



Laboratory Manual

POLYMER CHEMISTRY I

SIC2005 / SID2002 / SCES2242



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EXPERIMENT 1

IDENTIFICATION OF POLYMERS FROM SOLUBILITY TESTS

Objective

To identify polymer using solubility test.

Introduction

A macromolecule becomes a single phase in solution according to the same thermodynamics laws as the micromolecular solution substances. However, differences in molecular size influence the solubility properties of both substances. For example, a macromolecule dissolves slowly due to its entangled constitution opposing the penetration of the solvent. On contrary, though micromolecular substances normally are much easier to dissolve than the polymer, the solubility of micromolecules is generally limited to saturated solution.

The solvent of a macromolecule can be considered good by one of these two standards, i. e. the kinetic standard or the thermodynamic standard. A good solvent from the kinetic point of view is a solvent that easily dissolves the polymer in a short time. The solubility can be made faster by decreasing the particle size of the polymer sample because more of its surfaces are exposed to the solution. From the thermodynamic point of view, a good solvent must be able to strongly interact with the solution substances due to its similarity in their chemical structure. Thus, a good solvent in terms of kinetics is fast while that in terms of thermodynamics is efficient.

An amorphous polymer contains a network of entangled and flexible chains in a continuous motion. When the polymer is sunk in a solvent, the polymer network will swell from the osmotic activity of the solvent thus increase the segmental motion. Provided the solvent is still available, the polymer will continue to expand and increase its freedom to move. When the solvation process has sufficiently advanced to allow transitional movement to the chains, the substances will separate out to form a solution. Consequently, as the solution becomes more diluted, the intermolecular forces that exist between the polymer chains will become less and finally the solution properties will only exhibit polymer-solvent interaction forces.

Solubility of a polymer will happen if the free energy of the solution (G), given by Equation (1):

$$\Delta G = \Delta H - T\Delta S \quad (\text{Eqn. 1})$$

having a negative value. Entropy of the solution (ΔS) is normally having a small and positive value, thus the sign and magnitude of the enthalpy of the solution (ΔH) will determine whether the dissolution process can happen or not.

Scatchard-Hildebrand equation can be written as Equation (2):

$$\Delta H / V\Phi_s\Phi_p = (\delta_s - \delta_p)^2 \quad (\text{Eqn. 2})$$

where V is the total volume of the mixture, Φ_s and Φ_p are the volume fractions of the solvent and polymer respectively, while δ_s and δ_p are the solubility parameters of the solvent and polymer

respectively. Generally, if $(\delta_s - \delta_p) = 0$, from Equation (2), $\Delta H = 0$ and the dissolution process will happen because of the ΔS factor.

Solvent solubility parameter can be calculated from the expression

$$\delta_s = [(\Delta H_v - RT) / (M/d)]^{1/2} \quad (\text{Eqn. 3})$$

where ΔH_v is the molar heat of vapourization, M and d are the molecular mass and density of solvent respectively.

Polymer solubility parameter is obtained from:

$$\delta_p = d' \Sigma G/M' \quad (\text{Eqn. 4})$$

where d' is the density of polymer with repeating units of molecular mass M' , and G is the molar attraction constants (see Table 1.1). Here, Σ refers to the total of all the chemical structure groups in the repeating unit of the polymer. Normally without strong interactions like hydrogen bonds, the solubility of a polymer can be predicted if $|\delta_s - \delta_p| < 1$.

Methodology

Materials and Apparatus

- (i) Small test-tubes (13 mm x 100 mm), measuring cylinder, glass stirring rod and water bath.
- (ii) Unknown polymer samples, different type of solvents (refer to Flow-chart 1.1)

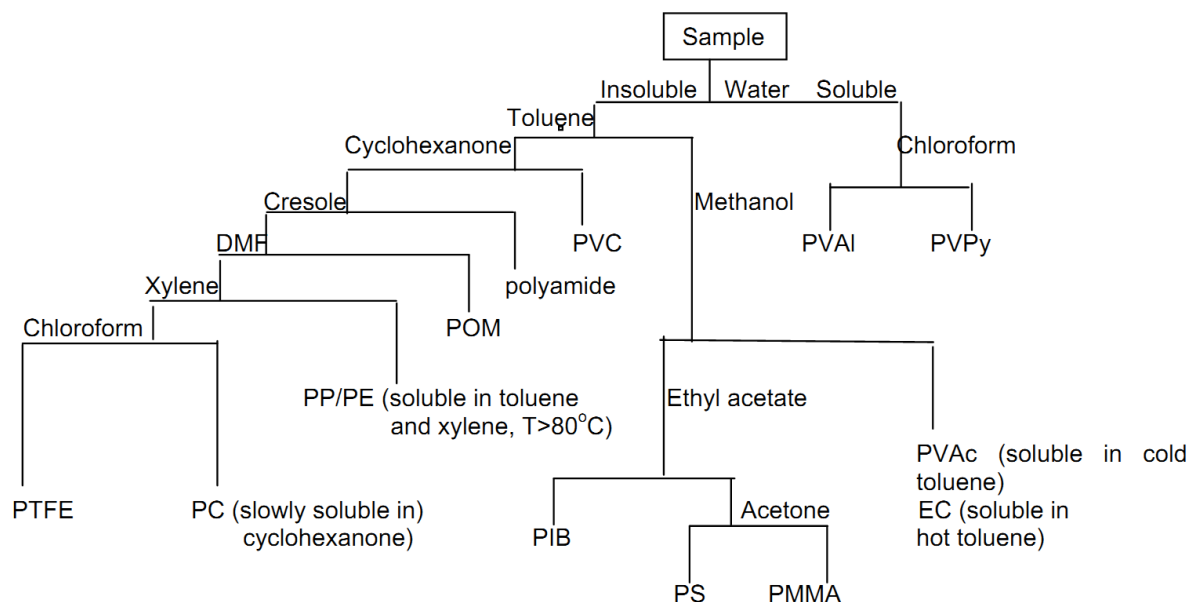
Polymer identification

Each student is provided with 2 unknown polymer samples for identification. Place ~0.001 g of the polymer sample in a small test-tube (13 mm x 100 mm) and add 5 mL of the solvent required for the test. Shake the test-tube and/or stir with a glass stirring rod. The dissolution process can be made faster by heating the test-tube in a hot water-bath in the fume cupboard.

A soluble polymer will form a homogeneous solution with the solvent (solvent category), while an insoluble polymer will remain as a separate phase from the solvent (non-solvent category). The solubility test is considered negative if i) the two phases still remain after stirring with a glass rod or ii) two phases are formed again after the solution temperature reduced to room temperature.

The following flow-chart must be used as a guide to identify the unknown polymers. Use the solvent indicated down the chart. If the polymer is soluble in the solvent or the test result is positive, move towards the right arm of the chart. However, if the polymer is insoluble (test result is negative), move towards the left arm of the chart. Continue the solubility test until the type of polymer is discovered.

