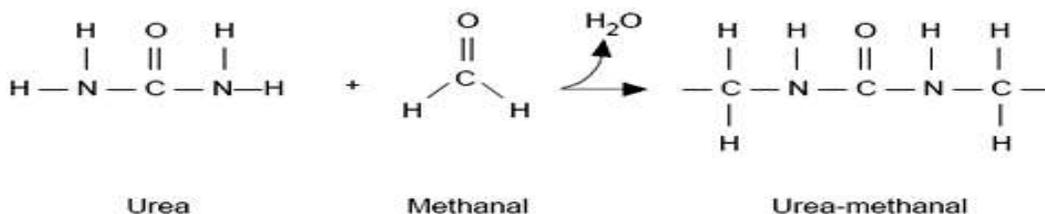


## Polymer Laboratory

### Exp.1: Urea-Formaldehyde [Methanal] polymerization

Urea is dissolved in aqueous formaldehyde in a throw-away container. Acidification of this solution initiates condensation polymerization, and a hard, white, thermosetting polymer is formed within a few minutes. After washing, the properties of this substance can be investigated. If a mould is used, the experiment can be extended to show the formation of plastic articles made in a mould by condensation polymerization. The reaction is a condensation polymerization in which water is eliminated as the hydrogen atoms from the ends of one amino-group from each of two urea molecules combine with the oxygen atom from a formaldehyde molecule. The remaining  $-\text{CH}_2-$  group from the formaldehyde molecule then forms a bridge between two neighboring urea molecules, as shown below. This process, repeated many thousands of times, forms long chains of urea and formaldehyde molecules linked in this way.

Sometimes the second hydrogen atom on an amino-group will also react with a formaldehyde molecule, producing a branch in the chain, and chains may even become cross-linked to each other. Eventually a random three-dimensional network of cross-linked chains is formed, giving a rigid structure and thus a hard, inflexible material. The product has many cross links: Because the tangle of cross-linked chains is almost impossible to separate, the material does not melt on heating, although it will eventually break down at high temperature, decomposing and giving off small molecules such as steam and nitrogen, leaving a charred mass which is largely carbon.





## **Exp.2: The Condensation Polymerization of Phenol and Formaldehyde :Bakelite**

The first completely synthetic organic polymer was Bakelite, named for its discoverer Leo Baekeland .He was a Belgian chemistry professor who invented the first successful photographic paper, Velox .He then turned his attention to finding a replacement for shellac, which comes from the Asian lac beetle .At the time, shellac was coming into great demand in the fledgling electrical industry as an insulator. The polymer Baekeland produced is still used for electrical plugs, distributor caps in automobiles, switches, and the black handles and knobs on pots and pans .It has superior electrical insulating properties and very high heat resistance .It is made by the base-catalyzed reaction of excess formaldehyde with phenol .In a low-molecular-weight form it is used to glue together the plies of ply wood or mixed with a filler such as sawdust .When it is heated to a high temperature, cross linking occurs as the polymer "cures". Most polymers are amorphous, linear macromolecules that are thermoplastic and soften at high temperature . In Bakelite the polymer cross links to form a three-dimensional network and the polymer becomes a dark, insoluble, infusible substance.

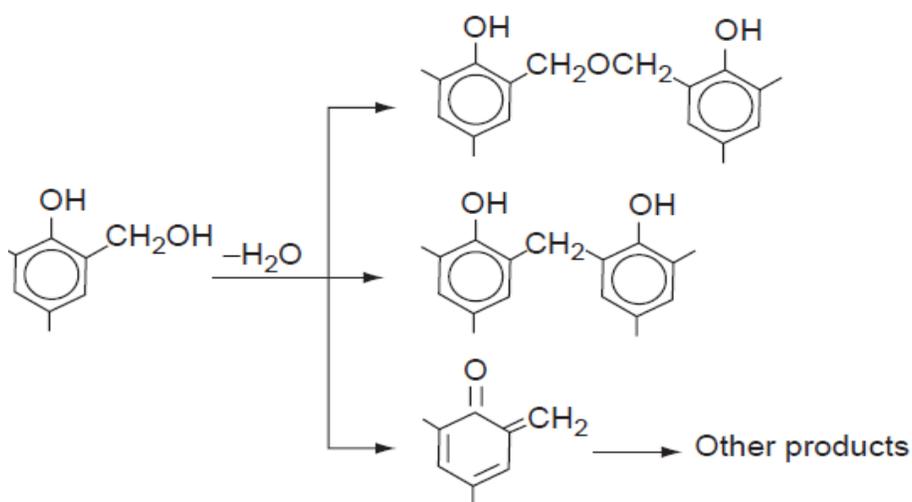
Since the cross-linked polymer of phenol-formaldehyde reaction is insoluble and infusible, it is necessary for commercial applications to produce first a tractable and fusible low-molecular-weight prepolymer which may, when desired, be transformed into the cross-linked polymer .The initial phenol-formaldehyde products prepolymers may be of two types : resols and novolacs.

### **Resols:**

Resols are produced by reacting a phenol with a molar excess of formaldehyde commonly about 1:1.5–2by using a basic catalyst ammonia or sodium hydroxide .This procedure corresponds to Baekeland's original technique .Typically, reaction is carried out batchwise in a resin kettle equipped with stirrer and jacketed for heating and cooling .

The resin kettle is also fitted with a condenser such that either reflux or distillation may take place as required. Two classes of resins are generally distinguished .

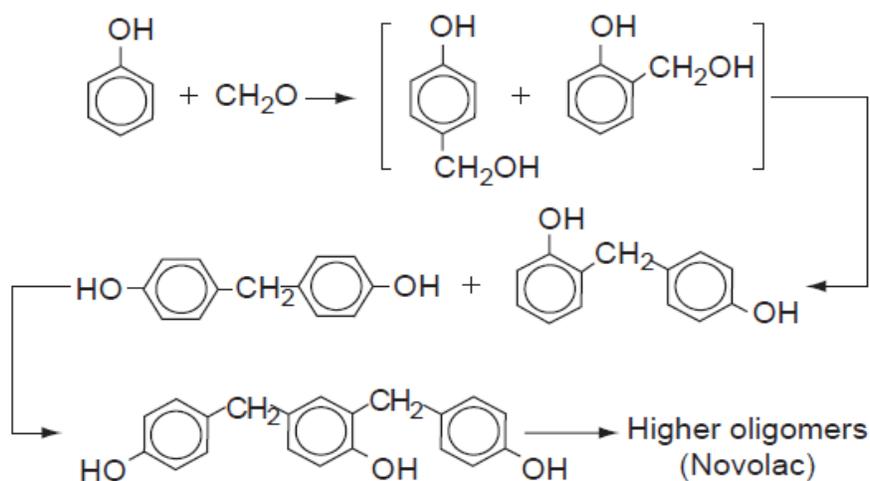
Resols prepared with ammonia as catalysts are spiritsoluble resins having good electrical insulation properties. Water-soluble resols are prepared with caustic soda as catalyst .In aqueous solutions with a solids content of about 70 %these are used mainly for mechanical grade paper and cloth laminates and in decorative laminates. The reaction of phenol and formaldehyde in alkaline conditions results in the formation of *o* -and *p*-methylol phenols .These are more reactive towards formaldehyde than the original phenol and undergo rapid substitution with the formation of di -and trimethylol derivatives .The methylol phenols obtained are relatively stable in an alkaline medium but can undergo self-condensation to form dinuclear and polynuclear phenols of low molecular weight in which the phenolic nuclei are bridged by methylene groups .Thus in the base-catalyzed condensation of phenol and formaldehyde, there is a tendency for polynuclear phenols, as well as mono-, di-, and trimethylol phenols to be formed.



