Q1. If trifluoroacetic acid is added drop wise to styrene at room temperature, no polymerization occurs. However, styrene is added to trifluoroacetic acid at room temperature, high molecular weight polymer forms rapidly. Suggest explanation for this experimental observation. (Given that dielectric constants at 25°C for styrene and trifluoroacetic acid are 2.4 and 39, respectively) (2 Marks)

Sol6 F

Q4. Mark following statements as TRUE or FALSE (5 Marks, -0.5 mark for every wrong answer, no answer no marks)

(a) The rate of polymerization is diffusion controlled in interfacial polymerization _____

(b) The rate and the degree of polymerization can be increased together in bulk polymerization _____

(c) Kinetic features of suspension polymerization are similar to those of bulk polymerization TRUE

(d) Surfactant concentration falls below CMC after stage II of emulsion polymerization FALSE

(e) Copolymerization of stilbene and maleic anhydride always produces an alternate copolymer TRUE

(f) An ideal copolymer is formed when $r_1 > r_2 > 1$ FALSE

(g) Reactivity ratio for a monomer is a constant and doesn't depend on mode of polymerization FALSE

(h) It is desirable in interfacial polymerization that high molecular weight polymer should not precipitate out from the solvents TRUE

(i) In a living polymerization, polydispersity index (PDI) should be ≈ 1 TRUE

(j) Number of polymer particles remains constant after stage I in emulsion polymerization TRUE

3

Q11 The standard enthalpy and entropy of polymerization of vinyl chloride at 25°C are -72 kJ/mol and -100 J/K mol respectively. Can you use the polymer that is obtained after polymerization at 25°C safely if it is known that vinyl chloride monomer is carcinogenic above 500 ppm. (R = 8.314 J K mol). (3 Marks)

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow \Delta G^\circ = \left(-72 - \frac{298 \times (-100)}{1000}\right)$ kJ/mol

$= -72 + \frac{29800}{1000} = -42.2$ kJ/mol

As we have to find

So, Monomer Conc at 25° would be,

$\Delta G^\circ = -RT \ln [M]$

$\Rightarrow -42.2 \times 1000 = 8.314 \times 298 \times \ln [M]$

$\Rightarrow [M] = 4.01 \times 10^{-8}$ mol/L

As Conc. is much less than 500 ppm., so it is safe to work with vinyl chloride monomer at 25°C.

(2 Marks)

20.5/30

TXL130 – Polymer Chemistry
Minor – 2
7th October 2016

Time: 1 Hour **Name:** Dhawal Parmar **Entry No.** 2015 T T10890 **Total Marks:** 30

Instructions:
Please write your name and entry number at the space provided on top of the sheet
There are total 13 questions, some have negative marking
Write your answers within the space provided with every question
No additional sheet will be provided
Write your answers in legible and step-wise manner

Q1 In the model for emulsion polymerization, it is assumed that most of the primary free radicals produced in aqueous phase enters the micelles rather than the monomer droplets. How would you justify this assumption? (2 Marks)

The free radicals produced in aqueous phase has to react with monomers. The size of micelles is of the order of nano-metres. While the size of monomer droplets is of the order of milli-meters. So, if we assume the volume of both monomers droplets and micell is same, then the surface area of micelle is higher than monomer droplet, and due to that larger surface area, the rxn. in micelle is more preferable.