Flow-chart 1.1: Polymer identification from solubility test



EC = ethyl cellulose
 PVAI = poly(vinyl alcohol)
 POM = polyoxymethylene
 PE = polyethylene
 PVC = poly(vinyl chloride)
 PTFE = polytetrafluoroethylen
 PS = polystyrene

A = poly(methyl methacrylate)
 PC = polycarbonate
 Ac = poly(vinyl acetate)
 PP = polypropylene
 PIB = polyisobutylene
 PVPy = poly(vinyl pyrrolidone)

Supplementary Informations:

Table 1.1: Molar attraction constants at 25°C (Van Krevelen)



Group	$G \text{ (J}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}\text{)}$	Group	$G \text{ (J}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}\text{)}$
-CH ₃	420	-F	164
-CH ₂ -	280	-Cl	471
-CH-	140	-OH	754
-C-	0	-O-	256
-CH=CH-	444	-C-O-	512
-C=CH-	304	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$	
	1517	-C-NH-	1228
	1377	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$	
5 or 6 membered ring	200	-C-N-	430
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$	

Table 1.2: Density of polymers (g cm^{-3})

Polymer	Code	Amorphous	Crystalline
Ethyl cellulose	EC	1.15	-
Polyamide-6,6	PA66	1.09	1.24
Poly(ethylene)	PE	0.85	1.00
Poly(isobutylene)	PIB	0.91	1.94
Poly(carbonate)	PC	1.20	-
Poly(methyl methacrylate)	PMMA	1.17	1.23
Poly(oxymethylene)	POM	1.25	-
Isotactic poly(propylene)	PP	0.85	0.94
Poly(styrene)	PS	1.05	1.12
Poly(tetrafluoroethylene)	PTFE	2.00	2.40
Poly(vinyl alcohol)	PVAI	1.29	1.35
Poly(vinyl acetate)	PVAc	1.19	-
Poly(vinyl chloride)	PVC	1.41	1.44
Poly(vinyl pyrrolidone)	PVPy	1.25	-

Table 1.3: Solvent solubility parameters

Solvent	$\delta_s (\text{J cm}^{-3})^{1/2}$	H-bonding
Water	48.0	s
Acetone	20.0	m
Dimethylformamide(N,N)	24.9	m
Ethyl acetate	18.6	m
Carbon tetrachloride	17.7	p
Chloroform	18.9	p
m-Cresole	22.7	s
Methanol	29.5	s
Cyclohexanone	19.5	m
Toluene	18.2	p
p-Xylene	17.9	p

Note: s = strong hydrogen bonding
 m = moderate hydrogen bonding
 p = poor hydrogen bonding

Calculation Example:

Polymer: Poly(vinyl acetate) = $-\text{[CH}_2\text{CH(OCOCH}_3\text{)]}_n-$

Density = 1.19 g cm^{-3} (amorphous)

Molecular mass of repeating unit = 86.1 g mol^{-1}

Group	G ($\text{J}^{1/2}\text{cm}^{3/2} \text{ mol}^{-1}$)
1 -CH ₃	420
1 -CH ₂	280
1 -CH	140
1 -COO	512
$\Sigma G =$	1,352

$$\delta_p = (\text{density} \times \Sigma G) / (\text{molecular mass of repeating unit})$$

$$= (1.19 \text{ g cm}^{-3} \times 1,352 \text{ J}^{1/2}\text{cm}^{3/2} \text{ mol}^{-1}) / 86.1 \text{ g mol}^{-1} = \underline{\underline{18.7 \text{ J}^{1/2} \text{ cm}^{3/2}}}$$

Discussion / Questions:

1. Calculate the polymer solubility parameter (δ_p) for the polymers that have been identified.
2. Calculate the solvent solubility parameter (δ_s) for one solvent under each of the following category:
 - i) solvent; and ii) non-solvent for the unknown polymer.
3. Based on value measured in 1 and 2, comment about the polymer relative solubility in solvent of both categories (solvent and non-solvent).
4. Discuss on how polymer dissolved in solvent?

EXPERIMENT 2

SEPARATION AND PURIFICATION OF POLYMER

Objective

To carry out separation and purification of polymer quantitatively.

Introduction

Polymers are always synthesized in the laboratory by solution or emulsion polymerization methods. Separation methods of polymers from the reaction mixture depend on the properties of the polymer and the system of polymerization. Polymers prepared in solution are usually isolated by adding the reaction mixture in excess non-solvent and this will cause the polymer to precipitate out and can be filtered or strained. Sometimes the precipitated polymer remains in the form of suspended colloid; the polymer can be removed by cooling the mixture with ice or by adding an electrolyte like sodium chloride or diluted acid solution. Other methods such as long stirring time, shaking or centrifuging can also complete the separation.

Separation of polymers from aqueous emulsion is often difficult to carry out. Methods frequently used are diluting using aqueous electrolyte solution, freezing or pouring or spraying into alcohol.

Polymers separated using methods described above are likely to get contaminated by impurities such as residual monomer, initiator, solvent and possibly additives like surfactant or transfer agent. Purification of the polymer using methods such as distillation and re-crystallisation is obviously impossible to carry out. Instead methods like re-precipitation, freeze-dry, normal drying and solvent extraction are used.

Methodology**Materials and Apparatus**

(i) Beaker, measuring cylinder, dropper, magnetic stirrer, volumetric flask, sintered glass and glass stirring rod.

(ii) Poly(methyl metacrylate), cinnamic acid, methanol, chloroform and acetonitrile.

Polymer separation and purification

Students will be provided with 10.0 ± 0.1 mL solution of poly(methyl metacrylate) in chloroform, having a concentration of about 5% w/v. The solution is contaminated with cinnamic acid to a level of about 1% w/v. The polymer is separated and purified using the re-precipitation method.

In the first purification step, the polymer is separated from the polymer solution by precipitating it in methanol. Add the polymer solution drop-wise into the methanol with a volume of more than 5 times the volume of the polymer solution (~50 mL). While adding the polymer solution into the methanol, the mixture must be stirred vigorously either with a magnetic stirrer or glass rod.

When precipitation is completed, filter the polymer using a clean and dried sintered glass. Wash the polymer with a small amount of methanol and leave it to dry by suction using vacuum pump for about

20 min. Transfer the polymer into small plastic container with its mass known beforehand. Dry the sample in vacuum oven at about 50°C at least for 24 hours. After drying, record the weight of the dried polymer product.

Keep about 0.02 – 0.05 g of the dried polymer and label it as Polymer 1. The remaining of the dried polymer is used to carry out the second purification step by dissolving it in not more than 5 mL of chloroform and re-precipitating as in the first purification step, as described above. The polymer obtained from this step is labelled as Polymer 2.

UV analysis

The purified polymers will be analysed by UV method. The UV test is done on the Polymer 1 and 2 obtained from first and second purification steps. For each UV analysis, weight out accurately ~0.01 g polymer sample and dissolve it in 25 mL acetonitrile. Get the UV spectrum of the solution in the range of 300 – 200 nm.

Table 2.1: UV absorption

Reagent	$\epsilon_{215 \text{ nm}} / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	$\epsilon_{215 \text{ nm}} / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$
Poly(methyl methacrylate)	1.7×10^2	1.5
Cinnamic acid	?	1.89×10^4

Note:

In the case of polymer with an unknown molecular mass, the extinction coefficient is reported as the mole of the repeating unit. For example, in this case, the repeating unit of poly(methyl methacrylate) is $-\text{CH}_2-\text{C}(\text{CH}_3)\text{COOCH}_3-$ and is equivalent to molecular mass of 100.

Data Analysis

Beer's Law: $A = \epsilon \cdot b \cdot c$ (Eqn. 1)

A = absorption (directly obtained from the UV chart)

ϵ = molar extinction coefficient

b = cell distance (in this case, b = 1 cm)

c = concentration (mol dm^{-3})

Discussion / Questions:

1. Calculate the percentage of cinnamic acid presence in Polymer 1 and Polymer 2 (if any).
2. Please suggest different type of solvents that can be used to replace methanol and chloroform in this experiment. Explain your answer.

