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### Poly(vinyl acetate)

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 Protocol  
 Poly (vinyl acetate);  
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**Background.** Simple bulk polymerization is of limited industrial use because of the difficulty of temperature control. Several techniques have been developed to overcome this limitation. For example, in emulsion polymerization, the monomer is emulsified in water with surfactants and a water-soluble initiator is used. Polymerization occurs to give an emulsion of polymer particles. The system can be stirred during polymerization and the heat of the reaction is dissipated throughout the water so that close temperature control is possible. In this experiment an emulsion of poly(vinyl acetate) is prepared and can be used subsequently to prepare a paint. Such emulsion paints are now very widely used. It will be noticed that in this experiment a small proportion of the monomer, octyl acrylate is present. This becomes incorporated in the final polymer and lowers the softening point, thereby assisting the coalescence of particles to give a continuous film when the paint is applied to a surface. A polymer which is derived from two or more monomers is known as a copolymer.

#### Equipment

- 1 Reactor (about 500 ml) fitted with condenser, dropping funnel, electric stirrer and thermometer (0-110°C) (see Fig. 2 for examples of suitable assemblies)
- 5 Weighing bottles
- 1 Measuring cylinder (100 ml)
- 2 Water baths
- 1 Tripod and gauze
- 1 Bunsen burner

#### Materials

- Vinyl acetate (inhibitor free)
- Octyl acrylate (inhibitor free)
- Hydroxyethylcellulose
- Poly(ethylene glycol) ether of lauryl alcohol
- Sodium dodecylbenzenesulphonate
- Sodium bicarbonate
- Potassium persulphate

#### Hazards

Vinyl acetate and octyl acrylate are inflammable liquids and should be handled carefully. The polymerization is exothermic and a cold water bath should be kept ready to that, is necessary, the reactants can be rapidly cooled.

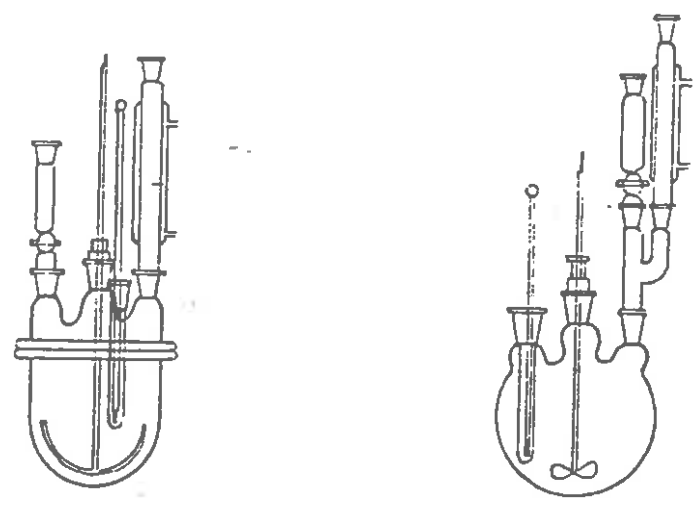
#### Experimental procedure

Place water (100 ml) in the measuring cylinder and weight out in separate weighing bottles the following ingredients:

Hydroxyethylcellulose (2.5 g) (protective colloidal); poly(ethylene glycol) ether of lauryl alcohol (2.5 g) (surfactant); sodium dodecylbenzene-sulphonate (0.1 g) (surfactant); sodium bicarbonate (0.5 g) (buffer).

Transfer these ingredients to the reactor using small portions of the water to wash out the weighing bottles so that the full weight of each material finds its way into the reactor. Use the remaining water to wash down any material adhering to the sides of the reactor. Start the stirrer and heat the mixture to 60°C using a water bath. Mix vinyl acetate (100 ml) and octyl acrylate (20 ml) in the dropping funnel. Add potassium persulphate ...

(0.5 g) (initiator) to the reactor, followed by a portion (about 20 ml) of the mixed monomers. Raise the temperature of the reactants to 75-80°C. When reflux has ceased (if it does not subside after 30 minutes add a further quantity (0.5 g) of potassium persulphate) add the remaining monomer mixture dropwise over a 2 hour period. Keep the temperature at 75-80°C throughout this time; if it should rise above this range stop the addition of monomer and apply the cooling bath until the required temperature is regained. When all the monomer mixture has been added maintain the temperature of the reactants at 75-80°C until reflux has ceased. Still stirring, cool the emulsion to room temperature. Retain the emulsion for use in the next experiment of the preparation on an emulsion paint.



