

Intro to Polymer Science

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Contents

1	Introduction	2
1.1	Brief History	2
1.2	Classes	2
1.3	Molecular Weight Distribution	2
2	Polymer Chain Conformations	2
2.1	Freely Joint Chain	2
2.2	Real Chains	2
2.2.1	Free Rotation	2
2.2.2	Hindered Rotation	3
2.2.3	The Kuhn Length	3
2.3	Scaling Laws for the SAW	3
3	Crystallization, Melting, and Glass Transition	3
3.1	Nucleation	3
3.2	Thermodynamics	3
3.3	Melting Temperature	3
3.4	Glass Transition Temp.	3
4	Thermodynamics of Polymer Phase Separation	4
4.1	Entropy of Mixing	4
4.2	Enthalpy of Mixing	4

1 Introduction

1.1 Brief History

"gun cotton", using cellulose, 1843

Vulcanized rubber, 1844

First fully-synthetic: Bakelite, 1907

First linear fully-synthetic: Nylon, 1937, W. Carothers

H. Wieland – large mol is junk

H. Staudinger – No! (article: Über Polymerisation)

polystyrene – most difficult to recycle, (all landfill in US)

substitute: polylactic acid (decompose in land)

How large is large? What's the cutoff?

1.2 Classes

1. Thermosets (much cross-linked, stable under heat)
2. Thermoplastics (no cross-linked, melt easily)
 - (a) Semi-crystalline (Note: No fully crystallized polymer)
 - (b) Amorphous
3. Elastomers (little cross-linked)

1.3 Molecular Weight Distribution

2 Polymer Chain Conformations

2.1 Freely Joint Chain

1D free walk of R. Feynman

$$R_1^2 = \ell^2 \tag{1}$$

$$R_N = R_{N-1} + \ell, R_{N-1} - \ell \tag{2}$$

$$\langle R_N^2 \rangle = R_{N-1}^2 + \ell^2 = \dots = N\ell^2 \tag{3}$$

$$\sqrt{\langle R_N^2 \rangle} = \ell\sqrt{N} \tag{4}$$

other ways to derive that:

1. radial Gaussian distribution function

2.2 Real Chains

def: characteristic ratio C_∞

$$\sqrt{R_N^2} = \ell\sqrt{C_\infty N} \tag{5}$$

2.2.1 Free Rotation

$$\sqrt{R_N^2} = \ell\sqrt{N} \sqrt{\frac{1 + \cos \theta}{1 - \cos \theta}} \tag{6}$$

where $\theta = 180^\circ - 109.47^\circ$, thus

$$\sqrt{R_N^2} = \ell\sqrt{2N} \tag{7}$$

2.2.2 Hindered Rotation

$$\sqrt{R_N^2} = \ell \sqrt{2N} \sqrt{\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}} \quad (8)$$

ϕ	$\cos \phi$	E_i	$p(E_i)$
-120			
0			
120			

$$\sqrt{\langle R_N^2 \rangle} = \ell \sqrt{6.9N} \quad (9)$$

2.2.3 The Kuhn Length

def: Kuhn segment length ℓ_k

$$\sqrt{R^2} = \ell_k \sqrt{N_k} \quad (10)$$

2.3 Scaling Laws for the SAW

$$\sqrt{\langle R^2 \rangle} = \ell (C \cdot N)^\nu \quad (11)$$

3 Crystallization, Melting, and Glass Transition

3.1 Nucleation

3.2 Thermodynamics

critical lamellar thickness

$$l^* = \frac{4\sigma_{face}}{\Delta g_{vol}} \propto \frac{1}{\Delta T} \quad (12)$$

where $\Delta T = T_m - T$

crystallization requires $l > l^*$.

Why polymer crystallize in a chain folding manner, rather than an extended chain? – kinetics.

3.3 Melting Temperature

Why polymers melt over a range of temperature?

factors that affect T_m

1. backbone stiffness
2. non-covalent interaction
VdW, dipole-dipole (PVC), H-bonding (Nylon 6)

3.4 Glass Transition Temp.

factors that affect T_g

1. molecular weight

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad (13)$$

2. backbone stiffness
3. Side Chains
4. Non-covalent interactions

5. corss linking
6. Dilutents/Plasticizer
7. copolymerization and blending
blend miscibility

4 Thermodynamics of Polymer Phase Separation

4.1 Entropy of Mixing

4.2 Enthalpy of Mixing

$$\Delta H_m = n_A f_B z \Delta \varepsilon_{AB} \quad (14)$$

def: interaction parameter

$$\chi = \frac{z \Delta \varepsilon_{AB}}{kT} \quad (15)$$

Flory-Huggins Eq.

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (16)$$

$$\frac{\Delta G}{kT} = n_A \Phi_B \chi + n_A \ln \Phi_A + n_B \ln \Phi_B \quad (17)$$

$m = DP$ for an approximation.

UCST: Upper critical solution temperature

Since $\chi \sim 1/T$, we can calculate χ_c at T_c

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}} \right)^2 \quad (18)$$

for polymer solution

$$\chi_c = \frac{1}{2} \left(1 + \frac{1}{\sqrt{m_p}} \right)^2 \rightarrow \frac{1}{2} \quad (19)$$