Relative high pressure crystallization behaviour of cis — and trans-1, 4— polyisoprenes

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Cis — and trans-1, 4-polyisoprenes have different ranges of crystallization temperatures, the respective ranges of degree of supercooling, however, are similar.

The variation of the crystal growth rate with temperature can be represented at all pressures by an equation derived from the Lauritzen and Hoffman theory.

For the trans- isomer it appears crystals of the same form grow by the same mechanism as at atmospheric pressure. The major effect is on the melt rather than on the crystals. The variation of the crystal growth rate with pressure can be largely accounted for by the increases in T_m and T_f.

INTRODUCTION

Trans-1, 4—polyisoprene (TPI) and cis-1, 4—polyisoprene (CPI) differ only in the position of the —CH_3 group with respect to the double bond. However, the maximum crystal growth rate, at atmospheric pressure, of TPI is ≈25 times that of CPI. These two isomers are the only polymers, in the knowledge of the authors, whose crystal growth rate as a function of pressure has been studied [1, 3].

TPI crystallizes in two forms; low melting form (LMF) and high melting form (HMF), with equilibrium melting temperatures of 78 and 87° C respectively [4]. LMF spherulites contain only crystals with an orthorhombic unit cell and HMF spherulites crystals with a monoclinic unit cell [5, 7]. CPI crystals have an equilibrium melting point of 39° C [8] and its unit cell is monoclinic [6], etc.

The effect of pressure on actual melting temperatures and on the equilibrium melting point for LMF and HMF-TPI has been reported previously [9] as 15 K kbar⁻¹. For CPI it has been estimated to be 13.25 K kbar⁻¹[10].

If crystal growth of chain-folded crystals at a temperature T, can be described by a secondary nucleation model [11], the linear growth rate can be represented by an equation of the form:

\[ G = G_o \exp \left( -\frac{U^*}{R(T - T_m)} \right) \exp \left( -\frac{a b \sigma_e}{\Delta G_c k T} \right) \]  

The first exponential is a mobility term and contains the activation energy (U*) for transport of “segments” of molecules to the site of crystallization. T_m is a hypothetical temperature at which all motion associated with viscous flow ceases, and is somewhat below the glass transition temperature. R is the gas constant.

The second exponential is a driving force term and contains the Gibbs free energy change on crystal formation (ΔG_c) and the work per area to create the fold surface (σ_e) and side surfaces (σ). The value of α will be 4 if only one nucleus per growth face is formed (regime I) and 2 if multiple nucleation occurs on the growth face (regime II). b is the thickness of the layer added to the growth face measured in the growth direction and k is the Boltzmann constant.

The preexponential factor G_o contains terms largely insensitive to temperature compared to the exponential terms. It contains the segmental jump frequencies and has dimensions of length per time.

Equation 1 is often expressed by

\[ G = G_o \exp \left( -\frac{U^*}{R(T - T_m)} \right) \exp \left( -\frac{K_s}{(T - T_0) f} \right) \]  

where

\[ K_s = \frac{a b \sigma_e T_m}{\Delta H_m k} \]  

and

\[ f = \frac{2 T}{T_0 + T} \]  

this expression assumes that ΔG_c can be expressed by

\[ \Delta G_c = \left( \Delta H_m \frac{\Delta T}{T_m} \right) \left( \frac{2 T}{T_m} \right) \]
CRYSTAL GROWTH RATES

The growth rates at all temperatures and pressures are given for LMF crystals in Fig. 1, for HMF crystals in Fig. 2 and for CPI crystals [10] in Fig. 3. The experimental details for the obtaining of Figs. 1 and 2 have been given elsewhere [1]. When these figures are compared a difference in behaviour between TPI and CPI crystals is evident - both forms of TPI present a decrease in the maximum crystal growth rate with increasing pressure up to 3.5 kbar whilst CPI presents an initial increase of crystal growth rate with increasing pressure up to 1.0 kbar and then this maximum remains approximately constant up to 3.5 kbar.

Using the equilibrium melting temperatures of the two crystalline forms of TPI [14, 9] and CPI [8, 10], the crystal growth rates for LMF and HMF-TPI and CPI crystals are plotted as a function of degree of supercooling at pressures of 1 bar, 2 kbar and 3, kbar in Figs. 4 to 6. From these graphs it is interesting to notice that whilst TPI and CPI have different ranges of crystallization temperatures, the respective ranges of AT are similar. The curves for LMF and HMF-TPI crystals present a cross-over point at all pressures. The values for the degree of supercooling at which the cross-over points occur are given in Table I for all pressures. The cross-over point can be considered to be pressure independent. It suggests that the major effect of pressure is on the melt rather than on the crystal properties. The value of the crystallization temperature at which LMF and HMF-TPI have equivalent growth rate together with this growth rate are listed in the same table. The variation of the cross-over point temperature with pressure is depicted in Fig. 7. It shows a linear increase with temperature. the equivalent growth rate as a function of crystallization pressure is shown in Fig. 8. It decreases with increasing crystallization temperature analogously to the maximum growth rate.