### Novolac :

Novolac resins are normally prepared by the reaction of a molar excess of phenol with formaldehyde commonly about 1.25:1 under acidic conditions .The reaction is commonly carried out batchwise in a resin kettle of the type used for resol manufacture .

Typically, a mixture of phenol, formalin, and acid is heated under reflux at about 100°C . The acid is usually either hydrochloric acid 0.1–0.3 % on the weight of phenol or oxalic acid 0.5–2.% Under acidic conditions the formation of methylol phenols is rather slow, and the condensation reaction thus takes approximately 2–4 h .When the resin reaches the requisite degree of condensation, it become hydrophobic, and the mixture appears turbid. Water is then distilled off until a cooled sample of the residual resin shows a melting point of 65–75°C .The resin is then discharged and cooled to give a hard, brittle solid novolac.



Condensation of phenol with formaldehyde is a base-catalyzed process in which one resonance form of the phenoxide ion attacks formaldehyde .The resulting trimethylol phenol is then cross linked by heat, presumably by dehydration with the intermediate formation of benzyl carbocations .The resulting polymer is Bakelite .Since the cost of phenol is relatively high and the polymer is somewhat brittle, it is common practice to add an extender such as sawdust to the material before cross linking .The mixture is placed in molds and heated to form the polymer .The resulting polymer, like other thermosetting polymers, is not soluble in any solvent and does not soften when heated.



## **Procedure:**

In a 25-mL round-bottomed flask place 3.0g of phenol and 10mL of 37% by weight aqueous formaldehyde solution .The formaldehyde solution contains 10-15 %methanol which has been added as a stabilizer to prevent the formaldehyde from polymerizing .Add 1.5 mL of concentrated ammonium hydroxide to the solution and reflux it for 5 min beyond the point at which the solution turns cloudy, a total reflux time of about 10 min .

In the hood pour the warm solution into a test tube and draw off the upper layer.

Immediately clean the flask with a small amount of acetone .Warm the viscous milky lower layer on the steam bath and add acetic acid drop wise with thorough mixing until the layer is clear, even when the polymer is cooled to room temperature .Heat the tube on a water bath at 60-65°C for 30 min .Then, after placing a wood stick in the polymer to use as a handle, leave the tube, with your name attached, in an 85°C oven overnight or until the next laboratory period .To free the polymer the tube may need to be broken.

## **Polymer Laboratory**

### **Exp.3: Preparation of Polystyrene by Bulk polymerization**

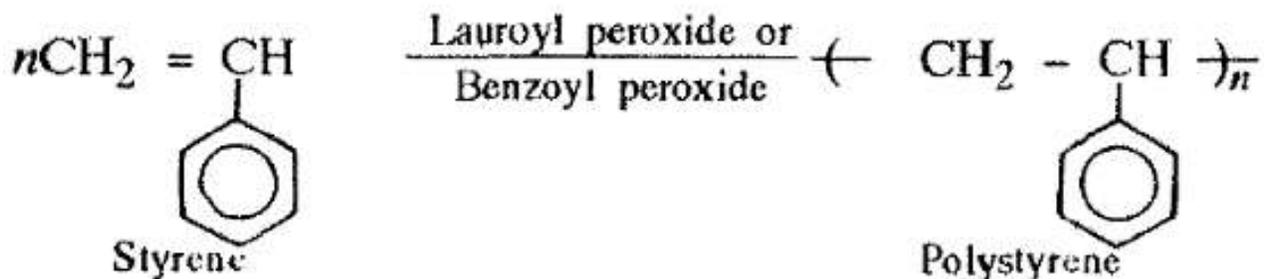
#### **Theory:**

Bulk polymerization consists of heating the monomer without solvent with initiator in a vessel .The monomer-initiator mixture polymerizes to a solid shape fixed by the shape of the polymerization vessel .A free radical catalyst or initiator is dissolved in the monomer which is then heated and stirred in a suitable vessel .The polymerization is exothermic and dissipation of heat through cooling may be required. In the use of polystyrene, the polymerization reaction is exothermic to the extent of 17 Kcal/mol or 200 BTU/lb .As the reaction progresses, the system become viscous making stirring difficult .The method is economical and the product is of high purity .The main practical disadvantages of this method are the difficulty in the removal of polymer from a reactor or flask and the dissipation of the heat evolved by the polymerization.

The technique is used for preparing polyvinyl chloride [PVC], polystyrene [PS] and poly methyl methacrylate [PMMA]

Polystyrene is a brilliantly clear, high-refractive-index polymer familiar in the form of disposable drinking glasses .It is brittle and produces sharp, jagged edges when fractured. It softens in boiling water and it burns readily with a very smoky flame .But it foams readily and makes a very good insulator; witness the disposable, white, hot-drink cup .It is used extensively for insulation when properly protected from ignition .The addition of a small quantity of butadiene to the styrene makes a polymer that is no longer transparent but that has high impact resistance .Blends of acrylonitrile,

butadiene, and styrene [ABS] have excellent molding properties and are used to make car bodies .One formulation can be chrome-plated for automobile grills and bumpers



### Procedure:

#### Polymerization of styrene:

- 1 .Add 50 g of inhibitor-free dry styrene [Wash the styrene monomer twice with 25-ml portions of 25 %aqueous sodium hydroxide in order to remove the inhibitor .Then wash twice with 25 ml of distilled water to remove any residual caustic reagent.], to a test tube.
- 2 .Flush the tube with nitrogen and add 1.0 g of benzoyl peroxide .Gently shake, stopper, and place the tube in an oil bath at 80°C for 1-2 hr.
- 3 .When the styrene becomes syrupy and viscous and before it stops flowing, dissolve the contents in 50 ml of toluene and then pour into 500 ml of methanol in order to precipitate the polystyrene that is formed.
- 4 .Isolate the polymer by filtration and dry in order to calculate the percentage conversion after this time of reaction.

## **Exp.4 :Determination of the Molecular' Weight of a polystyrene Sample by Viscometer**

### **Theory:**

Polymers have high molecular weights, which may vary from 10,000 to several millions .The molecular weight of polymers is related to the chain length and the extent of cross-linking between different chains, the extent of cross-linking depends on the concentration during polymerization of the monomer having functionality higher than two and increases with increase in the functionality .Both the chain length and the extent of cross-linking depend on the reactivity of the monomers and increase with the reaction time in case of condensation polymerization which proceeds via the step-growth mechanism .In case of addition polymerization, which follows a chain mechanism, the length of the chain depends on the relative rates of propagation and termination reactions, a high molecular weight results if the rate of propagation is much more than the rate of termination step .The actual length of the polymer chain in both cases depends on the random encounter between the monomer and the reactive site of the chain .Because of this randomness, some polymer chains may grow longer than the others .The product will thus not be a single chemical species but a mixture of chains of different lengths and therefore of different molecular masses .A polymer sample is thus in homogeneous mixture of different molecules and the range of molecular weight' is fairly wide, therefore, the experimentally determined molecular weight of a polymer sample is always some sort of, an average of the molecular weights of the molecules present .The kind of average depends on the method of measurement. The two most common averages used are the number average and the weight average.

