Total No. of Questions : 4] **[Total No. of Pages : 2**

P356

[3631] - 31
M.Sc.
POLYMER SCIENCE
PS - 310 : Kinetics Mechanism of Polymerization Processes

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic table / Calculator is allowed.***

SECTION - I

Q1) Attempt any four of the following: **[20]**

a) How do addition and condensation polymerizations differ from each other?

b) Discuss the effect of by-product removal on the molecular weight built up of the polymer formed in step reaction polymerization with a suitable example.

c) What is importance of stoichiometric ratio of the reactants in condensation polymerization? Illustrate it with suitable example.

d) In a typical polyesterification, self catalysed reaction is of the third order with respect to carboxylic acid concentration. However it is much slower than the similar reaction with strong acid as a catalyst, which is second order with respect to the carboxylic acid concentration. Explain.

e) What will be the effect of monofunctional and trifunctional chemicals in condensation polymerization? How will it affect gel point?

f) Derive relation between number average degree of polymerization and extent of reaction for step reaction polymerization process, when stoichiometry is not maintained.

Q2) Attempt any four of the following: **[20]**

a) Discuss cationic mechanism of addition polymerization.

b) In a radical polymerization, is it advisable to use retarder for inhibiting the reaction? Comment on it.

c) What are chain transfer agents? Describe its effect on the rate expression and molecular weight obtained in their presence.

P.T.O.

d) Compare the steps involved in cationic and anionic polymerization.
e) Enlist assumptions made for deriving rate expression for typical polyesterification reaction. Describe its suitability based on experimental evidences.
f) Discuss effect of temperature and pressure on chain polymerization.

SECTION - II

Q3) Attempt any four of the following: **[20]**

a) Unlike in free radical polymerization both cationic and anionic polymerizations show a marked dependence on type of solvent used. Discuss the causes behind it.
b) Describe the structure of Ziegler-Natta catalyst used in co-ordination polymerization of olefins. Write any one mechanism.
c) Discuss the influence of ion pair on polymerization by cationic and anionic mechanisms.
d) Write a short note on ring opening polymerization.
e) Write a short note on living polymer.
f) Rate of radical polymerization needs to be doubled. Suggest various alternatives to achieve it.

Q4) Attempt any four of the following: **[20]**

a) Derive copolymer composition equation. Explain the assumption under which it is derived.
b) Describe anyone method for estimation of reactivity ratio.
c) Describe importance of reactivity of monomers and reactivity of radicals in explaining mechanism of copolymer formation.
d) Describe Q-e scheme. Discuss its advantages and limitations.
e) For the following values of r_1 and r_2 what type of polymers will be expected?
   i) r_2 and $r_1 = 1$; ii) $r_1 >>> 0$, $r_2 = 1$;
   iii) r_1 = infinity, $r_2 = 0$. Justify your answer.
f) Is it possible to predict length of units derived from monomer A and monomer B, in a given binary copolymer of A and B? Elaborate.

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Total No. of Questions : 4] **[Total No. of Pages : 2**

P358

[3631] - 33
M.Sc.
POLYMER SCIENCE
PS - 312 : Polymer Processing

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic table / Calculator is allowed.***

SECTION - I

Q1) Attempt any four of the following **[20]**

a) Discuss importance of compounding.

b) Define vulcanization. Discuss sulphur or non sulphur mechanism of vulcanization.

c) What are accelerators and activators? Discuss their importance in rubber vulcanization.

d) Enlist any five synthetic elastomers; write their structure, special properties, applications.

e) Explain what are re-enforcing and non -reinforcing fillers. Discuss theory of re-enforcement action of carbon black.

f) Draw and explain curves showing effect of vulcanization time / temperature on various properties of rubber.

Q2) Attempt any four of the following **[20]**

a) What are different methods of spinning synthetic fibers? Describe any one in details.

b) Define, continuous and staple fiber, Deniere, Tenacity, moisture contents and moisture regain, and crimp.

c) What fiber properties are important in textile uses?

d) Write notes on dye take up; crease resistance and crease retention; and mercersation of finished fiber.

e) How does the stress strain curve differ in silk like and wool like fibers?

f) What are the features of nonwoven fibers? Give examples.

P.T.O.

SECTION - II

Q3) Attempt any four of the following **[20]**

a) Why are the additives needed for polymers? Explain plasticisers with their role. Give examples of different plasticisers.

b) Explain the 'role of design of object' in deciding the suitable polymeric process.

c) Describe typical processing parameters for compression molding.

d) Explain defects occurring in transfer molding. Suggest the measures to avoid the defects.

e) Describe different zones in the barrel of an extruder. Explain variation in the screw in each zone.

f) Write a note on co-rotating twin screw extruder with a neat diagram.

Q4) Attempt any four of the following **[20]**

a) Write the important features of injection molding.

b) Explain various defects and their causes in injection molding.

c) Describe process of RIM and RRIM.

d) Compare the processes of blow molding and rotamolding.

e) Describe the process of calendering. Explain the variation in roller arrangement with variation in the nature of the polymer processed.

f) Explain the variation in thickness in the product formed by thermoforming.

