

Code -

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**Maharashtra Institute of Technology, Aurangabad**

(An Autonomous Institute)

END SEMESTER EXAMINATION

**Second Year B.Tech (Plastic and Polymer Engineering) –**

**Feb/Mar-2023**

Course Code: PPE 203  
Polymers




Course Name: Physical Chemistry of

Duration: 2 Hrs

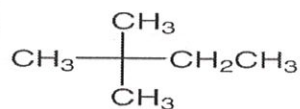
Max. Marks: 50

Date: 08/02/2023

Solution and Marking Scheme

Q. 1	Solve/Answer Any Four (Marks: 4)
	Questions
a)	<p>Solvent quality: interaction monomer – solvent</p>  <p>good solvent: maximization of monomer-solvent contacts → chain expansion, „swollen chain”</p> <p>theta solvent: balanced interactions → unperturbed (ideal) chain</p>  <p>poor solvent: minimization of monomer-solvent contact → chain collapse, clustering, precipitation</p> 
b)	<p><b>Process of polymer dissolution: two step</b></p> <ul style="list-style-type: none"><li>•Step 1: the solvent diffuses into polymer masses to make a swollen polymer gel</li><li>•Step 2: swollen polymer gel breaks up to solution</li></ul>
c)	<p>Conformations are different <u>spatial arrangements</u> of a molecule that are generated by <u>rotation about single bonds</u>. (1mark)</p> <p>Three points: (1mark)</p> <ol style="list-style-type: none"><li>1. free rotation around single bonds.</li><li>2. ability to adopt different conformations arises from the rotational degree of freedom around the single chemical bonds connecting the backbone atoms.</li><li>3. gives a different 3D form of the same molecule.</li></ol>

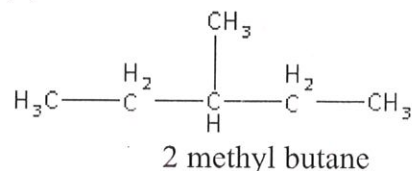
d)	<p>Methylene dichloride is a good solvent and tetrahydrofuran a poor solvent for the polycarbonate the reverse is true for PVC yet all four materials have similar solubility parameters. The explanation is that a form of hydrogen bonding occurs between the polycarbonate and methylene dichloride and between PVC and tetrahydrofuran. In other words, there is a specific interaction between each solvent pair.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{CH}_2 \\   \\ \text{Cl}-\text{C}-\text{H} \cdots \cdots \text{O} \\   \\ \text{CH}_2 \end{array}</math> <math display="block">\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\   \\ \text{CH}_2 - \text{CH}_2 \end{array}</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{R} \\   \\ \text{O} \\    \\ \text{C} = \text{O} \cdots \cdots \text{H} - \text{C} - \text{Cl} \\   \\ \text{Cl} \end{array}</math> </div> </div>
e)	$\delta = \left( \frac{\Delta E}{V} \right)^{1/2} = \left( \frac{\Delta H - RT}{M/D} \right)^{1/2}$ <p>Where <math>\delta</math> is the solubility parameter  <math>\Delta E</math> the energy of vaporisation  <math>V</math> the molar volume  <math>\Delta H</math> the latent heat of vaporisation  <math>R</math> the gas constant  <math>T</math> the temperature  <math>M</math> the molecular weight  <math>D</math> the density.</p>
f)	<p>Thomas Young (13 June 1773 - 10 May 1829) proposed treating the contact angle of a liquid with a surface as the mechanical equilibrium of a drop resting on a plane solid surface under the restraints of three surface tensions:</p> <ul style="list-style-type: none"> <li>• <math>\gamma_{lv}</math> (at the interface of the liquid and vapor phases),</li> <li>• <math>\gamma_{sl}</math> (at the interface of the solid and liquid phases) and</li> <li>• <math>\gamma_{sv}</math> (at the interface of the solid and vapor phase). This lead to <i>Young's equation</i>:</li> </ul> $\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (1.1)$ <p>This equation is deceptively simple, but there are a few difficulties with it because of the definitions of the surface tension of the solid-vapor and solid liquid phases.</p>
g)	<p>The Gibbs free energy change at temperature T is expressed as,</p> $\Delta G = \Delta H - T \Delta S$ <p><math>\Delta G</math> = Free energy change  <math>\Delta H</math> = Enthalpy change  <math>T</math> = Absolute temperature  <math>\Delta S</math> = Entropy change</p>
h)	<p>Cohesive Energy is the energy that must be supplied to the solid to separate its constituents into neutral free atoms at rest and at infinite separation with the same electronic configuration.</p> <p>The adhesive energy is the energy which is released when one liquid or solid surface comes in contact with another liquid or solid surface.</p>
Q. 2	<p>Sight down the C-2--C-3 bond, and draw Newman projection formulae for the (a)</p>



2,2, dimethyl butane

Draw the Newman projection formula with C2 as front and C3 as back carbon atoms or vice versa.

