P1181   **[4028]-31**
M.Sc.
POLYMER SCIENCE
PS - 310 : Kinetics and Mechanism of Polymerization Processes
(Old Syllabus)

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

a) Compare and contrast addition, condensation and ring opening polymerization reactions with respect to the kinetics and molecular weights obtainable.

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 catalyzed 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 organic compounds in condensation polymerization? How will it affect gel point?

f) Calculate X_w, X_n for an equimolar mixture of a diacid and a glycol at the following extent of reaction 0.990, 0.999 when the stoichiometric imbalance is 0.99.

Q2) Attempt <u>any four</u> 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 their effect on the rate expression and molecular weights obtained in their presence chain transfer agents.

   d) Compare and explain 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 <u>any four</u> 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) Is it possible to control molecular weight and MWD in cationic and anionic polymerization? Explain.

   f) Under what conditions does cyclization take place in a polycondensation reaction? What is importance of such reaction?

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

a) Vinyl cinnamate does not readily form copolymer with acrylic acid. However it forms copolymer very easily with vinyl acetate. Explain this phenomenon. Predict copolymerization of vinyl acetate with acrylic acid.

b) Explain "Q and e" scheme in estimating reactivity ratios in copolymerization. Discuss its advantages and limitations.

c) Write and explain copolymer composition equation. Under what assumptions is this equation derived?

d) Write any one graphical method of determining reactivity ratio in binary copolymerization. State its limitations.

e) Predict the values of reactivity ratios for obtaining the copolymers as described as follows:

   i) Random copolymer,

   ii) Block of 1 with short group of 2 and

   iii) Long block of 1 separated by one unit of 2.

f) Is it possible of take a feed ratio for preparation of copolymer that is directly observed in the copolymer formed? Explain with appropriate diagram.

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P 1182   **[4028] - 32**
M.Sc.
POLYMER SCIENCE
PS - 311 : Synthesis, Structural Aspects, Properties and Applications of Polymers
(Old syllabus)

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

Instructions to candidates :

1) *All questions are compulsory.*
2) *Answer 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) Write the structure of lignin. What are the different types of bonds joining chains? How is pulp sulfated? What happens to lignin and why is the process called sulfate pulping?

b) Concerning aromatic polyamides, please explain the following:

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

   ii) How are aromatic polyamides prepared by interfacial polymerization?

c) Explain the mechanism by which oils dry in air using linoleic acid as an example.

   Explain:

   i) The formation of hydroperoxides.

   ii) Primary decomposition,

   iii) Induced temperature, and

   iv) Termination steps.

d) Methylethyl ketone peroxide and cyclohexanone peroxide are commercially available. Please write their structure and explain the role of cobalt octoate and the role of the octoate radical as an accelerator.

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e) In the preparation of cellulose triacetate and secondary cellulose, comment on the following

    i) Use of $CH_2 Cl_2$

    ii) Use of CH_3COOH

    iii) Addition of 50% aq/ H_3COOH

    iv) No addition of sodium acetate

    v) Boiling with very dilute H_2SO_4.

f) Explain the following regarding alkyd resins

    i) Though semi-drying oils are still tacky after air drying for seven days, the resins prepared from these oils undergo effective air drying;

    ii) Such resins are preferred to those from drying oil resins for obtaining high gloss white finishes;

    iii) In the free fatty acid process the solvent process is preferred to the fusion process; and

    iv) Alkyd resins can not be prepared by heating a mixture of oil, polyol and dibasic acid.

