**Exp. No. (1)**

# Preparation of Poly Methyl Methacrylate (PMMA) by Addition Polymerization

## Introduction

A polymer is a long-chain molecule that is composed of a large number of repeating units of identical structure.

The repeat unit of polymer is usually equivalent or nearly equivalent to the monomer such as the report unit of polyethylene $(-CH_2-CH_2-)_n$ is $nCH_2=CH_2$.

The number of repeat unit a long the polymer chain is called the degree of polymerization.

Monomer is the compound or compounds, used in the preparation of polymer.

For example ethylene is a monomer that can be polymerized to polyethylene:

$$\underset{\text{Monomer}}{\boxed{CH_2=CH_2}} \longrightarrow \underset{\text{Polymer}}{—CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2—}$$

Two monomer molecules first react together to form a dimer. The dimer may then react with a third monomer to yield a trimer and so on.

It is convenient to classify polymers according to the kinetics of the polymerization:

1. Chain-growth polymerization (addition polymerization).
2. Step-growth polymerization (condensation polymerization).

Chain-growth polymerization is that attachment of a monomer to an (active) chain. The active end may be a free radical or an ionic site (i.e., anion or cation). High-molecular-weight polymer is formed in the early stages of a chain-growth polymerization.

Chain-growth polymerization has three principal steps:

1. Initiation process, in which active monomer is formed

$$I{-}I \xrightarrow{K_d} 2\ I^{\cdot} \qquad \text{(dissociation step)}$$

$$I^{\cdot} + M \xrightarrow{K_a} IM^{\cdot} \qquad \text{(association step)}$$

2. Propagation or growth of the active chain by sequential addition of monomers

$$IM_x^{\cdot} + M \xrightarrow{K_p} IM_xM^{\cdot}$$

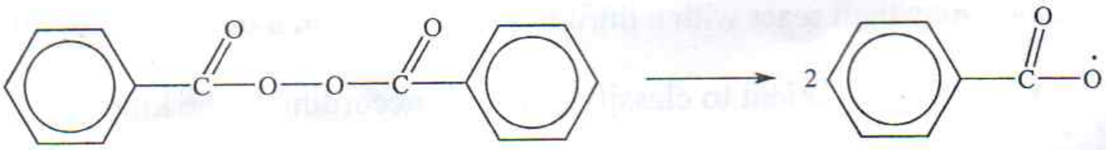
3. Termination of the active chain to give the final polymer product by different reaction

$$IM_{x-1}M^{\cdot} + {}^{\cdot}MM_{y-1}I \xrightarrow{K_{tc}} IM_{x-1}MM_{y-1}I \qquad \text{(combination)}$$

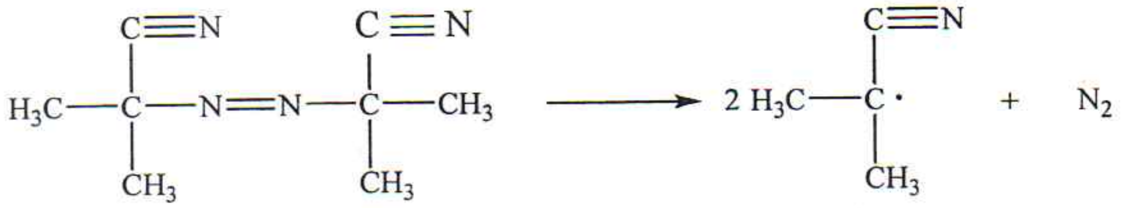
$$IM_{x-1}M^{\cdot} + {}^{\cdot}MM_{y-1}I \xrightarrow{K_{td}} IM_x + IM_y \qquad \text{(disproportionation)}$$

$$IM_{x-1}M^{\cdot} + SH \xrightarrow{K_{tr}} IM_{x-1}MH + S^{\cdot} \qquad \text{(chain transfer)}$$

Initiator is usually molecule that can be decomposed thermally or by irradiation to yield a pair of initiating radicals, such as peroxides, azo compounds and redox system.



Benzyl peroxide



Azobisisobutyronitrile (AIBN)

Redox system

1. $S_2O_8^{2-} + S_2O_3^{2-} \longrightarrow SO_4^{2-} + \overset{\cdot}{SO_4}$

   persulfate thiosulfate

2. $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \overset{\cdot}{OH} + OH^-$

**Apparatus**

1. Balance
2. Heavy-walled glass tube (test tube)
3. Beaker
4. Watch glass
5. Thermometer
6. Oven

**Reagent and materials**

1. Methyl methacrylate MMA (monomer)
2. Benzoyl peroxide (Initiator)
3. Ethanol (precipitator)

## Procedure

1. Put 2 ml of methyl methacrylate individually in two tubes.
2. 0.03g of benzoyl peroxide is added to added to each tube and shake gently, the tubes are heated inside water bath at 80°C for 15 min.
3. When the contents of the tubes become viscous due to polymerization process, one of MMA tubes is transfer to dry beaker.
4. 10ml ethanol is added to the content of the beaker gradually with shaking, and the precipitated is collected and transferred to the watch glass then dried in oven at 40°C and weighted .
5. The second tube of MMA monomer is heated for 20min, and the same procedure of polymer precipitation in first tube is applied to the second tube and the precipitate is collected, dried and weighted.
6. Calculate the yield percentage of the PMMA prepared by the two procedures.

**Exp. No. (2)**

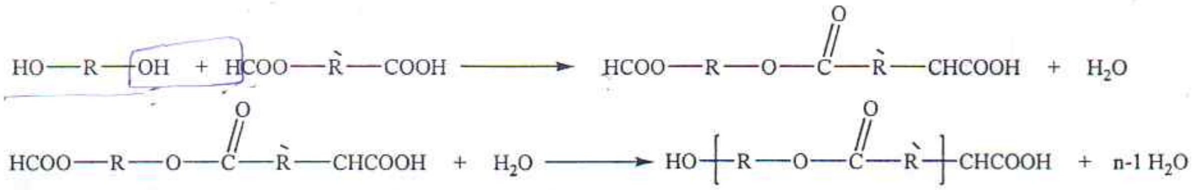
# Preparation of Polyester by Condensation Polymerization

## Introduction

Step-growth polymerization is a random reaction of two molecules that may be any combination of a monomer, oligomer, or a longer-chain molecule, and usually small molecules like $H_2O$, $CH_3OH$, $HCl$, etc. are eliminated. ~~High-molecular-weight polymer is formed in the early stages~~

An example of this type of polymerization is the formation of laminating resin polyester (Glyptal) from the reaction of glycerol and phthalic acid.

Polyesters are being commercially produced from the combination of two different monomers, one have two (or more) hydroxyl groups and the other have two (or more) carboxyl groups:



$$HO-R-OH + HCOO-\grave{R}-COOH \longrightarrow HCOO-R-O-\overset{O}{\overset{\|}{C}}-\grave{R}-CHCOOH + H_2O$$

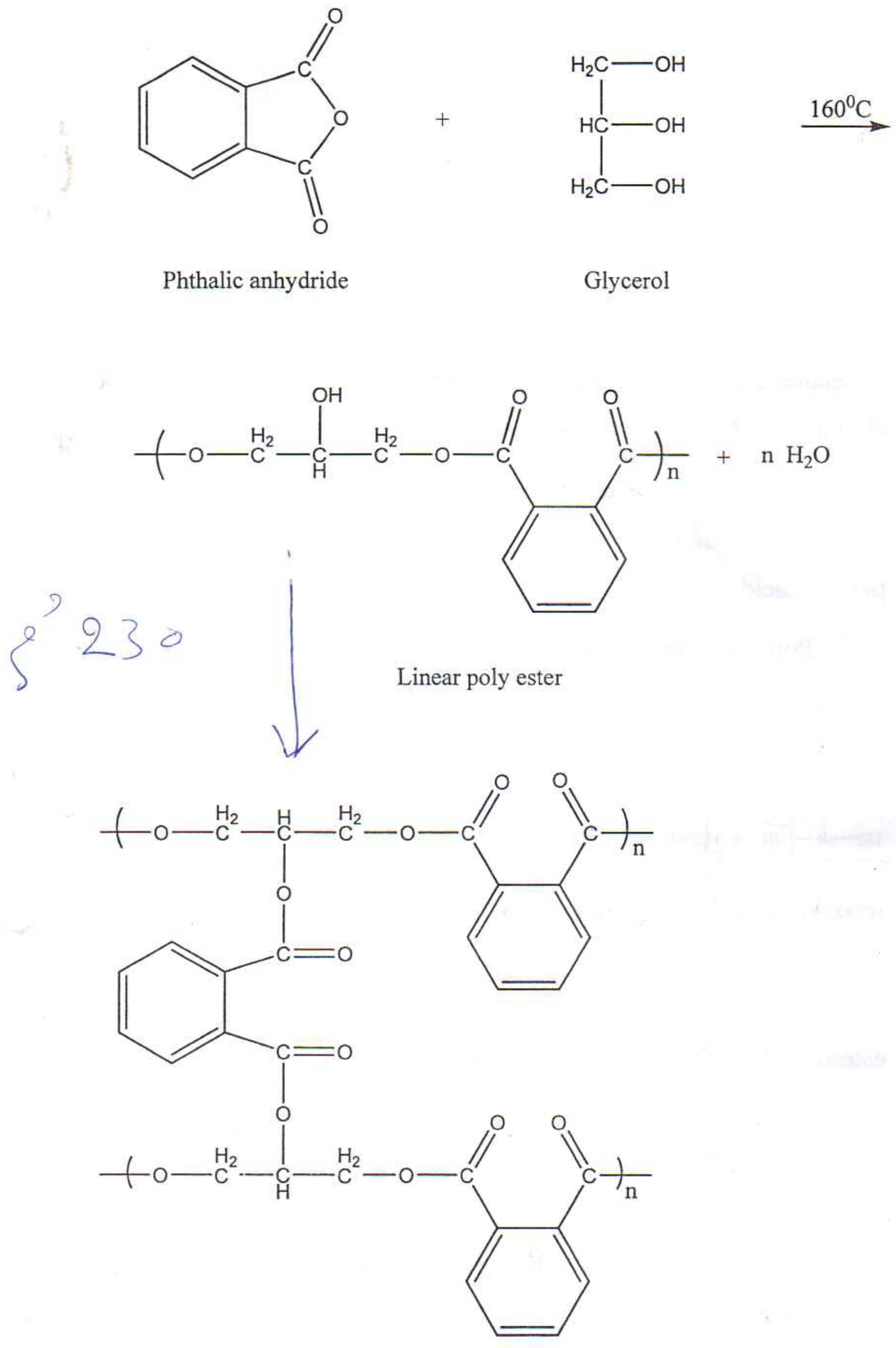
$$HCOO-R-O-\overset{O}{\overset{\|}{C}}-\grave{R}-CHCOOH + H_2O \longrightarrow HO\left[R-O-\overset{O}{\overset{\|}{C}}-\grave{R}\right]CHCOOH + n\text{-}1\ H_2O$$