2

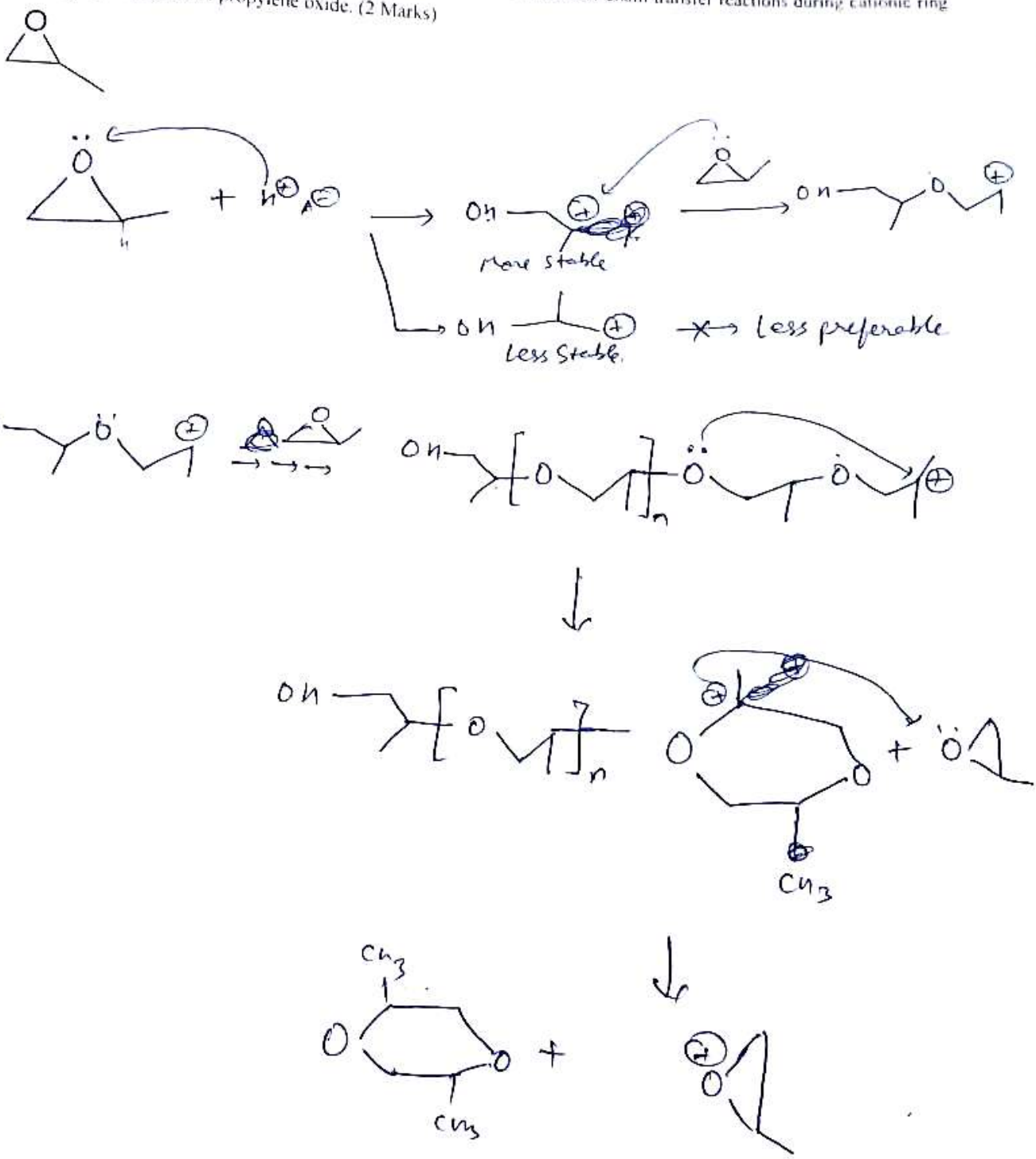
Q2. Write two disadvantages of high pressure process for polyethylene production. (2 Marks)

1. Through this, with high pressure, we can have more packed polymer and so its rigidity is higher, can be used in buckets. 2

(2) It has high MP. 2

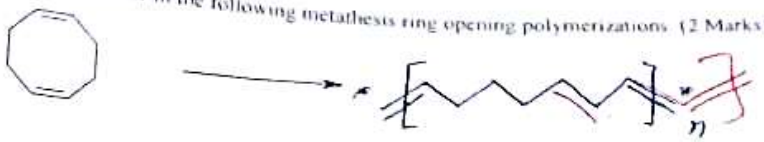
0

Q13. Write the reaction scheme and products formed after intra-molecular chain transfer reactions during cationic ring opening polymerization of propylene oxide. (2 Marks)



2

Q5. Write the missing monomer / polymer in the following metathesis ring opening polymerizations. (2 Marks)