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

a) Using load deflection curves, explain why flexible foam present from hydroxyl terminated polyethers are preferred to those prepared from hydroxyl-terminated polyesters for upholstery application. By contrast the opposite is true for use as shoulder pads for coats. Why?

b) Explain how spectroscopy can be used to determine the average number of styrene units to crosslink two chains of linear unsaturated polyesters. What are the assumptions involved in this method? How is this assumption justified? How can the validity of this assumption be confirmed experimentally?

c) Describe mechanism and the process of photonitrosation for conversion of cyclohexane to caprolactam. What are its advantages as compared to the usual process?

d)   A typical formulation of rigid foam is given below. Comment on the role of different compounds and their quantities. Give the structure of DABCO. Low molecular weight polyether polyols (100 parts by weight); crude MDI (stoichiometric + 5%); $CFCl_3 50$; glycerine 10; DABCO 0.5; silicone block copolymer 1.0.

e)   Give the structures of the polymers A and B. What are the terminal groups in A.? What types of links are formed in conversion of A to B? In the polymer B, what are the hard and soft segments? Why are these characteristics observed? What happens when this polymer is stretched and when the stretching force is withdrawn? What class of fiber is B?
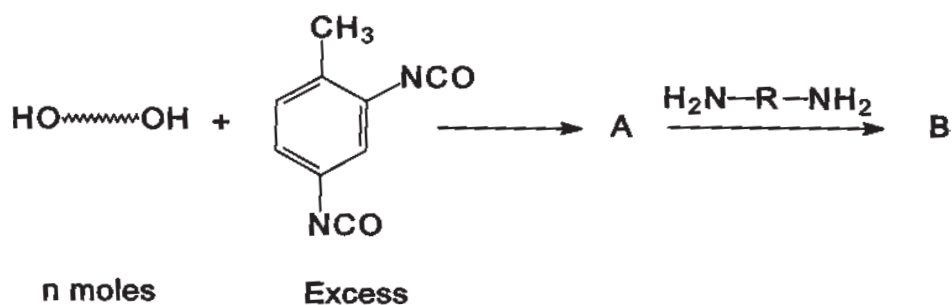
f)   How are the aromatic polyamides Nomex and Kevlar prepared? What are their advantages? Where are these used? What are their drawbacks?

SECTION-II

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

a)   Explain the role of aliphatic and aromatic polyamines in the curing of epoxy resins. Describe the differences in the adhesive properties of both the adhesives.

b)   Write importance of chemical modification of the M-F resins. Explain the equations involved in such modifications.

c)   Describe any one method of manufacturing silicon containing polymers. Explain the applications of the manufactured polymer.

d)   Compare crosslinking reactions in phenol-formaldehyde and urea-formaldehyde resins.

e)   Write a short note on the preparation and applications of silicone containing polymers.

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

    a) Give a synthetic method for the preparation of

        i) Acrylonitrile,

        ii) Vinyl acetate,

        iii) Styrene, and

        iv) Acrylic acid.

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

    c) Describe variation in the manufacturing of LDPE, LLDPE, and HDPE.

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

    e) Write a short note on Ziegler-Natta catalyzed manufacture of polyethylene. Explain the advantages of gas phase over solution phase process.

    f) Citing advantages and limitations, describe the bulk polymerization of styrene.

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P1183

[4028]-33
M.Sc.
POLYMER SCIENCE
PS-312 : Polymer Processing
(Old Syllabus)

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) Why is there a need for polymers to be processed? How do the polymer processes differ from that of metals?

   b) Explain the need and role of various additives that are added to a polymer before processing? Explain with respect to any non elastomeric polymer.

   c) Explain citing suitable examples, the role of plasticizer and thermal stabilizer.

   d) Differentiate between re-enforcing and non-reinforcing fillers. Discuss theory of re-enforcement action of carbon black.

   e) What are the different processes that can be used to make a cup like object of about 900 cubic centimeters? Which criteria should be applied to choose a specific process?

   f) Size, complexity and number of pieces of objects required influence the choice of polymer processing. Explain.

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

   a) What are merits and demerits of compression molding over other processes to get a similar product?

   b) If temperature control is not efficient in a transfer molding operation, what will be the defects caused in the product.

   c) Describe the transfer molding process citing typical processing parameters.

   d) Compare compression molding with transfer molding.

   e) With the help of suitable diagram explain the role of different zones in extuder barrel.

   f) What is the importance of flight angle, root diameter and pitch in designing a screw in extrusion?

