THERMAL PROPERTIES - Crystallization



MEASURING THERMAL PROPERTIES BY DSC



A plot of specific volume as a function of temperature for linear polyethylene samples. From R. Chiang and P. J. Flory, JACS, 83, 2857 (1961).

POLYMER CRYSTALLIZATION

WHAT DO WE KNOW FROM EXPERIMENTAL OBSERVATION ?

•Crystallization occurs relatively slowly

•At high undercoolings

•And results in the formation Of chain folded lamellae





MELT

DILUTE SOLUTION

POLYMER CRYSTALLIZATION



APPLICATION OF THERMODYNAMICS

WHAT TYPE OF STRUCTURE MINIMIZES THE FREE ENERGY ?



FREE ENERGY OF CRYSTAL = G_c = $G_s + bG$ surface bulk

Surface free energy - larger free energy than bulk. Chains are not in minimum energy conformation

$$\begin{array}{rcl} G_c &=& (4xl \) &+& (2x^2 \) & e & -& (x^2l \) \ f \\ & sides \ of & folds & bulk \\ & crystal \end{array}$$

FREE ENERGY OF A CRYSTAL



$$G_{c} = (2x)^{2} \left\{ \frac{2I}{X} + e \right\} - (x^{2}I) f$$

FREE ENERGY OF A CRYSTAL

But that answer was obvious ! Why bother with an equation ?

It turns out that this equation can be used to obtain additional things

1. AN EXPRESSION FOR THE EQUILIBRIUM MELTING POINT (It's always higher than the experimentally observed melting point)

2. AN EXPRESSION FOR THE FOLD PERIOD AND IT'S DEPENDENCE ON SURFACE ENERGY AND Tm

FREE ENERGY OF A CRYSTAL

Back to the obvious - the free energy is minimized when the surface area is minimized

i.e. the chains would be fully extended



THEN WHY DO POLYMERS CRYSTALLIZE AS FOLDED CHAINS ?

AS WE WILL SEE, ONCE AGAIN KINETICS REARS ITS UGLY HEAD!

THE CRYSTAL MUST FIRST FORM BY A PROCESS OF NUCLEATION FROM THE MELT (OR SOLUTION)

What is the probability of Obtaining one chain in the Fully extended state ?



Then what is the probability Of getting a bunch of chains To form an extended chain Nucleus ?

KINETIC THEORY OF CRYSTALLIZATION

An initial nucleus of folded chains is formed that is then "Locked in" by subsequent growth. We can distinguish Two stages; primary nucleation, then subsequent growth On the sides of this nucleus by a process of secondary Nucleation



• CRYSTALLIZATION KINETICS

PRIMARY VS SECONDARY NUCLEATION

Bell shaped curves are obtained Because of a balance between two Factors;



- A. Formation of nucleus
- **B.** Transport of chains to growth front



Note; a larger number of smaller crystals are formed as the Crystallization temperature is decreased. This affects Properties in various ways

CRYSTALLIZATION REGIMES

Three crystallization regimes have been identified. We will only mention primary and secondary





. Reproduced with per-mission from J. D. Hoffman, T. Davis and J. I. Lauritzen, Treatise on Solid State Chemistry, Vol. 3, *Chapter 7, Plenum Press, New York, 1976.*

CRUCIAL POINTS

- Polymers would like to crystallize In the form of extended chain crystals
- But they cannot get there ! the initial Nucleus is chain folded and its Formation is governed by kinetic factors
- Subsequent crystal growth proceeds by a secondary nucleation process That locks the crystal into its folded Chain form
- (Tm < tm because of fold surface)
- The lower the crystallization temperature, The more crystals are formed (what about The fold period ?)

THERMAL PROPERTIES - Tg



Volume changes as a function of temperature

THE ORDER OF A PHASE TRANSITION



MEASURING THERMAL PROPERTIES BY DSC