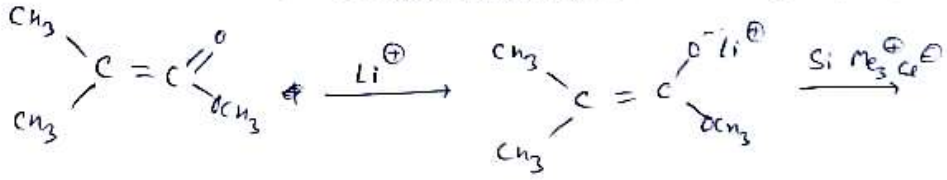
(a) 

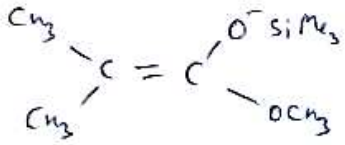
(b) 

1

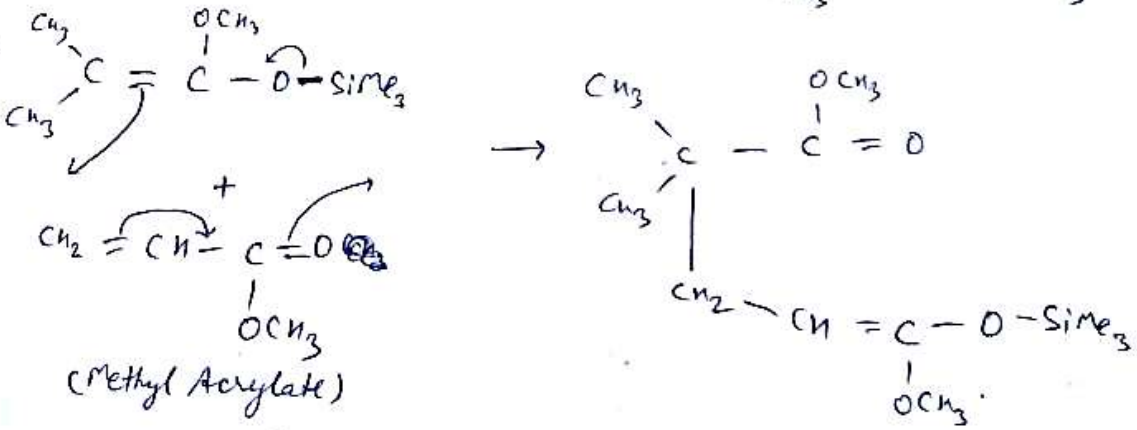
Q6. Write initiation and propagation steps to show Group Transfer Polymerization of Methyl acrylate. (2 Marks)

Initiation:

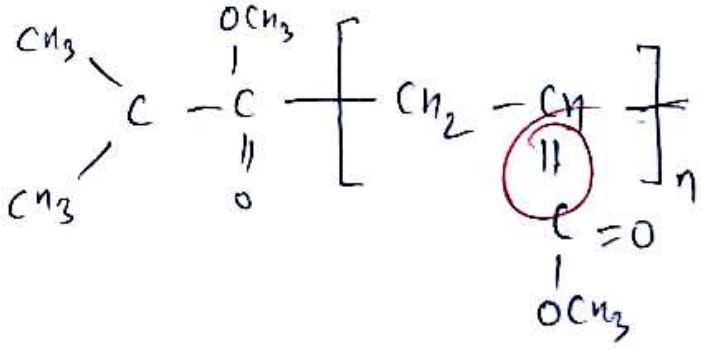




Propagation:



(Methyl Acrylate)



2

Q7. It is desired to form a copolymer of two monomers M_1 and M_2 that contains equal moles of M_1 as M_2. The monomers copolymerized ideally with monomer reactivity ratios $r_1 = 2.0$ and $r_2 = 0.5$. Calculate the feed composition you should take to make this copolymer. (2 Marks)