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Total No. of Questions : 4] **[Total No. of Pages : 2**

P360

[3631] - 401

M.Sc.

POLYMER SCIENCE

PS - 404 : Special Topics in Polymer Science

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections must be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic tables / Calculators is allowed.***

SECTION - I

Q1) Attempt any four of the following: **[20]**

a) Describe difficulties involved in recycling of polymeric materials.

b) Enlist the important polymers that are extensively recycled. Give reasons for the same.

c) What are different applications of biodegradable polymers?

d) Write the peculiarities of biological degradation of small molecule which are not met with in the degradation of polymers.

e) Explain the advantages and disadvantages of obtaining functional polymer by chemical modification of polymer.

f) Describe functional polymers as a separation aid in organic synthesis.

Q2) Attempt any four of the following: **[20]**

a) Explain the term liquid crystallinity and describe different phases in LCP.

b) Write an account of different applications of LCP.

c) What are polymer blends? Explain synergistic blends and miscible blends.

d) To obtain a polymeric material with desired property profile, blending, functional polymers and copolymerisation are the important strategies. Explain importance of blending as compared to the other two strategies.

e) Describe the methods of increasing thermal stability of polymers.

f) Discuss synthesis of Kevlar and Nomex. Mention their applications.

P.T.O.

SECTION - II

Q3) Attempt any four of the following: **[20]**

a) Compare the suitability of polymers vis a vis other traditional materials for biomedical applications.

b) Suggest the polymers for entire synthetic heart, artificial skin and kidney.

c) How does one select polymeric materials for structural/engineering applications? Discuss the concept of HDT.

d) Discuss preparations and important applications of polyacetals as engineering plastics.

e) What are polymeric membranes? Discuss mechanism of separation of liquids using polymeric membranes.

f) Discuss the applications of polymeric membranes in food and fruit juice processing.

Q4) Attempt any four of the following: **[20]**

a) Discuss various mechanisms of controlled release.

b) What are electroactive polymers? Discuss the mechanism of conducting polymers using concept of solitons and polarons.

c) Discuss the mechanism and applications of polymers filled with conducting fillers.

d) Discuss the applications of inherently conducting polymers.

e) Write importance of general purpose (GP) resins in composites.

f) Write short notes on Economics of selecting engineering plastics for various applications.

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Total No. of Questions : 4] **[Total No. of Pages : 2**

P362

[3631] - 403

M.Sc.

POLYMER SCIENCE

PS - 411 : Structure & Properties of Bulk Polymers

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic tables / Calculators is allowed.***

SECTION - I

Q1) Attempt any four of the following **[20]**

a) What is glass transition temperature? Do highly crystalline polymers exhibit glass transition temperature? Explain your answer.

b) When a polymer is heated it shows several transitions. With a help of a suitable diagram explain the different transitions. Explain your answer with reference to amorphous polymers and elastomers.

c) Explain the thermomechanical method of determination of Tg of polymers. Sketch a thermomechanical curve for an amorphous polymer and lable Tg on this curve.

d) Discuss various factors which affect the crystallinity of PET.

e) Polycarbonate based on BPA is as transparent as glass. After annealing at about 150° C it looses transparency. Explain.

f) Taking the example of PP, discuss the effect of tacticity on the crystallinity of stereoregular PP.

Q2) Attempt any four of the following **[20]**

a) Explain how the X-ray scattering data can be used to determine the percent crystallinity and the size of the crystallites.

b) Discuss the phenomenon of chain folding in polymer. Provide evidence in support of chain folding and the conditions under which it occurs.

c) What is shish kabab model? How is it obtained? What is its significance?

P.T.O.

d) Compare the structure of polymers when they are crystallized from melt and from polymeric solutions.

e) Name two techniques to study the kinetics of the development of crystallinity in polymers What is Avarami expression? Explain the terms involved in it.

f) Discuss various factors influencing the glass transition temperature of polymer.

SECTION - II

Q3) Attempt any four of the following **[20]**

a) Describe advantages of adhesives over traditional techniques of joining substrates.

b) Describe the classification of adhesives on the basis of origin, citing suitable examples.

c) Describe influence of mechanical properties on the choice of adhesives.

d) Explain the procedures to quantify the performance of adhesive in paper industry.

e) Describe adhesives used in the field of stationary. Justify the selection.

f) Give various purposes of the different types of surface coatings?

Q4) Attempt any four of the following **[20]**

a) Discuss importance of selecting pigment to binder ratio in paint formulation.

b) Discuss the property of polymeric material as the film former in surface coating. Enlist various commercial polymers / resins used in surface coating applications.

c) Discuss the importance of barrier properties of packaging materials in the packaging of biological air sensitive materials.

d) Discuss the important property requirements of polymer for packaging applications.

e) Compare special purpose and general purpose packaging techniques.

f) Describe the preparation of thermocol from styrene monomer.