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SECTION - II

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

    a)   Enlist the fiber properties that are important in textile uses?

    b)   Enumerate the different methods of spinning synthetic fibers. Describe any one method in details.

    c)   Define the following : Denier, tenacity, moisture contents and moisture regain, and crimp.

    d)   Describe preparation and applications of non woven fiber.

    e)   Give three examples polymers used for synthetic fibers. Describe preparation of any one of them.

    f)   Write a short note on spinning of inorganic fibers.

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

    a)   Discuss importance of compounding.

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

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

    d)   Enlist any three synthetic elastomers. Write their structures, special properties and applications.

    e)   Compare and contrast reinforcing and non-reinforcing fillers. Describe the theory of reinforcement action of carbon black.

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

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P1009

[4028] - 301
M.Sc. (Sem. - III)
POLYMER SCIENCE
PS - 310 : Chain Polymerization
(2008 Pattern) (New)

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) Comment on the effect of chain transfer agent on the rate expression and molecular weight obtained in free radical polymerization.

b) Discuss mechanism of Group Transfer Polymerization.

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

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

e) Write a note on random, graft and block copolymers.

f) Write a note on Fineman-Ross method for the determination of reactivity ratios.

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

a) Explain in detail ring opening polymerization.

b) Describe Reversible Addition Fragmentation Termination polymerization.

c) Derive the expression for degree of polymerization in cationic polymerization.

d) Write a note on coordination polymerization.

e) Write a note on nitroxide mediated polymerizations.

f) Write a note on SAN polymers.

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

    a)   What is the influence of ion pair on polymerization by ionic mechanism?

    b)   Describe the structure of Ziegler-Natta catalyst used and mechanism of co-ordination polymerization in which they are used.

    c)   Describe methods to control molecular weight and polydispersity in cationic and anionic polymerization. Explain your answer.

    d)   Write short note on living polymer.

    e)   In the manufacture of polyethylene, explain the advantages of gas phase over solution phase polymerization. What is the importance of chlorosulphonation of polyethylene?

    f)   What reactivity ratio values would you require for obtaining the following copolymers :

        i)   Random copolymers.

        ii)   Block of 1 with a short group of 2, and

        iii)   Long block of 1 separated by one unit of 2.

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

    a)   Write a note on Q.e scheme for copolymerization.

    b)   How is isobutylene polymerized? State the important properties of the resulting polymer.

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

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

    e)   Write a note on alternate copolymer formation.

    f)   Describe the polymerization of acrylamide. State the important applications of polyacrylamide and its copolymers.

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P1010

[4028] - 302
M.Sc. (Sem. - III)
POLYMER SCIENCE
PS - 311 : Condensation Polymerization
(New Syllabus) (2008 Pattern)

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

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

b) State the requirements to achieve high conversions to synthesize high polymers by condensation polymerization.

c) Distinguish between step reaction and chain reaction polymerization.

d) Discuss with suitable examples, carbonyl addition-elimination mechanism of condensation polymerization.

e) Explain ring versus chain formation by condensation polymerization.

f) Explain how the molecular weight of a linear condensation polymerization can be controlled by keeping the concentration of one of the reactants away from the stoichiometric balance. Derive the necessary equation.

*Q2)* Attempt <u>any four</u> of the following : **[20]**

a) Draw a plot of $\dfrac{1}{(1-P)^2}$ versus time for self catalyzed condensation polymerization and state the reasons for non-linearity in high conversion region.

b) Derive the rate equation for step polymerization in presence of catalyst. Name the catalysts.

c) Derive the equation : $P = \dfrac{2}{f_{avg}} - \dfrac{2}{\overline{X}n \, f_{avg}}$

d) Discuss the plots of number fraction distribution and weight fraction distribution function for linear step reaction polymerization.

e) Write a note on multi chain polymerization.

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 and number fractions of monomer in the resulting polymer.