As given, $F_1 = F_2 = 0.5$, $r_1 = 2$ $r_2 = 0.5$

We Ans. $$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$0.5 = \frac{2 f_1^2 + f_1 f_2}{2 f_1^2 + 2 f_1 f_2 + 0.5 f_2^2}$$

$$\Rightarrow 2 f_1^2 + 2 f_1 f_2 + 0.5 f_2^2 = 4 f_1^2 + 2 f_1 f_2$$

$$\Rightarrow 2 f_1^2 = 0.5 f_2^2 \quad \rightarrow \frac{f_1}{f_2} = \sqrt{\frac{0.5}{2}}$$

$$\therefore \frac{f_1}{f_2} = \sqrt{\frac{1}{4}} = \frac{1}{2} \Rightarrow 2 f_1 = f_2$$

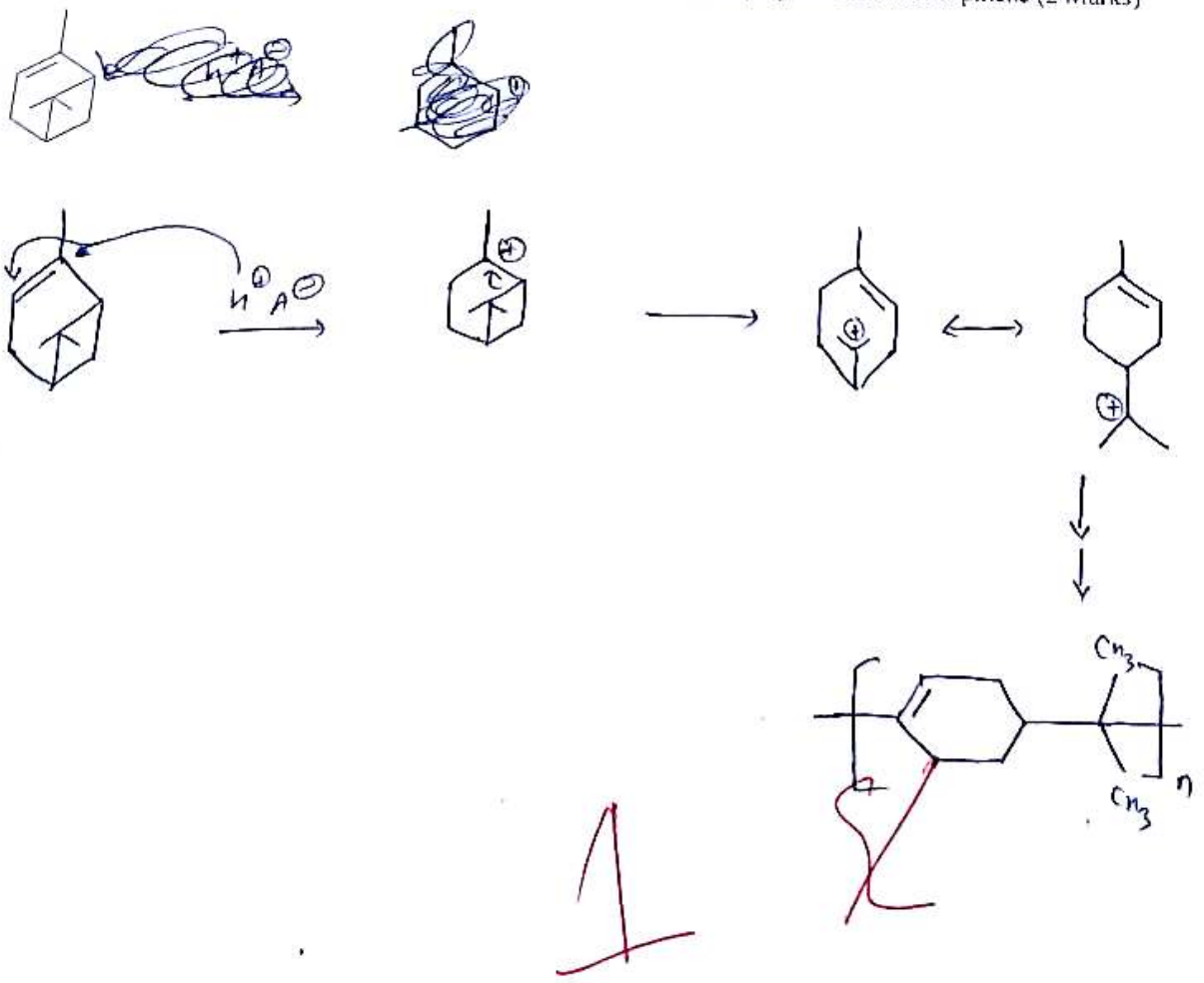
Also, $f_1 + f_2 = 1 \Rightarrow f_1 + 2 f_1 = 1$ $\therefore$ $\boxed{f_1 = \frac{1}{3}}$ & $\boxed{f_2 = \frac{2}{3}}$