EXPERIMENT 3

EMULSION POLYMERIZATION OF STYRENE

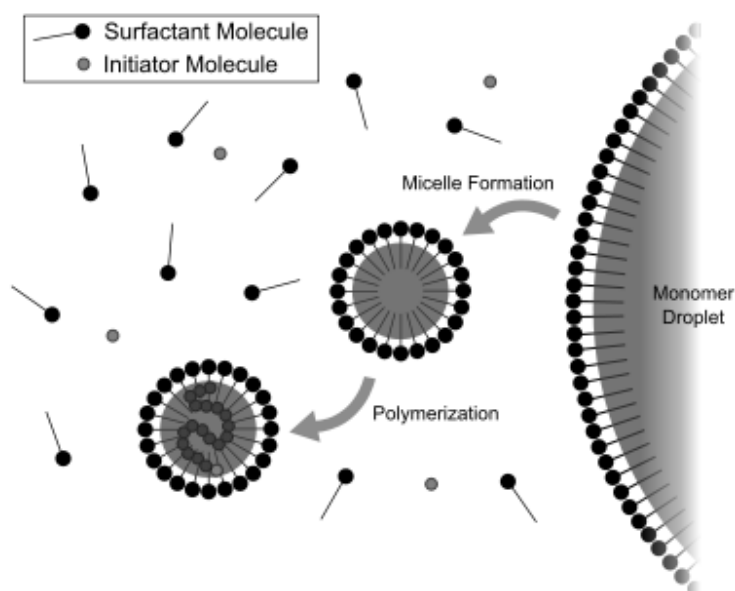
[This experiment involves 2 students in a group]

Objective

To investigate the effect of concentration of emulsifier and monomer on the kinetic of emulsion polymerization of styrene.

Introduction

At the beginning of an emulsion polymerization, three phases are present: a continuous aqueous phase containing the water-soluble initiator, suspended droplets of monomer, kept from coagulating to a continuous organic phase by agitation; and surfactant micelles containing a small proportion of monomer. Initiator fragments enter some of the micelles, where polymerization takes place, supplied with monomer by diffusion from the monomer droplets through the aqueous phase. As these micelles grow, they are stabilized by more surfactant at the expense of uninitiated micelles, which eventually disappear. The polymerization rate depends upon the number of micelles, and this in turn on the concentration of the surfactant. Other than the surfactant, this experiment also aims to investigate how the concentration of monomer affects the polymerization rate.



Methodology**Materials and apparatus**

- (i) Chemical storage bottle with cap (Glass, 250 mL) and water bath set at 70 °C.
- (ii) Nitrogen gas.
- (iii) Styrene, potassium persulfate, sodium hydrogen phosphate, sodium laurylsulphate (SLS) or sodium dodecyl sulphate (SDS), aluminium sulphate, methanol, and sodium hydroxide.

Preparation of styrene monomer

Styrene is a reactive monomer that can easily polymerize by itself when stored over a short period of time. It is normally stabilized with inhibitor such as hydroquinone or t-butylpyrocatechol. Prior to use, the inhibitor must be removed by washing with 10% dilute NaOH solution.

Mix roughly equal parts of styrene and 10% NaOH solution in a separating funnel by shaking it gently for 1-2 minutes. Allow the mixture to stand until it separates into two distinct layers. Drain off the aqueous phase and repeat the procedure again. Finally, wash the styrene with distilled water for three times, or until the water is no longer alkaline.

[Suggestion: 2 students in a group. The total amount of styrene monomer needed in this experiment is 180 mL. Each student has to wash 100 mL of styrene monomer each.]

Emulsion polymerization

Prepare 12 chemical storage bottles and into each of the glass bottle, add distilled water, $K_2S_2O_8$, Na_2HPO_4 and surfactant (SLS or SDS) according to the amount stated in Table 1. Record the actual weight of each chemicals used. Shake the flasks slowly until all the chemicals are dissolved in the water.

Table 3.1: Emulsion polymerization formulations

Bottle	Water / mL	$K_2S_2O_8$ / g	Na_2HPO_4 / g	Surfactant / g	Styrene / mL
1	60.00	0.03	0.03	0.05	15.00
2				0.10	
3				0.15	
4				0.20	
5				0.25	
6				0.30	
7				0.35	
8				0.35	
9					
10					
11					
12					

[NOTE: Styrene to be added at the last stage, one bottle at a time]

Add **PRECISELY** 15 mL of styrene to the first bottle (Bottle 1) and immediately bubble nitrogen gas through the mixture for 2 minutes and quickly cap the bottle. Shake vigorously to mix the monomer and the aqueous phase to form emulsion (looks like milk or latex). Clamp the bottles in water bath that has been pre-heated to 70°C and record the time as the starting time for Bottle 1. Repeat this step for the remaining bottles and the amount of styrene to be added in each bottle is based on Table 1.

During polymerization, make sure to shake/swirl the bottles for few seconds in every 15-20 minutes intervals. Do not remove the bottles from the water bath during shaking.

For Bottle 1 to Bottle 7, stop the reaction after 90 mins for each bottle, while for Bottle 8 to 12, the time ranges from 30 to 105 mins. Details are shown in Table 2.

Table 3.2: Duration of reaction for each bottle

Bottle	Duration of reaction / (mins)
1 – 7	90
8	75
9	105
10	120
11	150
12	180

To stop the reaction, remove the bottle from the bath, open the cap of the bottle, and add in 10 mL of 2.5% w/v of $\text{Al}_2(\text{SO}_4)_3$ (aq) (prepared by lab assistant). Filter out the coagulated polymer and wash the solid polymer with 30 mL methanol twice, followed by distilled water twice. Place the product in a plastic envelope and dry it in vacuum oven at 70°C. Record the weight of product obtained.

Discussion / Questions:

1. Calculate the concentration (mol m^{-3}) of $\text{K}_2\text{S}_2\text{O}_8$, styrene, and surfactant used in the experiment.
2. Discuss the role of $\text{K}_2\text{S}_2\text{O}_8$, NaHPO_4 and $\text{Al}_2(\text{SO}_4)_3$ in the experiment.
3. Rate of reaction \propto yield of Polystyrene (PS) = $[\text{surfactant}]^x$

Plot a graph of log PS yield vs log [surfactant] using results for Bottle 1 to Bottle 7. Determine the order of reaction with respect to the surfactant.

4. The rate law and order of reaction with respect to surfactant obtained in Question 3 is derived by taking yield of PS after 90 mins of reaction to reflect the rate of reaction. The duration of reaction is important in order for the relationship “rate of reaction \propto yield of PS” to remain valid. Elaborate this.

5. Assuming that the amount of styrene and PS in this experiment obeys the law of conservation of mass (no loss of reactant and products during the experiment),

$$M_{\text{styrene}} = M_{\text{styrene}}^0 - M_{\text{PS}} \text{ (Eqn.1)}$$

M_{styrene} = mass (g) of styrene at time t

M_{styrene}^0 = initial mass (g) of styrene

M_{PS} = mass (g) of polystyrene obtained

Based on the above equation and data collected from Bottle 7 to 12, plot the following graphs:

- (i) [styrene] vs time
- (ii) \ln [styrene] vs time
- (iii) $1/[\text{styrene}]$ vs time

6. By referring to the graphs obtained in Question 5, suggest the order of reaction with respect to the styrene. Explain your answer.

