Q12. In polyesterification of a hydroxyacid find the probability of formation of polymers chains having "x" repeat units and derive equations to relate the probability with number average molecular weight (M_n), weight average molecular weight (M_w) and PDI. (3 Marks)

Let $P \rightarrow$ Part of coolt being reacted

then $P(x) = \cdot P^{x-1}(1-P)$

↙ Probability of formation of polymer chains having 'x' repeat units.

$$\cdot \bar{M}_n = \sum_{x=1}^{n} M_x P(x)$$

$$M_x = x M_0$$

$$\Rightarrow \bar{M}_n = \sum_{x=1}^{n} x M_0 P^{x-1}(1-P)$$

$$\Rightarrow M_0(1-P) \sum_{x=1}^{n} x P^{x-1}$$

$$= M_0(1-P)\left(\frac{1}{1-P}\right)^2 = \frac{M_0}{1-P}$$

$$\bar{M}_w = \sum M_x \omega_x$$

$$\omega_x = \frac{N_x M_x}{\sum N_x M_x} = \frac{N_0(1-P)^2 P^{x-1} M_0 x}{\sum (x M_0)\left(N_0(1-P)^2 P^{x-1}\right)}$$

$$= \frac{N_0(1-P)^2 P^{x-1} M_0 x}{M_0 N_0 (1-P)^2 \left(\frac{1}{1-P}\right)^2} = x(1-P)^2(P^{x-1})$$

$$\Rightarrow \bar{M}_w = \sum \omega_x M_x = \sum x(1-P)^2(P^{x-1})\, x M_0$$

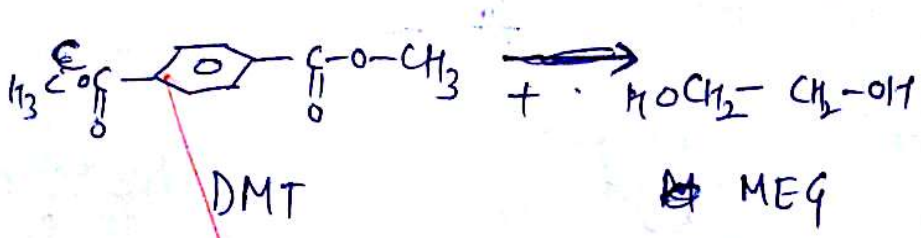
$$= M_0(1-P)^2\left(\sum x^2 P^{x-1}\right)$$

$$= M_0(1-P)^2\left(\frac{1+P}{(1-P)^3}\right) = \frac{M_0(1+P)}{1-P}$$

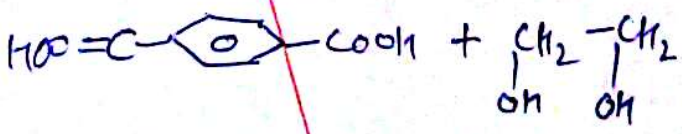
$$\Rightarrow PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{M_0(1+P)}{\quad} = \frac{1+P}{\quad}$$

Q6. Several side reactions may occur during EI step of PET synthesis in both DMT and PTA routes. Write two most important and difficult to avoid side reactions during EI step. (2 Marks)