The HMF crystals have faster growth rates than LMF at large supercoolings, whilst LMF crystals grow faster than HMF at small supercoolings. This occurs as the available driving force for growth is initially larger for LMF but increases much more rapidly with increasing supercooling for HMF crystals [19, 14]. CPI crystals have much slower growth rates than both TPI forms at atmospheric pressure. This difference, however, decreases as CPI crystal growth rate increases initially with pressure whilst LMF and HMF-TPI crystal growth rates decrease steadily with pressure. The curves for CPI and LMF-TPI crystals cross at 3 kbar (fig. 6).

Crystal growth rate parameters

The parameters \( G_0 \) and \( K \) can be calculated from experimental values of crystal growth rate using equation 2. Independently measure values of \( U^* \) and \( T_\infty \) are not available, partly as it is not clear what
“segment” lengths are involved in the thermally activated transport process. \( U^* \) and \( T_\alpha \) can either be considered as adjustable parameters or the term approximated by the William-Landel-Ferry relation [15]

\[
\frac{U^*}{R(T - T_\alpha)} = \frac{c_1}{R(c_2 + T - T_g)}
\]  

where \( T_g \) is the glass transition temperature, \( c_1 \) and \( c_2 \) are constants taken to be 17.24 kJ/mol and 51.6° C respectively. The application of the different methods for the calculation of \( K_g \) and \( G_0 \) for both crystal forms of TPI has been discussed elsewhere [16].

Table II gives the values of \( G_0 \) and \( K_g \) obtained. For CPI the value for \( U^* \) was floated to get the best fit and \( T_\alpha \) was assumed to be

\[ T_\alpha = T_g = 51.6\, ^\circ C \]

The \( T_g \) for TPI is known to increase 24° C per kbar⁻¹ [17], therefore \( T_\alpha \) at high pressure was considered to be

\[ T_\alpha = T_g + 24\, ^\circ C \times P_c - 51.6\, ^\circ C \]

where \( P_c \) is the value of the crystallization pressure expressed in kbar.

The values of \( K_g \) and \( G_0 \) for CPI are given in Table II. The Table shows that for TPI the values of \( G_0 \) and \( K_g \) are largely pressure independent, however, they show an increase at the highest pressure; for CPI there is a noticeable increase of both parameters from 1 bar to 3.0 kbar.

**Estimation of the regime of crystallization**

The nucleation constant \( K_g \) can take the values

\[ K_g(1) = \frac{4\sigma_c bT_m}{k\Delta H_m} \]

or

\[ K_g(II) = \frac{4\sigma_c bT_m}{k\Delta H_m} \]

or some value in between depending on the mechanism of crystallization [11].

The distinction between both regimes may be estimated by the dimensionless parameter [18].

\[
z \approx 10^{1.8} \frac{(L/a)^2}{X / \Delta T}
\]

where

\[ X = K_g(1) \quad \text{for } z \leq 0.01 \]

and

\[ X = 2K_g(II) \quad \text{for } z \geq 1 \]

It is possible to estimate the range of values of \( L \) consistent with regime I or regime II behaviour using the values of \( K_g \) in Table II.

\[
L(1) \leq 2 a \left\{ 10^{-5} \exp \left( \frac{K_g}{T \Delta T} \right) \right\}
\]

\[
L(II) \geq 2 a \left\{ 10^{-3} \exp \left( \frac{2K_g}{T \Delta T} \right) \right\}
\]

The value of \( L \) has to be “reasonable”. It is difficult, however, to decide which is a “reasonable” value for \( L \); estimates for polyethylene suggest that \( L \) is of the order of magnitude of 1-10 \( \mu \)m [19]. When \( L \) estimated is smaller than 1 \( \mu \)m it is assumed that regime II is approached. \( L(1) \) and \( L(II) \) are shown in Fig. 9 as a function of crystallization temperatures for LMF-TPI crystals obtained at 1 bar. Similar plots are obtained for LMF and HMF-TPI crystals at all pressures studied.
Both crystal forms of TPI follow a regime II type mechanism for a large part of the temperature ranges studied at all pressures, only at very low degree of supercooling an intermediate regime seems to describe the crystal formation better.

For CPI an intermediate regime is followed at atmospheric pressure at all temperatures studied, but it is displaced to regime I when pressure is increased.

Estimation of surface energies

The values of $\sigma$ can be obtained from the experimental values of $K_e$ using equation 3. From the estimation of the regime it can be assumed that $\alpha = 2$ for crystal forms of TPI. For CPI $\alpha$ was estimated to be 2.5 at 1 bar, 2.75 at 0.5 kbar, 3.0 for pressures 1-1.5 kbar, 3.5 at 2 kbar and 4 at 3 kbar. The values of $\sigma_e$ are listed in Tables III to V. It should be noted that these calculations assume that $\Delta H_m$ does not change with pressure as it is effectively observed for branched polyethylene [1, 20]. The values of $\sigma_e$ for TPI have been previously calculated [9]. Edwards [21] reports $\sigma_e$ for CPI crystallized at atmospheric pressure and assumes that it does not change significantly with pressure. The value of $\sigma$ can then be calculated by

$$\sigma = \frac{\alpha \sigma_e}{\sigma_e}$$
The values of $a$ for LMF and HMF-TPI and CPI crystals grown at several pressures are listed in Tables III to V.

