INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR
MID-SEMESTER EXAMINATION, SPRING 2008-09

Department: Chemistry **Year:** 4th yr of 5-yr int. M.Sc + 1st yr of 2-yr M.Sc
Subject Name: Int. to Polymer Chemistry **Subject No:** CY40012 + CY43004
Full Marks: 50 **Time:** 2 hours **No. of Students:** 5 + 29 = 34

Instructions: Answer all the questions

List of abbreviation used:
MW - molecular weight; *Xn* - no. average degrees of polymerization
Mn - number-average molecular weight
Mw - weight-average molecular weight; *Mv* - viscosity-average molecular weight
Ri- Rate of initiation; *Rp*- Rate of polymerization; *Rt*- Rate of termination

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1. (a) Calculate the *number-average molecular weight (Mn)* of an equimolar mixture of adipic acid (MW – 146) and hexamethylene diamines (MW-116) for extent of reaction (p) 0.990. What is the theoretical *Mw* for this polymer? **4**

   (b) A polyesterification reaction is been carried out in two condition; - in presence and in absence of an externally added catalyst. How would *no. average degrees of polymerization (Xn)* vary in the two cases with reaction time? **3**

   (c) Mention differences between *chain growth* and *step growth* polymerization with respect to the following features – (i) MW as a function of conversion; (ii) *Composition of reaction medium* if the reaction is stopped before completion (say at 75% Conversion) **3**

2. (a) A typical *radical polymerization* is being carried out with the following assumptions: initiation by thermal dissociation of initiator, steady state and equal reactivity of propagating radicals, termination of reaction is only by bimolecular coupling, and no chain transfer.
   What will happen to the *polymer molecular weight and polymerization rate* if one increases: (i) initiator conc. (ii) monomer conc. (iii) temperature? Justify your answer with brief explanation mentioning any assumption made about *Ri, Rp, Rt*. **6**

   (b) Arrange in increasing order of *Xn* of polymers obtained by polymerization of styrene initiated by thermal decomposition of benzoyl peroxide at 80°C in the following solvents – Benzene, 1-Butanethiol, Isopropylbenzene, Carbon tetrachloride. Assume chain transfer only to solvent. Briefly explain your answer. **2**

   (c) Define of *living polymerization*. Mention two benefits of *living polymerization* in general over *conventional (non-living)* polymerizations. **2**

3. (a) Write the main ingredients required in an *emulsion polymerization*. Mention one disadvantage and one advantage of *emulsion polymerization* over *dispersion polymerization*. How can one increase *Rp* without compromising on molecular weight in an *emulsion polymerization*? **4**

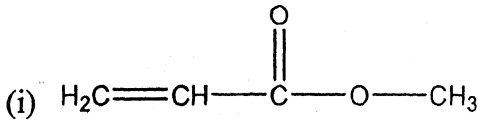
(c) How are *ionic chain polymerizations* different to *radical chain polymerization* in regard to solvent polarity and inherent termination steps? **3**

(c) Consider the following *reactivity ratios* for the copolymerization of three monomer pairs:

Case	r_1 (for M_1)	r_2 (for M_2)
(i)	0.0	0.0
(ii)	4.0	0.4
(iii)	1.0	1.0

Specify the *type of copolymer* and the *monomer* present in higher mole fraction in each case. Assume sample is isolated at low conversion, feed ratio of M1:M2 =1:1. **3**

4. (a) Write the names and the structures of the polymers that are synthesized using following monomer(s)

(i) 

(ii) 

2

(b) For a monomer of general structure CH_2=CHX, complete the following table. Put '+' if the monomer can be polymerized by the method mentioned at the top of the column, and '-' if polymerization by the method is not feasible. Briefly justify your answer.

X	Free radical	Anionic	Cationic
-CN			
-Ph			
$-OCH_3$			
$-OCOCH_3$			

4

(c) Write the general expression for *Mn*, *Mw*, and *Mv* of a *polydisperse* polymer sample.

For a *polydisperse* sample rank the above three according to their values.

In 10g of a polystyrene sample (*Mn* 30,000; *Mw* 60,000), you add 0.5g of a narrow-disperse polystyrene sample (*Mn* 10,000; *Mw* 10,250). How would *Mw*, *Mn*, *Mv* change (increase/decrease) and which of these three avg. MWs would change most?

4

5. (a) In a *living anionic polymerization* the ingredients used as follows – 1M acrylonitrile, 1M methylmethacrylate (MMA), and 0.01M C_4H_9Li. What would be the value of *Xn* and *nature of copolymer* in the following two cases? - (i) Both the monomers added simultaneously to the initiator, (ii) acrylonitrile was added separately after the MMA were polymerized? **4**

(b) Everything else remaining same, in which of the following two cases the chances of forming *cyclic products* is more for a *step-growth polymerization* process: – conc. of monomer is 2M, and 0.5M. Explain briefly. **2**

(c) Explain briefly "*autoacceleration*" in *radical polymerization*? Why does it happen? **2**

(d) Explain three types possible tacticity in polymers with suitable example. **2**