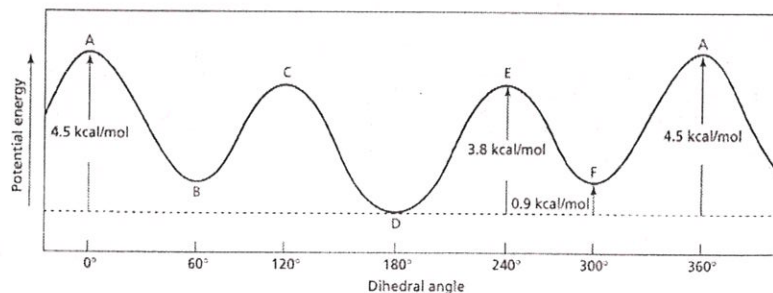
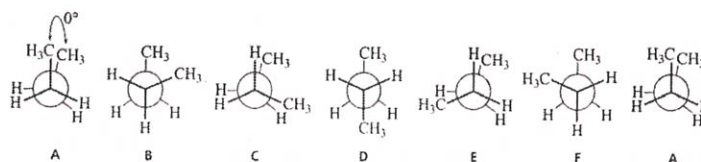
(b)



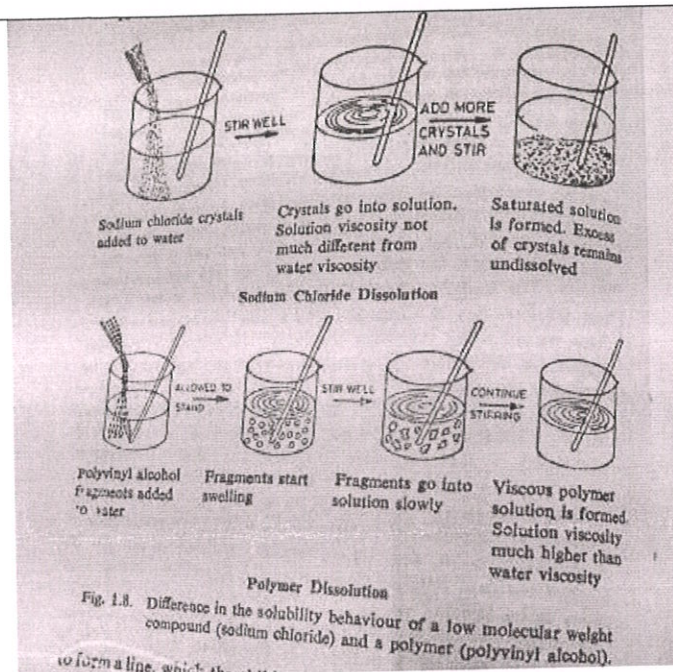
The most stable conformation" generally belongs to staggered conformation in organic chemistry. In this type of conformation, all the groups are away from each other, and therefore, less steric crowding is present.

OR

Potential energy of butane as a function of the degree of rotation about the C-2—C-3 bond. Letters refer to the conformers (A-F) shown above.



- we consider conformations related by rotation about the bond between the **middle two carbons** ( $\text{CH}_3\text{CH}_2\text{---CH}_2\text{CH}_3$ ).
- Unlike ethane, in which the staggered conformations are equivalent, two different staggered conformations occur in butane, shown in figure below.
- The methyl groups are gauche to each other in one, anti in the other. Both conformations are staggered, so are free of torsional strain, but two of the methyl hydrogens of the gauche conformation lie within 210 pm of each other.
- This distance is less than the sum of their van der Waals radii (240 pm), and there is a repulsive force between them. The destabilization of a molecule that results when two of its atoms are too close to each other is called **van der Waals strain**, or **steric hindrance** and contributes to the total steric strain.
- In the case of butane, van der Waals strain makes the gauche conformation approximately 3.2 kJ/mol (0.8 kcal/mol) less stable than the anti



