Sudan university of Science and Technology

Polymers preparation and their molecular weight determinations

A Dissertation submitted for the requirement of B.Sc.degree.

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2016 A.D.

Contents

Dedication to :

My beloved parents , Brothers , sisters and friends

قال تعالى(كل ذي علم عليم) ...

Acknowledgement

Thank God for giving me the will , strength , patience and guidance to go through all obstacles in order to complete this research project .

First of all , I would like to express my gratitude to Dr. Hamad Balla for his supervision , valuable ,critical ideas and useful comment

Abstract :

The present work was carried out to elucidate the preparations of some polymers in addition to determination of their molecular weights .First of all Bakelite was prepared from phenol and formaldehyde added and sulfuric acid and sodium chloride .

The preparation of the plastic milk (casein) carried out by adding acetic acid to the hot milk , and preparation of nylon done by polymerization of acid and amine functions . The molecular weights determined by many methods : the average molecule weight by use :

- Colligative properties .
- GPC chromatography .
- Osmotic measurement .
- Light scattering .
- Viscosity measurement .

Introduction

The meaning of polymer: poly"many" +mer"part"

1-1 Polymers Is a large molecule or macromolecule , composed of many repeated subunits. The unit composing polymers derived, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by jons Jacob Berzelius.

The modern IUPAC definition of polymer as covalently bonded macromolecular structures, was proposed in 1920 by Hermann Staudinger.

1-2 Types of polymers :

There are two types of polymers : *natural and synthetic* , both synthetic and natural polymers play an essential and ubiquitous role in everyday life. polymer range from familiar synthetic plastics such as polystyrene to natural biopolymer such as DNA and proteins that are fundamental to biological structure and function .

Natural polymeric materials such as shellac, wool, silk and natural rubber have been used for centuries. A variety of other natural polymers exist ,such as cellulose, which is the main constituent of wood and paper.

The list of synthetic polymers includes synthetic rubber ,phenol formaldehyde resin (or Bakilite) ,neoprene,nylon,polyvinyl chloride

,polystylene,polypropylene,polyacrylonitrile,PVB,silicon,and many other polymers .

*Polymers, both natural and synthetic are created via

polymerization of many relative small molecules, known as monomers.

1-3 Uses of polymers:

Polymers have many different uses. The use of polymer is related to its properties, as illustrated below:

Monomer	Polymer	Properties	Uses
Ethene	Polyethene	Flexible Cheap Electrical insulator	Plastic bags and bottles, coating on electrical wires
Propene	Polypropene	Flexible and strong	Buckets and crates
Chloroethene	**Polychloroethene or pvc**	Tough ,cheap and long lasting	**Window frames**
Tetrafluoroethene	**Polytetrafluoroethene)**	**Tough and non-stick**	**non-stick coating**

1-4 Industrial polymers:

This polymers are prepared from simple compounds ,contain different plastics and other materials .

This type are classified into :

1-Organic polymers :

Polyester , polyamide , polyethylene , polypropylene and polycarbonate …etc.

2-Inorganic polymers :

1-5 The physical and chemical properties of polymers:

Polymers properties are broadly divided into several classes, based on the scale at which the property is defined , as well as it is physical basis. The most basic property of a polymers is the identity of its constituent monomers.

A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of single chain . These basic structural properties play a major role, in determining bulk of physical properties of the polymer , which describes how the polymer behaves as continuous macroscopic material.

Chemical properties:

At the nano-scale , describes how the chains interact through various physical forces . At the macro – scale ,they describe how the bulk polymer interacts with other chemicals and solvents.

Physical properties , including toughness,viscolasticity , and tendency to form glasses and semicrystallin structures rather than crystals.

Physical properties : Monomers and repeat unit:

The identity of the repeat units (monomer residues , also known as "mers") appear in a polymer first as its most important attribute . Polymer nomenclature is generally based upon the type of monomer residues, comprising the polymer. Polymers that contain only a single type of repeat unit , are known as homopolymers , while polymers containing a mixture of repeat unit are known as copolymers . polystyrene , for example , is composed only of styrene monomer residues , and is therefore classified as a homopolymer . ethylene – vinyl acetate , on the other hand , contains more than one variety of repeat unit and is thus copolymer . some biological polymers are composed of a variety of different but structurally related monomer residues ; for example , polynucleotide's such as DNA are composed of a variety of nucleotide subunits . A polymer molecule containing ionizable subunits is known as polyelectrolyte or ionomer.