So, feed composition of $M_1 = \frac{1}{3}$

& of $M_2 = \frac{2}{3}$

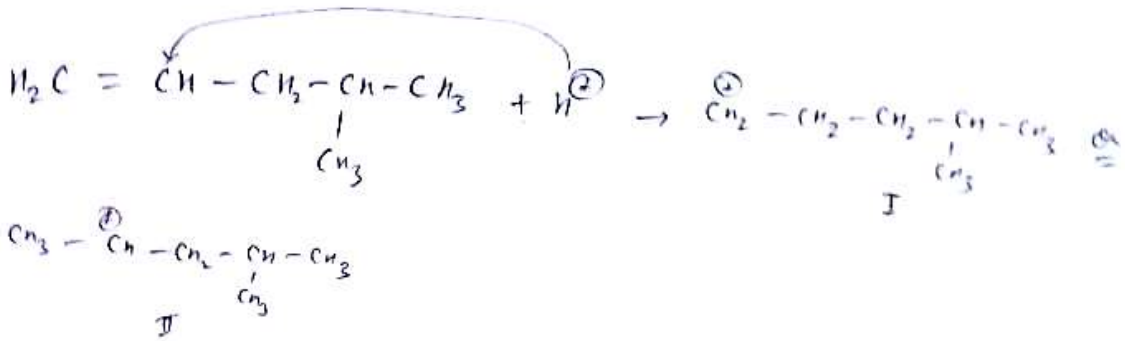
2

Q8. Write the repeat unit structure for polymer obtained after cationic polymerization of α-pinene (2 Marks)



1

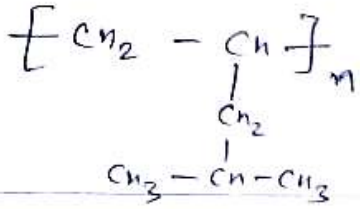
Q9. Write equations to show all structural units that may result from intra-molecular hydride shifts (at the end monomeric unit) in cationic polymerization of 4-methyl-1-pentene. Which of these structural units is most stable and why? (2 Marks)



I

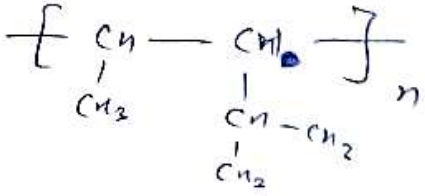
II

Ist will give →



0.5

If IInd will give →



??

Q10. In a polymerization it has been observed that ΔH = 64.964 kJ/mol and ΔS = 0.218 kJ/K-mol. With decrease in temperature from 100°C to 25°C what effect will you observe (Choose the right answer with proper justification) (2 Marks) (-1 for wrong answer)

(a) Conditions are never spontaneous towards polymer
(b) Conditions are always spontaneous towards polymer
(c) Floor Temperature
(d) Ceiling Temperature
(e) Telomerization

At 25°C, $\Delta G = \Delta H - T\Delta S$

$= 64.964 - 298 \times 0.218$

$= 64.964 - 64.964 = 0$

2

& at 100°C, $\Delta G = \Delta H - T\Delta S$

$= 64.964 - 373 \times 0.218 = 64.964 - 81.314$

$= -16.35$

As on ↑T, ΔG becomes -ive. So, it is its floor temp. & (c) & Cond^n are always spontaneous towards polymerisation (b).