The reaction between glycerol and phthalic anhydride is basically esterification, and $H_2O$ molecule is eliminated.

$HO-R-\overset{O}{\overset{\|}{C}}-O-\bar{R}-COOH + H_2O$

$H$ [illegible] $OH + HCOO-\bar{R}-COOH$

$HO-R-\overset{O}{C}-O-\bar{R}-COOH$



Cross linked poly ester

phthalic الوزن 2.5o20

**Apparatus**

1. Pyrex test tube
2. Thermometer
3. Crucibles

**Reagent and materials**

1. Phthalic anhydride
2. Glycerol
3. Conc. Sodium hydroxide solution
4. Conc. Sulfuric acid
5. Solvent (chloroform, acetone and ethanol)

**Procedure** ١٥ دقيقة

1. 2.5g of phthalic anhydride and 1g of glycerol are mixed in dry Pyrex tube with stopper and thermometer.
2. Heat slowly with careful stirring mixture inside the hood.
3. Rise the temperature to about 160°C and keep the reaction for 15 min at this temperature until all the solid is dissolved.
4. Some drops of produced polymer is pull in two crucibles for analysis. تسحب

   بعض القطرات الناتج
5. The temperature of polymerization reaction is then rised slowly until it become 200-240°C where cross-linked polymer is formed.
6. Another few drops of product cross-linked polymer is pull in another two crucibles for analysis.
7. The collected drops of polymer samples, two crucibles contain linear and two crucibles contain cross-linked polyester are tested as following:

a) *Conc. Sodium hydroxide test:*

3ml of conc. Sodium hydroxide is added to one linear polyester crucible and another 3ml for one cross-linked polyester crucible.

b) *Acid test:*

3ml of conc. $H_2SO_4$ is added to one linear polyester crucible and another 3ml for one cross-linked polyester crucibl.

c) *Melt test:*

Heating the prepared polymer samples (linear and cross-linked polyester) on a heater and recorder your notes.

d) *Solubility test:*

3ml of one of the following organic solvents as, chloroform, acetone, $CCl_4$, ethanol, or any available organic solvent in the lab.

8. Record your notes and obtained results.

A) Bulk →
بلمرة الكتلة
(طور واحد)

* الابتداء (تقوم) بالقيام على البلمرة والترسيب
* وسط البلمرة يكون متجانس خلال عملية البلمرة
* يكون التفاعل باعث للحرارة (من العيوب التوزيع الغير منتظم للحرارة)
* اللزوجة الزائدة للخليط
* تكون اللزوجة عالية بسبب عدم استخدام المذيب
* معوقات البلمرة هي
① صعوبة السيطرة على الحرارة الزائدة والتخلص منها
② - صعوبة الخلط التحريك لان السائل لزج جداً .

**Exp. No. (3)**

## Preparation of Synthetic Rubber (Thiokol)

### Introduction

Thiokol rubber is a kind of rubber that is resist the natural oxidation by oxygen, ozone and organic solvents such as oils and gasoline. This makes it useful for engine O-rings, gaskets and hoes which may come in contact with oils.

The preparation of Thiokol rubber involve two steps process:

The first step is the preparation of sodium polysulfide by the reaction of sulfur ($S_8$) with the strong base (NaOH)

$$S_8 + 2\ NaOH \longrightarrow Na_2S_8$$

At room condition, sulfur is normally in the form of $S_8$ rings and chain.

The reaction with sodium hydroxide produces a mixture of mostly $Na_2S_8$ with other chain lengths of sulfur presents, this mixture is called polysulfide.

The second step of preparation is the reaction of sodium polysulfide with 1,2-dichloroethane.

$$Cl-\overset{H_2}{C}-\overset{H_2}{C}-Cl + Na_2S_8 \longrightarrow \left[\overset{H_2}{C}-\overset{H_2}{C}-S_8\right]_n + 2\ NaCl$$

## Apparatus

1. Conical flask
2. Graduated cylinder
3. Beaker
4. Water bath

## Reagent and materials

1. Sodium hydroxide solution (20%)
2. Powdered sulphur
3. 1,2-dichloroethane
4. Distilled water

## Safety

1,2-dichloroethane is flammable, avoid any fires or sparks. It is also an irritant to the skin and eyes and it is toxic by ingestion, work only under a fume hood.

## Disposal

Dispose all liquid waters in the proper waste bottle provided.

## Procedure

1. 3g powder sulphur is keep in clean and dry round bottom flask.
2. 12ml (20%) NaOH solution is added to the sulfur powder.
3. 40ml distilled water is added to the mixture
4. Reflux the mixture for 30 minutes.

حتى يبرد

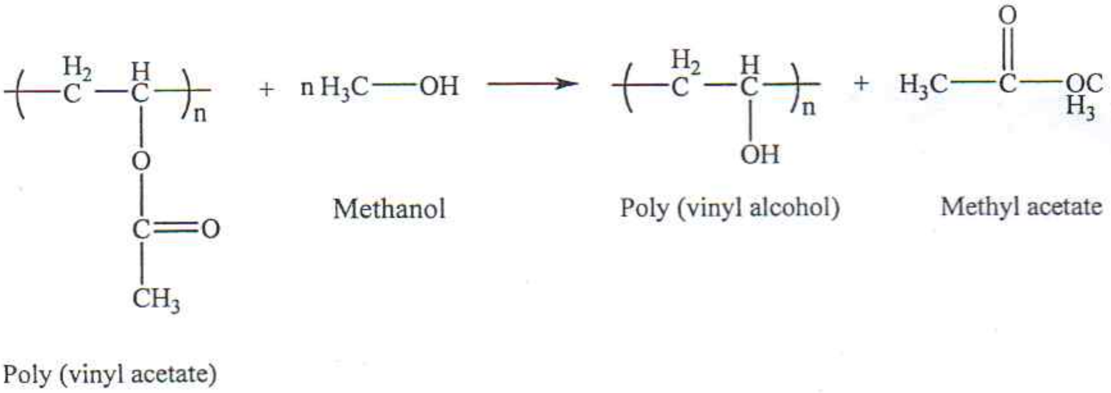
5. Keep the reflux contents to cool, filter the remaining mixture to remove the unreacted sulfur.
6. 15ml of the red brown filtrate solution of $Na_2S_x$ is added to another round bottom flask contain 5ml of dichloroethane.
7. Heat the mixture at 70°C use water bath with stirring for 45 minutes, the synthetic yellow rubber (Thiokol) is formed.
8. Cool the contents and wash the product well with distilled water.
9. Dry and weight the product.

**Exp. No. (4)**

## Preparation of Poly (vinyl alcohol) (PV~~C~~A)

### Introduction

The monomer vinyl alcohol ($H_2C=CH-OH$) is unstable and it transforms into the tautomeric acetaldehyde and it must be prepared by indirect methods, however the poly (vinyl alcohol) is prepared by the alcoholysis of poly (vinyl alcohol) (the less accurate term "hydrolysis" and "saponification").



Ethanol or methanol can be used to effect the alcoholysis with either acid or base as catalyst.

### Apparatus

1. Round bottom flask
2. Glass condenser
3. Water bath
4. Buchner funnel

## Reagent and materials

1. Poly (vinyl acetate)
2. Methanol
3. Potassium hydroxide
4. Distilled water

## Procedure

1. Set up reaction flask on a water bath.
2. Charge it with 0.6g of poly (vinyl acetate) (PVAc).
3. 15ml of methanol added to the flask.
4. Fit the flask with a reflux water condenser attached to a $CaCl_2$ drying guard tube.
5. Reflux the contents until PVAc dissolved (25-30) minutes.
6. Add 5ml of methanol containing 0.4g of potassium hydroxide when the contents of the flask are still warm.
7. Reflux the mixture further for 1 hour.
8. Poly (vinyl alcohol) formed due to the hydrolysis of PVAc.
9. Collect the product using Buchner funnel and wash it with 5ml of methanol.
10. Dry the product and weight it.
11. Report the yield.