## Poly(vinyl acetate) emulsion paint

In order to prepare a paint from a poly(vinyl acetate) emulsion it is necessary only to add a pigment dispersion in water.

Paints of this kind are widely used as household decorative paints. Since they contain no organic solvents they have the advantage of having little odour. Further they are fast drying since drying involves only evaporation of water and coalescence of the polymer particles; chemical reaction is not involved (unlike conventional paints which dry by evaporation of solvent and by reaction with atmospheric oxygen). However, the emulsion paints do contain appreciable quantities of water-soluble ingredients which render them somewhat water sensitive and less satisfactory for outside use.

### Equipment

1 Beaker (1000 ml)  
 1 Beaker (100 ml)  
 1 Measuring cylinder (250 ml)  
 1 Measuring cylinder (50 ml)  
 1 Electric stirrer  
 1 Glass rod  
 1 Weighing bottle

### Materials

Poly(vinyl acetate) emulsion  
 (either a commercial product  
 or the emulsion prepared in  
 experiment)  
 Rutile titanium dioxide  
 Talc  
 China clay  
 Sodium hexametaphosphate  
 Sodium carboxymethylcellulose  
 Butyl cellosolve acetate

### Hazards

The paint is difficult to remove once drying has occurred. Any spillages should therefore be promptly cleaned off with a wet cloth.

### Experimental procedure

Dissolve sodium carboxymethylcellulose (1.5g) (thickener) in water (30 ml) by stirring with the glass rod in the small beaker. Transfer the solution to the large beaker. Dissolve sodium hexametaphosphate (0.4 g) (dispersant) in water (10 ml) in the small beaker and also transfer this solution to the large beaker. Add water (140 ml) and butyl cellosolve acetate (12 ml) (coalescing agent) to the large beaker. Stir the resulting solution rapidly with the electric stirrer and slowly add the following ingredients.

Rutile titanium dioxide (180 g) (white pigment); talc (20 g) (extender); china clay (40 g) (extender).

Maintain rapid stirring for 1 hour and then, still with stirring, slowly add poly(vinyl acetate) emulsion (200 ml). Maintain stirring for further 15 minutes. The paint is then ready for use. A coloured paint may be produced by adding an organic dye to the white paint.

## Determination of the glass transition temperature ( $T_g$ ) of a polymer by the dilatometric method

### Purpose

The purpose of this experiment is to show how the glass transition temperature ( $T_g$ ) of a polymer sample can be determined by a "home" made cheap dilatometer, with which the change of the specific volume of the sample versus temperature can be recorded.

### Background

The specific volume in milliliters per gram (cgs) or cubic meters per kilogram (SI) of an amorphous polymer changes linearly with increasing temperature up to the transition region, where a change of the slope occurs (steeper gradient). At the glass transition temperature ( $T_g$ ), the rate of change increases and a discontinuity is formed in the specific volume curve (Fig I). The glass transition temperature ( $T_g$ ) is usually defined as the point at which the tangents of the curves intersect. Such curves are obtained by dilatometric measurements.