*Microstructure:

The microstructure of a polymer (sometime called configuration) relates to the physical arrangement of monomer

residues along the backbone of the chain . These are the elements of polymer structure, that require the breaking of a covalent bound in order to change . Structure has a strong influence on the other properties of a polymer . for example , two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers .

*Polymers architecture:

An important microstructure feature of a polymer is its architecture and shape , which relates to the way branch points lead to deviation from a simple linear chain . A branched polymer molecule is composed of main chain with one or more substituent side chain or branches . Types of branched polymers include star polymers, comb polymers , brush polymers , deodorized polymers, ladders, and dendrimers.

*Chain length:

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain . For example , as chain length is increased , melting and boiling temperatures increase quickly . Impact resistance also tends to increase with chain length , as does the viscosity , or resistance to flow , of the polymer in its molten state .so that increase in polymer chain length result in a viscosity increase of over 1000 times. Increasing chain length furthermore tends to decrease chain mobility , increase strength and toughness, and increase the

glass transition temperature (Tg).
This is a result of the increase in chain interaction such as van der Waals attractions and entanglements that come with increased chain length.

A polymer's size may also be expressed in terms of molecular weight . Since synthetic polymerization techniques typically yield a polymer product, including a range of molecular weights, the weight is often expressed statistically to describe the distribution of chain length present . common examples are the number average molecular weight and weight average molecular weight.

*Monomer arrangement in copolymers:

- Alternating copolymers.
- Periodic copolymers.
- Statistical copolymers.
- Block copolymers.
- Graft or grafted copolymers.

*Tactility:

Tactility describes the relative stereochemistry of chiral centers in neighboring structural units within a macromolecule. There are three types:

1. Isotactic.
2. Atactic.
3. Syndiotactic.

*Polymer morphology.

* crystalline.

*chain conformation.

*Melting point.

*Glass transition temperature.

Chemical preoperties

The attractive forces between polymer chains play a large part in determining polymer`s properties. Because polymer chains are so long , these interchaine forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymers can lend the polymer to ionic bonding or hydrogen between its own chains . these stronger forces typically result in higher tensile strength and higher crystalline melting point.

The intermolecular forces in polymers can be affected by dipoles in the monomer unit. Polymers containing amide or carbonyl group can form hydrogen bounds between adjacent chains ; the partially positively charged hydrogen atom in N-H group of one chain are strongly attracted to the partially negatively charged oxygen atom in C=O group on anther. These strong hydrogen bounds , for example , result in the high tensile strength and melting point of polymers containing urethane or urea linkages. Polyesters have dipole – dipole bonding between the oxygen atom in C=O group and the hydrogen atoms in H-C groups . Dipole bonding is not as strong as hydrogen bounding , so a

polyesters melting point and strength are lower than Kevlar's (Twaron) , but polyesters have greater flexibility.

Ethene , however , has no permanent dipole. The attractive forces between polyethylene chains arise from weak van der Waals forces. Molecules can be thought of as being surrounded by a cloud of negative electrons. As two polymer chains approach , their electron clouds repel on another. This has the effect of lowering the electron density on one side of a polymer chain, creating a slight positive dipole on this side. This charge is enough to attract the second polymer chain. Van der Waals forces are quite weak, however, so polyethylene can have a lower melting temperature compared to other polymers.

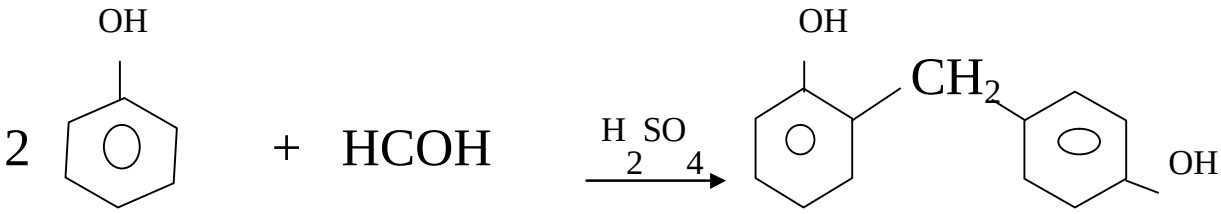
Polymerization :

The process of converting a monomer or a mixture of monomers into a polymer. In polymer chemistry , polymerization is a process of reacting monomer molecules together in a chemical reaction , to form polymer chain or three-dimensional networks.