**Exp. No. (5)**

# Preparation of Urea-Formaldehyde Resins

## Introduction

Urea-formaldehyde resins is prepared by step-growth polymerization (condensation polymerization).

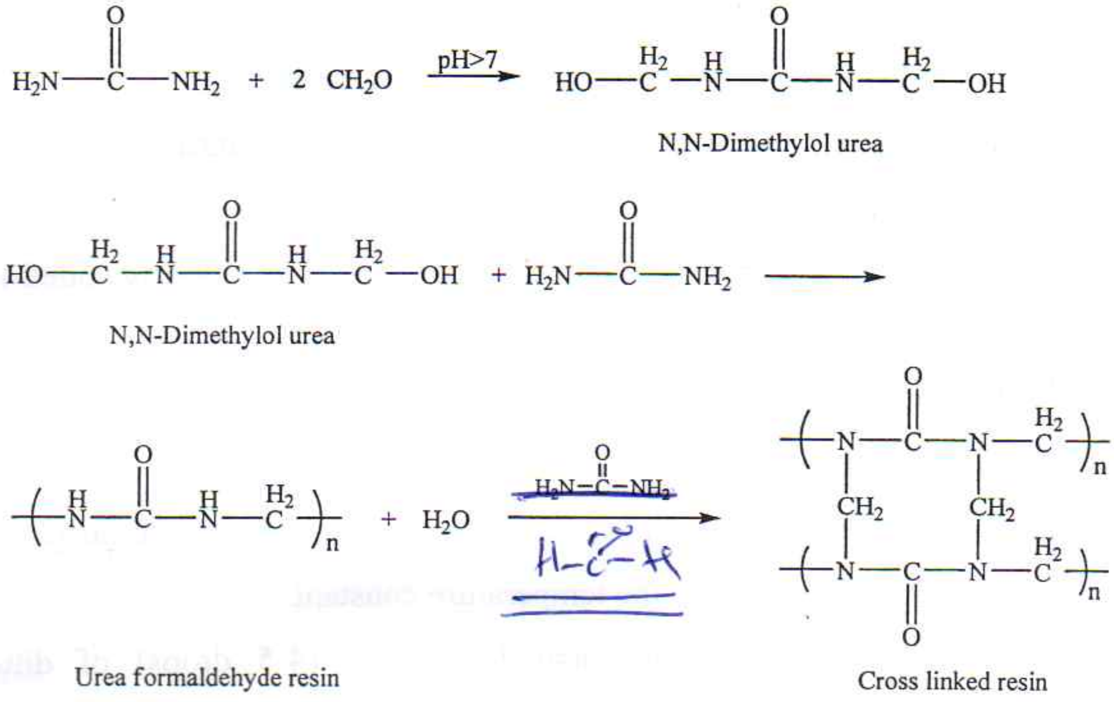
The resin is used as adhesive for the bounding of plywood and other structure wood products, because urea formaldehyde resins are lighter in color than phenol formaldehyde resins, they are used for interior plywood and decorative paneling. [illegible]

[illegible]

The reaction between urea and formaldehyde involved two steps, The first step is the addition of formaldehyde to urea to form methylol~~ated~~ urea, the second step is the condensation between methylol and amino group to form methylene-linked polymers or between two methylol groups to form cross-linked polymers.

As in phenolic resins, the formation of urea formaldehyde resins is known to be greatly influenced by both acid and base catalysts.

The condensation of methylol unites to yields polymer is shown in the following reaction:



## Apparatus

1. Beaker
2. Round bottom flask
3. Condenser
4. Buckner funnel
5. Water bath
6. Thermometer

## Reagent and materials

1. Urea
2. Formaldehyde
3. NaOH (dilute)
4. HCl (dilute)
5. Filter paper
6. Litmus paper

**Procedure**

1. Weight 3.5g of urea and crushed it in dry beaker.
2. Add 10ml of formaldehyde solution and stirr until solid urea is dissolve.
3. Few drops (4-5 drops) of sodium hydroxide solution is added for solution medium to become basic, use litmus paper as indicator.
4. Pour the mixture into dry and weight round bottom flask with coke fit condenser.
5. Heat the mixture in water bath for 1 hour at 70-80°C use thermometer to keep the temperature constant.
6. Cool the mixture and add few drops (4-5 drops) of dilute hydrochloric acid to neutralize the mixture (pH = 6-7). Use litmus paper as indicator.
7. Filter the solution using Buckner funnel. Dry the product and weight it for yield percentage.

العبوة المحدودة بالتفاعل الى فاعلي الاول للهيئة لمن احيا (تفاعلون) وصلفسرها الى العظم
بروا أكثفيات .

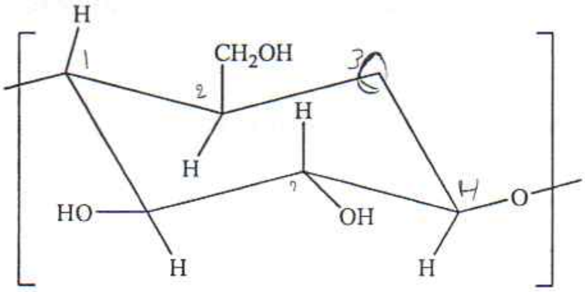
* لا يذوب في الماء والكحول ولكن يذوب في $H_2SO_4$ واحسن مذيب له هو $Cu(NH_3)_3(OH)_2$

**Exp. No. (6)**

## Preparation of Rayon (Pure Cellulose)

### Introduction

Cellulose is among the simplest of the natural polymers, consist of D-glucose repeat unit linked through carbon 1 and 4 by β-linkages.



سليلوز طبيعي Cellulose

القطن والخشب هو اكثر مصادر السليلوز بعد ازالة المواد الشمعية والبكتينية الموجودة في القطن الخام)

Cotton and wood is the most important source of cellulose. Wood has now become the main source of cellulose, the substance must be extracted by pulping.

الخشب المصدر الرئيسي للسليلوز الان والمصدر النقي له هو القطن

هناك ٣ انواع في السليلوز

There are three kinds of cellulose; α-, β-, γ-cellulose:

1. α-cellulose: it is the part which is not dissolved in 18% NaOH solution, it is called pure cellulose, which has high molecular weight and long chain. سلاسل طويلة غير متفرعة
2. β-cellulose: it is part which is dissolved in 18% NaOH solution, it can be precipitated by acid and has low molecular weight.
3. γ-cellulose: it is dissolved in 18% NaOH solution and cannot precipitated by acid.

Cellulose can be prepared in two processes:

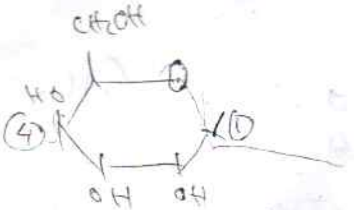
1. Cupper ammonium process.
2. Viscous process. → a- steeping process عملية النقع
   b- viscous prepartaion
   c- pure نقي cellulose fiber prepration

تأخذ منه الطريقة

The viscous process cellulose is soaked in caustic soda solution for about 3hr. the alkaline solution is removed and the product is treated with $CS_2$ this gives cellulose xanthate, which is dissolved in NaOH solution to give viscous solution. The solution filtered and forced through a spinnert into a dilute $H_2SO_4$ solution.

In this experiment pure cellulose can be prepared by viscous which includes:

a. Steeping process. عملية النقع
b. Viscous preparation. تحضير
c. Pure cellulose fiber preparation.



**Reactions**

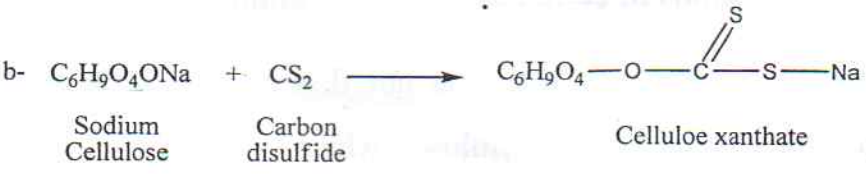
1) يعامل مع 18% من NaOH حيث يتم تحويل السليلوز الى صوديوم سليلوز والماء (٢١)

الخطوة الاولى عملية النقع

a- $C_6H_9O_4OH + NaOH \longrightarrow C_6H_9O_4ONa + H_2O$

Cellulose 18% Sodium Cellulose

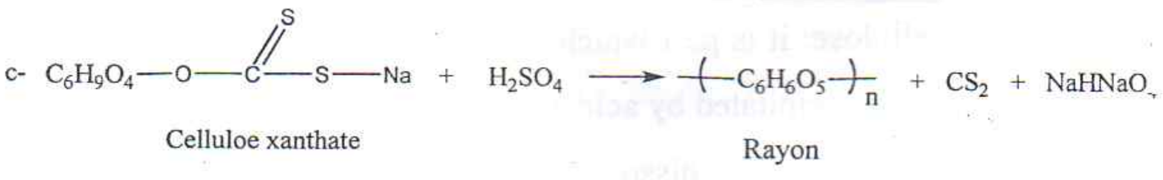
2) يتم فصل γ , β عن α
تذوب لا تذوب



b- $C_6H_9O_4ONa + CS_2 \longrightarrow C_6H_9O_4{-}O{-}C({=}S){-}S{-}Na$

Sodium Cellulose Carbon disulfide Celluloe xanthate

3) ← خطوة الزانثيت ←



c- $C_6H_9O_4{-}O{-}C({=}S){-}S{-}Na + H_2SO_4 \longrightarrow -\!\!\left(C_6H_6O_5\right)\!\!-_n + CS_2 + NaHNaO$

Celluloe xanthate Rayon

$-\!\!\left(C_6H_{10}O_5\right)\!\!-_n$

**Note: Cellophane production** [illegible]

When viscose is extruded through a slit die into an acid bath, a film of regenerated cellulose known as *cellophane* were results.