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Total No. of Questions : 5] **[Total No. of Pages :4**

P357

[3631] - 32

M.Sc.

POLYMER SCIENCE

PS - 311 : Synthesis, Structural Aspects, Properties and Applications of Polymers

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***

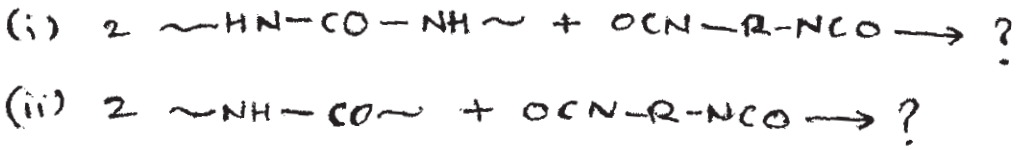
SECTION - I

Q1) Answer any four of the following : **[16]**

a) Explain the following regarding polyurethanes.
   i) Reactions of polyols with diisocyanate are more widely used than reactions of diols with polyisocyanates.
   ii) Hydroxy terminated polyethers are preferred to hydroxyl terminated polyesters.
   iii) The structural differences when diols or polyols react with diisocyanates.

b) A typical formulation of a flexible foam is given below. Comment on the role of different components and their quantities. Give the structures of the last three components. Hydroxy terminated polyester (slightly branched) 100 parts; TDI 33 parts, Water 4 parts; N-methylmorpholine 2.0 parts; N,N dimethyl cetyl amine 2.0 parts; Ammonium oleate 2.0 parts.

c) Isocyanate curing of polyurethane elastomer is shown below. Indicate the nature of cross links obtained. How are the urea and amide groups introduced in the starting polymer?



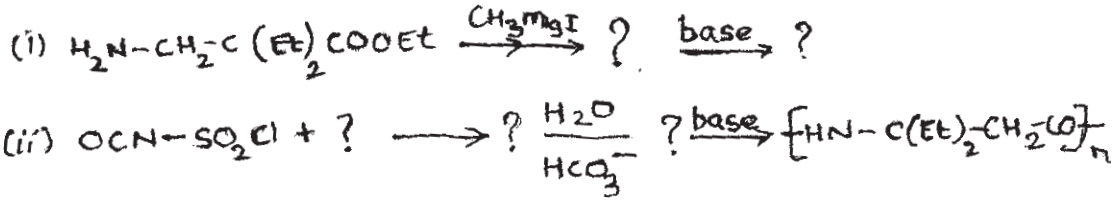
What is the structure of the dimmer of TDI? How does this act as a curing agent at about 150ºC?

P.T.O.

d) Comment on the properties of different nylons given below:

	6,6	6	6,10	11	12
Tensile strength in 1000 lb/ in^2	11.5	11	8.5	5.5	6.6
% water absorption at saturation	8.0	9.0	2.4	2.0	1.8
% elongation at break	80-100	100-200	100-150	280-300	200

e) Complete the syntheses of differently substituted nylon -3 in the reaction shown below. Why is it more difficult to prepare unsubstituted nylon -3?



f) Give the structure of the polymers formed by reaction C1-CO-R CO-Cl with (i) NH_2-NH_2 and (ii) H_2N-NH-CO-R'-$CONHNH_2$. Why is the reaction with (ii) preferred over that with (i)? When the reaction is carried out with NH_2-NH_2 the first reaction is faster than the second. Why?

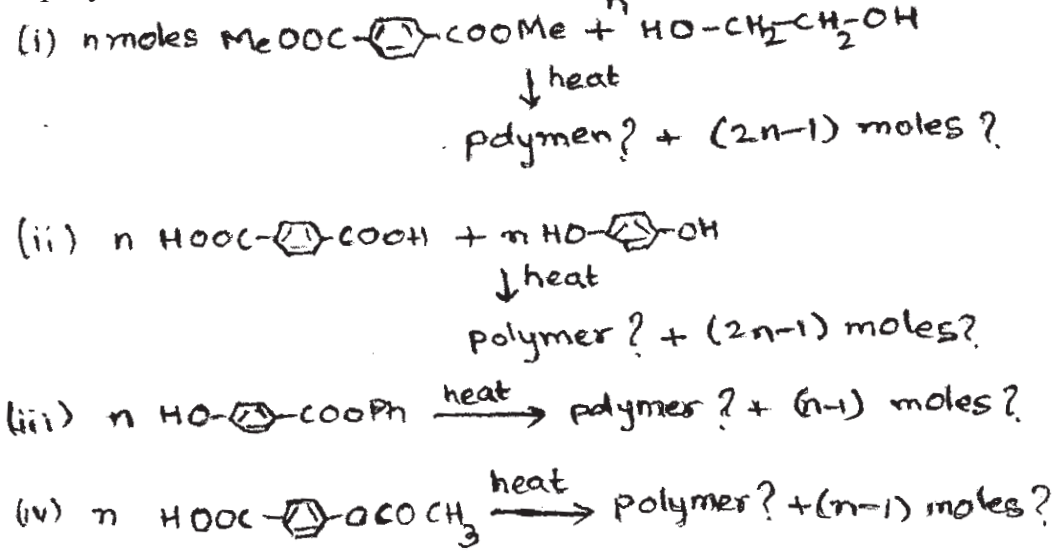
g) Explain the following regarding aromatic polyamides.

i) These have not attained the commercial importance of aliphatic polyamides mainly because of production and processing difficulties.

ii) How these polymers are prepared by interfacial polymerization?

