

Polymers

L-5

weight average & o.Average molecular weight

mhttps://youtu.be/FyQCjD_1tx4

<https://youtu.be/T0rKGecWvdQ>

polymer

<https://www.slideshare.net/sagarsavale1/polymer-56240652>

mpf

Diblock Copolymers

It will become clear that universality makes it possible to think about phase transitions in an abstract manner and develop novel and experimentally verifiable conclusions based on a general understanding of the principles and mechanics underlying phase transitions.

A diblock copolymer is a polymer consisting of two types of monomers, A and B. The monomers are arranged such that there is a chain of each monomer, and those two chains are grafted together to form a single copolymer chain. A large collection of diblock copolymers is called a polymer melt, and below a certain temperature this melt will exhibit a phase transition. Above the transition temperature the amount of A and B is equally distributed throughout the material. This is the disordered state of the material and exhibits no spatial variance, and thus possesses the same type of translational symmetry found in liquids.

As with any thermodynamic system there is a competition between entropy and enthalpy which can be expressed as the minimization of a free energy. At high temperatures when entropy dominates the polymer melt is highly disordered and the distribution of A and B is even within fluctuation around mean zero.

Below a certain transition temperature the polymer melt orders. The ordering results in the formation of a periodic distribution of A and B, and many exotic geometries have been observed in experiment. Below the transition temperature, however, the monomer segments will segregate and form regular, periodic structures. That is, the A and B segments of each copolymer chain will come together and display macroscopic order.

Some of the common shapes that have been observed experimentally are lines (lamellar), hexagonal cylinders, and stacked balls (body centered cubic, BCC). Copolymers are important as a class of materials because they can be engineered to exhibit specific physical properties. Each geometry could potentially possess different physical characteristics, and thus the ability to readily switch between the phases could allow for materials with tunable properties.

The various phases of a diblock copolymer melt can be succinctly described by a phase diagram. Unlike the previously shown phase diagrams, temperature is no longer an explicit parameter. Rather, the two parameters that define the phase diagram are the Flory parameter, which is a measure of the strength of interactions between monomers (alike and different) and the bulk fraction of monomer A.

The Flory parameter is temperature dependent in a non-trivial manner, but since it is a monotonic function of temperature, the phase diagram qualitatively says all the same things that a diagram that had temperature explicitly would. The bulk fraction f is quite literally the fraction of A monomer to total monomer in the melt.



Spheres (BCC)



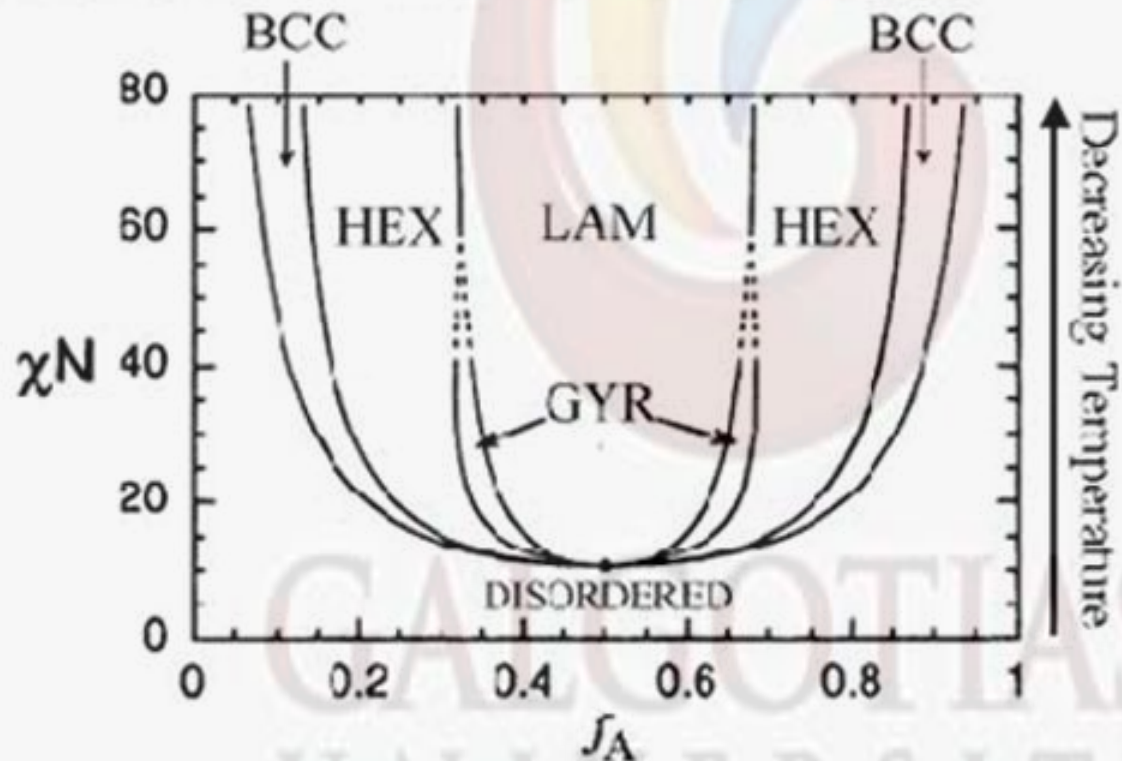
Cylinders (HEX)