SECTION - II

Q3) Attempt <u>any four</u> of the following : **[20]**

a) Calculate $\overline{X}n$ and $\overline{X}w$ for an equivalent mixture of a diacid and a glycol at the reaction 0.750.

b) Write a short note on synthesis and utility of alternating and block copolymers.

c) Give the structures of A, B and C in the reaction shown. How is step (i) and step (ii) carried out? The formation of voids in step. (ii) is a problem. What causes this and how can it be avoided?
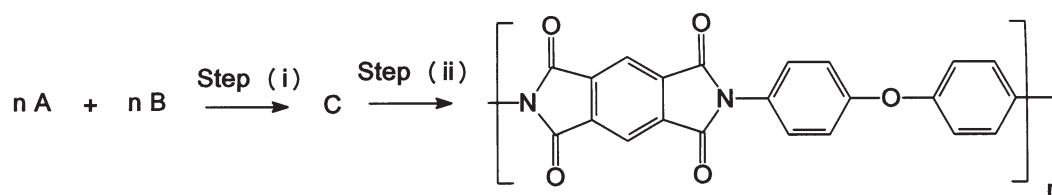
d) Discuss the properties of the different nylons listed below :

	Tensile strength, 1000 lb/in²	% Water Absorption	% Elongation at break
Nylon 66	11.5	8.0	80–100
Nylon 6	11	9.0	100–200
Nylon 6,10	8.5	2.4	100-150
Nylon 11	5.5	2.0	280–300
Nylon12	6.6	1.8	200

e) In polyurethane chemistry, explain why
   i) Reactions of polyols with diisocyanates are more widely used than the reaction of diols with poyisocyanates.
   ii) Hydroxyl terminated polyethers are preferred to hydroxyl terminated polyesters.
   iii) The structural differences when diols or polyols react with diisocyanates.

f) Write a short account of the preparation of unsaturated polyesters and alkyds.

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

a) BPA-PC is prepared by the following method. Please explain with appropriate equations :
   i) A mixture of pyridine and chloroform is used.
   ii) Phosgene is passed into a solution of BPA 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.

b) Explain with suitable chemical equations the synthesis of nylons by interfacial polymerization.

c) Explain ROP with respect to the polymerization of D_3 and D_4 monomers. Enlist the properties of resulting polymer.

d)   What are hyperbranched polymers and dendrimers? Give at least three routes for the synthesis of the same.

e)   Write a note on the concept of generation in hyperbranched polymers. What type of monomers are generally employed for the preparation of hyperbranched polymers?

f)   Write a note on the manufacture and application of cyanate ester resins.

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P1011

[4028] - 303
M.Sc. (Sem. - III)
POLYMER SCIENCE
PS - 312 : Physical Chemistry of Polymers
(2008 Pattern) (New)

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

a) Enlist and explain the factors that influence glass transition temperature in polymers.

b) Define crystallinity and crystallizability. Explain if it is possible to obtain 100% crystalline and 100% amorphous polymers.

c) Draw a neat diagram and mark the different transitions observed in a polymer in the solid state. How are these measured?

d) Explain what happens when a polymer in the liquid state is suddenly cooled to the solid state.

e) Mentioning the types of plasticization, explain their role in polymers.

f) Write a note on the observed Tg values in a homologous series of polyacrylates.

Q2) Attempt <u>any four</u> of the following :   **[20]**

a) Writing the structures of the following polymers, arrange them in decreasing order of Tg. Give reasons for your answer :
   Natural rubber (cis and trans) and polybutadiene (cis and trans).

b) What are spherulites? How are they formed? Provide evidence in support of chain folding and the conditions under which it occurs.

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c) Write a note on the strain induced crystallization. What does it signify?

d) How does hydrogen bonding in polymers affect the Tg and Tm in polymers? Nylon 66 and Kevlar form fibers. Which is more crystalline and why?

e) Name the techniques employed to study the kinetics of the development of crystallinity in polymers. Explain the terms involved in Avrami equation.

f) Write a note on theories of glass transition temperature.