Q2) Answer any four of the following : **[16]**

a) Complete the reactions shown below and indicate the structure of the polymers.



Why is higher temperature needed for reaction (ii) as compared to (i)? What is the role of COOPh in reaction (iii) and of $OCOCH_3$ in reaction (iv)?

b) Using linoleic acid depict the mechanism by which oils dry in air. Clearly indicate (i) the formation of hydroperxides (ii) the primary decomposition (iii) induced decomposition and (iv) termination steps.

c) Explain the following regarding the preparation of linear unsaturated polyesters (i) Phthalic anhydride is preferred to phthalic acid. (ii) in the conversion of naphthalene to phthalic anhydride 4.5 moles of oxygen are used to give CO_2 and H_2O (2 moles each) as bye products (iii) for the manufacture of the anhydride o-xylene is preferred to naphthalene.

d) Explain the following in the preparation of polycarbonates by solution method. (i) a mixture of pyridine and chloroform is used (ii) phosgene is passed into a solution of bisphenol A in the above. (iii) the resulting mass is washed with HCl and then with water (iv) in the above process pyridine is used as solvent, catalyst and reagent.

e) Calculate the % yield of acetic acid and % acetyl content of cellulose acetate with D.E = 2.6. Clearly show your calculation.

f) What is the structure of cellobiose? How does this differ from maltose? How is the stereochemistry of the glycoside linkage established in these two isomers? How is the structure of cellobiose established?

g) Answer the following regarding cellulose esters. (i) Cellulose nitrate and cellulose acetates are both esters (ii) Cellulose nitrate with DE 1.9 to 2.0 can be used both as a lacquer and as a plastic. What is the difference in the two? (iii) In the production of cellulose nitrate the degree of substitution is controlled by choice of reaction condition. Why? This is not possible in the case of cellulose acetate. Why?

SECTION - II

Q3) Attempt any four of the following : **[16]**

a) Compare the reactions of phenol with formaldehyde when carried out in the presence of sulphuric acid, oxalic acid and sodium acetate, respectively.

b) Describe the manufacture of epoxy polymer. How is the molecular weight of epoxy prepolymer controlled?

c) Explain manufacture of UF resins. State their important applications.

d) Illustrate the preparation of D_3, D_4 siloxane monomers explain ROP of these monomers to yield polysiloxanes. Mention two important properties and uses of poly (dimethyl siloxane).

e) What are UF resins? With suitable chemical reactions, explain curing of UF resins.

f) Describe the chemistry involved in the preparation of Novolak polymers using strong acids and weak organic acids.

Q4) Attempt any two of the following : **[16]**

a) Give a synthetic method to prepare (i) acrylonitrile, (ii) vinyl acetate, (iii) styrene, and (iv) acrylic acid.

b) Describe the bulk polymerization process for the preparation of polystyrene. State the advantages of the process. What are the limitations?

c) Describe one method each of preparation of HDPE and LDPE. Describe the differences in the properties of both the polymers.

Q5) Attempt any two of the following: **[16]**

a) Explain polymerization of propylene yielding stereoregular polymer. Describe the change in the properties with varying the type of tacticity.

b) Describe the polymerization of vinyl chloride. Explain the variation in the structure of the polymer. State the important applications of PVC.

c) Describe briefly Ziegler-Natta catalyzed manufacture of polyethylene. Explain the advantages of gas phase over solution phase. What is importance of chemical modification to sulphochlorination?

Total No. of Questions : 4] **[Total No. of Pages :2**

P359

[3631] - 34

M.Sc.

POLYMER SCIENCE

PS-313 : Polymer Chains and Their Characteristics

Time : 3 Hours] ***[Max. Marks :80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic table / calculator is allowed.***

SECTION - I

Q1) Attempt any four of the following : **[20]**

a) Define virial coefficients. Explain theta solvent, good, poor and non solvent.

b) What are the different stages of polymer dissolution? How can this process be hastened?

c) Differentiate between ideal, regular and strictly regular solutions.

d) Define Flory temperature (Θ) describe one method of determining it from thermodynamic considerations.

e) Write short note on Flory-Huggins theory.

f) Write short note on phase separation in polymeric solution.