- Dissolution of a polymer is generally a slow process, which can take even several weeks, depending on the structure and the molecular weight of a given polymer.
- When a low molecular weight solute such as sucrose is added to water, the dissolution process takes place immediately. The sugar molecules leave the crystal lattice progressively, disperse in water, and form a solution.
- But polymer molecules are rather different. They constitute long chains with a large number of segments, forming tightly folded coils which are even entangled to each other. Numerous cohesive and attractive both intra and intermolecular forces hold these coils together, such a *dispersion, dipole-dipole interaction, induction, and hydrogen bonding.*

OR

A chemical will be a solvent for another material if the molecules of the two materials are compatible, i.e., they can co-exist on the molecular scale and there is no tendency to separate. This statement does not indicate the speed at which solution may take place since this will depend on additional considerations such as the molecular size of the potential solvent and the temperature. Molecules of two different species will be able to co-exist if the force of attraction between different molecules is not less than the forces of attraction between two like molecules of either species. If the average force of attraction between dissimilar molecules A and B is  $F_{AB}$  and that between similar molecules of type B  $F_{BB}$  and between similar molecules of type A  $F_{AA}$  then for compatibility  $F_{AB} \geq F_{BB}$  and  $F_{AB} \geq F_{AA}$ .

If either  $F_{AA}$  or  $F_{BB}$  is greater than  $F_{AB}$  the molecules with the highest intermolecular attraction will tend to congregate or cohere and they will expel the dissimilar molecule with the result that two phases will be formed.

When a polymer is added to a given solvent, attraction as well as dispersion forces begin acting between its segments, according to their polarity, chemical characteristics, and *solubility parameter.*

If the polymer-solvent interactions are  $>$  than the polymer-polymer attraction forces, the chain segment start to absorb solvent molecules, increasing the volume of the

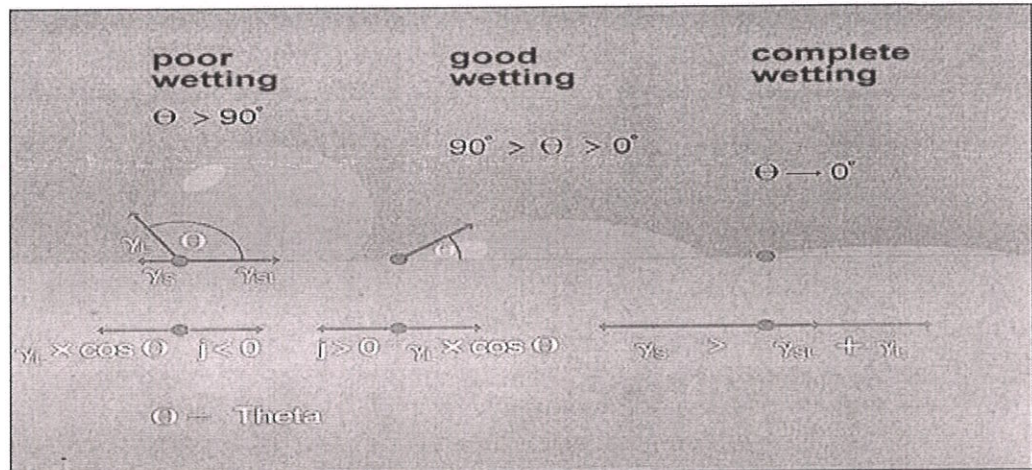
polymer matrix, and loosening out from their coiled shape.

We say the segments are now "solvated" instead of "aggregated", as they were in the solid state.

The polymer-solvent interactions are still strongly enough, the "solvation-unfolding-swelling" process will continue until *all* segments are solvated. Thus, the whole loosen coil will diffuse out of the swollen polymer, dispersing into a solution. At this stage, the disintegration of the swollen mass can be favored by stirring, which increases the rate of dissolution.

**Q.** Contact angle: It is the angle between the surface of the liquid and the surface of solid.

4



**Different contact angles ( $\Theta$ ) with different degrees of wetting**

OR

- a. There are three forces responsible for the cohesion of a solid:
  1. Coulomb force: This is the major contribution to the cohesion of a solid; it is the attractive force between electrons and the nuclei.
  2. Magnetic force: This has a weak contribution to cohesion.
  3. Gravitational force: It has a negligible contribution to cohesion
  
- b. Factors affecting adhesion.
 