SECTION - II

Q3) Attempt <u>any four</u> of the following :   **[20]**

a) Define solubility parameter. How would you measure solubility parameter of unknown polymer? Write the significance of solubility parameter.

b) Define viral coefficients. Explain theta solvent, good, poor and non solvent.

c) What is hydrodynamic volume? Give examples of application of hydrodynamic volume of linear and branched polymers.

d) Write an account of the different chain models to depict a linear chain in solution.

e) Comment on (i) the size of linear and branched polymers of identical molecular weight in size exclusion chromatography, and (ii) solubility of crystalline and amorphous polymers.

f) With the help of neat diagrams describe LCST and UCST. What is its significance?

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

a) Write a note on ideal solution, real solution, and strictly regular solution.

b) Write a note on the advantages and disadvantages of Flory Huggins solution theory.

c) Write a note on the type of radiation sources that are used in polymer preparation and modification.

d) Explain the role of high energy radiation in bringing out chemical changes in polymers. How are the properties of polymers affected?

e) What are the advantages and disadvantages of radiation-induced polymerization?

f) Determine the solubility parameter of poly-n-butyl acrylate 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-butyl acrylate is 1.05.

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P1012

[4028] - 304
M.Sc. (Sem. - III)
POLYMER SCIENCE
PS - 313 : Analytical Chemistry of Polymers
(New) (2008 Pattern)

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 the following :

 a) Determine the structure of a monomer **A** $C_6H_{10}O_2$ (Mol. Wt. 114) and the polymers **B** and **C** based on the data given below. Explain your answer.   **[6]**

	(i) Polymerization		(i) Hydrolysis*	
A	------------------>	Polymer **B**	------------------>	Polymer **C**
	(ii) Purification		(ii) Purification	

*Assume there is no backbone degradation during hydrolysis

A IR - 1720, 1625, 970 cm^{-1}; UV – 215 nm ε ~ 7000

B Mol. Wt. 3420; IR - 1735 cm^{-1}

C Mol. Wt. 3000; IR - 3300 – 2500 cm^{-1} (broad), 1730 cm^{-1}

 b) Deduce the structure of any two of the following compounds, all of which are $C_8H_8O_2$. Explain the given data.   **[6]**

 i) IR : 2730, 1680, 1605, 1495, 765 cm^{-1}; UV : 257 nm ε ~ 11000.

 ii) IR : 1760, 1600, 1505, 760, 680 cm^{-1}.

 iii) IR : 3300, 1680, 1595, 1495, 850 cm^{-1}; UV : 270 nm ε ~12000. It gives positive iodoform test.
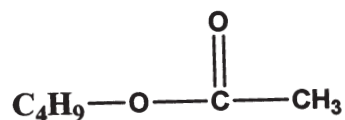
Q2) Answer any one of the following : **[10]**

a) Draw four possible isomers of

$$C_4H_9-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

indicate the number of signals expected for each of these compounds. For each compound indicate the expected chemical shift, multiplicity, coupling constant, integration (assume 1H = 4 mm) for the protons at highest and lowest field only, with reasons.

b) Make a neat sketch of the ^{1}H-NMR of Compound 1 which is one of the raw materials for making oil soluble resins for surface coatings. Consider chemical shifts, multiplicity, coupling constants, integration (assume 2H = 8 mm), intensity within the multiplet and comparative intensity within a multiplet and comparative intensities of different multiplets.

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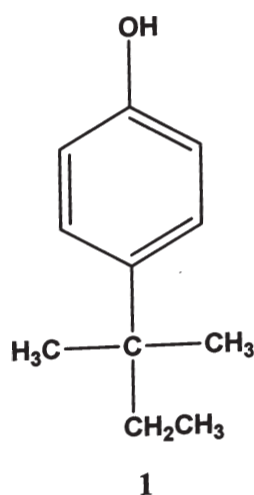
*Q3)* Attempt any two of the following : **[12]**

a) The CMR spectra of 2 and 3 are given below. Identify which spectrum corresponds to which compound, giving reasons. Assign the signals. Note that both compounds are diethyl esters of important polymer raw material.

i) 14(q)*, 62(t)*, 129(d), 130.5(d), 130.7(s)*, 134(d)*, 165(s)*.

ii) 12(q)*, 60(t)*, 128(d)*, 130(d)*, 131(s), 166(s).