Q2) Attempt any four of the following : **[20]**

a) Define excluded volume and discuss the difficulty in its evaluation.

b) Estimate solubility parameter of poly-n-hexyl methacrylate
Assume the following:

Group	Fsmall	Fvolume
- CH_2 -	133	16.45
> C <	- 93	4.75
- CH_3	214	22.8
- COO -	310	21.0

Density of poly-n-hexylmethacrylate is 1.05.

P.T.O.

c) Write notes on radiation induced polymerization and effect of radiation on polymethylmethacrylate and polyethylene.

d) Explain radiation curing of polymers and its significance.

e) Write a note on degradation of polymers by energy intensive radiations. Give examples.

f) What is oxidative degradation? Explain with examples.

SECTION - II

Q3) Attempt any four of the following : **[20]**

a) Explain the terms i) stress tensor, ii) Shear modulus, iii) Deborah number, iv) Normal stress, and v) shear thickening

b) Explain Hooke's law and Newtons law and their relevance to rheology.

c) Using dashpot and spring analogy explain Maxwell and Voigt visco-elasticity model.

d) Describe the rheological properties of polymeric melt. Explain how it partially behaves like a solid and partially like a fluid.

e) What is meant by relaxation and retardation of polymeric material?

f) Explain Burger model for deformation behavior of polymeric material.

Q4) Attempt any four of the following: **[20]**

a) What is power law model? Explain.

b) Draw stress strain curve for i) Hard and brittle, ii) Hard and strong, iii) Hard and tough, iv) Soft and weak, and v) Soft and tough polymers. Explain their behaviour.

c) Write short note on kinetic theory of rubber elasticity.

d) Describe dynamic mechanical model for testing of polymeric material.

e) Describe theory of visco-elasticity for amorphous polymeric material. Why it can not be extended to crystalline polymeric materials?

f) Explain shear thickening and shear thinning with respect to polymers.

Total No. of Questions : 4] **[Total No. of Pages : 2**

P858

[3631]- 301
M.Sc.
POLYMER SCIENCE
PS - 310 : Chain Polymerization

Time : 3 Hours] ***[Max. Marks : 80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic table/calculator is allowed.***

SECTION - I

Q1) Attempt any four of the following : **[20]**

a) Discuss anionic mechanism of addition polymerization.

b) Unlike in free radical polymerization both cationic and anionic polymerizations show a marked dependence on type of solvent used. Discuss the causes.

c) What are chain transfer agents? Describe its effect on the rate expression and molecular weight obtained in their presence.

d) With a suitable example explain Atom Transfer Radical Polymerization.

e) Discuss effect of temperature and pressure on chain polymerization.

f) Write a note on kinetic chain length in free radical polymerization.

Q2) Attempt any four of the following : **[20]**

a) Discuss mechanism of vinyl polymerization.

b) Differentiate between inhibition and retardation.

c) Describe the structure of Ziegler-Natta catalyst and mechanism of co-ordination polymerization with an example.

d) Write a short note on importance of controlled radical polymerization.

e) With a suitable example explain RAFT.

f) What do you understand by Group Transfer Polymerization? Discuss in detail.

P.T.O.

SECTION - II

Q3) Attempt any four of the following : **[20]**

a) Distinguish between random, graft and block copolymers. Describe one method each for the preparation of graft and block copolymers.

b) Write copolymer composition equation and explain the assumption under which it is derived.

c) Describe importance of reactivity of monomers and radicals in explaining mechanism of copolymer formation.

d) Write a note on Q-e Scheme.

e) Describe any one method for the synthesis of

i) Acrylic acid.
ii) Methyl methacrylate.
iii) Styrene.
iv) Vinylchloride, and
v) Chlorotrifluoroethylene.

f) Describe the manufacture of any methacrylate polymer. State its important applications.

Q4) Attempt any four of the following : **[20]**

a) Describe the process variations in the manufacturing of LDPE and HDPE.

b) Enlist synthetic methods for the preparation of different grades of poly (vinyl alcohol). Explain how chemical modifications result in different properties.

c) Describe at least three halogen containing polymers. Compare their different properties. State their applications.

d) How is 2-chloro-1, 3-butadiene synthesized? Explain crosslinking reactions in Neoprene. Illustrate the applications of this rubber in view of its properties.

e) Discuss any method to prepare polystyrene. Give its applications.

f) Write a short note on sulfur vulcanization of natural rubber.

Total No. of Questions : 4] **[Total No. of Pages : 3**

P859

[3631]- 302
M.Sc.
POLYMER SCIENCE
PS - 311 : Condensation Polymerization

Time : 3 Hours] ***[Max. Marks : 80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic tables/calculators is allowed.***

SECTION - I

Q1) Attempt any four of the following : **[20]**

a) Explain the mechanism of step reaction polymerization - carbonyl addition and nucleophilic substitution.

b) Explain how the rate of polymerization is independent of molecular size.

c) Derive the rate equation for step polymerization in the absence of catalyst and show that the molecular weight is proportional to the square root of time.

d) Describe briefly the factors responsible for the non-linearity in the third order plot for self-catalyzed step polymerization reaction.

e) Calculate the weight fraction of trimer in step polymerization carried to 99% conversion.

f) A polyester made with equivalent quantities of a dibasic acid and a glycol is stabilized in molecular weight at $\overline{X}n = 100$ by adding methanol. Calculate $\overline{X}w$ and the weight number fraction of monomers in the resulting polymer.