Experimental and Results

2-1 Bakelite :

The chemical formula $(C_6 H_6 O. H_2 O)_n$.



Is an early plastic . it is a thermosetting phenol formalaldehyde resin, it was developed by the Belgian–American chemist Leo Baekeland in new York in 1907.

One of the first plastics made from synthetic components. Bakelite was used for its electrical nonconductivity and heat–resistant properties in electrical insulators , radio and telephone casings and such diverse products as kitchenware , jewelry pipe. The "reto" appeal of old Bakelite products has made them collectible. Synthesis:

Chemicals:

Formaldehyde , phenol ,sulphuric acid (concentrated), and sodium chloride (solid) .

Preparation of Bakelite was a multi-stage processes .

The first step is the heating of phenol and formaldehyde in the presence of a catalyst, such as hydrogen chloride.

Procedure:

50ml of formaldehyde was transferred into a beaker , then 10ml of phenol was added to the beaker.
2gms of sodium chloride was placed in a conical flask, and 5ml of sulphuric acid was added drop-wise (using a dropper).

Observations :

1- Evaporation of hydrogen chloride gas while the sulphuric acid was dropping into the salt .This gas was passed to the beaker contents .
2- Formation of plastic , it is brown color ,solid and insoluble in water , also insoluble in organic solvents.

Result :

Bakelite formed from a condensation reaction of phenol with formaldehyde in presence of catalyst such as hydrogen chloride gas .

2-2 Change of milk to plastic :

This plastic , known as casein plastic ,it was used to manufacture buttons , decorative buckles , beads and other jewelry as well as fountain pens and hand held mirrors and brush sets.

Synthesis :

The milk was boiled , then drops of vinegar or acetic acid was added to the boiling milk of the white slurry, without water .

Result :

The result is plastic that can be molded into many shapes.

2-3 Nylon :

Chemical formula $(C_{12}\ H_{22}\ N_2\ O_2)_n$

Nylon 66 is a type of poly amide or nylon .

Nylon 66 is made of two monomers each containing 6 carbon atoms . hexa methylylene diamine and adipic acid . it is used in fibers textiles , oil pans and pipes .

SYNTHESIS AND MANUFACTURING:

Equivalent amounts of reactants combined with water in a reactor , this is crystallized to make nylon salt , the nylon salt goes into the reaction vessel where polymerization process takes place . Continuously removing water, drives the reaction towards polymerization of acid and amine functions . Thus molten nylon 66 is formed .

2- 4 polystyrene:

Casts are prepared in polyethylene scoops like those used to measure coffee or Kool-Aid. Styrene monomer free of inhibitors and catalyst (containing methyl ethyl ketone peroxide) come from Iasco. Eight drops of catalyst are mixed with 13 g of styrene in a 3-oz. paper cup (we use Dixie bathroom cups). Because the styrene is so thick and messy, we measure it out for the students using a top-loading balance protected from drips by a sheet of glass or plastic. You should use something disposable

when handling it, because you can never clean it up. The mixture is poured into the polyethylene mold.

Methods of determination of molecular weight of polymers:

The techniques use to determine molecular weight are:

3-1 Colligative properties .

3-1-1 Elevation boiling point.

3-1-2 Depression freezing point.

3-1-3 Osmotic pressure.

3-1-4 Change in vapor pressure.

3-2 osmotic measurement.

3-3 GPC Chromatography.

3-4 light scattering.

3-5 viscosity measurement.

3-1-3 Osmotic pressure:

We have to talk about average molecular weights when we talk about polymers . the average molecular weights can be calculated by different ways , and each way has its own value .

- The number average molecular weight $\bar{M}_n$.

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 .

