerical values appeared in our previous paper;⁷⁾

$$\langle R_0^2 \rangle / M = 1.15 \times 10^{-16}$$

$$\phi_1 = 1.00$$

and the relation

$$\bar{v} = 1.152 \times 8.8 \times 10^{-4} t, \quad (t \text{ in } ^\circ\text{C})$$

for \bar{v} , given by Chiang and Flory.¹⁴⁾ The resulted curve is shown in Fig. 8, and whose

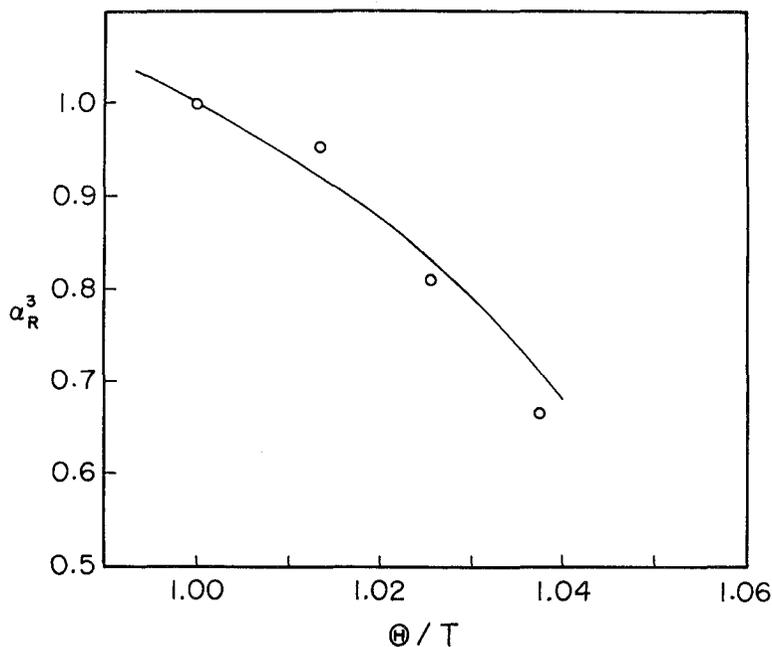


Fig. 8. Comparison of experimentally obtained temperature variation of expansion factor α_R below theta-temperature, for system linear polyethylene-diphenyl ether, with theoretical curve calculated from modified-Flory equation. Sample used is FIII ($M_w = 1.7 \times 10^5$).

Table 5. Temperature Variation of α_{η} and α_R for Sample FIII ($M_w = 1.7 \times 10^5$) in Diphenyl Ether.

Temp($^{\circ}$ C)	148	153	158	163.9
$T(^{\circ}$ K)	421.2	426.2	431.2	437.1 (θ)
θ/T	1.0377	1.0255	1.0137	1.0000
α_{η}^3	0.70	0.83	0.96	1.00
α_{η}	0.888	0.940	0.987	1.00
α_R	0.875	0.937	0.985	1.00

Table 6. Calculation of α_R According to Modified-Flory Equation, for Sample FIII in Diphenyl Ether.

Temp(°C)	148	153	158	163.9
\bar{v} (ml/g)	1.1533	1.1533 ₄	1.1534	1.1534 ₄
V_1 (ml)	163	168	172	177
$\alpha_R^5 - \alpha_R^3$	-0.1437	-0.0943	-0.0495	0
α_R	0.892	0.942	0.973	1

details of calculation being given in Table 6.

As obvious from Fig. 8, the experimental point is in accord with the theoretical curve at least in the temperature range from 163.9°C (θ -temperature) down to 153°C, but slightly deviates at 148°C. This fact may mean that the modified-Flory equation is valid even below θ -temperature ($\alpha_R < 1$) for such crystallizable polymer as polyethylene.

As mentioned above, the θ -temperature of crystallizable polymer is usually high, therefore, at temperatures slightly lower than the θ -temperature, polymer chain, owing to the thermal movement of the chain portions, may behave as a slightly contracted random coil.

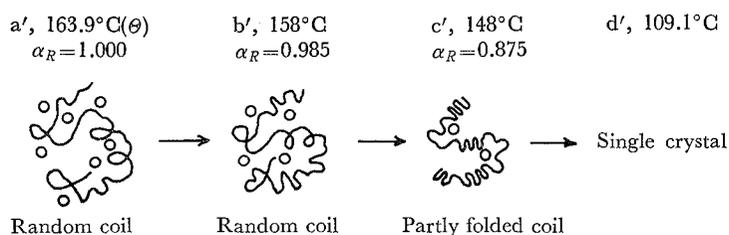


Fig. 9. Schematic representation of chain conformation of polyethylene FIII in diphenyl ether (bad solvent) in a temperature range below theta temperature.

Thus, we may propose schematic representations as shown in Fig. 9 for the change of chain conformation below θ -temperature. In the temperature range from θ down to T_{crit} , the polymer chain may be in random coil conformation, but below T_{crit} intra-molecular folding begin to take place, and with further decreasing temperature increased folding together with inter-molecular aggregation finally result in the formation of single crystal.

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