**Factors related to adherent**

  - **Surface energy**
  - Atoms and molecules at the surfaces of liquids and solids possess more energy than do those in the interior.
  - In case of solids, the **surface energy** is greater than the internal energy, because the outermost atoms are not equally attracted in all directions.
  - Surface energy is increased by: Increasing its surface area
  - Solids tend to reduce this surface energy by adsorption of atoms or molecules.
  - In case of liquids, the energy is called surface tension: the attraction force exists between the surface molecules of a liquid.
  - The molecules at the surface are farther apart owing to loss of molecules by evaporation. This greater average separation leads to a net attraction between molecules and a higher energy of attraction.
  - Surface tension is decreased by
  - increasing the temperature and impurities.
  - Liquids try to decrease its surface tension by minimizing its surface area.
  - The higher the surface energy of the adherent, the stronger the strength of the

adhesive junction.

Q.  
5

Concentration C (g/L)	Osmotic pressure $\Pi$ at 30°C - (atm)
2.7	0.00046
12.5	0.00210
17	0.00265
22	0.00323

Plot the graph between  $\pi/c$  vs  $c$ .

Find the slope and intercept of the best fit curve. From the intercept get the value of  $M_n$  and the slope will give the virial coefficient  $A_2$

Using Van't Hoff equation:  $\pi = A_2 c$

Intercept will provide the value of  $M_n$

OR

### Osmometric measurement

- Van't Hoff equation is for ideal, dilute solutions. In real solutions the equation will be following:

$$\frac{\pi}{c} = \frac{RT}{M_n} + Bc + Cc^2 + \dots$$

B, C are virial coefficients

- For the determination of molecular weight, 4-6 pressure measurements with different concentrations are required. When solutions are dilute enough,  $\pi/c$  can be obtained by extrapolation of  $c$  to 0. Average molecular weight can be calculated from:

$$\lim_{c \rightarrow 0} \frac{\pi}{c} = \frac{RT}{M_n}$$

- Polymer concentration is  $\text{g/dm}^3$  and  $\pi/c$  in  $\text{J/kg}$

- Osmotic pressure is a colligative property, which means that it is proportional to the concentration of solute.
- The van't Hoff equation is often presented in introductory chemistry for calculating osmotic pressure ( $\Pi$ ) from the moles of solute ( $n_{\text{solute}}$ ) that occupy a given volume ( $V$ ) and the absolute temperature ( $T$ ) of the solution

$$\frac{\pi}{c} = \frac{RT}{M_n} + A_2 c$$

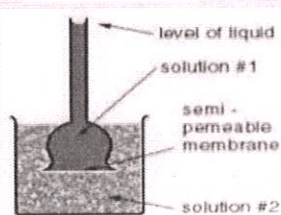
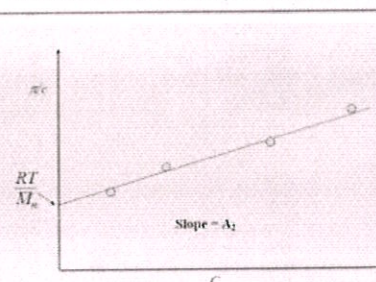


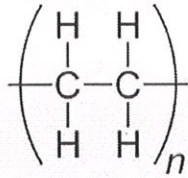
FIGURE 2.4 Plot of reduced osmotic pressure ( $\pi/c$ ) versus concentration ( $c$ ).



From the plot of  $\pi/c$  vs  $c$  find the slope and intercept of the best fit curve. From the intercept get the value of  $M_n$  and the slope will give the virial coefficient  $A_2$

Using Van't Hoff equation:  $\ln A_2c = A_2c$   
 Intercept will provide the value of  $M_n$

Q.  
6



M for repeating unit = 28

D for LDPE = 0.94 g/cc

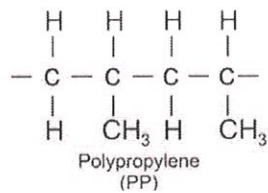
2 CH<sub>2</sub> at 133

$$G = 2 * 133 = 266$$

$$= (0.94 * 266) / 28 = 8.93 \text{ (cal/cm}^3\text{)}^{1/2} = 18.21 \text{ MPa}^{1/2}$$

OR

Estimate the solubility parameters of polypropylene (PP) (Data given in the next page)



M for repeating unit = 42

D for LDPE = 0.86 g/cc

1 CH<sub>2</sub> at 133

1 CH<sub>3</sub> at 214

1CH< at 28

$$G = 133 + 214 + 28 = 375$$

$$= (0.86 * 375) / 42 = 7.67 \text{ (cal/cm}^3\text{)}^{1/2} = 15.64 \text{ MPa}^{1/2}$$

*Swanda*