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Example :

N1= 100 , N2 = 200 , N3 = 90 , N4 = 150

M1 , M2 , M3 , M4

$$\bar{M}_n = \frac{100 \times M_1 + 200 \times M_2 + 90 \times M_3 + 150 \times M_4}{100 + 200 + 90 + 150}$$

- The weight average molecular weight , $\bar{M}_w$:
  The weight average is little more complicated . It is based on the fact that, bigger molecule contains more of the total mass of the polymer sample, than the smaller molecule do.

$$\bar{M}_w = \frac{\sum N_i M_i}{\sum N_i M_i}$$

Example :

$N_1 = 100$, $N_2 = 200$, $N_3 = 90$, $N_4 = 150$

M1 = 500 , M2 = 5×10^6 , M3 =50000 , M 4 = 5000

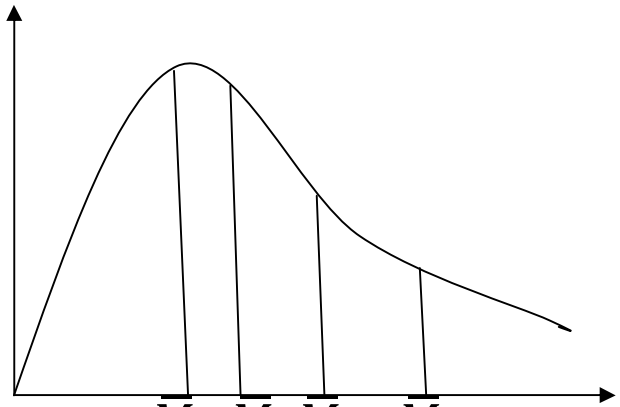
$$\bar{M}_w = \frac{(100+200+90+150) \times (500+5000000+50000+5000)^2}{540 \times 5055500}$$

- Viscosity average molecular weight ,$\bar{M}_v$

  Molecular weight can also be calculated from the viscosity of a polymer solution .The principle is a simple one : bigger polymers molecules make solution more viscous than small ones do.

$$\bar{M}_v = \left\{ \frac{(\sum N_i M_i)^{1+\alpha}}{\sum N_i M_i} \right\}^{1\backslash\alpha}$$

Molecular weight distribution curve:



Random distribution : $\bar{M}_{n:}\bar{M}_v : \bar{M}_w : \bar{M}_z$ = 1:2:3

Monodisperse distribution: $\bar{M}_n = \bar{M}_v = \bar{M}_w = \bar{M}_z$

Polydisperse distribution: $\bar{M}_n < \bar{M}_v < \bar{M}_w < \bar{M}_z$

3-5 Viscosity measurenmt:

$$\eta = KM^{\alpha}$$

$$\log \eta = \log K + \alpha \log M$$

$$(\log \eta - K) \div \alpha = M$$

3-2 Osmotic measurement:

$$\frac{\pi}{cRt} = \frac{1}{M_n} + A_1C$$

$$M_n \equiv molecular\ weight$$

Discussion

Bakelite is pink solid, it is not soluble in water, prepared from the condensation reaction between phenol and formaldehyde .It is used as electrical non conductivity and heat resistant properties in electrical in sulater radio and telephone .

Identification of Bakelite**:**

Effect of temperature:

In this study Bakelite was analyzed by heat and reduces the colour to brown.

Density: 1.3 g\cm^3

. Preparation of Bakelite was a multi-stage processes .
The first step is the heating of phenol and formaldehyde in the presence of a catalyst, such as hydrogen chloride.

Result:

Bakelite formed from a condensation reaction of phenol with formaldehyde in presence of catalyst such as hydrogen chloride gas .

Casein:

It is also plastic, product of boiled of milk with finger ,used in manufacture of buttons ..etc

The milk was boiled , then drops of vinegar or acetic acid was added to the boiling milk of the white slurry, without water .

The result is plastic that can be molded into many shapes.

Nylon: Is type of poly amide ,is made of two monomers each one ,containing 6 carbon atoms .

Equivalent amounts of reactants combined with water in a reactor , this is crystallized to make nylon salt , the nylon salt goes into the reaction vessel where polymerization process takes place .

polystyrene: Casts are prepared in polyethylene scoops like those used to measure coffee or Kool-Aid. Styrene monomer free of inhibitors and catalyst (containing methyl ethyl ketone peroxide) come from Iasco. Eight drops of catalyst are mixed with 13 g of styrene in a 3-oz.

conclusion

In this search we talk about polymers general, defined and many types were mentioned, besides their physical and chemical properties, also industrial polymers ,polymerization and usage...etc.