Addition of even a very small amount of a polymer to a solvent of low viscosity causes a sharp increase in its viscosity .The magnitude of increase in viscosity depends, in addition to other factors such as concentration, size and shape of the solute molecules, on the molecular weight of the' polymer .Mathematical manipulations have reduced the

problem of determination of the molecular weight of a polymer to a few simple viscometric measurements on the pure solvent and solutions of known concentration of the polymer in that solvent. The ratio or the coefficient of viscosity of the solution  $\eta_s$  to the coefficient of viscosity of the pure solvent  $\eta_o$  at the same temperature, is known as viscosity ratio or Relative Viscosity  $\eta_r$  which, by using expression,

$$\eta_1 = \eta_2 \frac{\rho_1 t_1}{\rho_2 t_2}$$

Can be written as:

$$\eta_r = \frac{\eta_s}{\eta_o} = \frac{\rho_s t_s}{\rho_o t_o}$$

Where  $\rho_s$ , and  $\rho_o$  are the densities of the polymer solution and the solvent respectively,  $t_s$  and  $t_o$  are the corresponding efflux times for the flow of some specified volume of the two through the same capillary [Viscometer] of narrow bore and a long efflux time of about 200 seconds] .For a dilute polymer solution [ $C < 0.5$  g/100ml] the density of the solution may be taken as equal to that of the solvent, i.e.,  $\rho_s = \rho$

Then :

$$\eta_r = \frac{t_s}{t_o}$$

Dividing [ $\eta_s - \eta_o$ ] the increase in viscosity of the solvent due to the presence of the solute, by [ $\eta_o$ ] the viscosity of the pure solvent, gives Specific Viscosity  $\eta_{sp}$ , of the polymer solution:

$$\eta_{sp} = \frac{\eta_s - \eta_o}{\eta_o} = \frac{\eta_s}{\eta_o} - 1$$

$$= \eta_r - 1 = \frac{t_s}{t_o} - 1$$

The ratio of the specific viscosity of the solution to its concentration  $C$ , expressed in grams per 100 ml [g/dl] is called Viscosity Number, Reduced Specific Viscosity or simply Reduced Viscosity,  $\eta_{red}$ . Therefore,

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

Whereas both  $\eta_r$  and  $\eta_{sp}$  vary sharply with concentration, the variation of  $\eta_{red}$  with concentration is somewhat less and regular, and the plot of  $\eta_{red}$  versus concentration is a straight line [Fig. 1] given by the equation

$$\eta_{red} = \frac{\eta_{sp}}{C} = mC + \text{constant}$$

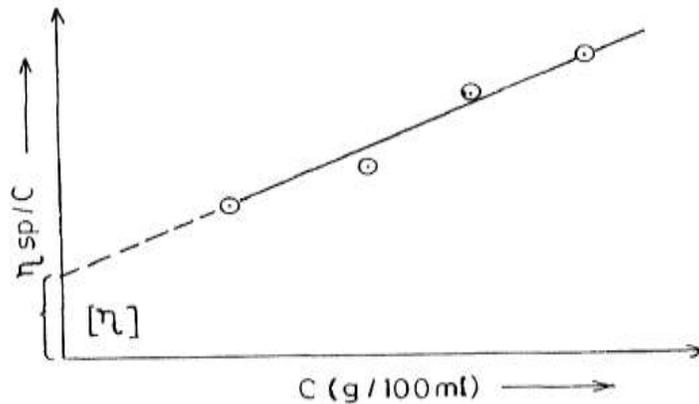


Fig.1 :Plot of Reduced Viscosity versus Concentration

Where  $m$  is the slope of the line.

The value of the constant is given by the intercept on the ordinate obtained by extrapolating the graph to zero concentration [infinite dilution]. This constant which becomes independent of concentration is the limiting value of the reduced viscosity and is termed as Limiting Viscosity Number or Intrinsic Viscosity  $[\eta]$ .

Mathematically.

$$[\eta] = \lim_{C \rightarrow 0} \left( \frac{\eta_{sp}}{C} \right)$$

or

$$\frac{\eta_{sp}}{C} = mC + [\eta]$$

For linear polymers, the intrinsic viscosity  $[\eta]$  and the molecular weight  $[M]$  are generally found to obey the [Mark-Kuhn-Houwink ] empirical equation.

$$[\eta] = KM^a \quad \dots\dots\dots[1]$$

Where  $[K]$  and  $[a]$  are constants for a particular polymer / solvent/ temperature system .

$[K]$  and  $[a]$  values are known for many systems some of which are given in Table 1

Polymer	Solvent	Temperature (°C)	$K \times 10^4$	$a$
Polystyrene	Benzene	25	1.02	0.74
		30	1.10	0.735
	Toluene	25	1.1	0.72
		30	1.1	0.725
Polyisobutylene	Benzene	30	6.1	0.56
	Toluene	30	2.0	0.67
Polyvinyl acetate	Acetone	25	1.88	0.69
		30	1.02	0.72
Natural rubber	Benzene	30	1.85	0.74
	Toluene	25	5.0	0.67
Polymethyl methacrylate	Acetone	25	0.75	0.7
		30	0.7	0.7
	Toluene	25	0.75	0.71
		30	0.7	0.72

Table [1] Intrinsic viscosity-molecular weight constants  $[K]$  and  $[a]$  in above equatio] for some polymer/solvent systems.  
For most systems,  $[a]$  lies between 0.6 and 0.8 and  $[K [ 10^4]$  lies between 0.5 and 5.

**Procedure:**

**a-[Preparation of Polymer Solution]**

Weigh accurately  $500 \pm 1$  mg of the well-dried powdered polystyrene and transfer quantitatively to a 100-ml measuring flask .Add 90-95 ml of the solvent [benzene or toluene], stopper the flask and suspend it in the thermostat maintained at  $25^{\circ}\text{C}$  .Shake occasionally to dissolve the sample .When the solution has acquired the temperature of the bath, add more solvent to fill the flask up to the graduation mark. Filter the polymer solution through a coarse porosity sintered glass filter without suction into a suitable glass-stoppered clean dry container.

Concentration of this solution is 0.5 g/100 ml [0.5%] Make solutions of lower concentrations [0.1 %, 0.2%, 0.3 % and 0.4%]by appropriate dilution of the above solution with well-filtered solvent.

**b** -[Measurement of Flow Time with Ostwald Viscometer]:

Wash the Ostwald viscometer with chromic acid/sulphuric acid mixture, tap water and then with distilled water and dry in an air oven .Pipet 20 ml of the well filtered solvent into the wide arm reservoir [R] of the viscometer [Fig2] and attach it to the mounting support in the thermostat .Allow 5-10 min for attainment of temperature .Using a rubber ball, force air into the wide arm so as to raise the level of the liquid into the capillary arm above the higher mark [M 1]. Then release the pressure and with a timer, measure the time in which the liquid meniscus moves from the upper mark [M1] to the lower mark [M2] .Repeat to get five values and use the average as the flow time  $t_o'$

Now remove the viscometer from the thermostat and pour out the liquid from the wide arm, as completely as possible .Properly clean the viscometer, dry it and fill it with 20 ml of one of the solutions and determine the flow time as before. Similarly, determine the flow times for solutions of different concentrations, properly cleaning and drying the viscometer whenever the solution is to be changed .