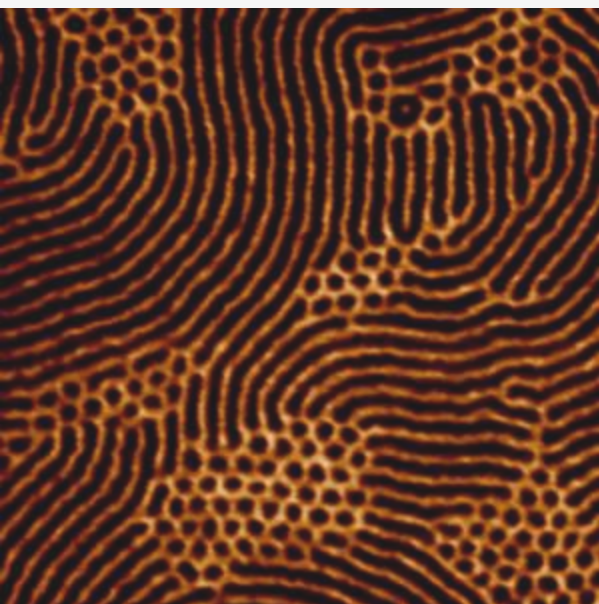


Gyroid (GYR)



Lamellar (LAM)





Much like the solidification of a liquid, the phase transition is first order and loses translational symmetry in the appearance of regular periodic structure. The order parameter is the difference between the local fraction of A, and the bulk fraction.

In the disordered state the order parameter is zero everywhere since the entire melt is homogenous, but in the ordered phase the order parameter is spatially varying with a periodicity.

This is another image of a diblock copolymer melt in the lamellar phase.

While the spatial correlation is not infinite, as there still is some variability in the lengths and angles with which the layers form, there is high and obvious correlation.

Triblock Polymers

There are other varieties of copolymer melts as well. A simple extension is the triblock, or n-block copolymer, which consists of a copolymer chain consisting of n different monomer chains. There is also the example of the randomly grafted copolymer (RGC).

The RGC consists of a 'backbone' of polymer A with chains of polymer B attached to it at locations randomly distributed on the backbone. Unlike the case of the diblock copolymer, which could be understood in terms of two parameters, there are three parameters necessary to describe the characteristics of an RGC melt. N is the length of the polymer backbone, m is the length of the branches it possesses, and p is the number of such branches.

The locations of the branches, although they can be located anywhere along the polymer backbone, are in essence fixed from one polymer to the next. The placement of the branches are thus an example of quenched randomness. The degree of freedom for each polymer chain as described by the locations of the branch points is not free, but is fixed. Special care must be taken with such problems which are often lead to intractable calculations where particular approximations must be made.

Number-average molecular weight

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i / M_i}$$

Weight-average molecular weight

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$

z-Average molecular weight

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}$$

Where,

n = Moles of molecules ($n_1 + n_2 + n_3 + \dots + n_i$) i.e. weight (w)/molecular weight (M)

w = Weight of individual molecules ($w_1 + w_2 + w_3 + \dots + w_i$)

M = Molecular weight of each molecules

Number Average Weight (M_n)

The number average molecular weight is not too difficult to understand. It is just the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample.