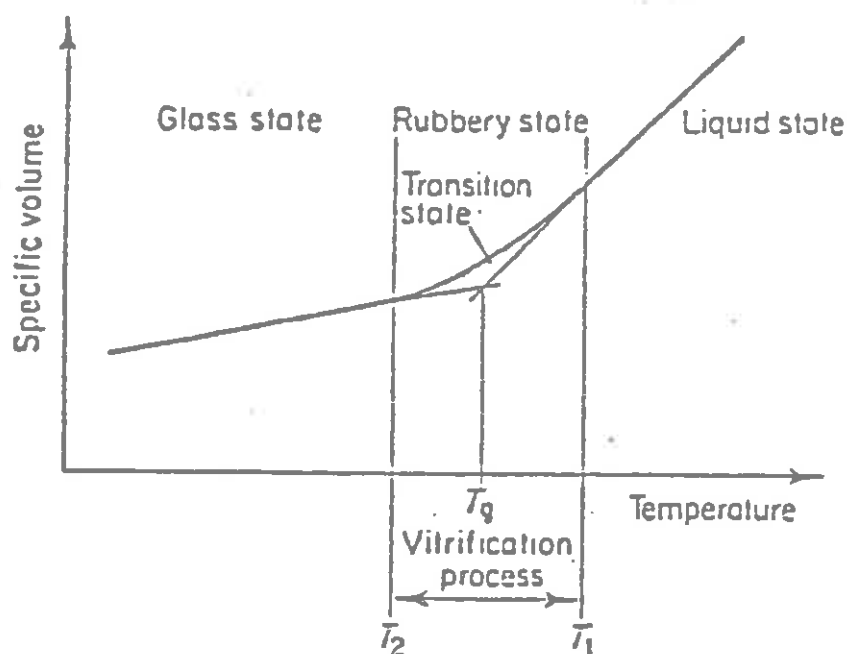


Fig.1 The specific volume as a function of temperature in the transition range

When a liquid polymer (melt) is cooled, the transition from highly viscous supercooled melt to the rigid glass begins at temperature  $T_1$  (Fig.1). At temperature  $T_2$  the solidification (vitrification) process is terminated. This phenomenon is called the glass transition because amorphous polymers exhibit a change from soft, elastic (rubbery) behaviour above  $T_g$  to glass-like behaviour below  $T_g$ .

If the polymer is crystallizable the specific volume curve shows a discontinuity at the melting point. A typical behaviour of a semi-crystalline polymer forming both a glassy and a crystalline state is shown in Fig.2,  $T_m$  represents the melting point and  $T_{g1}, T_{g2}, \dots$  the glass transition temperatures obtained at various cooling rates. In the region between  $T_m$  and  $T_g$  supercooling occurs and sudden crystallization takes place. Below  $T_g$  the rapid crystallization is

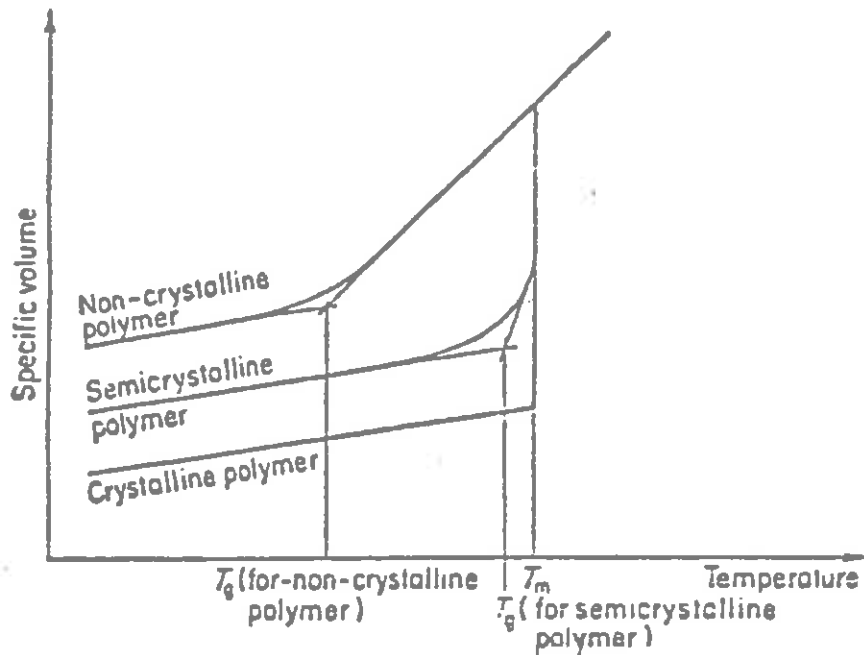


Fig.2 The specific volume as a function of temperature of a glass-forming polymer cooled at various rates

not possible by reason of an increase of viscosity, and the polymer remains in the disordered glassy state. When the cooling rate is slower the supercooling persists to lower temperatures and the transition  $T_{g2}$  occurs at a lower temperature than  $T_{g1}$ . If an infinite time were allowed, a limiting value  $T_g$  would be reached. The glassy states obtained by different cooling rates differ in  $T_g$  and also in density. Completely crystalline polymers should not exhibit a glass transition temperature. Semicrystalline polymers exhibit glass transition temperature of their amorphous region and melting temperature of their crystalline region.

Equipment

- Dilatometer shown in Fig.3. It is composed of a 10ml flask with a perforated rubber stopper which carries tightly in its hole a 60cm long, thick wall, precision bore, capillary of 1mm internal diameter, on which a scale with 1mm divisions is attached.
- Thermometer 100°C with at least 0.1°C divisions.
- Water bath or oil bath in a glass container with 200ml transparent automotive lubricating oil as a heat transfer liquid or silicone oil if available.
- Magnetic stirrer with a heating plate or an immersion resistance for heating.
- Ring stand.
- Two small clamps.
- Magnetic bar.
- Beaker 250ml.