Use below table to calculations:

Polymer Solution	Flow time (sec.)	Relative viscosity	Specific viscosity	Reduced viscosity
Concentration C(g/ dl)	Average of 5 measurements $\frac{t_1+t_2+t_3+t_4+t_5}{5}$	$\eta_r = \frac{\eta_s}{\eta_o} = \frac{t_s}{t_o}$	$\eta_{sp} = \eta_r - 1$	$\eta_{red} = \frac{\eta_{sp}}{C}$

**c- Determination of Intrinsic Viscosity:**

Plot the various values of reduced viscosity against the corresponding concentrations and extrapolate the graph to zero concentration [Fig.1] Read the value of intercept on the ordinate .Record it as the value of  $[\eta]$

Calculation of Molecular Weight

Substitute the value of  $[\eta]$ ,  $[K]$  and  $[a]$  in equation [1], and calculate the value of  $M$

$$\begin{aligned} [\eta] &= KM^a \\ \log [\eta] &= \log K + a \log M \\ \log M &= \frac{\log [\eta] - \log K}{a} \\ M &= \text{Antilog} \left[ \frac{\log [\eta] - \log K}{a} \right] \end{aligned}$$

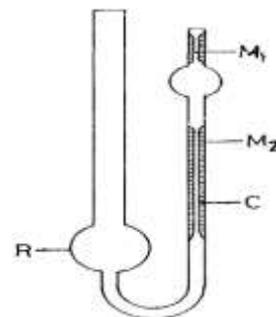


Figure 2 :Ostwald Viscometer

**Polymer Laboratory**  
**Exp.5 :Preparation of Nylon 6,6 and Nylon 6,10 by**

## Interfacial Polycondensation

### Theory:

In interfacial polycondensation the reaction takes place at the interface between solutions of the reactants in immiscible solvents. Increasing the interface by thorough agitation of the two solutions substantially increase the rate of polymerization. Exact stoichiometry is not necessary and a high molecular weight product can be easily formed. Being very simple, the method is widely used for the production of polyamides, polyesters, polyurethanes and polysulphonamides. Difference in the reactivity of materials can be utilized to prepare ordered copolymers which otherwise are very difficult to produce. The technique is however limited to reactants having highly reactive functional groups that can readily react at the ambient temperatures. When an aqueous solution of the diamine is carefully brought in contact with the solution of the diacid dichloride in an organic solvent [immiscible with water], the reactants diffuse to the interface where the polycondensation reaction takes place:

The polymer film, which is insoluble in both the solvents, is formed at the Interface and, using a pair of forceps, can be drawn out in the form of a thread or a rope.



appears at the interface, hold it gently at its Centre with a pair of forceps and lift out of the beaker .As it comes out in the form of a thread or rope, wrap it around a thick glass rod or a test tube .

For continuous and automatic wrapping of the thread, a mechanical or an electrical wind-up device may be placed up the beaker.

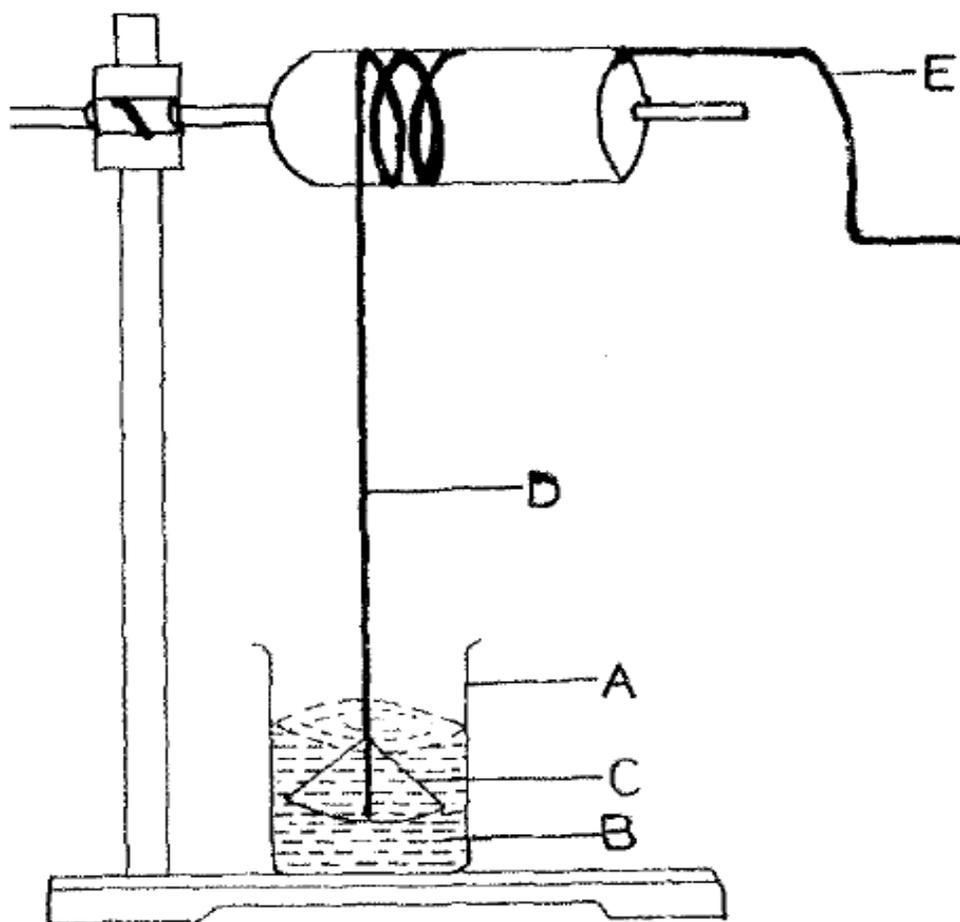


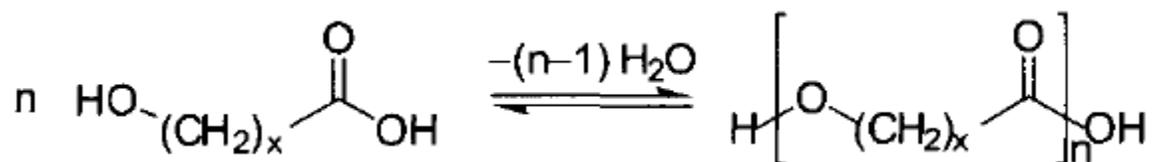
Figure 1 :Preparation of Nylon 'Thread

### **Petrochemistry laboratory**

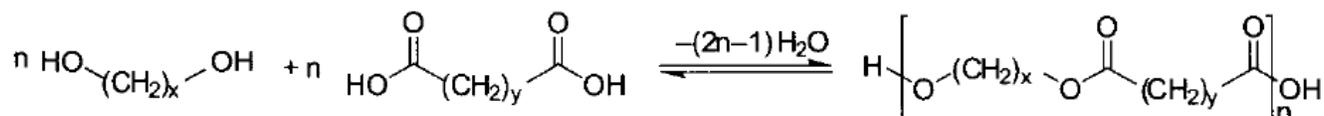
### **Exp.6: Preparation of phthalic alkyde resin**

Condensation polymerizations [polycondensations] are stepwise reactions between bifunctional or polyfunctional components, with elimination of small molecules such as water, alcohol, or hydrogen and the formation of macromolecular substances. For the preparation of linear condensation polymers from bifunctional compounds [the same considerations apply to polyfunctional compounds which then lead to branched, hyperbranched, or crosslinked condensation polymers] there are basically two possibilities. One either starts from a monomer which has two unlike groups suitable for polycondensation [AB type], or one starts from two different monomers, each possessing a pair of identical reactive groups that can react with each other [AABB type].