Consider a polymer, which contains four molecular weight polymers in different numbers and weight and these

Polymer entity	Number of unit in each entity, n	Weight of each grams, M(g)	Total weight of each entity, $W = nM(g)$
Poly-1	2	10	20
Poly-2	4	20	80
Poly-3	6	100	600
Poly-4	3	250	750
Total	15	-	1450

Total number of polymer in containing each entity of poly-1, poly-2, poly-3 and poly-4 is = 15

Number of Poly-1 present in the polymer = 2

Number of fraction of poly-1 = $2/15$

Similarly, Number of fraction of poly-2 = $4/15$, Number of fraction of poly-3 = $6/15$, Number of fraction of poly-4 = $3/15$

Contribution made by poly-1 towards the average weight of polymer = number of fraction of each polymer x weight of each poly entity

Therefore, each poly contribution is

$(2/15) \times 10 = 1.33\text{g}$, $(4/15) \times 20 = 5.33\text{g}$, $(6/15) \times 100 = 40\text{g}$, $(3/15) \times 250 = 50\text{g}$

Summing up the contribution to get Number Average Molecular Weight=

$$1.33 + 5.33 + 40 + 50 = 96.66\text{g}$$

Generalization of Concept

Total number of molecules (n) is given by

$$n = n_1 + n_2 + n_3 + n_4 + \dots = \sum n_i$$

Number fraction of each molecule is = $\frac{n_i}{\sum n_i}$

Number average weight contribution of each entity is = $\frac{n_i M_i}{\sum n_i}$

Number average weight molecular weight is

$$\frac{n_1 M_1}{\sum n_i} + \frac{n_2 M_2}{\sum n_i} + \frac{n_3 M_3}{\sum n_i} + \frac{n_4 M_4}{\sum n_i} + \dots = \frac{\sum n_i M_i}{\sum n_i} = M_n$$

Weight Average Molecular Weight (Mw)

Total weight of each poly present in the polymer =1450g

Weight of poly-1 present in polymer = 20g

Weight fraction of poly-1 = 20/1450, Weight fraction of poly-2 = 80/1450, Weight fraction of poly-3 = 600/1450, Weight fraction of poly-4 = 750/1450

Contribution made by each poly towards average weight of polymer = weight fraction of poly-1 x weight of each unit

For poly-1 (20/1450) x 10 = 0.14g

For poly-2 (80/1450) x 20 = 1.10g

For poly-3 (600/1450) x 100 = 41.38g

For poly-4 (750/1450) x 250 = 129.31g

Summing up the contribution made by each poly to get weight average molecular weight is

$$0.14 + 1.10 + 41.38 + 129.31 = 171.93g$$

Generalization of Concept

Total number of molecules (n) is given by

$$n = n_1 + n_2 + n_3 + n_4 + \dots = \sum n_i$$

Total weight of the polymer is = $\sum N_i M_i$ W

Weight fraction of each molecule is = $\frac{n_1 M_1}{W} = \frac{n_1 M_1}{\sum n_i M_i}$

Weight average weight contribution of each entity is = $\frac{n_1 M_1 M_1}{\sum n_i M_i} \frac{n_i M_i^2}{\sum n_i M_i}$

Number average weight molecular weight is

$$\frac{n_1 M_1^2}{\sum n_i M_i} + \frac{n_2 M_2^2}{\sum n_i M_i} + \frac{n_3 M_3^2}{\sum n_i M_i} + \frac{n_4 M_4^2}{\sum n_i M_i} \dots = \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

For synthetic polymers M_w is greater than the M_n . If they are equal then they will consider as perfectly homogeneous. (Each molecule has same molecular weight).

Molecular weight and degree of polymerisation

Number of repeating unit in a polymer called as *degree of polymerisation* (DP). DP provides the indirect method of expressing the molecular weight and the relation is as follows;

$$M = DP \times m$$

Where, M is the molecular weight of polymer, DP is the degree of polymerisation and m is the molecular weight of the monomer

$$(\text{DP})_n = \frac{\sum n_i (\text{DP})_i}{\sum n_i} \text{ and } (\text{DP})_w = \frac{\sum n_i (\text{DP})_i^2}{\sum n_i (\text{DP})_i}$$

Each of these averages can be related to the corresponding molecular weight average by the following two equations;

$$M_n = (\text{DP})_n \cdot m$$

$$M_w = (\text{DP})_w \cdot m$$

Influence of Molecular weight of Polymers

The influence of molecular weight on the bulk properties of polyolefin's, an increase in the molecular weight leads to

Increase in:

- **Melt viscosity**
- **Impact strength**

Lowers in:

- **Hardness**
- **Stiffness**
- **Softening point**
- **Brittle point**

High molecular weight polymer does not crystallize so easily as lower molecular weight material crystallizes due to chain entanglement and that reflect in bulk properties of the high molecular weight polymer.