7. Propose the mechanism of polymerization of styrene in this experiment.

EXPERIMENT 4

PREPARATION OF POLYESTER VIA CONDENSATION POLYMERIZATION

[This experiment involves 2 students in a group]

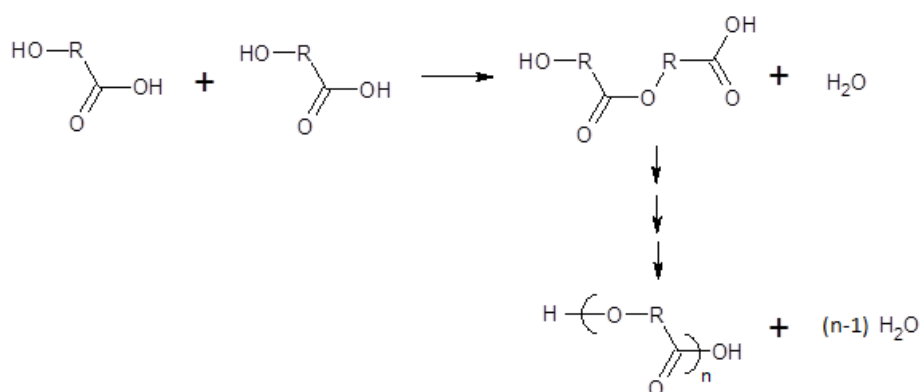
Objective: To study condensation polymerization via synthesis of poly(ethylene terephthalate), PET

Introduction

Step growth polymerization and polyester

Condensation polymerization is an example of step growth polymerization. There are several unique features of step-growth polymerization that differentiates it from chain growth polymerization. In step growth polymerization, any two molecules in the system carrying suitable functional groups can react with each other. Initially, the monomers react to form dimers, dimers can react with another dimers to form tetramers, and so on. Step reactions can therefore be characterized by the disappearance of monomer at relatively early stage of the polymerization, and "relatively uniform" progress of reaction.

Polyester is an example of polymer which is usually synthesized via condensation polymerization. In principle polyester can be produced from monomer that has both $-OH$ and $-COOH$ functional groups per molecule, such as the lactic acid. The general reaction is represented by:



It is however difficult to obtain such type of monomer in pure state, since reaction can begin even when the monomer is being stored. Besides, it will be difficult to control the molecular weight of the polyester produced from such monomer. More frequently, polyesters are being commercially produced from the combination of two different monomers, one with two or more hydroxyl groups and the other with two or more carboxyl groups. The general reaction is as follows:



Basic Carothers equation

Degree of polymerization, p and amount of water, W

For simplicity, we consider the synthesis of polyester from **equimolar** amount of diol and diacid. One molecule of diol contains 2 groups of $-OH$, hence the functionality, $f = 2$. The same goes for diacid (dicarboxylic) molecule contains 2 groups of $-COOH$, and the functionality $f = 2$.

Initially, A_0 and C_0 represents the total amount $-OH$ and $-COOH$ groups respectively, while $\frac{1}{2} U_0$ represents the amount of diol or diacid. Since each molecule of diol or diacid contains 2 $-OH$ or 2 $-COOH$ each,

$$A_0 = C_0 = U_0 \quad (\text{Eqn. 1})$$

After time t , the amount of $-OH$ and $-COOH$ left can be noted as A_t and C_t respectively.

The extent of polymerization, p after time t can be expressed as:

$$p = \frac{\text{amount of functional group that has reacted}}{\text{initial amount of functional group}}$$

$$p = (A_0 - A_t) / A_0 = (C_0 - C_t) / C_0 \quad (\text{Eqn. 2})$$

Considering the relationship shown in Eqn. 1, Eqn. 2 can also take the following forms:

$$p = (C_0 - C_t) / U_0$$

$$pU_0 = C_0 - C_t \quad (\text{Eqn. 3})$$

(The same applies for equation using A_0 and A_t)

In polyesterification, since one H_2O is produced from every $-COOH$ that was consumed in the reaction (or from every $-OH$ consumed), the amount of water, W produced can be expressed as follows:

$$W = C_0 - C_t \quad (\text{Eqn. 4})$$

Substitute Eqn. 3 into Eqn. 4,

$$W = p U_0$$

$$p = W / U_0 \quad (\text{Eqn. 5})$$

Average degree of polymerization, P_n

The polymer molecules formed at any time t would most likely have different molecular weight (or different chain length). The average degree of polymerization, P_n can be estimated from the extent of polymerization, p .

Considering the nature of the product, a polyester, one end of the polymer chain comprised of $-\text{COOH}$ and another comprised of $-\text{OH}$. The total number of polymer chains at time t , N_t can therefore be estimated based on the amount of $-\text{COOH}$ or $-\text{OH}$ present at time t :

$$N_t = (1-p) U_0 \quad (\text{Eqn. 6})$$

[Reminder: U_0 here can corresponds to the total initial amount of $-\text{COOH}$ or $-\text{OH}$]

Total amount of molecules in the system = $\frac{1}{2} U_0(\text{of acid}) + \frac{1}{2} U_0(\text{of alcohol}) = U_0$, and these would become the total number of molecules in the system at start.

Average degree of polymerization, P_n at time t :

$P_n = \text{number of molecules at start} / \text{number of molecules (including polymer) at time } t$

$$P_n = U_0 / (1-p)U_0$$

$$P_n = 1 / (1-p) \quad (\text{Eqn. 7})$$

Eqn. 7 forms the basic Carothers equation which allows one to relate the extent of polymerization with average degree of polymerization. Based on the equation, relationship of p and P_n as follows:

p	0	0.5	0.75	0.9	0.95	0.99	0.999	1
P_n	1	2	4	10	20	100	1000	∞

In this experiment, we are going to make polyester from phthalic anhydride and ethylene glycol, and keep the extent of reaction p between 70-80%, so that the polymer would have a low degree of polymerization, $3 < P_n < 10$.

The resulting polyester should be in the form of a viscous liquid.

Methodology

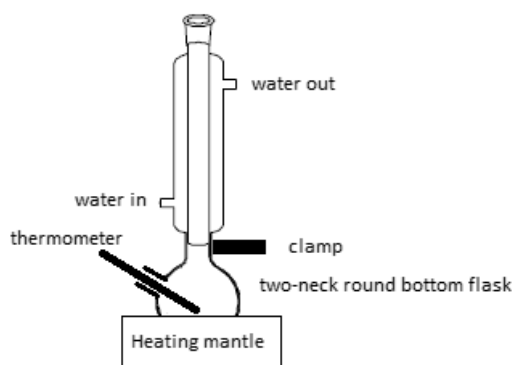
Materials and apparatus

(i) Phthalic anhydride and ethylene glycol, KOH, ethanol, potassium hydrogen phthalate (KHP), toluene, isopropanol, phenolphthalein.

(ii) 2-necked round bottom flask, thermometer, heating mantle, condenser and adapters.

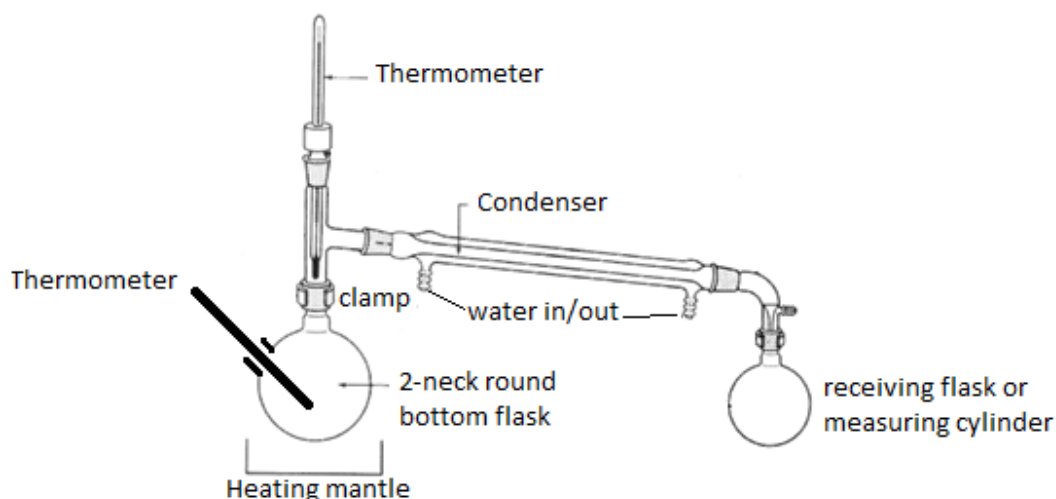
Synthesis of PET

Introduce 74.10 g (0.50 mol) phthalic anhydride into a 2-necked round-bottom flask. Add in equimolar amount of ethylene glycol (31.00 g). The round bottom flask must be secured in a heating mantle with a retort stand, fixed with a thermometer and condenser in reflux setup:



Heat the mixture slowly, and swirl the flask from time to time. Let the temperature to gradually rise to 160-180°C and hold for about 20 minutes or until all of the components in the mixture has “dissolved”. At this stage, there is no water evolved.