[illegible]

## Apparatus

1. Beaker (250ml)
2. Glass rod
3. Cock fit conical with stopper
4. Syringe

## Reagent and materials

1. Filter paper or cotton
2. NaOH solution
3. Carbon disulfide $CS_2$
4. Dilute $H_2SO_4$
5. Sodium bisulfite $Na_2SO_3$
6. Zinc sulfate $ZnSO_4$

## Procedure A

① تحلل السليلوز ح
18% NaOH

1. Put 1g of filter paper or cotton in conical flask or beaker.
2. 25ml of 18% NaOH solution is added to the conical flask.
3. Leave the conical flask contents for 1hr use stirring from time to time.
4. The contents of the conical flask is squeeze between two watch glass, then the squeezed filter paper is cutted into small pieces.

5. Put the pieces in dry conical flask with stopper and left it to the next week.

## Procedure B

مادة خطرة جداً وأبخرتها كريهة لذا نرتدي الكمامات الكبيرة

1. Add 12.5ml of $CS_2$ to the conical flask which containing cutted pieces of filter paper (prepared last week).
2. Close the conical flask by stopper and keep for 1 hr with stirring from time to time until the color of the filter paper became tallow-red.
3. Pour the excess of $CS_2$ and squeeze the pieces of paper in mortar and 3-5 drops of 4% of NaOH solution is added to prepare viscous solution with yellow-red color.

## Procedure C

حمام الغزل

1. Spin bath is prepared by mixing the following materials.
   a) 5ml of $H_2SO_4$
   b) 6.2g of $Na_2SO_4$
   c) 0.5g of $ZnSO_4$
   d) 34.5ml of water

هذه المادتان تزيدان من الشد السطحي

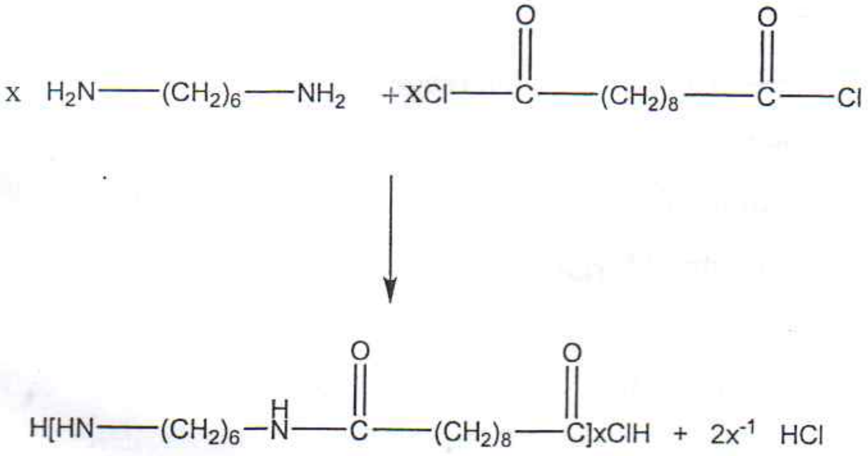
2. Inject the viscous solution into the spin bath to produce regenerated cellulose fibers.
3. Remain the cellulose fibers in spin for 10sec.
4. The prepared rayon filaments are washed, dried and weighted.

## Exp. No. (7)

# Preparation of Poly (Hexamethylene Sebacamide), Nylon 610 by Interfacial Polycondensation Method

## Introduction

Nylon 610, poly (hexamethylene sebacamide), is formed by a simple method and at room temperature called interfacial poly condensation method.



$$x\ H_2N{-}(CH_2)_6{-}NH_2\ +XCl{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}Cl$$

$$\downarrow$$

$$H[HN{-}(CH_2)_6{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}]xClH\ +\ 2x^{-1}\ HCl$$

In interfacial polymerization, two complementing monomers (for example, a diamine and a diacid chloride as in this experiment) are dissolved in two immiscible solvents, neither of which is a solvent for the resulting polymer. When the solution are mixed, a film of high polymer is immediately formed at the interface. This can be pulled out as a continues fiber (the "nylon rope trick"); or, if the solution are mixed with violent agitation to produce a large surface area, polymer can be formed in high yield very rapidly. This nonequilibrium method eliminates three of the disadvantages of bulk polymerization: the need for high temperatures, long reaction times, and exact stoichiometric equivalence.

## Warning

The reaction need steam of nitrogen to prevent explosion may occur in presence of oxygen.

## Apparatus

1. Separator funnel (300ml).
2. Large fritted-glass filter, 45-inch diameter, or equivalent.

## Reagent and materials

1. Hexamethylene diamine, reagent grade.
2. Sebacoyl chloride
3. Sodium hydroxide
4. Carbon tetrachloride ($CCl_4$)
5. Acetone
6. Methanol

## Procedure

1. Dissolved 2.32g hexamethylene diamine and 1.6g sodium hydroxide in 330ml distilled water, and place it in blender.
2. Dissolve 4.78g sebacoyl chloride in 250 ml $CCl_4$ and place in separator funne;. Support the separator funnel with its stem passing through the cover of the blender (beaker have magnetic bar).
3. Turn the blender on to maximum speed, and add the contents of the separator funnel rapidly (15 sec.). continue to stir vigorously for about 3 min.
4. Stop the blender, and collect the polymer on the fritted-glass filter.

5. Return the polymer to the blender, and wash with 500ml of 1:1 water : methanol for 2-5 min. then repeat step 4.
6. Repeat step 5 using a water : acetone mixture.
7. Dry the polymer in a vacuum oven for 24 hr. at about 80°C.
8. The produced polymer could be used for primary identification of polymers.

**Exp. No. (8)**

# Preparation of Phenol-Formaldehyde resin (Bakelite)

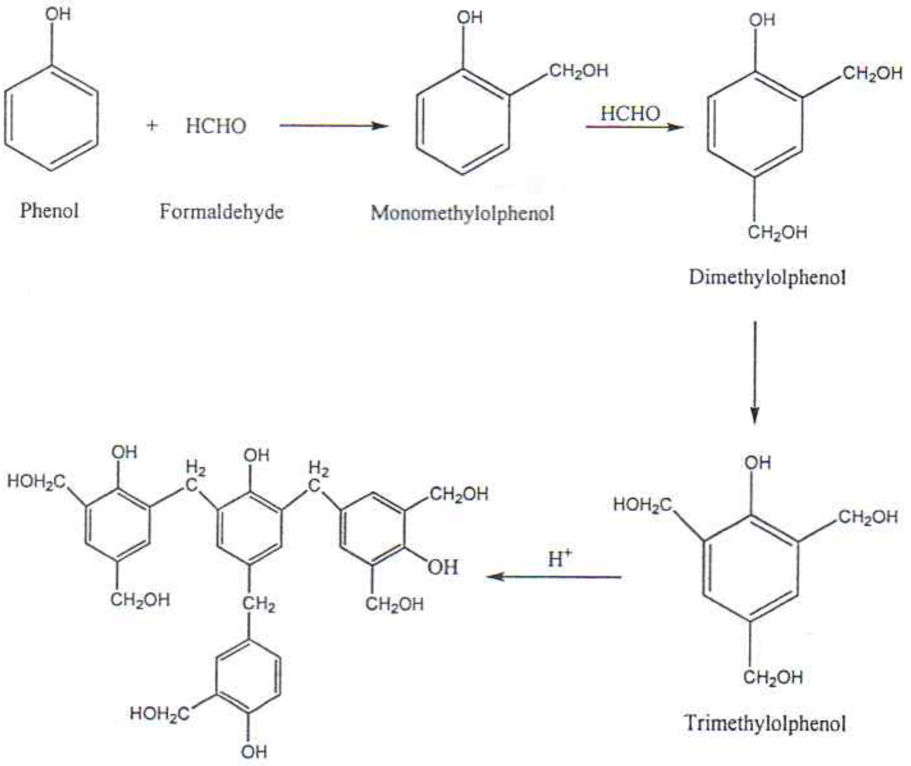
## Introduction

Phenolic resin was the first totally synthetic coating material. In 1909, the Bakelite was the first phenolic resin produced commercially and it was replace for cellulose nitrate.

The base-catalyzed addition of formaldehyde to phenol would form *Resole formation* and acid-catalyzed reaction would form *Novolac formation.*

In resole formation the reaction of phenol and excess formaldehyde under basic conditions would form mono-, di-, an trimethylolphenols.

The resole formation can also be obtained by an initial acid-catalyzed reaction of formaldehyde with excess phenol.



Representative structure of a resole

## Apparatus

1. Beakers
2. Conical flask
3. Glass rod
4. Water bath
5. Cylinder

## Reagent and materials

1. Glacial acetic acid.
2. Formaldehyde solution 40%
3. Phenol
4. Concentration hydrochloric acid
5. Distill water

## Procedure

1. Pour 5ml of glacial acetic acid in a beaker.
2. Add 2.3ml of formaldehyde solution in same beaker.
3. Add 2g of phenol with stirring and heating (phenol should be stirred in the formaldehyde solution for 10 minutes to make saturated solution).
4. Add 2-3ml of concentrated HCl to the mixture (concentrated HCl should be added stepwise with continuous stirring for heat dispersion.
5. Filter the large piece of pink resin from its mixture.
6. Wash several time with distilled water, dry the resin and calculate its yield percentage.