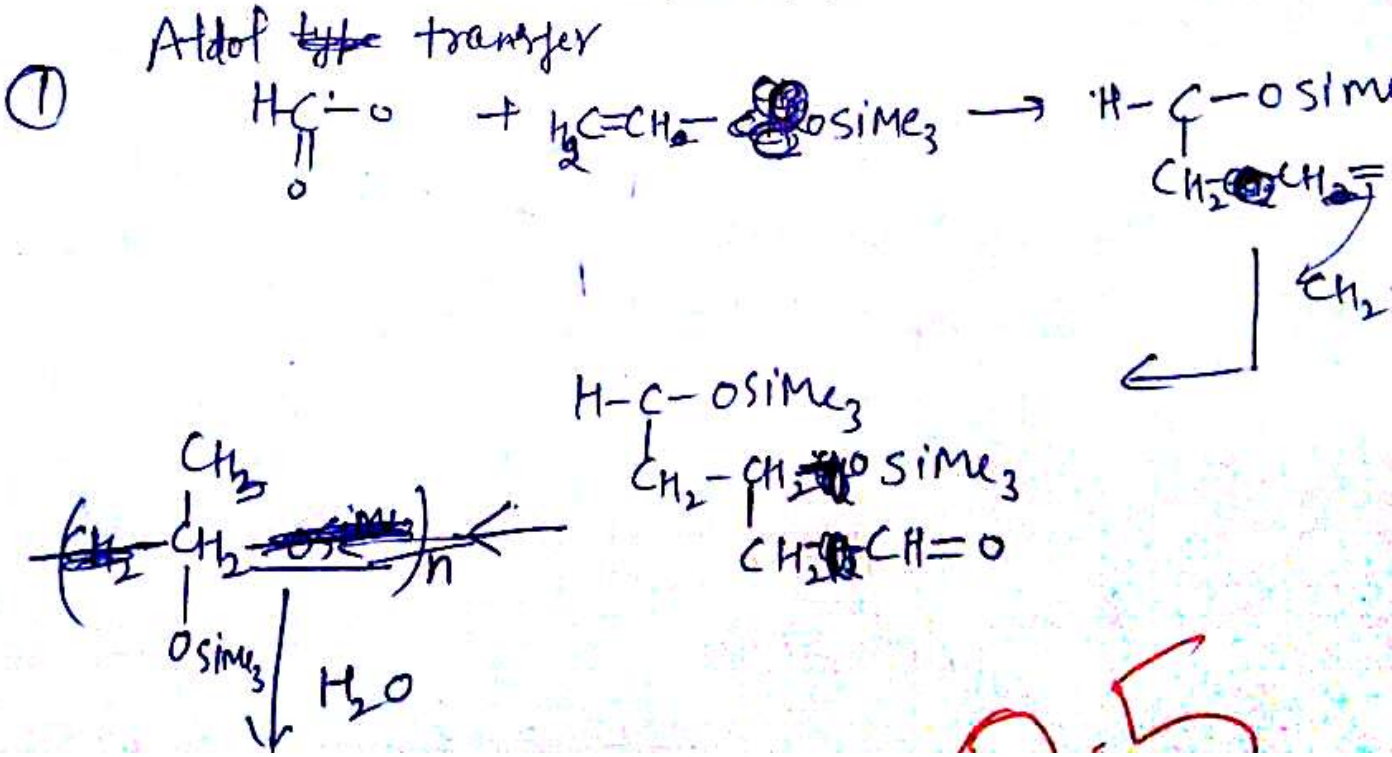
DMT



DMT MEG



Q7. Write TWO possible reaction schemes to synthesize poly(vinyl alcohol). (2 Marks)