Allow the reaction mixture to cool down to $\leq 120^\circ\text{C}$. Rearrange the apparatus, and set up for distillation, as shown below:



Restart heating and increase the temperature gradually until the lower thermometer reaches **200°C** (*time, t = 0*), and hold the temperature constant for 1.5 hour. Monitor the temperature of the higher thermometer as well to ensure that no reactant is lost. After 1.5 hour, gradually increase the temperature of the reaction mixture to 220°C and hold it constant until the reaction is complete. Make sure the temperature does not exceed 240°C.

Note that the water of reaction may be generated as early as around 180°C, which would then distill over as steam and condense through the condenser. Make sure receiving flask/ graduated tube is placed at the end of the condenser to collect the water produced.

Withdraw approximately 1.0 g of the reaction mixture at $t = 30, 60, 90$ and 120 mins (note that $t=0$ when temperature of the mixture reaches 200°C). The withdrawn samples need to be analyzed for their acid value. Make sure to record the cumulative amount of water collected at the graduated tube/receiving flask during each sample withdrawal.

Stop heating when the total amount of water collected is approximately 7.0 g and withdraw another 1.0 g of the reaction mixture to measure the final acid value of the product (polyester). Take note of the time when the reaction stops ($t = y$).

Allow the temperature to fall below 100°C. Dismantle the apparatus, and pour your product into a sample bottle. Label with your name, group, and date of synthesis.

Submit small amount of the final product for GPC analysis.

Acid value measurement

(i) Preparation of standardised KOH solution.

Dissolve 3.3 g of potassium hydroxide (KOH) in 500 mL of ethanol. Standardize the KOH solution with potassium hydrogen phthalate solutions (1.0 g KHP in 50 mL water) and few drops of phenolphthalein solution as the indicator (Note: record the actual amount of KHP used). Calculate the concentration of KOH solution, K in the unit of milligrams of KOH per millilitre of solution.

[Phenolphthalein solution to be prepared by lab assistant: Dissolve 1 g of phenolphthalein in 100 mL ethanol]

(ii) Preparation of neutral solvent

Prepare 400 mL of neutral solvent by mixing equal parts by volume of isopropanol and toluene.

(iii) Acid value measurement of sample

Dissolve about 1.0 g of sample in 25 mL of neutral solvent. Mix until the sample is fully dissolved, warm it using water bath if necessary. Let it cool to room temperature, add few drops of phenolphthalein indicator solution and titrate with the KOH solution to the end point.

Acid value (mg KOH/mL) can be calculated using the following equation:

$$\text{Acid value} = (V \times K) / s \quad (\text{Eqn. 8})$$

V = volume of KOH solution used in the titration, mL

K = strength of KOH solution, mg KOH/mL

S = amount of sample, g

Discussion / Questions

1. Give the chemical equation for the formation of PET from the reaction between phthalic anhydride and ethylene glycol.
2. From the amount of water of reaction collected, calculate the actual extent of reaction, p and average degree of polymerization, P_n .
3. What would be the average molecular weight of the polyester based on the P_n ?
4. Compare and discuss the molecular weight that you calculated in question 3 with the one obtained from GPC analysis.
5. What would happen if the extent of reaction, p approaches 100%?
6. Initial acid value of a mixture is usually calculated based on the amount of reactant introduced into the mixture. Calculate the initial acid value (mg KOH/g) of the reaction mixture based on the amount of phthalic anhydride introduced in the reaction.
7. Calculate the expected final acid value based on the final amount of water collected.
8. Compare the value that you calculated in question 7 with the actual final acid value measured from the experiment.
9. Plot a 3-axes graph of acid value and water collected vs time. Briefly comment on the change in acid value and water collected throughout the polymerization.

Duration of reaction / mins	Acid value	Water collected (mL)
0 (Initial)	Value calculated from question 6	0
30	Measured	Measured
45	Measured	Measured
60	Measured	Measured
90	Measured	Measured
y	Measured	Measured

EXPERIMENT 5

VISCOSITY-AVERAGE MOLECULAR WEIGHT

Objective

To measure viscosity-average molecular weight of polymer using viscometer.

Introduction

Measurements of the viscosity of dilute polymer solution provide the simplest and most widely used technique for routinely determining molecular weights of 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 0.5 g/100 mL of solvent by determining the flow time of a certain volume of solution through a capillary of fixed length. Flow time in seconds is recorded as the time for the meniscus to pass between two designated marks on the viscometer. Viscosities of the polymer solutions are measured at constant temperature; usually at $30.0 \pm 0.1^\circ\text{C}$.

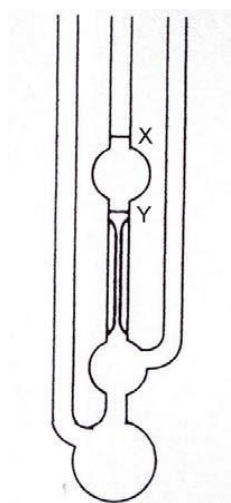


Figure 5.1:Ubbelohde viscometer

The Ubbelohde type of viscometer is the most convenient to use as it is not necessary to have exact volumes of solution to obtain reproducible results. Furthermore, additional solvent can be added (as long as the total volume can be accommodated by the reservoir); thus the concentration can be diluted without evacuating and refilling the viscometer.

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 the capillary tube would affect the flow time.

Viscosity can be expressed in several ways as described below.

Relative Viscosity, η_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.

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (\text{Eqn. 1})$$

where η and η_0 are the viscosities of the solution and solvent, respectively; t and t_0 are the respective flow time of the solution and the solvent, respectively.

Specific viscosity, η_{sp}

Specific viscosity is the fractional increase in viscosity, defined as,

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 \quad (\text{Eqn. 2})$$

Both η_r and η_{sp} are dimensionless (i.e. without a unit). As concentration increases, so does the viscosity. Hence to account for the concentration effects, the specific viscosity is divided by concentration to give the reduced viscosity, η_{red}

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad (\text{Eqn. 3})$$

Not uncommonly, viscosities are determined at a single concentration and the inherent viscosity (η_{inh}) as defined below is used as an approximate indication of molecular weight

$$\eta_{inh} = \frac{\ln \eta_r}{c} \quad (\text{Eqn. 4})$$

where concentration c is commonly expressed as g per 100 ml.

The change in solution viscosity with increasing concentration can be expressed as a series in concentration c as given by the Huggins Equation and the Kraemer equation as shown below.

$$\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c \quad (\text{Eqn. 5})$$

(M. L. Huggins, J. Am. Chem. Soc., 64(1942) 2716)

$$\frac{\ln \eta_r}{c} = [\eta] + k' [\eta]^2 c \quad (\text{Eqn. 6})$$

(E. D. Kraemer, Ind. Eng. Chem., 30(1938) 1200)

Both the inherent and reduced viscosities extrapolate to give the intrinsic viscosity, $[\eta]$, at zero concentration.