## Precautions

1. The reaction sometimes is vigorous and it may jump from the beaker, be aware the beaker while adding conc. HCl.
2. Phenol should be stirred with formaldehyde solution for 10min. for saturated solution formation.
3. Conc. Hydrochloric acid should be added drop wise carefully.

**Exp. No. (9)**

# Successive Precipitation of Polymers

## Introduction

Most of polymers are consisted of different chain length. So there are differences in their molecular weights. The polymer in this case is called (polydispersed) polymer, while polymer which have chain with similar in their molecular weight is called (monodispersed) polymer. Separation of mixture of molecules with different or similar molecular weights are impossible by the ordinary methods, like distillation or crystallization. Separation is often done by methods depend upon the ability of polymer chains to dissolve according to their molecular weights (their ability to dissolve is decrease as their molecular weight is increase). The separated parts with almostly similar range of molecular weight are measured in their molecular weights. The successive methods followed for separation of polymers according to their chain lengths:

1. Precipitation separation
2. Separation by using different solvent
3. Gradual thermal
4. Column separation

The method used in this experiment is precipitation method which depends on precipitating agent added to the polymer solution while the polymer molecules are not homogenous in their molecular weights so it precipitate gradually according to their molecular weights (this mean big molecular precipitate first then it is followed by the smaller one and so on).

### Apparatus

1. Burette 25ml
2. Beaker 150ml
3. Glass rod

### Reagent and materials

1. Polystyrene
2. Butyl acetate
3. Ethanol or methanol

### Procedure

1. Dissolved 2.5g of polystyrene in 25ml *n*-butyl acetate.
2. Fill burette with precipitating agent like ethanol or methanol.
3. The precipitating agent is added stepwise from the burette with continuous stirring till white precipitate is appeared.
4. Stop the addition of the precipitating agent and separate the white precipitate.
5. The precipitating agent is further added as drops to the separated white precipitate for extra collection.
6. The remained clear solution is treated further with precipitating agent for collection of second part of polymer precipitate, and the procedure is repeated till three different polymer chain lengths are collected.

Each part is putted alone in individual crucible and left next week to dry, then its molecular weight will be calculated.

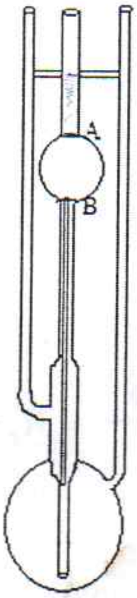
**Exp. No. (10)**

## Viscosity Average Molecular Weight Determination

### Introduction

Measurement of the viscosity of dilute polymer solution provide the simplest of most widely used technique for routinely determining molecular weights for polymer samples.

However, it is not an absolute method because each polymer system must first be calibrated with absolute molecular weight determinations (usually by light scattering) run on fractionated polymer samples. Viscosities are measured at concentrations of about 2 $gdL^{-1}$ of solvent by determining the flow time of a certain volume of solution through capillary of fixed length. Flow time in seconds is record as the time for the meniscus to pass between two designated marks on the viscometer as shown in fig (1). Viscosities of the polymer solutions are measured at constant temperature usually at 30.0±0.1°C.



Ubbelohde viscometer

Thus concentration can be reduced without having to empty and refill the viscometer, the additional advantage is that dilution of solution can be done in the viscometer itself.

***Caution*:** It is necessary to ensure that the polymer solution is free from any solid particle, either due to dust or incompletely dissolved polymer, as any particle that got stuck at capillary tube would affect the flow time.

Viscosity can be expressed in several ways as described below.

### Relative viscosity ($\eta_r$)

Relative viscosity is the ratio of solution viscosity to solvent viscosity, which is proportional to a first approximation for dilute solutions to the ratio of the solution flow time to solvent flow time.

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad (1)$$

Where $\eta$ and $\eta_o$ are the viscosities of the solution and solvent respectively, t and $t_o$ are the respective flow time of the solution and the solvent respectively.

### Specific viscosity ($\eta_{sp}$)

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 \qquad (2)$$

Both $\eta_r$ and $\eta_{sp}$ are dimensionless (without a unit). As concentration increases, so does viscosity. Hence to account for the concentration

ID: mahmoodalhassoy

effects, the specific viscosity is divided by concentration to give the reduced viscosity ($\eta_{red}$)

$$\eta_{red} = \frac{\eta_{sp}}{C} \qquad (3)$$

Where concentration C is commonly expressed as g per 100 ml.

## Apparatus

1. Ubbelohde viscometer
2. Water bath
3. Thermometer
4. Beaker
5. Pipet (10ml)
6. Stop watch

## Reagent & material

1. Polystyrene
2. Benzene

## Procedure

### *(a) Determination of* $t_0$

1. Set the water bath at 30.0±0.1°C. Measure 10 ml of benzene (which has been filtered through a filter stick) into an ubbelohde viscometer. Allow the system to attain thermal equilibrium (let the viscometer be in the water bath for at least 2 minutes).

2. Allow the solution to flow under gravity. Start timing with a stopwatch when the upper meniscus reaches A, and stop the timing when the meniscus reaches B. Repeat 2 to 3 times, and take the average of the three most consist readings to be the solvent flow time $t_0$.
3. Pour out all benzene and hang the viscometer upside down in the fume cupboard to drip dry while you prepare the polystyrene solution as follow.
4. Prepare a solution of the polystyrene sample (0.2g/10ml) by weighing accurately 0.2 g of polystyrene into the beaker. Add 10ml of benzene into the beaker and allow the polystyrene to dissolve completely (need to wait at least 15 minutes, with occasional shaking).

### *(B) Determination of solution flow time t*

5. Pour the prepared polystyrene solution into the viscometer. Follow the same procedure as in (a) to measure the solution flow time (t).
6. Dilute the concentration of the solution in the viscometer by adding 2 ml of solvent directly into the viscometer. Make sure you shake the viscometer for a few minutes to ensure homogeneous mixture, before you start to determine the solvent flow time.
7. Repeat the dilution 2 to 3 times, each time by adding 2ml solvent into the viscometer. For each concentration, repeat measurement of flow time at least 3 times and the average value is computed.

*Note*: At the end of the experiment, pour the content of the viscometer into a waste bottle. Fill the viscometer with clean solvent, before you return it back to the laboratory assistance.

## Analysis of data

Tabulate your results as follow:

Measurement of solvent flow time $t_0$

| **No.** | **Solvent flow time $t_o$/s** |
|---|---|
| 1 | |
| 2 | |
| 3 | |

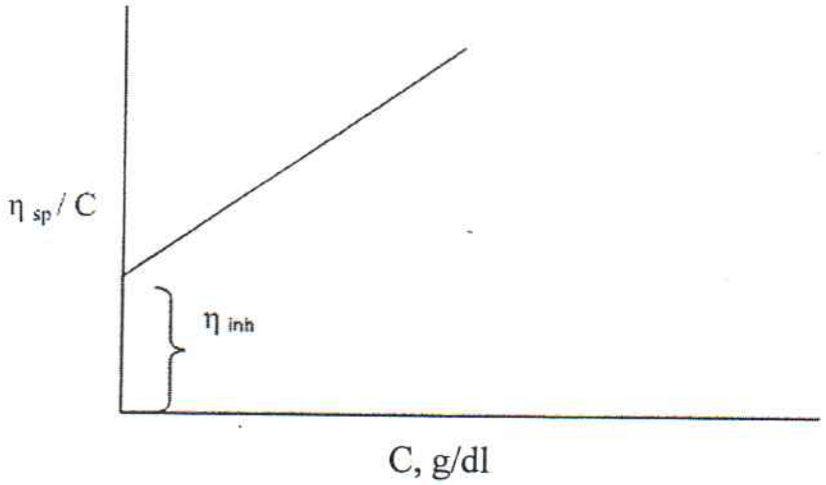
Average of three most constant measurement

| **$gdL^{-1}$** | **Solution flow time (sec)** | | | **Average t (sec)** | **$\eta_r = t/t_o$ Relative viscosity** | **$\frac{t}{t_o} - 1 = \eta_{sp}$ Specific viscosity** | **$\eta_{sp}/C$ Reduced viscosity** |
|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |

Plot ($\eta_{sp}$/C) versus (C) in graph paper, and determine the intrinsic viscosity [η]. Determine the viscosity average molecular weight of your polystyrene sample.

The intrinsic viscosity of a polymer is related to the viscosity average molecular weight by the Mark-Houwink Equation.

$$[\eta] = K (M_v)^a$$



Where K and a are constant for a specific polymer and are dependent on the temperature and solvent.