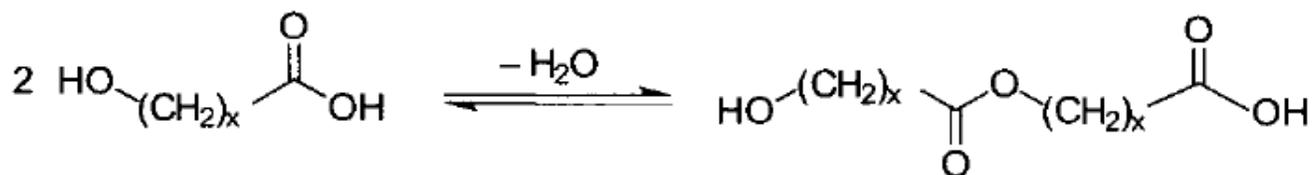
An example of the AB type is the polycondensation of hydroxycarboxylic acids:



An example of the AABB type is the polycondensation of diols with dicarboxylic acids:



The formation of a condensation polymer is a stepwise process. Thus, the first step in the polycondensation of a hydroxycarboxylic acid [AB type] is the formation of a dimer that possesses the same end groups as the initial monomer:



The end groups of this dimer can react in the next step either with the monomeric compound or with another dimer molecule, and so on. The molecular weight of the resulting macromolecules increases continuously with reaction time, unlike many addition polymerizations, e.g., radical polymerizations. The intermediates that are formed in

independent, individual reactions, are oligomeric and polymeric molecules with the same functional end groups as the monomeric starting compound

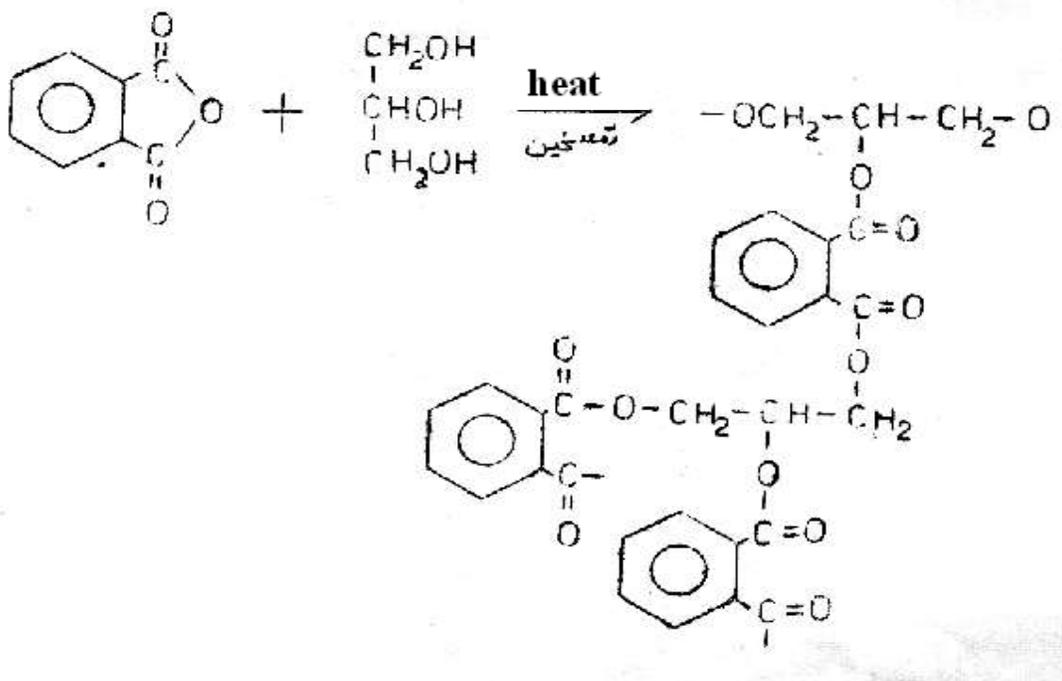
One class of crosslinkable polyesters is the so-called alkyd resins. Alkyd resins are defined as branched or crosslinked polyesters obtained, for example, by polycondensation of a dicarboxylic acid with a polyfunctional alcohol. Branching and crosslinking occur consecutively in a controllable manner. Thus, in the polycondensation of glycerol with phthalic acid anhydride, there is first formed a branched polyester that remains soluble and fusible as long as the polycondensation is interrupted before more than about 75 mol% of the hydroxy or carboxyl groups have reacted. If this degree of condensation is exceeded the branched polyester transforms by further polycondensation [self crosslinking] into completely insoluble products. Since one is dealing with crosslinking by polycondensation here, a temperature of about 200 °C is generally required [baking varnishes]. Of course, if carboxylic acids containing double bonds are incorporated into the alkyd resins they can be crosslinked by the action of atmospheric oxygen at lower temperatures. However, the crosslinking then proceeds by a different mechanism. The dicarboxylic acids normally employed are phthalic acid or its anhydride, or mixtures of them with for example, adipic acid or unsaturated acids. The polyhydroxy compounds generally used are glycerol, trimethylolpropane, or pentaerythritol. In the preparation and crosslinking of alkyd resins [with the exception of some unsaturated alkyd resins] the reaction is practically always carried out in the melt.

For many years, resins resulting from the polycondensation of polyacids and polyols have been used in the paint industry. They have been named in many different ways which have led to ambiguities, as to the composition and utilisation of these products. Alkyds, Polyesters, Glycerols, Glycerophthalics, Oil-free Polyesters"

Alkyd resins are a class of polyester coatings derived from the reaction of an alcohol and an acid or acid anhydride hence the term alk-yl from "alcohol and acid or anhydride]" and are the dominant resin or "binder" in most "oil-based" coatings sold to the consumer market.

The term "Glycerophthalic" arises from the fact that the first resins were based on glycerol and phthalic anhydride. Alkyd resins today are typically manufactured from acid anhydrides such as phthalic anhydride or maleic anhydride and polyols such as glycerine [which is the first polyol used in production of alkyd resins] or pentaerythritol and are modified with unsaturated fatty acids [from plant and vegetable oils] to give them air drying properties.

The reaction between phthalic anhydride and glycerine, is a multistage reaction, if it stopped in its earlier stages, it will give a viscous solution used in manufacturing of some types of paints, and if the reaction continued for higher temperature, the product will solidify and more interlaced, which is used in varnish production and some types of paints after the addition of the unsaturated fatty acids to give which is known as alkyd paints.



### Procedure.

- 1- Put 6g from phthalic anhydride after grinding it, with 4g from glycerol in a large test tube and mix them.
- 2- Heat with mixing for one hour using an oil bath at temperature [150-180 °C].

**3-** One group of students will stop the reaction and take a part of the solution on a filter paper which become viscous not solid.

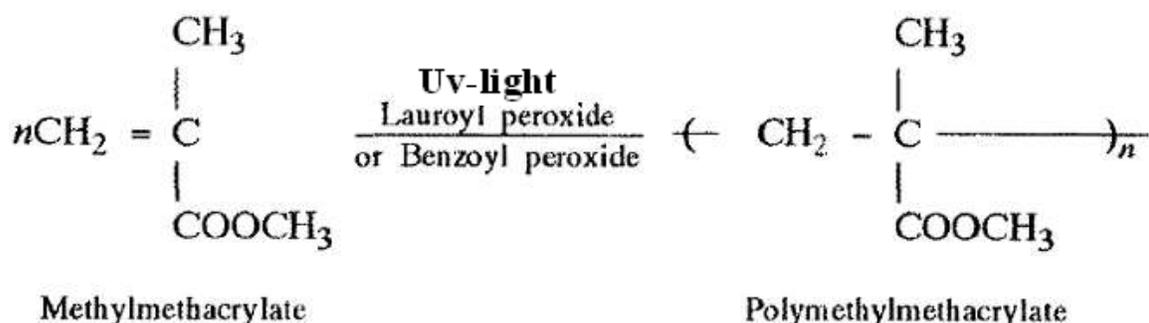
**4-** The second group will continue the reaction by increasing the temperature to [200-230 °C], where it will agglomerate, and the completion of the reaction can be noticed by taking a drop from the solution on a filter paper, if it solidified after cooling, that is indication to the completion of the reaction, and the alkyd resin is formed.

**5-**After the reaction is completed, pour the solution on a filter paper and let it to cool and solidify, then grind it.