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c=0} = \left(\frac{\ln \eta_r}{c} \right)_{c=0} \quad (\text{Eqn. 7})$$

The Huggins constant k_1 is related to the molecular structure and the degree of association of the polymer chains in the solvent. It could be shown mathematically that the two equations (5 & 6) would converge to intercept at the y-axis to the same $[\eta]$ value and

$$k_1 + k' = \frac{1}{2} \quad (\text{Eqn. 8})$$

Methodology

Materials and Apparatus

(i) Viscometer (Ubbelohde type), water bath, stop watch, rubber pipetting bulbs, beaker & volumetric flask.

(ii) polystyrene sample (H, L or X) & solvent (toluene).

Determination of t_0

Set the water bath to 30.0 ± 0.1 °C. Measure 10 ml of toluene (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).

Apply nitrogen gas to force the toluene to rise through up the capillary tube to fill the bulb between the marks X and Y and reach the bulb above X. (Get the demonstrator or the laboratory assistant to show you the correct technique).

Allow the solution to flow under gravity. Start timing with a stop-watch when the upper meniscus reaches X, and stop the stop-watch when the meniscus reaches Y. Repeat 4 to 5 times, and take the average of the three most consistent readings to be the solvent flow time t_0 .

Pour out all the toluene, and hang the viscometer upside down in the fume cupboard to drip dry while you prepare the polystyrene solution as follow.

Preparation of 1% w/v polystyrene solution

Prepare a solution of the polystyrene sample (H, L or X, get it from the laboratory assistant) by weighing accurately about 0.25 g of the polystyrene into a 25 mL volumetric flask. Add toluene into the flask and allow the polystyrene to dissolve completely (need to wait for at least 15 minutes, with occasional shaking), adjust to the mark of the volumetric flask.

Determination of solution flow time t

Pipette 10 mL of polystyrene solution into the viscometer. Follow the same procedure as in the measurement of the solution flow time.

Reduce the concentration of the solution in the viscometer by adding 3 mL of solvent directly into the viscometer. Make sure you shake the viscometer for a few minutes to ensure homogeneous mixing, before you start to determine the solvent flow time.

Repeat the dilution 4 to 5 times, each time by adding 3 ml solvent into the viscometer. For each concentration, repeat the measurement of flow time at least 4 times and then compute the average value.

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

Analysis of data

Tabulate your results as follow:

Measurement of solvent flow time t_0

No.	Solvent flow time t_0 /s
1	
2	
3	
4	
5	

Average of three most consistent measurement =

c g/100 ml	Solution flow time /s				Averaget	$\eta_r = t/t_0$	η_{sp}	η_{sp}/c	$\ln \eta_r/c$
	1	2	3	4					

Plot (η_{sp}/c) and ($\ln \eta_r/c$) versus c in the same graph paper, and determine the intrinsic viscosity $[\eta]$. 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.

$$[\eta] = K (M_v)^a \quad (\text{Eqn. 9})$$

where K and 'a' are constants for a specific polymer and are dependent on the temperature and solvent.

In the case of polystyrene in toluene at 30°C, $K = 9.2 \times 10^{-3} \text{ ml g}^{-1}$ and $a = 0.72$.

EXPERIMENT 6

DETERMINATION OF GLASS TRANSITION TEMPERATURE, TG: DILATOMETRY TECHNIQUE

Objective

To determination of glass transition temperature, T_g using dilatometry technique.

Introduction

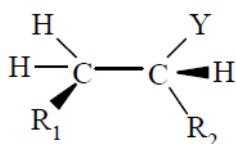
Macromolecules exist in a variety of aggregate states according to the structure, temperature and other environmental conditions. Four of these states are rubbery, glassy, crystalline and liquid. One polymer may exist in all of these states or some of them. Polymers are different compared to materials with lower molecular weight, because they normally exist in more than one state for the same sample and in rare special condition exhibit 100% crystalline state. Therefore, in one polymer sample, some may exist in the form of rubbery or glassy portion and some in crystalline portion.

In crystalline state, polymeric chains are arranged in order, forming crystal lattice, while in rubbery or glassy state, polymeric chains are in random orientation and is called amorphous. Characteristic that differentiate between the crystalline with amorphous states is not orientation, but motion. Below the glass transition temperature (T_g), the segmental motion of polymer chains, especially short segment rotations (≈ 5–10 carbon atom) stop and will be in the glassy state.

It should be noted that the transformation from a rubbery state to a glassy state or vice versa is a second order transition, i.e. no transition in polymer chain orientations, therefore there is no change in volume. It is different compared to the change from crystalline state to rubbery state or liquid, where there are changes in both polymer orientations and movements, followed by a change in volume. This is called first order transition.

The actual value of glass transition depends on several factors, but the main factor is the structure of repeating unit of that polymer. The glass transition is correlated to the beginning or stopping (freezing) of segmental motion through the bond rotation which in turn depends on the structure of repeating unit.

For organic molecules with low molecular weight, e.g:

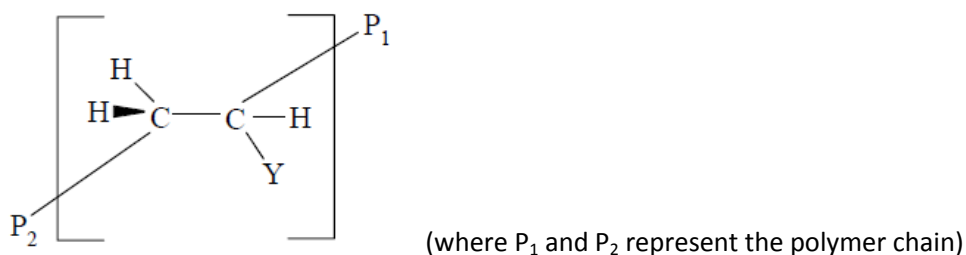


the activation energy for rotation of C-C bond depends on the properties of the substituted groups. An increase in size or polarity of the substituted groups can restrict the bond rotation, thus activation energy will increase. The frequency of bond rotation can be categorized by Arrhenius equation:

$$K = X e^{-\left[\frac{E_a}{RT}\right]} \quad (\text{Eqn. 1})$$

where X is assumed to have the same value as the frequency of torsional oscillation of C-C bond and E_a is activation energy of the bond rotation. Consequently, when the temperature is reduced, a value can be derived where the frequency of C-C bond rotation takes longer time than the experimental time period and rotation can no longer be detected. At this critical temperature, rotation is assumed to have stopped.

Polymers can also be treated in the same way. In normal repeating unit, e.g:



will contain two big substitutions, P_1 and P_2 (if C-C bond is not part of the end group, beside the other substituted units). Activation energy for C-C bond rotation in polymers is usually in the order of 10-20 kcal mol⁻¹ and depends on the size and polarity of the substituted groups. Therefore, the critical temperature (T_g) where the rotation can be observed to have stopped is in the range of -100°C to +200°C.

At glass transition temperature, there is a unique transformation in polymer properties, from hard and relatively brittle at lower temperature to a rubbery state at high temperature. Beside an abrupt change in hardness and brittleness at glass transition, other properties such as the thermal expansion coefficient, heat transition, heat capacity, dielectric constant and deflection index also change. By observing the changes in these properties against temperature, T_g can be determined. In this experiment, T_g will be determined with dilatometry technique, i.e. by observing the change in height of the meniscus of the capillary tube / specific volume (thermal expansion coefficient) of the polymer over a certain temperature range. (Eqn. 1)

Methodology

Materials and Apparatus

- (i) Dilatometer, hypodermic tube, grease, water bath & beaker.
- (ii) Poly(isobutyl methacrylate), ice-cube & distilled water.