Q2) Attempt any four of the following : **[20]**

a) Derive and plot the number distribution and weight distribution function for linear step reaction polymerization function for linear step reaction polymerization.

b) Explain how molecular weight of a polymer can be controlled by changing the concentration of one of the reactants away from the stoichiometric balance.

P.T.O.

c) What are hyperbranched polymers and dendrimers? Give the three routes for the synthesis of the same. Draw diagrams.

d) Write a short note on host guest chemistry of dendrimic macromolecules. Are hyperbranched polymers and dendrimers true polymers or high molar mass compounds? Comment.

e) What do you mean by generation in hyperbranched polymers and dendrimers? What type of monomers are normally used for the preparation of the same.

f) Write a note on multi-chain polymerization.

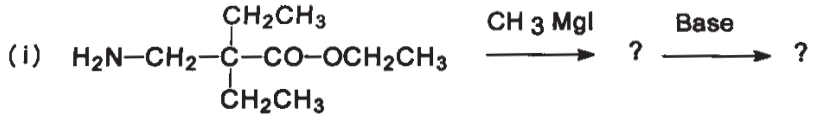
SECTION - II

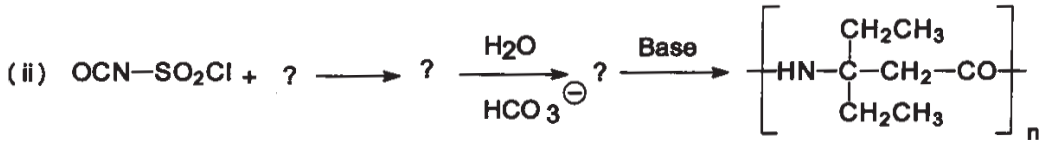
Q3) Attempt any four of the following : **[20]**

a) Comment on the properties of different nylons given below :

	6,6	6	6,10	11	12
Tensile strength in 1000 lb/in^2	11.5	11	8.5	5.5	6.6
% Water absorption at saturation	8.0	9.0	2.4	2.0	1.8
% Elongation at break	80-100	100-200	100-150	280-300	200

b) Complete the syntheses of differently substituted nylon -3 in the reaction shown below. Why is it more difficult to prepare unsubstituted nylon -3?





c) Give the structure of the polymers formed by reaction Cl-CO-R-CO-Cl with

i) NH_2-NH_2 and (ii) H_2N-NH-CO-R'-CONHNH_2. Why is the reaction with (ii) preferred over that with (i) ? When the reaction is carried out with NH_2- NH_2 the first reaction is faster than the second. Explain why?

d) Using linoleic acid depict the mechanism by which oils dry in air. Clearly indicate :

i) the formation of hydroperoxides,
ii) the primary decomposition,
iii) induced decomposition and
iv) termination steps.

e) Explain the following in the preparation of polycarbonates by solution method.

i) a mixture of pyridine and chloroform is used,
ii) phosgene is passed into a solution of Bisphenol A in the above,
iii) the resulting mass is washed with HCl and then with water,
iv) in the above process pyridine is used as solvent, catalyst and reagent.

f) Give at least three methods of synthesis of polyamides. Give four applications.

Q4) Attempt <u>any four</u> of the following : **[20]**

a) What is simplest route for the synthesis of polyether ketones? With suitable examples enlist their applications.

b) Describe the chemistry involved in the preparation of novolak polymers using strong acids and weak organic acids.

c) Describe the manufacture of epoxy polymer. How is the molecular weight of epoxy prepolymer controlled?

d) Illustrate the preparation of D_3 and D_4 siloxane monomers. Explain ROP of these monomers to yield polysiloxanes. Mention two important properties and uses of poly (dimethyl siloxane).

e) Explain the manufacture of UF resins. State their important applications.

f) What is malemine? How is it prepared? Give applications of malemineformaldehyde resin.

Total No. of Questions : 4] **[Total No. of Pages : 2**

P860

[3631]- 303
M.Sc.
POLYMER SCIENCE
PS - 312 : Physical Chemistry of Polymers

Time : 3 Hours] ***[Max. Marks : 80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic tables/calculator is allowed.***

SECTION - I

Q1) Attempt any four of the following : **[20]**

a) Define heat capacity and heat flow in polymers. Write the structure of the following polymers and arrange them in increasing order of Tg. Give reasons for your answer :
Natural rubber (cis and trans) and polybutadiene (cis and trans).

b) Explain what is meant by free volume in polymers. Why is poly (vinylcarbazole) amorphous while poly (vinyl alcohol) is crystalline?

c) Taking the example of PP, discuss the effect of tacticity on the crystallinity of stereoregular PP.

d) What is *"shish kebab"* morphology in polymers? How is it obtained? What is its significance?

e) Explain how X-ray scattering data can be used to determine percent crystallinity and the size of the crystallites.

f) Arrange the polymers in order of increasing Tg/Tm :
Poly (butylmethacrylate) and poly (laurylmethacrylate). Write structures and justify your answer.