## **Polymer Laboratory**

### **Exp.7: Bulk Photopolymerization of Methyl Methacrylate:**

The initiation of polymerization by ultraviolet radiation has been of particular interest in the study of free radical processes. The test tube demonstration described here is simple and may be used to evaluate the polymerizability of new monomers or to study some of the physical properties of a polymer. Although the method is particularly effective for acrylic and methacrylic monomers, it may also be applied to the polymerization of a wide range of "vinyl"-type monomers. Generally, the method depends on the sensitization of the monomer to ultraviolet radiation with reagents such as biacetyl or benzoin. With sensitizers, initiation stops when the source of radiation is turned off, this is followed by a rapid decay of the polymerization process. When a conventional initiator, such as dibenzoyl peroxide, is also present, the process is more rapid than when the sensitizer is used by itself. It also seems to continue after the radiation source has been discontinued. It is presumed that ultraviolet [UV]-induced decomposition of the peroxide becomes involved in the process. By this method, polymerizations may be carried out at temperatures well below those normally used with thermal initiators such as organic peroxides.



## Procedure:

1. Fill the 12 cm X 12 mm test tube with some of the 0.5% solution of sodium stearate in isopropanol. In a hood, pour the solution off into a suitable container. Allow the inside of the test tube to dry thoroughly [see Note 1].
2. While the test tube dries, prepare a solution of 0.5 g of benzoin in 10 ml of methyl methacrylate. Then add 0.5 g of dibenzoyl peroxide [see Note 2].
3. When the test tube is ready for use, place the methyl methacrylate initiator solution in the test tube. Cover the neoprene stopper with the polyethylene film and stopper the test tube.
4. Place the test tube in a test tube rack or a beaker. Note the time and expose the test tube to sunlight. From time to time, note the time and observe the progress of the polymerization [see Note 3].

## NOTES

1. In this experiment, coat the inside of the test tube with a thin layer of sodium stearate [or a plain, nonperfumed soap]. This will assist in removing the product from the apparatus.
2. In the laboratory, the source of radiation may be a high-intensity mercury lamp. However, for simple test purposes, sunlight is quite suitable. Even a lightly overcast sky furnishes sufficient UV radiation for photo-induced polymerizations. Naturally, bright sunlight is more effective.
3. As the polymerization of methyl methacrylate is somewhat inhibited by atmospheric oxygen, the upper layer of the polymerizing monomer may still be fluid, even though most of the material has already been converted. Therefore, when checking on the progress of the experiment, do not simply shake the test tube. Instead, either invert the test tube or insert a probe [a long pin, a paper clip, etc.] to check on the process.

## Polymer Laboratory

## **Exp 8: Preparation of Poly Cellulose Acetate**

Numerous chemical conversions of macromolecular substances are of technical interest, like reactions that attach or alter small parts of a polar group. Examples are the introduction of carboxyl or hydroxy groups to increase hydrophilicity, crosslinking [vulcanization] of polydienes with sulfur, or conversions that proceed only at the terminal groups under retention of the molecular backbone [chain-analogous conversion].

Amongst the important chemical conversions of macromolecular substances are the various reactions of cellulose. The three hydroxy groups per constitutional repeating units [CRU] can be partially or completely esterified or etherified. The number of hydroxy groups acetylated per [CRU] are indicated by the names, i.e., cellulose triacetate, cellulose 2-acetate, etc. Another commercially important reaction of cellulose is its conversion to dithiocarboxylic acid derivatives [xanthates]. Aqueous solutions of the sodium salt are known as "viscose"; they are spun into baths containing mineral acid, thereby regenerating the cellulose in the form of an insoluble fiber known as viscose rayon.

Cellulose acetate used as osmotic-cell membrane, cigarette filters, magnetic tapes, photographic film, protective coating solutions, and acetate fibers.

### **Procedure:**

1-In a conical flask add 10 ml of acetic anhydride to 10 ml of acetic acid ,then add 2 drops of Conc. H<sub>2</sub>SO<sub>4</sub> .

2-Add about 1.5 g shredded cellulose [small parts of paper] to the acetic solution , warm it with stirring in a water bath until the cellulose parts just dissolve completely.

3- After completely dissolving the cellulose, cool the solution in ice /water with continuous stirring.

4-Filter the product [cellulose acetate] by buchner funnel, then wash with water.

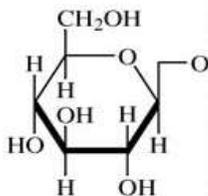
5-Dry the product in oven at 100°C .

6-Make powder of the product and test the solubility in Acetone, Acetic acid.

7-Calculate the product percentage as the following

### Calculations:

Theoretical weight:



**Mwt**

**1.5g**

→



**Mwt**

**X**

**Polymer Laboratory**

## Exp.7: Bulk Photopolymerization of Methyl Methacrylate:

A large number of alkyl methacrylates, which may be considered as esters of poly [methacrylic acid], have been prepared. By far the most important of these polymers is poly [methyl methacrylate], which is an established major plastics material. As with other linear polymers, the mechanical and thermal properties of poly- methacrylates are largely determined by the intermolecular attraction, spatial symmetry, and chain stiffness. As the size of the ester alkyl group increases in a series of poly [*n*-alkyl methacrylate]s, the polymer molecules become spaced further apart and the intermolecular attraction is reduced. Thus, as the length of the side chain increases, the softening point decreases, and the polymers become rubbery at progressively lower temperatures [Figure 7.1].

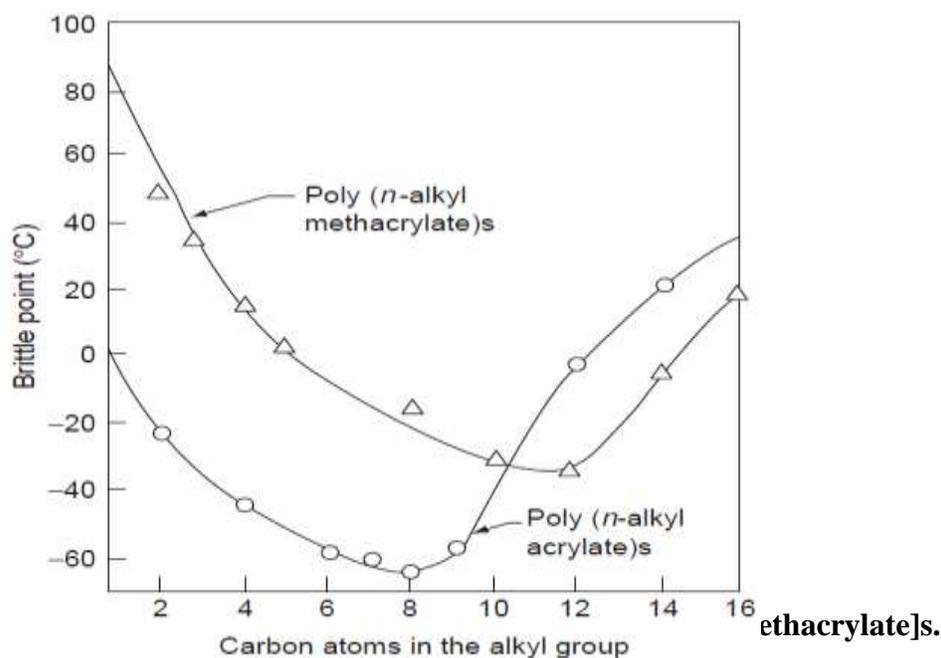


Figure 7.1 Bri

However, when the number of carbon atoms in the side chain exceeds 12, the polymers become less rubbery, and the softening point, brittle point, and other properties related to the glass transition temperature rise with an increase in chain length [Table 7.1 and Table 7.2]. As with the polyolefins, this effect is due to side-chain crystallization.