Table 1: The viscosities constants for some important polymers

| **Polymer** | **Solvent** | **Temp (°C)** | **K×$10^{-4}$** | **a** |
|---|---|---|---|---|
| Polystyrene | Benzene | 20 | 1.23 | 0.72 |
| | Benzene | 25 | 4.17 | 0.60 |
| | Benzene | 30 | 1.06 | 0.735 ✓ |
| | Toluene | 20 | 0.007 | 0.93 |
| | Toluene | 25 | 1.17 | 0.72 |
| | Toluene | 30 | 1.1 | 0.725 |
| Poly Methyl methacrylate | Acetone | 30 | 14.7 | 0.52 |
| | Benzene | 25 | 0.64 | 0.76 |
| | Toluene | 25 | 0.71 | 0.73 |
| | *n*-butylacetate | 25 | 2.5 | 0.68 |

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**Exp. No. (11)**

# Determination the Degree of Crystallinity

## Introduction

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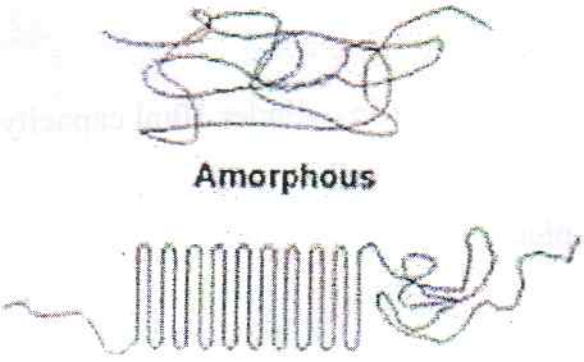
Crystallization of polymers have a significant effects on optical, mechanical, thermal and chemical properties of polymers.

The degree of crystallinity is estimated by different analytical methods and it typically ranges between 10 and 80%, thus crystallized polymer are often called (semicrystalline).

The properties of semicrystalline polymers are determined not only by the degree of crystallinity, but also by the size and orientation of molecular chain.



The arrangement of molecular chains in amorphous and semicrystalline polymers

Most methods of evaluating the degree of crystallinity assume a mixture of perfect crystalline and totally disordered areas; the transition areas are expected to amount to several percent. These methods include *density* measurement, *differential scanning calorimetry* (DSC), *X-ray diffraction* (XRD), *infrared spectroscopy* and *nuclear magnetic resonance* (NMR). The measured value depends on the method used, which is therefore quoted together with the degree of crystallinity.

## Apparatus

1. Volumetric flask (5ml).
2. Glass rod.
3. Graduated cylinder.

## Reagent and materials

Many samples of crystalline and amorphous polymers such as PE, PS, PP, PET and PVA.

## Procedure

1. Put 5ml of distill water in cylinder 10ml capacity.
2. Put small piece of unknown polymer in the cylinder.
3. Notice the piece of polymer floated on the water surface or sink:

If

Sink

Density of polymer is higher than density of water

1. Add salt solution (NaCl or $Na_2S_2O_3$) with stirring.
2. When the piece of polymer raise in the solution and settled in the middle, it means density of polymer = solution density

Float

Density of polymer is less than density of water

1. Add ethanol or methanol drop by drop with stirring
2. When the piece of polymer move inside solution and settled in the middle it means Density of polymer = solution density

4. The quantity of solution is weighted with volumetric flask ($W_2$).
5. Calculate the density of solution which equal the density of polymer as

$$\text{Density} = \frac{W_2 - W_1}{V}$$

Where $W_1$ = weight of volumetric flask and V = volume of volumetric flask.

Volume

6. Determined the degree of crystallinity of polymer by

$$\%\ \text{Crystallinity} = \frac{P - P_{am}}{P_{cry} - P_{am}} \times 100$$

Where $P$ = density of polymer sample, $P_{am}$ = density of amorphous polymer and $P_{cry}$ = density of crystalline polymer.

7. Discussion of the results.

Table 2: Densities of crystalline and amorphous polymers

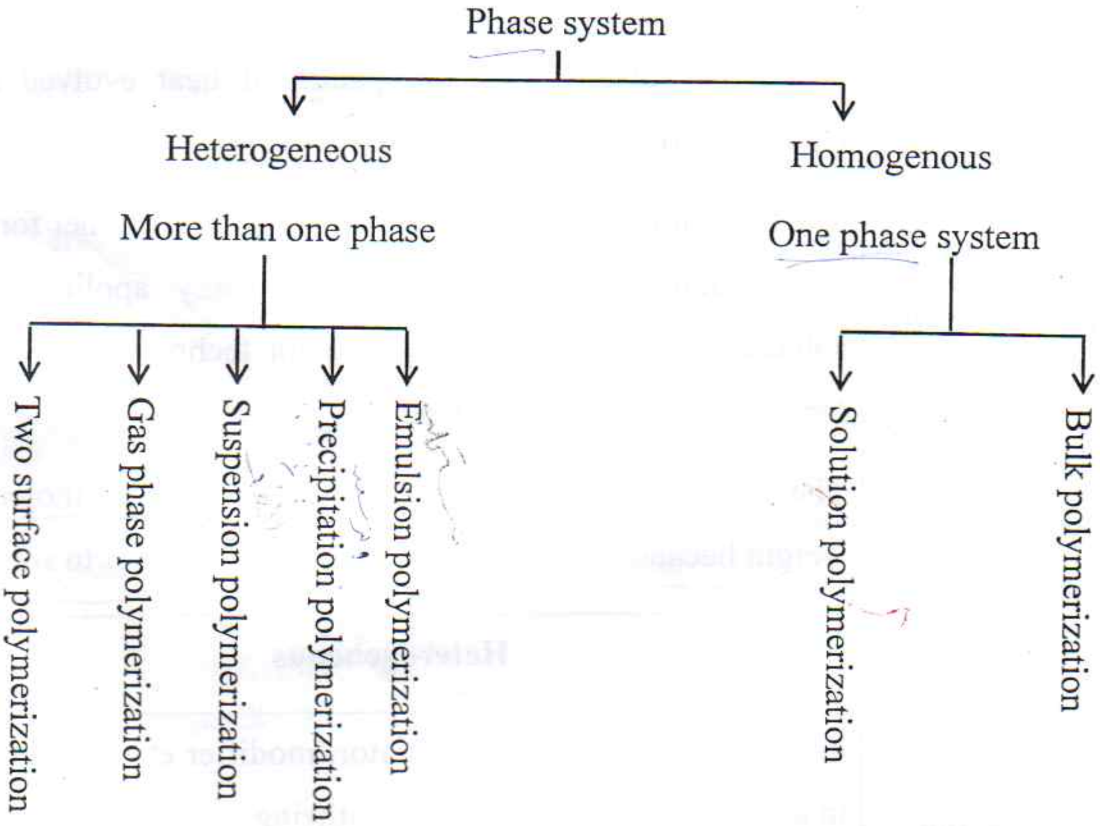
| **Polymer** | **Cryslalline $P_{cry}$** | **Amorphous $P_{am}$** | **$P_{cry} - P_{am}$** |
|---|---|---|---|
| PE | 1.00 | 0.852 | 0.148 |
| PP | 0.937 | 0.854 | 0.083 |
| PS | 1.11 | 1.054 | 0.057 |
| PET | 1.455 | 1.335 | 0.120 |
| P.V.al | 1.345 | 1.269 | 0.076 |

**Exp. No. (12)**

# Techniques of Polymerization

## Introduction

Phase systems in polymerization can be classified as:



In this experiment we shall discuss bulk polymerization and suspension polymerization:

Method /

The characterization of these methods shown in table 3.

| **Method** | **Homogenous** |
|---|---|
| ***Bulk polymerization*** | The reaction is carried out within the monomer which is catalyzed by initiator, highly exothermic process, increasing in viscosity.<br>Ex. Preparation of PMMA, PVC, PVA. |
| ***Solution polymerization*** | Both the monomer and the polymer produced are soluble in a suitable solvent, easy dissipation تبديد توزيع of heat evolved as a result of exothermic reaction.<br>يحجز تماماً<br>The solvent is occluded and firmly traps the polymer for this reason solution polymerization is mainly applied when solutions of polymer are required for technical application for e.g. as lacquers, adhesives.<br>The products of this method are relatively low molecular weight because of the possibility of chain transfer to solvent. |
| | **Heterogeneous** |
| ***Suspension polymerization*** | The monomer containing initiator, modifier معدلات etc. is dispersed in a solvent (water) by vigorous شديد stirring.<br>For a stable suspension of monomer in the solvent some stabilizers are added.<br>These may be protective colloids. الغرويات الواقية |

**Apparatus**

1. Beaker
2. Test tube (3)
3. Thermometer
4. Glass rod
5. Watch glass
6. Water bath

**Reagent and materials for**

***Procedure A***

1. Methyl methacrylate monomer
2. Benzoyl peroxide
3. Ethanol

***Procedure B***

1. Methyl methacrylate monomer
2. Benzoyl peroxide
3. Benzene
4. Ethanol

***Procedure C***

1. Methyl methacrylate monomer
2. Benzoyl peroxide
3. Distilled water
4. Ethanol

### *Procedure A*

(Bulk polymerization of methyl methacrylate)

1. Add 2.5ml of methyl methacrylate monomer in dry test tube with 0.03g of benzoyl peroxide.
2. Heat the mixture in water bath at 80°C for a time (15min) with stirring.
3. Take the mixture out of water bath, then add (5ml) of ethanol with stirring to precipitate the polymer.
4. Separate the precipitate polymer from the solution, then carry it to weight filter paper.
5. Dry, weight the polymer and calculate the yield percentage.

### *Procedure B*

(Solution polymerization of methyl methacrylate)

1. Add 2.5ml of methyl methacrylate monomer in dry test tube with 0.03g of benzoyl peroxide and 2.5ml of benzene.
2. Heat the mixture in water bath at 80°C for a time (15min) with stirring.
3. Take the mixture out of water bath, then add (5ml) of ethanol with stirring to precipitate the polymer.
4. Separate the precipitate polymer from the solution, then carry it to weight filter paper.
5. Dry, weight the polymer and calculate the yield percentage.