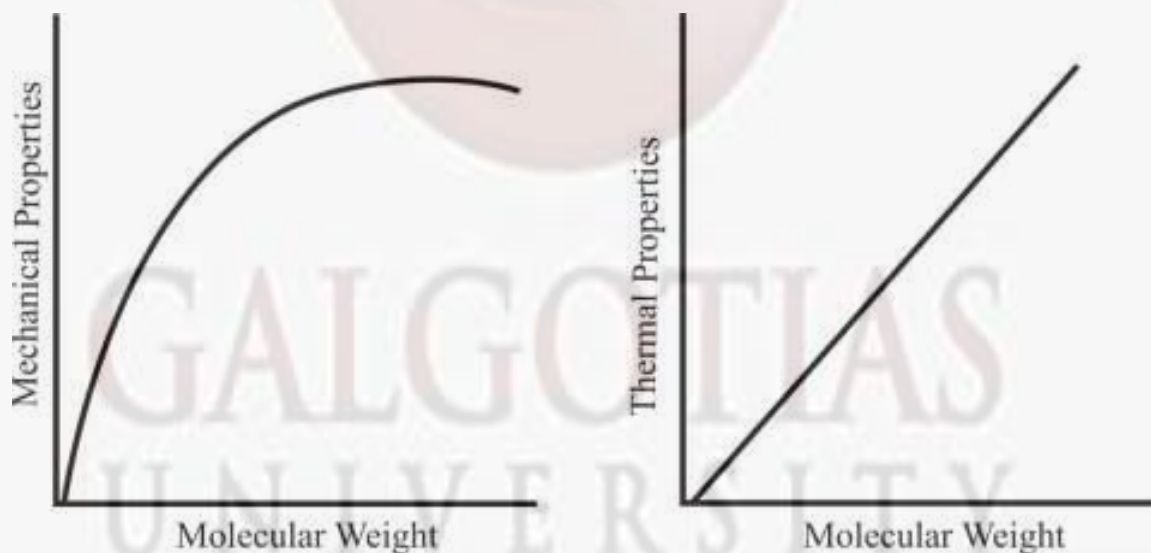
Effect of Molecular Weight on Properties of Polyolefins

Property	With Increase Molecular Weight
Melt Viscosity	↑
Melt Strength	↑
Melt Viscosity	↑
Toughness	↑
Abrasion Resistance	↑
Ultimate Strength	↑
Resistance to Creep	↑