Q2) Attempt any four of the following : **[20]**

a) How does hydrogen bonding affect the Tg and Tm in polymers? Nylon 66 and Kevlar form fibers. Write structures and explain which one is more crystalline and why?

b) Discuss with suitable examples the various factors which affect the crystallizability of polymers.

c) Write a note on the theories of glass transition temperature.

d) What type of polymers exhibit glass transition temperature? What structural features help increase or reduce Tg. Give two examples each.

P.T.O.

e) Write notes on :

i) Spherullites.
ii) Lamella and
iii) Cold drawing.

f) Explain the melting point behaviour of a polymer where n = 2 is much higher than when n = 3. n is the number of carbon atoms in repeat unit.

SECTION - II

Q3) Attempt any four of the following : **[20]**

a) What are Virial Coefficients? Explain theta solvent, good, poor and non solvent.
b) What are the different stages of polymer dissolution? Can this process be hastened?
c) What are the differences between ideal, regular and strictly regular solutions? Elaborate.
d) Define Flory temperature (θ). Describe one method of determining it from thermodynamic considerations.
e) Write a shot note on Flory-Huggins theory.
f) Write a short note on phase separation in polymeric solution.

Q4) Attempt any four of the following : **[20]**

a) Define excluded volume and discuss the difficulty in its evaluation.
b) Estimate solubility parameter of poly-n-hexyl methacrylate assume the following :

Group	Fsmall	Fvolume
$-CH_2-$	133	16.45
> C <	-93	4.75
$-CH_3$	214	22.8
-COO-	310	21.0

Density of poly-n-hexyl methacrylate is 1.05.

c) Describe the various effects of high energy radiations on polymeric materials.
d) Describe radiation polymerization of monomers. What are the merits and demerits of this method?
e) Describe the application of high energy radiations for the curing of polymeric materials and polymer based coatings. Comment on the safety aspects involved in the radiation processing of polymeric materials.
f) Describe a method to prepare graft or block copolymers using high energy radiations.

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Total No. of Questions : 4] **[Total No. of Pages : 4**

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[3631]- 304
M.Sc.
POLYMER SCIENCE
PS - 313 : Analytical Chemistry of Polymers

Time : 3 Hours] ***[Max. Marks : 80***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answers to the two sections should be written in separate answer books.***
3) ***Figures to the right indicate full marks.***
4) ***Use of logarithmic tables/calculators is allowed.***

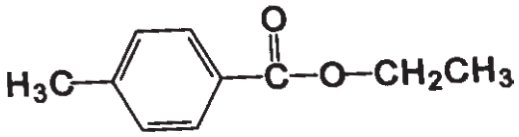
SECTION - I

Q1) Attempt any four of the following : **[20]**

a) Discuss the importance of five preliminary tests of a polymeric sample.

b) What is the need of testing and analyzing for elements in polymers? Explain ashing and combustion flask methods for the determination of elements in polymers.

c) Make a neat sketch of the ^{1}H-NMR spectrum of 1.



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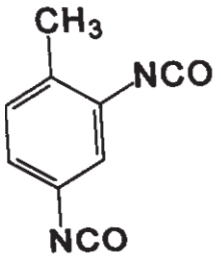
Consider chemical shifts, multiplicity, integration, coupling constants, intensity of lines within a multiplet and comparative intensity of different lines of different multiplets.

d) Identify the different isomers of $C_5H_{10}Cl_2$ from the ^{1}H-NMR data given below :

i) 1.1 (s, 6H), 3.7 (s, 4H);
ii) 0.9 (t, 6H); 2.5 (q, 4H);
iii) 0.9 (d, 6H), 1.75 (m, 1H), 4.15 (m, 2H); 4.9 (m, 1H);
iv) 1.3 (quintet, 2H), 1.9 (m, 4H), 3.75 (m, 2H);
v) 1.0 (s, 9H), 5.7 (s, 1H).

P.T.O.

e) Tolylene diisocyanates 2 and 3 are important raw materials for the preparation of polyurethanes. Indicate the differences in the ^{1}H-NMR of each of the aromatic protons for both these compounds. Consider integration, chemical shift, multiplicity and coupling constants :



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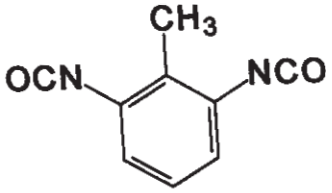

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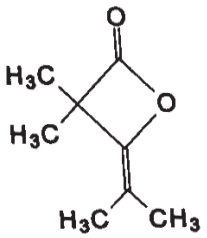
f) Decide, giving reasons which of the four structures given below is consistent with the given CMR data. Assign the CMR signals 15.2 (q), 15.4 (q), 20 (q, strong), 54 (s), 104 (s), 142 (s) 173 (s).