In special cases we show the synthesis of Bakelite and casein. Also we determined the molecular weights . In case of Bakelite :

50ml of formaldehyde was transferred into a beaker , then 10ml of phenol was added to the beaker.
2gms of sodium chloride was placed in a conical flask, and 5ml of sulphuric acid was added drop-wise (using a dropper).

Casein: The milk was boiled in beaker , then drops of vinegar or acetic acid was added to the boiling milk by dropper,formation of white slurry, without water then the solution was filtered .

We determine molecular weight by different way :

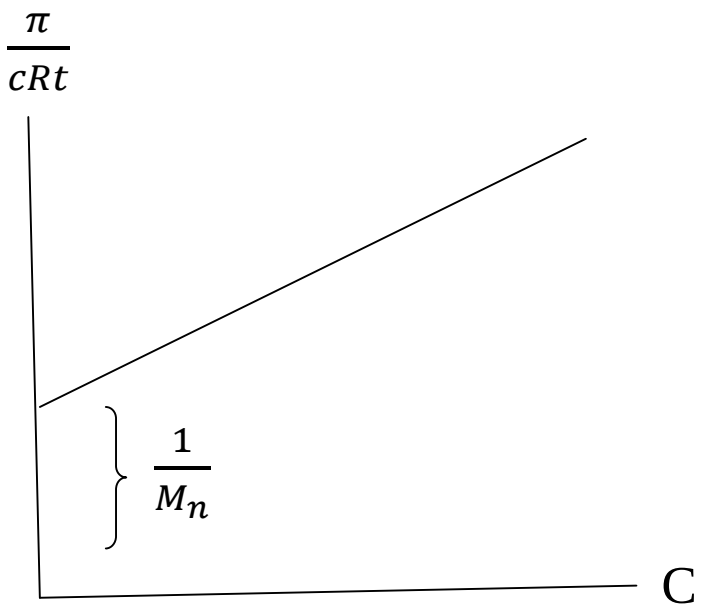
Osmotic pressure contain :

- Number average molecular weight $\overline{M_n}$.
- Weight average molecular weight $\overline{M}_w$.
- Z average molecular weight$\overline{M}_z$.
- Viscosity average molecular weight $\overline{M}_v$.

Also we determine it by curves like osmotic measurement according to law :

$$\frac{\pi}{cRt} = \frac{1}{M_n} + A_1c$$

We draw $\frac{\pi}{cRt}$ against C :



References

1- Roiter , y.; minko, s.(2005). "AFM single molecule experiments at the solid – liquid interface : in situ conformation of adsorbed flexible polyelectrolyte chains" . Journal of the American chemical society 127 (45) : 15688-15689 .doi: 10.1021/Ja0558239. PMID1677495.

2 - Polymer – definition of polymer "the free dictionary. Retrieved 23 July 2013 .

3- Define polymer "Dictionary Reference . Retrieved 23 July 2013 .

4- Painter , paul c.; Coleman,Michael M.(1997) . fundamentals of polymer science : An introductory text . Lancaster ,pa: technomic co.p.1. ISBN 1-56676-559-5 .

5 - McCrum ,N.G; Bukley ,c.B.(1997).principles of polymer engineering . oxford ; new York : oxford university press.p.1.ISBN0-19-856526-7

6- http://goldbook.org\M03667.html; accessed 7 October 2012.

7 - IUPAC, Compendium of chemical terminology, and ed (Gold Book)(1997). Online corrected version : (2006) "macromolecule (polymer molecule)".

8 - jons Jacob Berzelius(1833)"isomeri,Unterschediung von damit anlagen verhaltnissen".

9 -Originally published in 1832 in swedish as :Jons Jacob Berzelius (1832) .

10- Jensen , William b .(2008) "Ask the historian :the origin of the polymer concept" (PDF).Journal of chemical education 88:624-625 .Sperling p.11. Spelling p.15.

11 - Membranes on polyolefin plants vent recovery , improvement economics program. By nitrates , ISBN978-0615678917.

12- Rubinstein ,p.5.McCum p.37. **McCrum p.30.**

13- Rubinstein p.3.McCrum p.33.Rubinstein p.23-24.Painter p.22 Rubinstein p.50.Painter,p14.