CONCLUSIONS

The crystal growth rate versus temperature curves for LMF and HMF-TPI crystals are of the same form at all pressures studied. Crystallization at increasing pressures shifts the curves to higher temperature ranges. The maximum crystallization growth decreases continually with increasing pressure for both forms of TPI and increases up to 1.0 kbar, remaining thereafter constant for CPI. TPI and CPI have different ranges of crystallization temperatures, the respective ranges of degree of supercooling, however, are similar.

The variation of the crystal growth rate with temperature can be represented at all pressures by an equation derived from the Lauritzen and Hoffman theory [11].

For TPI it appears that, over the pressure range studied, crystals of the same form grow by the same mechanism as at atmospheric pressure. The major effect is on the melt rather than on the crystals. The variation of the crystal growth rate with increasing pressure can be largely accounted for by the increase of 15 K Kbar$^{-1}$ of $T_m$ [9] and of 20 K kbar$^{-1}$ of $T_g$ [2].

For CPI however, the estimates for the regime of crystallization suggests that a change in mechanism of crystallization occurs when pressure is increased.

TPI and CPI have appreciable differences in melting behaviour. The differences of the thermodynamic variables on melting of CPI and TPI might account largely for the differences in crystallization.

The enthalpy change on melting of TPI is appreciably greater than that for CPI ($> 3$ times). As a general rule, for low molecular weight hydrocarbons, isomers in transconfigurations have greater enthalpy change on melting than those with cis-configurations. However, the differences are not so great as in this case. A possible explanation has been given [22] considering the greater asymmetry of the chains in the CPI crystals where left and right handed helices are alternated.

The configurational entropy on melting for TPI is also much greater than for CPI ($> 2.5$ times). This has been attributed [22] to a greater flexibility of the TPI chains in the liquid state. This factor favours the TPI crystallization, the difference in the arrangement of TPI and CPI molecules within the crystal, however, seems to be a more significant factor. LMF-TPI molecules are asymmetric but all the molecules passing through any one crystal are identical — either right handed or left handed molecules [6]. CPI presents left and right handed molecules in the same crystal; this effect seems to be particularly important since adjacent chains in the considered growing plane [110] present different orientations. A segregation may then occur for LMF-TPI, but while this segregation may be slight it is probably much more significant for CPI. This segregation could result in a decrease of the growth rate.

At high pressures the change in mechanism of CPI seems to be the main reason for the difference in behaviour.

**TABLE I**

<table>
<thead>
<tr>
<th>$P_c$ (kbar)</th>
<th>$\Delta T$ (°C)</th>
<th>$G$ (nms$^{-1}$)</th>
<th>$T_c^{\text{LMF}}$ (°C)</th>
<th>$T_c^{\text{HMF}}$ (°C)</th>
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### Table II

PARAMETERS FOR THE GROWTH RATE EQUATION

<table>
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<tr>
<th>$P_c$ (kbar)</th>
<th>$G_0^\text{LMF}$ (m$^{-1}$)</th>
<th>$K_r^\text{LMF} \times 10^{-5}$ (K$^2$)</th>
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<th>$K_r^\text{CPI} \times 10^{-5}$ (K$^2$)</th>
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### Table III

SURFACE ENERGIES FOR LMF-TPI CRYSTALS

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<th>$P_c$ (kbar)</th>
<th>$\Delta H_m$</th>
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### Table IV

SURFACE ENERGIES FOR HMF-TPI CRYSTALS

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### Table V

SURFACE ENERGIES FOR CPI CRYSTALS

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### Footnotes

**TABLES III AND IV**

☆ Calculated considering $\Delta H_m$ pressure independent.

® Obtained from lamellar thickness data.

**TABLES V**

☆ Calculated considering $\Delta H_m$ pressure independent.

® Obtained from lamellar thickness data [22].

### Abreviations

- CPI: cis-1,4-polyisoprene.
- HMF: high melting form.
- LMF: low melting form.
- TPI: trans-1,4-polyisoprene.
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SYMBOLS

b    thickness of a monomolecular layer in the crystal.
f    correction factor for $\Delta H_m$.
$G_0$    crystal growth rate constant.
G    Crystal growth rate.
$\Delta G_c$    change of Gibbs free energy on crystalization.
$\Delta H_m$    change of enthalpy on melting.
k    Boltzmann constant.
$K_n$    nucleation constant.
$K_{g(I)}$    nucleation constant for regime I.
$K_{g(II)}$    nucleation constant for regime II.
L    length of a crystal.
P    pressure.
R    gas constant.
T    temperature.
$T_g$    glass transition temperature.
$T_m$    melting temperature.
$T_m^*$    equilibrium melting temperature.
$T_{\infty}$    theoretical temperature somewhat below $T_g$.
$\Delta T$    supercooling.
$U^{*}$    activation energy.
Z    dimensionless parameter.
$\alpha$    constant whose value depends on crystallization mechanism.
$\sigma$    lateral surface energy.
$\sigma_e$    end surface energy.

REFERENCES