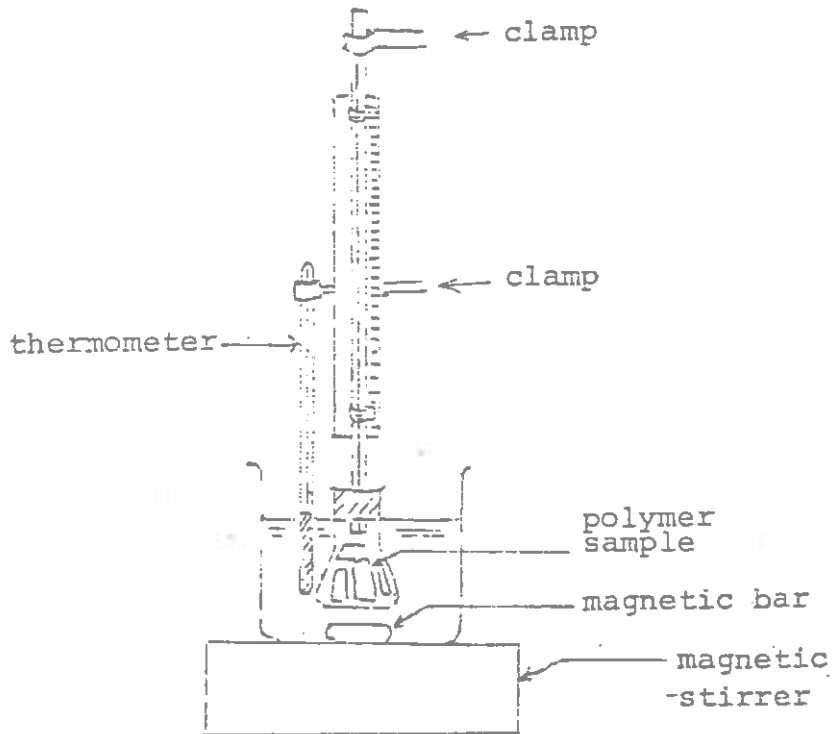


Fig.3 Experimental set up for the determination of T<sub>g</sub>

### Experimental procedure

A polymer sample in chips of approximately 5g and of a  $T_g$  between 30 and 70°C (e.g. Nylon 6) is transferred into the dilatometer flask. The flask is then filled with water (clean mercury can be used if available) up to the top. The water employed should be preboiled in a separate container (e.g. a 250ml beaker) to remove the dissolved air and then cooled to room temperature. The dilatometer flask is stoppered with the rubber stopper connected with the capillary tube and the attached scale. The lower tip of the capillary tube should initially stand out into the container, approximately 0,5-1cm below the lower surface of the rubber stopper.. Some water enters into the capillary and the rest overflows from the container. No airbubbles should be trapped in the dilatometer flask or in the capillary, otherwise the results will be erratic. The initial height of the meniscus of the water column in the capillary should be approximately 5-10cm, if not, it can be arranged by decreasing the standing out length of the capillary tube by carefully pulling it out by rotation.

The dilatometer flask is inserted into the bath and is carefully clamped perpendicularly from the top of the capillary tube onto the ring stand. The oil level should reach up to the height of the lower surface of the rubber stopper. The thermometer is clamped on the ring stand so that its bulb is immersed in the oil at the same depth and in contact with the dilatometer flask.

The magnetic stirring is started and the temperature of the bath is raised with a medium rate up to about 80°C. The temperature (every 1° or 2°C) and the corresponding height of the meniscus in the capillary are recorded. Fifteen to twenty readings are satisfactory.

After turning off the heating and after protection of the capillary with a piece of paper, the measurements can be repeated by lowering the temperature of the continuously stirred bath by blowing air with a small fan. Two different cooling rates can be employed separately in order to observe their effect on the obtained  $T_g$ .

### Processing of the results

A graph is drawn on a millimeter graph paper as follows:

The temperature (°C) is written on the x axis and the position of the meniscus (height in cm) is written on the y axis. The initial

and the final 5 to 7 points determine the positions of two straight lines of different slopes which therefore intersect. A straight line is drawn perpendicularly to the temperature axis passing through the point of intersection of the two previous lines. The temperature at the point of its intersection with the temperature axis determines the glass transition temperature of the polymer sample.

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