### *Procedure C*

عالق

(Suspension polymerization)

1. Add 2.5ml of methyl methacrylate monomer in dry test tube with 0.03g of benzoyl peroxide and 2.5ml of distilled water, 0.1g PVA or CMC.
2. Heat the mixture in water bath at 80°C for a time (15min) with stirring.
3. *Take the mixture out of water bath, then add (5ml) of ethanol with* stirring to precipitate the polymer.
4. Separate the precipitate polymer from the solution, then carry it to weight filter paper.
5. Dry, weight the polymer and calculate the yield percentage.

*Note:* Add PVA or CMC for protective colloids.

**Exp. No. (13)**

# Primary Identification of Polymers

## Introduction

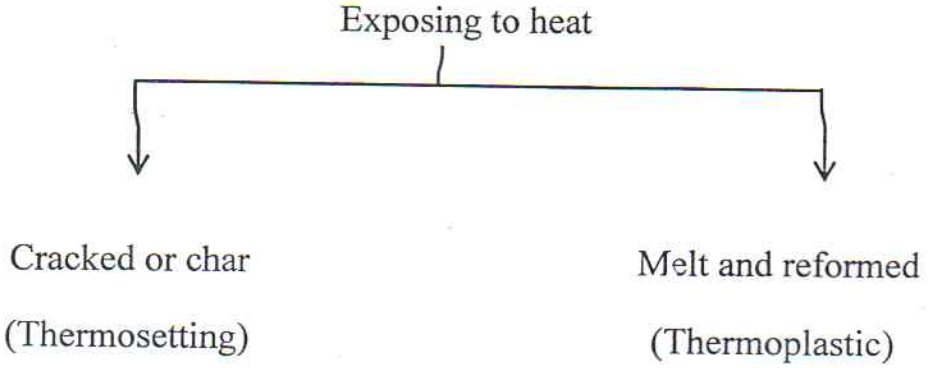
The reaction of various tests are directly related to the structure of the polymeric materials.

A useful link can be made in this way between structure and behaviors.

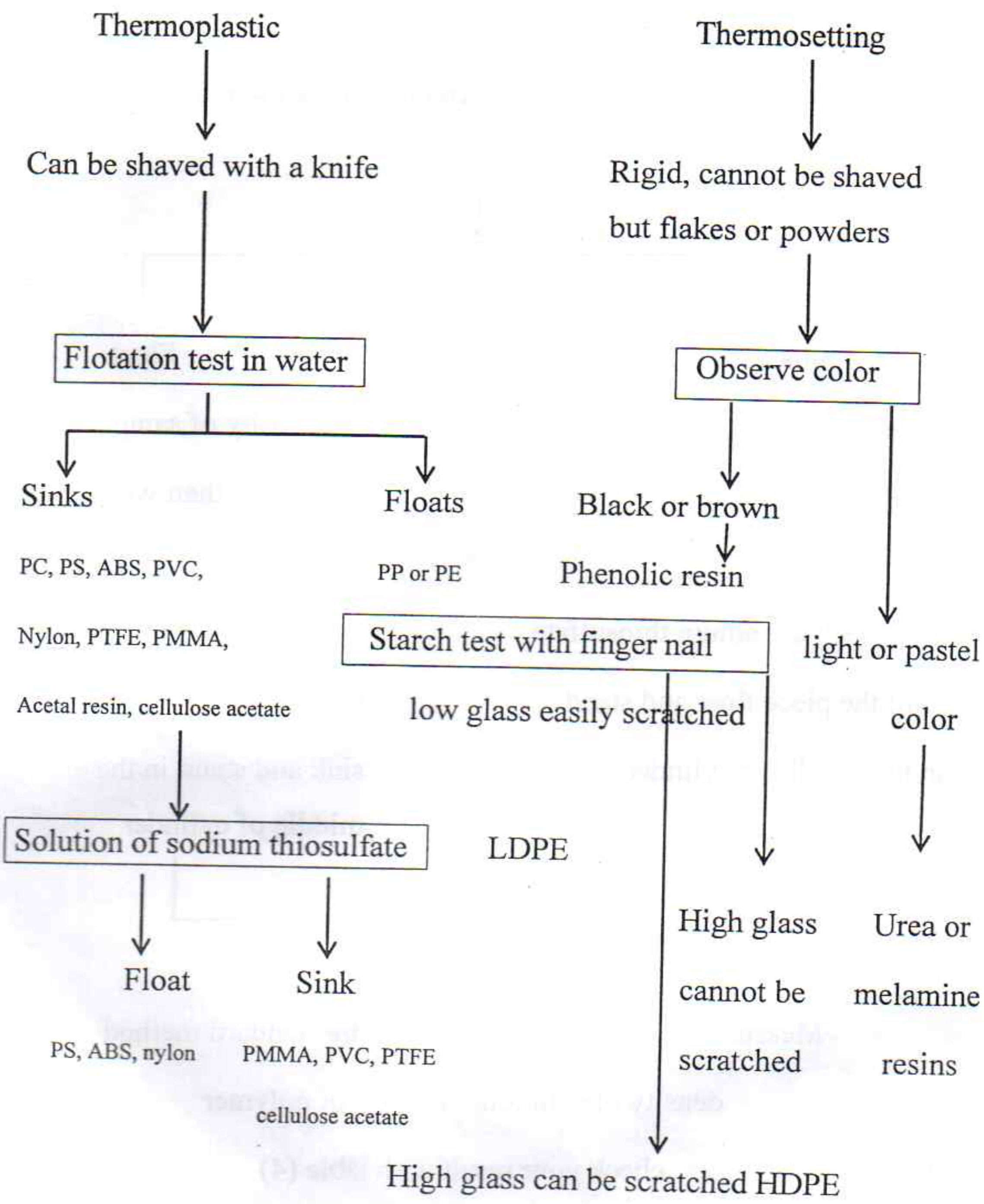
It should be realized that these simple tests is not always possible to give a positive identification of every type of plastic material. As some plastics are modified by additions, fillers, colors … etc.

### *1st test: Thermosetting or Thermoplastic*

The material should be cutted to a small pieces, exposing to heat and notice if

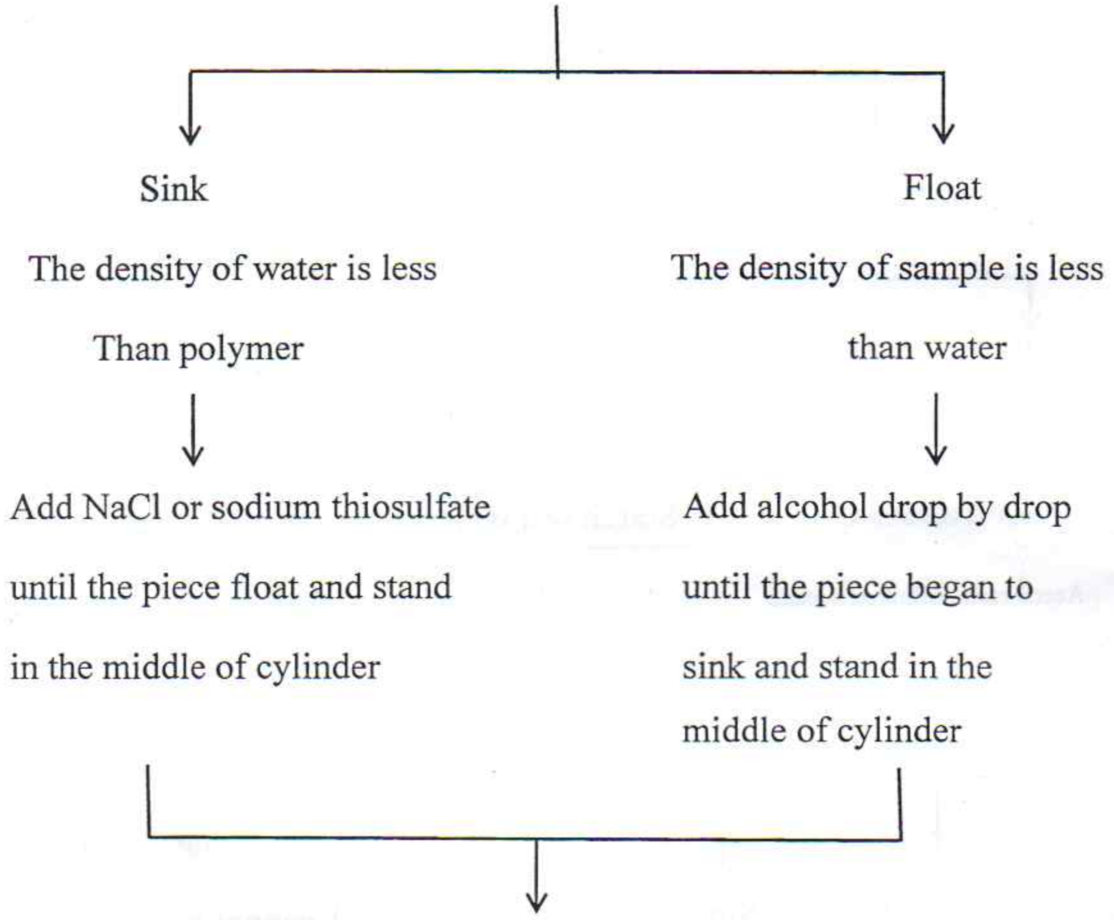


Another tests are followed.