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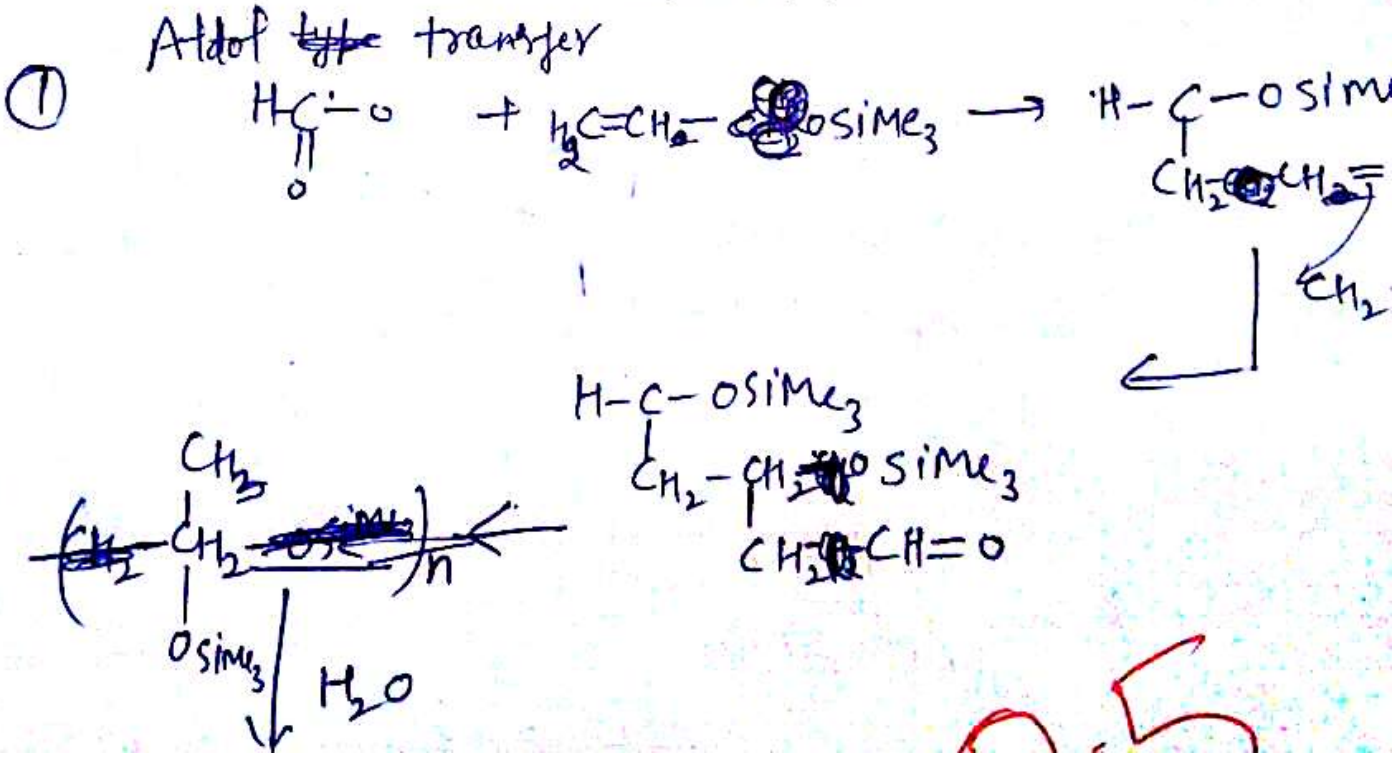


Q13. Write the full form of following terms (4 Marks, -0.5 for every wrong answer, no answer no mark)

(a) PET Poly ethylene terephthalate

(b) HDPE High density poly ethylene

(c) NMP

(d) ABS Acrylonitrile butadiene styrene

(e) GPC Gel permeation chromatography

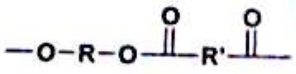
(f) DMT Dimethylterephthalate

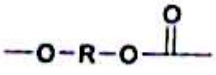
(g) CRP Controlled radical polymerisation

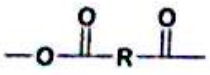
(h) SFRP

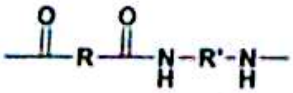
2

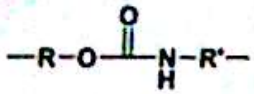
Q14. Write generic name of the polymer from the functional group written below (3 Marks, -0.5 for every wrong answer, no answer no mark)

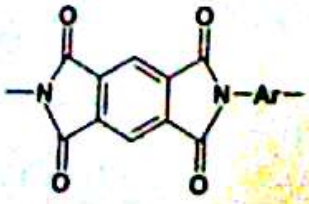
(a) 

(b)  Poly

(c) 

(d) 

(e) 

(f) 

Q8. Calculate the maximum average molecular weight that can be obtained when ethylene glycol ($HO\text{-}(CH_2)_2\text{-}OH$) is polymerized with adipic acid ($HOOC\text{-}(CH_2)_4\text{-}COOH$) containing 1% monocarboxylic acid as impurity? (3 Marks)

$$r = \frac{N_A + 2N_A'}{N_B}$$

Let one mole be N_A & 1 mole be N_B

then $N_A' = 0.01$ mole

$$\Rightarrow r = \frac{1 + 0.02}{0.1} = 1.02$$

mass of 1 unit = 172 g

$$\overline{X_n} = \frac{1+r}{1+r-2rp}$$

When $p = 1 \Rightarrow \overline{X_n} = \frac{1+r}{1-r} = \frac{2.02}{0.02} = 101$