**Table 7-1: Vicat Softening Points of Polymethacrylates Derived from Monomers of Type  $\text{CH}_2=\text{C}[\text{CH}_3]\text{COOR}$**

R-	Softening Point ( $^{\circ}\text{C}$ )
$\text{CH}_3-$	119
$\text{CH}_3-\text{CH}_2-$	81
$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	55
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	30
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	— <sup>a</sup>
$(\text{CH}_3)_2\text{CH}-$	88
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-$	67
$(\text{CH}_3)_3\text{C}-$	104
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2-$	46
$(\text{CH}_3)_3\text{C}-\text{CH}_2-$	115
$(\text{CH}_3)_3\text{C}-\underset{\text{CH}_3}{\text{CH}}-$	119

<sup>a</sup> Too rubbery for testing.

Poly[alkyl methacrylate]s in which the alkyl group is branched have higher softening points [see Table 7.1] and are harder than their unbranched isomers. This effect is not simply due to the better packing possible with the branched isomers. The lumpy branched structures impede rotation about the carbon-carbon bond on the main chain, thus contributing to stiffness of the molecule and consequently a higher transition temperature. Similarly, since the  $\alpha$ -methyl group in polymethacrylates reduces chain flexibility, the lower polymethacrylates have higher softening points than the corresponding polyacrylates do.

Poly [methyl methacrylate PMMA] is by far the predominant polymethacrylate used in rigid applications because it has crystal clear transparency, excellent weatherability [better than most other plastics], and a useful combination of stiffness, density, and moderate toughness. The glass transition temperature of the polymer is  $105^{\circ}\text{C}$

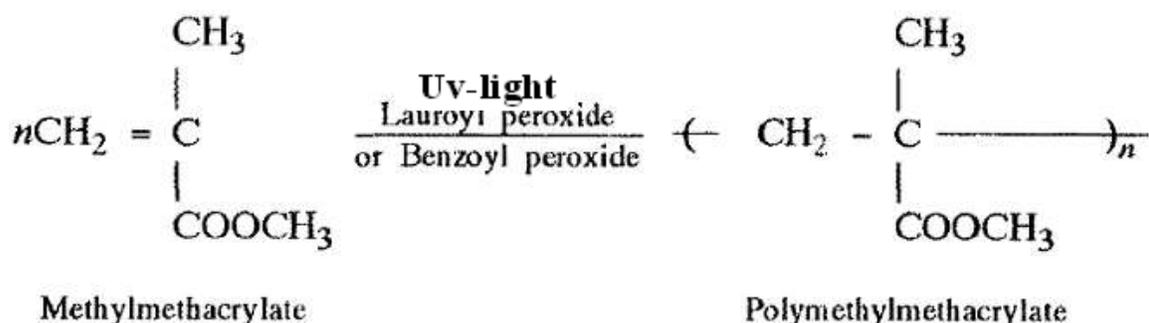
[221°F], and the heat deflection temperatures range from 75 to 100°C [167–212°F]. The mechanical properties of PMMA can be further improved by orientation of heat-cast sheets. PMMA is widely used for signs, glazing, lighting, fixtures, sanitary wares, solar panels, and automotive tail and stoplight lenses. The low index of refraction [1.49] and high degree of uniformity make PMMA an excellent lens material for optical applications. Methyl methacrylate has been copolymerized with a wide variety of other monomers, such as acrylates, acrylonitrile, styrene, and butadiene. Copolymerization with styrene gives a material with improved melt-flow characteristics. Copolymerization with either butadiene or acrylonitrile, or blending PMMA with SBR, improves impact resistance. Butadiene–methyl methacrylate copolymer has been used in paper and board finishes.

**Table 7-2: Glass Transition Temperatures of Polymethacrylates**

Ester Group	$T_g$ (°C)
Methyl	105
Ethyl	65
<i>n</i> -Butyl	20
<i>n</i> -Decyl	– 70
<i>n</i> -Hexadecyl	– 9

Higher *n*-alkyl methacrylate polymers have commercial applications. Poly[*n*-butyl-], poly[*n*-octyl-] and poly[*n*-nonyl] methacrylates are used as leather finishes; poly[lauryl methacrylate] is used to depress the pour point and improve the viscosity-temperature property of lubricating oils. Mention may also be made here of the 2-hydroxyethyl ester of methacrylic acid, which is the monomer used for soft contact lenses. Copolymerization with ethylene glycol dimethacrylate produces a hydrophilic network polymer [a hydrogel]. Hydrogel polymers are brittle and glassy when dry but become soft and plastic on swelling in water. Terpolymers based on methyl methacrylate, butadiene, and styrene [MBS] are being increasingly used as tough transparent plastics and as additives for PVC.

The initiation of polymerization by ultraviolet radiation has been of particular interest in the study of free radical processes. The test tube demonstration described here is simple and may be used to evaluate the polymerizability of new monomers or to study some of the physical properties of a polymer. Although the method is particularly effective for acrylic and methacrylic monomers, it may also be applied to the polymerization of a wide range of "vinyl"- type monomers. Generally, the method depends on the sensitization of the monomer to ultraviolet radiation with reagents such as biacetyl or benzoin. With sensitizers, initiation stops when the source of radiation is turned off, which is followed by a rapid decay of the polymerization process . When a conventional initiator, such as dibenzoyl peroxide, is also present, the process is more rapid than when the sensitizer is used by itself. It also seems to continue after the radiation source has been discontinued. It is presumed that ultraviolet [UV]-induced decomposition of the peroxide becomes involved in the process. By this method, polymerizations may be carried out at temperatures well below those normally used with thermal initiators such as organic peroxides.



## Procedure:

1. Fill the 12 cm X 12 mm test tube with some of the 0.5% solution of sodium stearate in isopropanol. In a hood, pour the solution off into a suitable container. Allow the inside of the test tube to dry thoroughly [see Note 1].
2. While the test tube dries, prepare a solution of 0.5 g of benzoin in 10 ml of methyl methacrylate. Then add 0.5 g of dibenzoyl peroxide [see Note 2].
3. When the test tube is ready for use, place the methyl methacrylate initiator solution in the test tube. Cover the neoprene stopper with the polyethylene film and stopper the test tube.
4. Place the test tube in a test tube rack or a beaker. Note the time and expose the test tube to sunlight. From time to time, note the time and observe the progress of the polymerization [see Note 3].

## NOTES

1. In this experiment, coat the inside of the test tube with a thin layer of sodium stearate [or a plain, nonperfumed soap]. This will assist in removing the product from the apparatus.
2. In the laboratory, the source of radiation may be a high-intensity mercury lamp. However, for simple test purposes, sunlight is quite suitable. Even a lightly overcast sky furnishes sufficient UV radiation for photo-induced polymerizations. Naturally, bright sunlight is more effective.
3. As the polymerization of methyl methacrylate is somewhat inhibited by atmospheric oxygen, the upper layer of the polymerizing monomer may still be fluid, even though most of the material has already been converted. Therefore, when checking on the progress of the experiment, do not simply shake the test tube. Instead, either invert the test tube or insert a probe [a long pin, a paper clip, etc.] to check on the process.

## Procedure No.2:

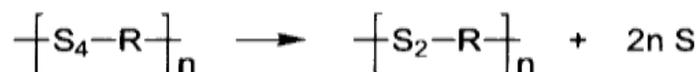
Add a pinch [20-30 mg] of Benzoyl peroxide or lauroyl peroxide to [3-4ml] of methylmethacrylate taken in a hard glass test tube and shake to dissolve. Using a clamp stand, secure the test tube in a water bath maintained at 60°C. As the polymerisation progresses, the liquid in the test tube slowly starts thickening and in about one hour changes to a transparent solid.