Thermoplastic
Can be shaved with a knife
Flotation test in water
Sinks
PC, PS, ABS, PVC,
Nylon, PTFE, PMMA,
Acetal resin, cellulose acetate
Solution of sodium thiosulfate
Float
PS, ABS, nylon
Sink
PMMA, PVC, PTFE
cellulose acetate
Floats
PP or PE
Starch test with finger nail
low glass easily scratched
LDPE
High glass cannot be scratched
High glass can be scratched HDPE
Thermosetting
Rigid, cannot be shaved
but flakes or powders
Observe color
Black or brown
Phenolic resin
light or pastel
color
Urea or
melamine
resins

### $2^{nd}$ *test: Density measurement (Specific gravity)*

Put small piece of plastic material in cylinder containing water and the floatation.



Sink

The density of water is less Than polymer

Add NaCl or sodium thiosulfate until the piece float and stand in the middle of cylinder

Float

The density of sample is less than water

Add alcohol drop by drop until the piece began to sink and stand in the middle of cylinder

Measure the density of the solution by standard method

density of solution = density of polymer

check your result with table (4)

Table 4: Density and specific gravity of some polymer

| | Polymer | Density | Specific gravity |
|---|---|---|---|
| Float on water | PP | 0.850 | 0.90 |
| | LDPE | 0.90 | 0.92 |
| | HDPE | 0.96 | 0.96 |
| Sink in water | PS | 1.04 | 1.07 |
| | ABS | 1.10 | 1.10 |
| | Nylon | 1.10 | 1.10 |
| Sink in hypo | PMMA | 1.20 | 1.20 |
| | PVC | 1.40 | 1.40 |
| | UREA | 1.50 | 1.50 |
| | PTFE | 2.00 | 2.75 |
| | Cellulous | 1.28 | 1.30 |

### *3rd test: Burning test*

The plastic materials can be classified into three types according to their burning characteristic.

1. Burned and did not extinguish after the fire source was keep back (extinguishable) e.g. PS, PE, PP, …
2. Burned and self extinguish after the fire source was keep back (extinguishable) e.g. PVC, Rubber.
3. Unburned, PTFE.

**Procedure**

Hold a small in flame. If it ignites, withdraw it from the flame a distance of about 6cm. Make observations as listed below:

1. Degree of flammability: burns; self extinguishing or not, dose not burn.
2. Color of flame: yellow and orange, blue, blue with yellow edge, etc… (notice the tip and the base of the flame).
3. Color of smoke: no smoke; black, white.
4. Type of flame: steady, tall, short, sputtering.
5. Vapor after extinguishing: acidic or basic by litmus paper.

Compare your results with table (5) to decide the type of the polymer.

Table 5: Typical results of burning tests

| **Polymer** | **Color of flame** | **Kind of smoke** | **Vapor** | **Other features** |
|---|---|---|---|---|
| PE | Blue with yellow tip | Absent | Neutral | Flaming plastic |
| PP | Yellow with blue base | Absent | Neutral | Flaming plastic |
| PTFE | Will not burn | Non | Non | Non |
| PS | Orange-yellow with blue base | Heavy black smoke | Neutral | Spurting burns |
| PVC | Yellow with green base | White smoke | Acid | Difficult to burn and self extinguish |
| Cellulose acetate | Yellow and turn brown at base | Light smoke | Acid | Burn, strong smell of vinegar |
| PMMA | Blue and yellow bubble at base | Little black smoke | Neutral | Burns and not extinguish |
| Nylon | Blue with yellow tip | Non | Neutral | Burns and flame lead to go out |
| Acetal resin | Pale blue | Non | Neutral | Burn |
| Poly carbonat | Yellow | Black smoke | Neutral | difficult to light |
| Phenol resin | Yellow with spark | Non | Neutral | Difficult to burn and self extinguish |
| Urea resin | Yellow with light blue edge | Non | Basic | Burn and flame lead to go out |
| Melamine resin | Pale yellow with light blue-green edge | non | Basic | Difficult to burn |
| Poly ester | Yellow with blue base | very dense smoke | Neutral | burn |
| Poly urethan | Yellow with blue base | Non | Neutral | burn |
| ABS | Yellow with blue base | Black smoke | Neutral | Difficult to burn and self extinguish |

### *4th test: Melting and odor characteristics*

Heat a metal plate over a Bunsen flam or electric plate and piece of polymeric material on it.

Observe the melt behavior (softness, hard, flows, bubbles, swells does not char but melts and chars). For odor, use a description by relating it to a familiar smell (burning rubber, sweet fruity, marigold, burning paperacid, rancid rubber). In most cases a strong odor will be noticed when the materoal is burning. Check your result against table 6.

Table 6: Melting and odor characteristics

| **Polymer** | **Melting behavior** | **Odor** |
|---|---|---|
| PE | Melt and bubbles fiercely around the edge | Waxy burning candle |
| PP | Becomes soft, tends to forma ball | Waxy smell |
| PTFE | Dose not melt | Non |
| PS | Melt and bubbles around edges | Marigold (styrene) |
| ABS | Becomes soft but not fluid | Burning rubber |
| PVC | Softens and forms a ball, chars at the bottom | Characteristic smell |
| Cellulose acetate | Melt and emits white smoke boils and chars | Vinegar |
| PMMA | Boils and bubbles | Fruity, floral smell |
| Poly carnonat | Bubbles develops acellulor structures before decomposing | Non |
| Nylon | Melt round edge and chars | Burning hair or wool |
| Phenol resin | Does not melt | Carbolic smell |
| Urea resin | Does not melt | Fishy smell |
| Melamine resin | Does not melt | Fishy smell |

### 5th test: Solubility test

The solubility process of polymer is differ than the solubility of organic materials (small molecules). In polymer solubility, the polymer swell in primary stage. In some cases there are only swelling but no stability. This case is not solubility so the polymer dissolving need long time with stirring. In this test need two solvents acetone and *n*-propanol.

**Procedure**

1. Shave off small amount of plastic materials, place the shaving into a test tube.
2. Add just enough solvent to cover the shavings.
3. Stir with glass rod for a few minutes and note the results.
4. If the plastic dose not dissolve, leave for many minutes and stir again.

Check your results against table 7.

Table 7: Typical results at solubility tests

| Polymer | Dissolved in acetone | Dissolved in *n*-propanol |
|---|---|---|
| PE | × | × |
| PP | × | × |
| تفلون PTFE | × | × |
| PS | o | × |
| ABS | o | × |
| PVC | + | × |
| Cellulose acetate | o | + |
| PMMA | o | × |
| Nylon | × | × |
| All resin | × | × |

× = not soluble  o = Soluble  + = slightly soluble

**Exp. No. (14)** البلمرة الاستحلابية

# Emulsion Polymerization

## Introduction

In emulsion polymerization, the monomer is dispersed in water containing an emulsifying agent (كعامل مستحلب) such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse (تنتشر) into soap micelles (المذيلات) swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles to continue the reaction. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination, extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds called *chain transfer agents* are added that control the degree of polymerization.

خاصة Emulsion polymerization is widely used in industry, and is particularly useful for manufacturing water-based (latex) paints or adhesives.

جزيئة توتر سطحي

مذيلات

0.85 + 5

## Apparatus

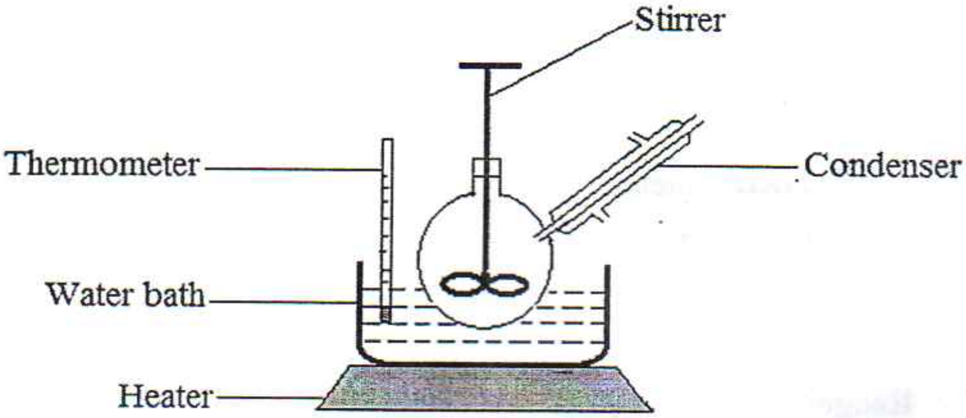
1. Round bottom flask with 2 neck.
2. Condenser.
3. Glass stirrer.
4. Thermometer.
5. Heating bed.

## Reagent and materials

1. Potassium thiosulfate.
2. Potassium persulfate.
3. Acrylo nitrile monomer.
4. Aluminum sulphate.

## Procedure

1. Charge the following materials in a 100ml two-necked round bottom flask:
   - 5ml of acrylo nitrile monomer.
   - 0.5g of liquid soap.
   - 0.03g of potassium thiosulfate.
   - 0.03g of potassium persulfate.
   - 30ml distilled water.
2. Connect the instruments as in the following scheme.
3. Heat in bath water at 70°C with vigorous stirring for 1hr.
4. Add 5ml of aluminum sulfate solution (2.5%).
5. Filter and wash with warm water and methanol.
6. Dry at 60°C, weight and calculate the percentage of the yield.


Stirrer
Thermometer
Condenser
Water bath
Heater