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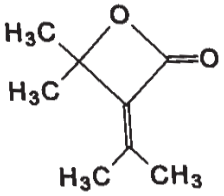

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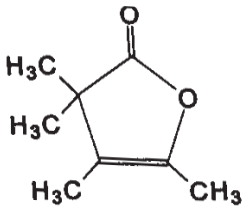

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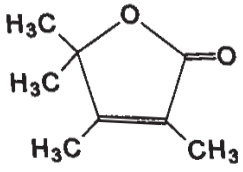

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Q2) Attempt any two of the following : **[20]**

a) Assign a structure to a possible polymer monomer based on the spectral data. Explain your answer. Assign the signals seen in CMR and ^{1}H-NMR Mol. formula $C_7H_{12}O_4$; UV featureless above 220 nm,

IR : 3400 to 2500 (broad), 1729 cm^{-1}.

CMR (in D_2O): 26 (q, strong), 32 (t), 38 (t), 42 (s), 182 (s), 185 (s)

^{1}H-NMR (in D_2O): 1.1 (s, 60 mm). 1.7 (t, J = 6 Hz, 20 mm); 2.2 (t, J = 6 Hz, 20 mm).

TABLE 1 - Some characteristics IR data in cm^{-1}. Values are approximate.

O-H 3600 (free)	NH 3300	C-H 3000
C ≡ N 2250	C ≡ C 2200	C = C 1620
Vinyl ester 1760	Saturated ester 1740	Saturated ketone 1720
Saturated amide 1650		

TABLE 2 - Approximate chemical shifts of protons (δ values).

CH_3-C 0.9	C = C-CH_3 1.6	O = C-CH_3 2.0
ROCH_3 3.8	-CO-CH_3 3.8	H_2C = C 4.6
C = C-H 5.1	HC = C-CO 6.3	C = CH-CO 5.7

TABLE 3 - Approximate CMR chemical shifts.

RCH_3 10-30	R_2CH_2 25-40	R_3-CH 30-50	H_3C-O 53-75
C ≡C 75-100	C ≡N 110-125	Benzene 128.5	C = C 100-140
C = N 145-162	RCOOR, R$COCH_2$, RCOOH 165-180	RCOR, RCHO, 190-210	

b) Draw structures of all eight benzene derivatives with the formula C_9H_{12}, assign each structure to a letter based on the CMR data given below :

Explain your answer

i) Isomer E shows 3 signals in the proton noise decoupled (PND) spectrum.

ii) Isomer F and G both show 6 signals in PND spectrum. For the sp^3 carbons F shows q (st), (d) while F show q (st), q in off resonance spectrum (SFORD).

iii) Isomer H and I both show 7 signals in PND spectrum. For the sp^3 carbons H shows q, q, t while I shows q, t, t (in SFORD).

iv) Isomer J, K and L each shows nine signals in PND spectrum for the sp^3 carbon J shows q, q, q, while K and L each shows q, q, t (in SFORD spectrum). In ^{1}H-NMR K shows one aromatic hydrogen as a triplet with J = 2 Hz.

c) Determine the structures of two monomers A and B and that of copolymers C and D from the data given below. Infer the ratio of A and B in the copolymer C. Explain your answer.

Monomer A ($C_3H_4Cl_2$) IR; 1630, 900 cm^{-1}
Monomer B (C_9H_7N) IR; 2260, 1635, 1600, 1495, 960, 765, 695 cm^{-1}
Copolymer C Mol wt. 11820 IR; 2240, 1600, 1495, 765, 695 cm^{-1}
Copolymer D Mol wt. 12580 IR 3300 to 2500 (broad), 1730, 1600, 1495, 765, 695 cm^{-1}

Assume no backbone degradation during hydrolysis.

SECTION - II

Q3) Attempt any four of the following : **[20]**

a) Draw a typical TGA curve of a polymer and explain various regions.

b) Explain the phenomenon of glass transition temperature.

c) Write a short note on Freeman and Carroll method used in TGA.

d) Discuss the maximization method used in TGA.

e) State Bragg's condition of XRD analysis. Describe the single crystal method to study the feature of a crystal using XRD.

f) Explain powder camera method used in XRD.

Q4) Attempt any four of the following : **[20]**

a) Write a note on small angle scattering of X-rays by polymer.

b) Explain with reference to a simple example the analysis of molecular structure of a simple polymer using XRD technique.

c) Write a short note on DTG for polymer characterization.

d) Write a note on birefringence and dielectric properties of polymeric materials.

e) Explain the behavior of PTFE during TGA studies.

f) How is DTA useful in the study of first order and second order transitions in polymers?