**Polymer Laboratory**  
**Exp.8 :Poly[alkylene Sulfide]**

The reaction of suitable aliphatic dihalogen compounds with alkali or alkaline earth polysulfides results in the formation of linear, rubbery or resinous, poly[alkylene sulfide]s:



The most widely used dihalide is 1,2-dichloroethane. The use of polyhalides [e.g., 2% 1,2,3-trichloropropane] results in the formation of branched or cross-linked products. Sodium tetrasulfide [ $\text{Na}_2\text{S}_4$ ] is generally used as the polysulfide since it contains scarcely any of the monosulfide which reacts with dihalides to form cyclic by-products with unpleasant odors. Sulfur can be removed from the poly[alkylene sulfide] with the aid of sulfur-binding agents; for example, by treatment of an aqueous dispersion with  $\text{Na}_2\text{S}$ ,  $\text{NaOH}$ , or  $\text{Na}_2\text{SO}_3$  at 30-100 °C, the sulfur content can be reduced to two atoms per constitutional repeating unit of the macromolecule:



Further desulfurization results in degradation of the poly[alkylene sulfide]s to low-molecular-weight products. Vulcanization of the linear poly[alkylene sulfide]s yields cross-linked elastic materials which are commercially important because of their solvent and oil resistance. They are also less sensitive to oxygen and light than most synthetic rubbers. The technical properties can be modified especially by changing the sulfur content, as well as by admixture of fillers. Poly[alkylene sulfide]s are used as solvent-resistant rubbers, sealing compounds, and adhesives. Aromatic polysulfides [poly arylene sulfides, PPS] possess substantially higher glass transition temperatures. Hence these polymers can be used as temperature-stable thermoplastics. Poly[alkylene sulfide]s are prepared by allowing the dihalide to drip slowly under vigorous stirring into a moderately concentrated aqueous polysulfide solution [generally in 10-20% excess]. Temperature and reaction time depend mainly on the dihalide being used: for 1,2-dichloroethane, temperatures between 50 and

80 °C, and reaction times of about 5 h suffice; on the other hand, long-chain dihalides require 20-30 h at 100 °C. Since the poly[alkene sulfide]s are insoluble in water and very easily agglomerate into lumps, thereby making further reaction and subsequent washing very difficult, it is expedient to carry out the polycondensation in the presence of a dispersing agent [for example, 2-5% magnesium hydroxide]. Emulsifiers are not recommended since they make the workup difficult. When the reaction has finished, the mixture is freed from sodium chloride and unreacted sodium polysulfide by slurring several times with water. It is then acidified with concentrated hydrochloric acid in order to coagulate the poly[alkene sulfide]. The resulting yellow-white spongy cake has an unpleasant smell. It is dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. The dry product is partially soluble in carbon disulfide. Poly[alkene sulfide]s can also be prepared by ring-opening polymerization of episulfides.

**Polymer Laboratory**  
**Exp.9: Making a Plastic from Potato Starch**

In polymer chemistry, polymerization is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains.

In chemical compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds, and their inherent steric effects explained by VSEPR Theory. In more straightforward polymerization, alkenes, which are relatively stable due to  $\pi$ -bonding between carbon atoms form polymers through relatively simple radical reactions; in contrast, more complex reactions such as those that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize.

There are many forms of polymerization and different systems exist to categorize them.

#### 1- *Biopolymers*:

- produced by living organisms :
- structural proteins :collagen, keratin, elastin...
- chemically functional proteins :enzymes, hormones, transport proteins...
- structural polysaccharides :cellulose, chitin...
- storage polysaccharides :starch, glycogen...
- nucleic acids :DNA, RNA

#### 2- *Synthetic polymers*:

used for

- plastics—fibers, paints, building materials, furniture, mechanical parts, adhesives :
- thermoplastics :polyethylene, Teflon polystyrene, polypropylene, polyester, polyurethane, polymethyl methacrylate, polyvinyl chloride, nylon, rayon, celluloid, silicone, fiberglass...
- thermosetting plastics :vulcanized rubber, Bakelite, Kevlar, epoxy...

This activity can be used simply as a practical to enhance the teaching of polymers or plastics. It can be used to introduce further work on biopolymers and bio-plastics and/or it can be used as an example of the effects of plasticizers. A similar process is used in

industry to extract starch, which is then used in a number of products including food and packaging.

If students extract their own potato starch then they can use that .It is a wet slurry rather than a dry powder so they need about 4 g with about 22 cm<sup>3</sup> water .

Starch is made of long chains of glucose molecules joined together .Strictly it contains two polymers :amylose which is straight-chained and amylopectin which is branched . When starch is dried from an aqueous solution it forms a film due to hydrogen bonding between the chains .However, the amylopectin inhibits the formation of the film .Reacting the starch with hydrochloric acid breaks down the amylopectin, forming more satisfactory film .This is the product that students make without propane-1,2,3-triol .The straight chains of the starch [amylose]can line up together and although this makes a good film, it is brittle because the chains are too good at lining up .Areas of the film can become crystalline, which causes the brittleness.

Students should be able to see a difference in the two films that they make .The one without the propane-1,2,3-triol is far more brittle, the one with it shows more plastic properties.

Adding propane-1,2,3-triol makes a difference due to its hydroscopic water attracting properties .Water bound to the propane-1,2,3-triol gets in amongst the starch chains and stops the crystalline areas from forming, preventing the brittleness and resulting in more ‘plastic’ properties, thus acting as a plasticiser .This can be explained to students without mentioning water – just that the propane-1,2,3-triol acts as a plasticiser.

## **Procedure:**

### **Extracting the starch:**

**A** -Grate about 100 g of potato .The potato does not need to be peeled, but it should be clean .Put the potato into the mortar.

**B** - Add about 100 cm<sup>3</sup> of distilled water to the mortar, and grind the potato carefully.

**C** -Pour the liquid off through the tea strainer into the beaker, leaving the potato behind in the mortar.

**D** - Repeat steps **B** and **C** twice more.

**D** - Leave the mixture to settle in the beaker for 5 minutes .

**E** -Decant the water from the beaker, leaving behind the white starch which should have settled in the bottom .Put about 100 cm<sup>3</sup> of distilled water in with the starch and stir gently . Leave to settle again and then decant the water, leaving the starch behind.

#### **Making the plastic film:**

**A**-Put 22 cm<sup>3</sup> of water into the beaker and add 4 g of the potato starch slurry from the previous step or 25 cm<sup>3</sup> water and 2.5 g of commercial potato starch, 3 cm<sup>3</sup> of hydrochloric acid and 2 cm<sup>3</sup> of propane-1,2,3-triol.

**B**-Put the watch glass on the beaker and heat the mixture using the Bunsen burner .Bring it carefully to the boil and then boil it gently for 15 mins .Do not boil it dry .If it looks like it might, stop heating.

**C**-Dip the glass rod into the mixture and dot it onto the indicator paper to measure the pH .Add enough sodium hydroxide solution to neutralize the mixture, testing after each addition with indicator paper .You will probably need to add about the same amount as you did of acid at the beginning 3 cm<sup>3</sup>.

**D**-You can then add a drop of food coloring and mix thoroughly .

**E**-Pour the mixture onto a labeled petri dish or white tile and push it around with the glass rod so that there is an even covering.

**F**-Repeat the process, but leave out the propane-1,2,3-triol.

**G**-Label the mixtures and leave them to dry out .It takes about one day on a radiator or sunny windowsill, or two days at room temperature .Alternatively, use a drying cabinet . It takes about 90 mins. at 100 °C.