Effect of Molecular Weight Distribution on Properties of Polyolefins

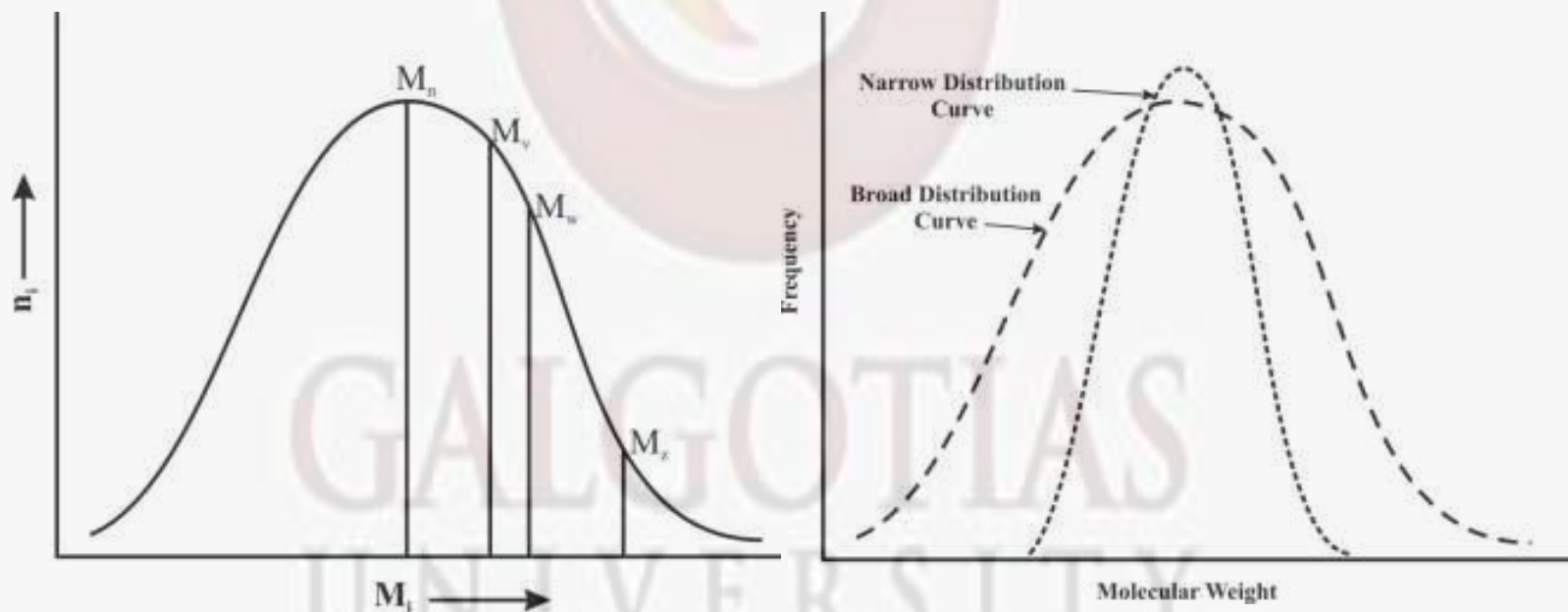
Property	Molecular Weight Distribution Increasing
Melt Viscosity(High Shear)	↓
Surface Gloss	↓
Toughness	↓
Optical Properties	↓
Melt Strength (Low Shear)	↑

- A high molecular weight polymer increases the mechanical properties. Higher molecular weight implies longer polymer chains and a longer polymer chain implies more entanglement thereby they resist sliding over each other.
- Increasing the molecular weight and the chain length of the polymer increases impact strength.
- Thermal properties can also improved by increasing the molecular weight.



Polydispersity Index for Molecular weight of Polymers

Polydispersity is a very important parameter and it gives an idea of lowest and the highest molecular weight species as well as the distribution pattern of the intermediate molecular weight species. Plastics processing are affected by the molecular weight distribution.



Determination of Molecular Weight



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Determination of Molecular Weight

1. Number-average Molecular Weight

a) End-group Analysis:

If functional groups present in a given weight of the sample and this is expressed as a functional group equivalent/100 g. From knowledge of the functional group equivalent and the functionality, The molecular weight is calculated using the equation:

$$M_n = \frac{\text{Functionality}}{\text{Functional group equivalent}}$$

Then the functionality of the polymer sample can be given by the equation

$$\text{Functionality} = \text{molecular weight} \times \text{functional equivalent}$$

References

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^ McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. (1997). *Principles of polymer engineering*. Oxford; New York: Oxford University Press. p. 1. [ISBN 978-0-19-856526-0](#).

^ Jensen, William B. (2008). ["Ask the Historian: The origin of the polymer concept"](#)(PDF). *Journal of Chemical Education*. **85** (5): 624–625. [Bibcode:2008JChEd..85..624J](#). [doi:10.1021/ed085p624](#).

^ Staudinger, H (1920). ["Über Polymerisation"](#) [On polymerization]. *Berichte der Deutschen Chemischen Gesellschaft (in German)*. **53** (6): 1073–1085. [doi:10.1002/cber.19200530627](#).

^ Allcock, Harry R.; Lampe, Frederick W.; Mark, James E. (2003). *Contemporary Polymer Chemistry (3 ed.)*. Pearson Education. p. 21. [ISBN 978-0-13-065056-6](#).

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School of Basic & Applied Sciences

Course Code : BSCC3004

Course Name: Organic Chemistry V



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.

3. Principle of Polymerization by George Odian, Wiley

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