Determination of t_0

Fill a dilatometer, containing about 17 g poly(isobutyl methacrylate) with distilled water. Use long hypodermic tube until the water reaches about 1/3 of capillary tube. Grease oil can be used at the joints if necessary. Place dilatometer into the water bath set at 70°C to remove any air bubbles by rotating it. Then cool it down to room temperature. Immerse the dilatometer with the whole bulb in a water bath, equipped with temperature controller and heater. Take the value of the meniscus for every 3°C increase within the temperature range of 20-70°C. Temperature must be controlled to constant value (+ 1.0°C) for 5 minutes before the value of the meniscus is noted down.

Data Analysis

Plot the change in value of the meniscus against temperature. The point of inflexion in the curve gives the T_g value.

EXPERIMENT 7

Determination of Glass Transition Temperature, T_g of Natural Rubber and Butyl Rubber

Objective

To determine of the glass transition temperature, T_g of Natural Rubber and Butyl Rubber using Rebound Resilience Method

Introduction

When stress is applied on a piece of elastomeric material, the rate of opening-up of the polymer molecule chain at any particular time depends on the proportion of the molecules which are still immobile. The rate of which can be given as $1/\tau$, known as stress relaxation time, defined as the time taken for the shape to deform $(1 - 1/\tau)$ of its equilibrium time. The time-deformation curve after the application of stress on a polymeric mass is given by the equation,

$$D_t = D_\infty [1 - e^{-t/\tau}] \quad (\text{Eqn. 1})$$

Where D_t refers to the deformation at time t and D_∞ the deformation after infinite time (Figure 7.1.)

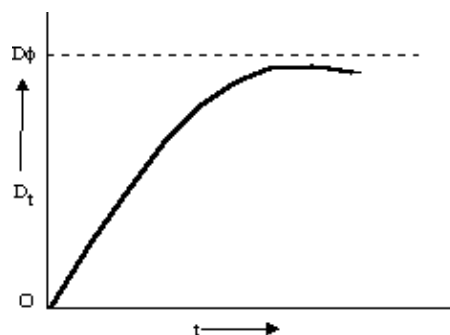


Figure 7.1: Deformation of a highly elastic material on application of stress.

A very important consequent of this theory is that for a particular material, whether it behaves as rubber or glass depends on the **test time scale**. For example, when the time taken to highly deform a material is extremely short, $t \ll \tau$, the material will behave like a glass, but at longer test time, $t \gg \tau$, the material will behave like rubber.

While t is influenced by the speed of the test, relaxation time is influenced by test temperature and obeys the normal exponential rate law

$$\tau = A e^{E/RT} \quad (\text{Eqn. 2})$$

where E is related to the activation energy of a bond rotation. By combining equations (1) and (2), we will obtain

$$D_r/D_\phi = 1 - e^{[-t/Ae^{E/RT}]} \quad (\text{Eqn. 3})$$

At high activation energy, the equation shows that D_t/D_ϕ changes from 0 to 1 for only a small change of temperature (Figure 7.2)

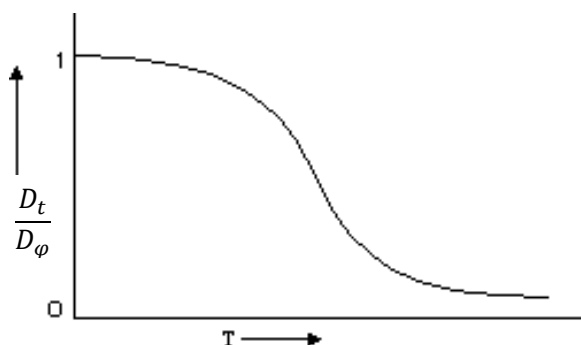


Figure 7.2: Change of D_t/D_ϕ with temperature T at fixed t , A and E .

As such, a sharp change from glassy to rubbery is expected to occur within a small range of temperature at a particular test speed. According to this theory, the actual T_g will depend on the speed of the test conducted. Tests at lower speed will show lower T_g .

This experiment shows the significance of both parameters, time and temperature, in determining the elasticity of an elastic material.

When an elastomeric ball is dropped onto a hard surface it will rebound; the time of contact between the ball and the surface is very brief. The extent of rebound depends on the temperature and can be shown by the rebound resilience defined as the ratio of regained energy in relation to the applied energy.

If h_0 is the initial height, and h is the rebound height, the rebound resilience, is given by h/h_0 and the energy loss for each rebound is $(1 - h/h_0)$. In this experiment, a plot of h/h_0 against T will produce a curve which will go through a minimum at which the value T corresponds to the glass transition temperature, T_g .

Methodology

Materials and Apparatus

- (i) Dewar flask, metal tong, ruler, thermometer, beaker & hot-plate.
- (ii) Natural rubber ball, butyl rubber ball, liquid N_2 , distilled water & acetone.

Determination of T_g

Two samples, a natural rubber (NR) ball and a butyl rubber ball, are used in this experiment. At room temperature, the NR ball will rebound higher than the butyl rubber ball. The experiment will be conducted at temperatures from -80°C to $+60^\circ\text{C}$. Temperature below 0°C is obtained by mixing liquid N_2 with water.

Use a dewar flask to prepare a sub-zero environment. Immerse the rubber balls, together with the metal tong, in the flask for 3 minutes. Set up a meter ruler to read vertically upwards. Using the tong, hold the rubber ball at a height of 60 cm (h_0), then release it to drop onto a hard surface of your work-bench. Note the height of the rebound (h). Take two readings. Repeat the process with the other sample.

Continue the experiment for other temperatures.

Discussion / Questions:

Analysis of Data

1. Plot h/h_0 against temperature for each rubber on a single graph. Determine the temperature at lowest value of h/h_0 .

This temperature is closely related to the transition temperature, T_g . The relationship is given by the William-Landel-Ferry (WLF) equation below:

$$T_g = T_g' + \frac{51.6 \log a}{17.4 - \log a} \quad (\text{Eqn. 4})$$

where $a = t'/t$. here, T_g is obtained from a technique of known test time t , while T_g' corresponds to t' . The values of t for different test are given in the Table 7.1 below:

Table 7.1: Test time (t)

Test	t(s)
Thermal expansion	10^4
Mechanical Loss	$1 - 10^4$
Rebound Resilience	10^{-5}
Dielectric loss	$10^{-2} - 10^{-8}$
Broadline NMR	$10^{-4} - 10^{-5}$

Example of Calculation using WLF Equation

If, in the rebound resilience experiment, minimum h/h_0 occurs at 100K, the T_g of the material can be predicted using the values corresponding to the thermal expansion as follows,

$$T_g = 100 \text{ K}, \quad t = 10^{-5} \text{ s (rebound resilience) ;}$$

$$T_g' = ? \text{ K}, \quad t' = 10^4 \text{ s (thermal expansion).}$$

$$\text{So, } a = 10^9$$

Equation (5) gives,

$$T_g = T'_g + \frac{51.6 \log a}{17.4 - \log a}$$
$$100 = T'_g + \frac{51.6 \log 10^9}{17.4 - \log 10^9}$$
$$100 = T'_g + 55.3$$
$$T'_g = 44.7 \text{ K}$$

Similarly, T_g for the rubber sample in the experiment can be determined based thermal expansion.

2. What are precaution steps needed during the experiment?

EXPERIMENT 8

Crosslink Parameters of a Vulcanised Natural Rubber

Objective

To determine the crosslink parameters of a vulcanised natural rubber

Introduction

This experiment is divided into two parts

PART A: Stress-Strain Method

A special feature of natural rubber (NR) is elasticity. Materials such as metal and glass can only be deformed elastically to a small degree, normally less than 1%, while NR can be extended to 700% or more. Elastic deformation means a material will recover to its original shape and dimension when released after being deformed.