extent of reaction

Total maximum avg. molecular wt. $= (172)(\overline{X_n})$

$= 17372$ g

Q9. In conducting a free radical polymerization of styrene with benzoylperoxide the molar ratio of monomer to initiator ([M] / [I]) is reduced to half in experiment 2 as compared to experiment 1. Calculate the change in kinetic chain length of polystyrene formed in experiment 2 as compared to experiment 1 assuming that initiator efficiency is 100% and all termination occurred by combination in both experiments. (2 Marks)

$$b = \frac{2}{2-a}, \quad a = \text{[illegible]} \Rightarrow b = 2$$

$$\nu = \frac{R_p}{R_i}$$

$$R_p = k_p [M^\cdot][M]$$

$$R_i = R_t = 2k_d [M][I] = 2k_t [M^\cdot]^2$$

$$\Rightarrow M^\cdot = \left(\frac{k_d}{k_t}\frac{[M][I]}{\phi}\right)^{1/2}$$

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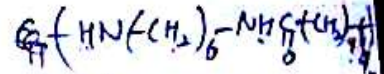
$$\Rightarrow M^\cdot = \left(\frac{k_d}{k_t}\frac{[M][I]}{\phi}\right)^{1/2}$$

ν = [illegible]

Q11. What feed ratio (r) of hexamethylene diamine and adipic acid should be taken in order to obtain a polyamide of number average molecular weight (M_n) = 10,000 g/mol at 99% conversion? Identify the end groups of this product based on the feed ratio. (3 Marks)

$P = 0.99$

$\overline{X_n} = \dfrac{1+r}{1+r-2rp}$



Mol wt. = 226 g

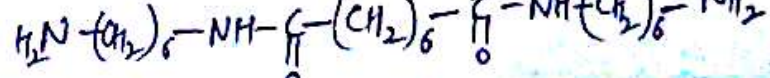
$\overline{X_n} = \dfrac{\overline{M_n}}{M_0} = \dfrac{10000}{226} \times \dfrac{g}{g} = 88.5$

$\Rightarrow 88.5 = \dfrac{1+r}{1+r-0.98r+1} = \dfrac{1+r}{1-0.98r}$

$\Rightarrow r = 0.997$

So it has hexamethylene diamine as excess

So end products would be as



Arrested by NH_2 at both ends.

88.5 − 0.98×88.5r = 1+r

87.5 / 87.72

3

Q15. Multiple Choice questions, select only ONE correct answer for every question (4 Marks, -0.5 for every wrong answer, no answer no mark)

(A) Which of the following viscosity parameters is equal to η/η_0 (the viscosity of the solution divided by the viscosity of the pure solvent)?

(i) Relative viscosity

(ii) Reduced viscosity

(iii) Specific viscosity

(iv) Intrinsic viscosity

(B) Which of following recipe will produce only a branched polymer, given that, A_f or B_f are tri-functional monomers, A group can not react with A, B group can not react with B.

(i) A-A + B-B + A_f

(ii) A-A + B-B + A_f + B_f

(iii) A-B + B-A + A_f

(iv) A-B + A-A + B_f

(C) Consider the properties of the following two polyethylene samples. Sample 1 was produced by a radical polymerization while sample 2 was synthesized using controlled radical polymerization.

	Polyethylene 1	Polyethylene 2
Mol wt. (g/mol)	200,000	200,000
Density (g/cm3)	0.92	0.96
Crystalline melting point (°C)	108	133

Which of the following statements is true?

(i) Sample 2 is more branched than sample 1

(ii) Sample 1 is more branched than sample 2

(iii) Sample 1 is more atactic

(iv) Sample 1 is more isotactic

(D) 10 moles of each of three monodisperse polystyrene samples of molecular weight 10,000, 20,000 and 30,000 are mixed. What would be the polydispersity index of the mixture?

(i) 1.2

(ii) 1.12

(iii) 1.14

(iv) 1.16

$$P = \frac{\sum N_i M_i^2 \times 3}{(\sum N_i M_i)^2}$$

$$= \frac{10(10^3)^2 + 20(20^3)^2 + 30(30^3)^2}{3 \times (10 \times 10^3 + 20 \times 20^3 + 30 \times 30^3)^2}$$

$$= \frac{8 \times (14)}{36} = 12$$