The basis of elasticity in NR is that polymer chains without any external application of strain, will have the most appropriate configuration, statistically; i.e. randomly coiled. When strain is applied, the chain will be effectively extended to a longer, less appropriate configuration, followed by a decrease in entropy. If the strain is released, the chain will return to the most probable configuration and maximum entropy in accordance to the Boltzman expression:

$$S = k \log W \quad (\text{Eqn. 1})$$

The idea that polymer, with its high molecular weight, should display elasticity, obviously, is not totally true because there are actually four basic criteria for the elasticity of rubber:

- (i) The material must be made up of long chain molecules which can rotate freely,
- (ii) Has weak intra-molecular attractive forces
- (iii) The molecules are joined or crosslinked along the chains, and
- (iv) The polymer is above its glass transition temperature T_g

Unvulcanised rubber does not fulfil these criteria because the polymer chains are not crosslinked. However, apparent crosslinks exist from the entanglement of the polymer chains. The elasticity of NR can be improved by chemically introducing the crosslinks through a process known as vulcanisation or curing.

Although rubber does not behave like solid, gas or liquid, part of its behaviour can be understood from the analogy of the properties of a perfect gas. Pressure exerted by gas on the wall of a vessel is caused by the continuous and random bombardment of the gas molecules; tension on an extended rubber is caused by the random thermal movement of segments of the polymer chain. Gas molecules are inclined towards a most probable distribution in space. Similarly, the segments of the polymer chains are inclined towards the most probable, randomly coiled condition.

We can also produce an equation for rubber, similar to the ideal gas equation, $P = nRT/V$. the equation for the situation is,

$$F = \frac{dRT}{M_c} (\lambda - \lambda^{-2}) \quad (\text{Eqn. 2})$$

where F is the tensional force (i.e. the force per cross-sectional area of the unextended rubber sample, kg cm^{-2}), d is the density of rubber (g cm^{-3}), R the gas constant, T the absolute temperature (K), M_c is the molecular weight between crosslinks, and λ the ratio of the extended length to its original.

Just as no gas behaves as ideal gas, similarly, rubber will display a deviation from its ideal behaviour, such that the equation is modified to fit actual observation,

$$F = \frac{gdRT}{M_c} \left(1 - 2\frac{M_c}{M}\right) (\lambda - \lambda^{-2}) \quad (\text{Eqn. 3})$$

where g is a correction factor for the additional (apparent) crosslinks caused by the physical entanglement of polymer chains, M the molecular weight of the elastomer, and the expression $(1 - 2M_c/M)$ is a modification which takes into consideration the existence of free ends in a 3-dimensional network.

In this experiment, the degree of vulcanisation, M_c as determined by the Mooney-Rivlin eqn. 3 will only be true at low extension ($\lambda < 1.5$).

Methodology

Mark two positions, a distance of 5 cm (l_0) on the rubber sample. Grip the sample with 2 clips; make sure the markings are visible. Hang the sample as shown in Figure 8.1.

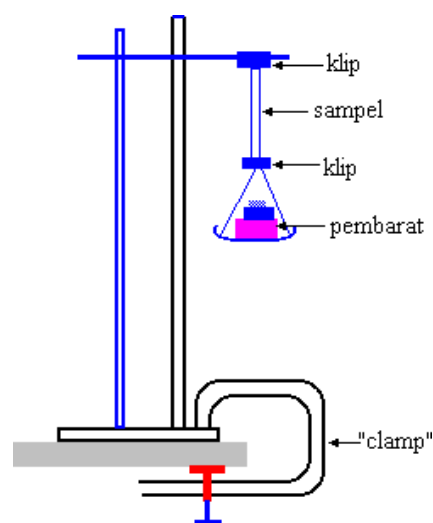


Figure 8.1: Experimental set-up.

Weigh the container which will be attached to the lower clip. Measure the distance between the markings. Add weights successively and measure the corresponding lengths (l) of the sample until it is extended to about 25 cm. Remove the weight successively and again measure the corresponding length of the sample.

Analysis of Data

Mooney-Rivlin equation is given as follows,

$$L/(\lambda - \lambda^{-2}) = l + S\lambda^{-1} \quad (\text{Eqn. 4})$$

where l and S are constants that can be determined from the plot $L/(\lambda - \lambda^{-2})$ against λ^{-1} . M_c can be calculated from the equation

$$M_c = W' RT/l \quad (\text{g/mol}) \quad (\text{Eqn. 5})$$

where $W' = \text{weight of sample}/l_0$ (g/cm)

$$R = 84.7 \text{ kg.cm.mol}^{-1}.\text{K}^{-1}$$

PART B: Swelling Method

Raw rubber (e.g. latex and unvulcanised rubber) can be perfectly miscible with good solvents such as toluene and chloroform; but once vulcanised, it becomes almost insoluble. It cannot be dispersed by solvent but will undergo swelling; the amount of solvent absorbed depends on the extent of crosslinking. This is almost similar to the solubility of a polymer. However, in swelling the penetration of solvent into the polymer network has an opposing effect to the elastic shrinkage of the network. At equilibrium, these two effects are in balance. The equilibrium degree of swelling can be understood from the combination of the theories of solution and elasticity of rubber. The equations enable the calculation of M_c from the degree of swelling of a rubber.

Experimental Procedure

TWO steps are involved.

(1) Determination of rubber density

Cut a portion of the rubber sample (~10 cm) and determine its ACCURATE weight. Fill a 5 ml measuring cylinder with distilled water to its 3.00 ± 0.05 ml. Cut the rubber into smaller pieces and put them into the measuring cylinder. Make sure there are no **AIR BUBBLES** on the rubber samples. Accurately read the new water level in the flask. Determine the volume (V) of the rubber. Hence, calculate the density of the rubber.

(2) Determination of swelling of the rubber sample

Cut about 3 cm of the rubber sample and **ACCURATELY** determine its weight. Place the sample in a conical flask containing 25 ml toluene. Stopper the flask and place it in a dark corner of a cupboard for at least 12 hours. Take the rubber out and place it on a wire mesh for 5 seconds. Transfer the rubber to a weighing bottle of known weight, close it and determine the weight of the rubber. The ratio of the volume of solvent trapped in the rubber sample is,

$$Q_m = \frac{\left[\frac{W_g - W}{d'}\right]}{\left[\frac{W}{d}\right]} \quad (\text{Eqn. 6})$$

where W_g is the weight of swollen rubber, W the initial weight of rubber, d' the density of toluene (0.867 g.ml^{-1}) and d the density of rubber [from Part B (1)]. The volume fraction of rubber in the swollen sample is,

$$V_2 = \frac{1}{1 + Q_m} \quad (\text{Eqn. 7})$$

The molecular weight, M_c can then be calculated from the following equation,

$$M_c = \frac{-dV_0V_2^{1/3}}{\ln(1 - V_2) + V_2 + \mu V_2^2} \quad (\text{Eqn. 8})$$

where V_0 is the molar volume of toluene (mol. wt / density), and μ is the interactive constant between natural rubber and toluene (0.42).

Discussion / Questions:

1. Analyse the obtained data as instructed below:

- Plot a graph of weight L (kg) against extension λ for both addition and removal of weights, in order to show the effect of hysteresis.
- Determine w' , the weight (g) per cm of the sample and use the data from the addition of weights to determine the molecular weight, M_c of the rubber using the given equations, Eqn. 4 – Eqn. 5.

2. Calculate the density of the rubber and determine the molecular weight, M_c of the rubber using Eqn. 6 – Eqn. 8.

3. What are precaution steps needed during the experiment in PART A and B?