*strong signals
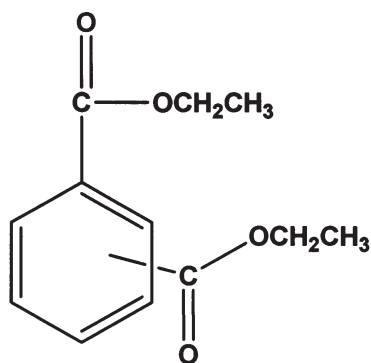
2 – ortho isomer; 3 – meta isomer

b) Identify the two possible monomers both C_4H_6O from their CMR data giving reasons. Assign the signals.

i) 76 (down, ab)*, 124 (up, up).

ii) 24 (down, ab)*, 67(down, ab)*, 98(up, up), 147(up, up).

The first word in brackets indicates result of DEPT 1, the second word that of DEPT 2. * ab = absent.

c) Assign the CMR signals in compound 4, giving reasons.

32(q, v. st),   35(s), 85(s), 92(s), 115(d), 121(s), 125(d, st), 131(d, st), 142(s).
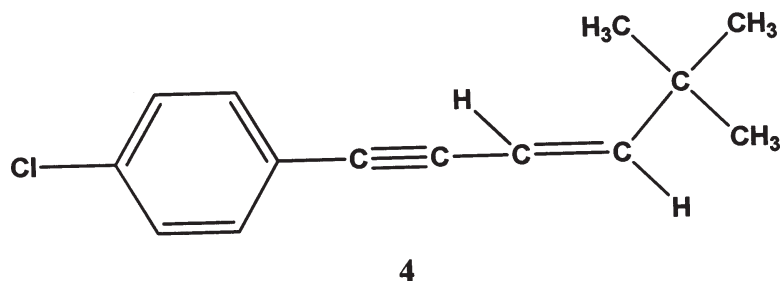
4

Q4) A possible monomer C_4H_7OCl shows the spectral data given below. Assign the signals. Use this to deduce the structure. Explain your answer. **[6]**

IR : 1633, 995, 910 cm^{-1}.

CMR : 41(t), 67(t), 87(t), 152(d).

^{1}H-NMR : 3.2(t, J=6 Hz, 20 mm); 3.45 (t, J=6 Hz, 20 mm); 3.9 (dd, J=3 and 8Hz); 4.0 (dd, J = 3 and 12 Hz, integration for 3.9 and 4.0, 20 mm), 6.25 (dd, J = 8 and 12 Hz, 10 mm).

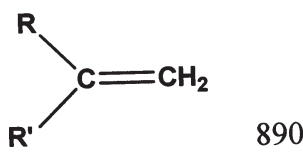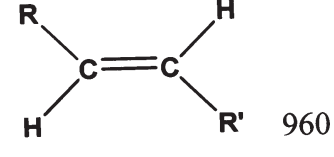Table 1 : Some characteristic IR data in cm^{-1}; Values are approximate.

OH - 3600 (free)	NH - 3300	$\equiv$ C-H 3300
C $\equiv$ N 2250	C $\equiv$ C 2200	C = C 1620
Vinyl ester 1760	Saturated ester 1740	Saturated ketone 1720
Saturated amide 1650	R, R' C=CH_2 890	R, H C=C H, R' 960

Table 2 : Approximate chemical shifts (δ values).

CH$_3$-C 0.9	C = C – CH$_3$ 1.6	O = C - CH$_3$ 2.0
R-OCH$_3$ 3.3	O = C – OCH$_3$ 3.8	H$_2$C = C 4.6
C = C – H 5.1	HC = C – CO 6.3	C = CH – CO 5.7
Ph – OCH$_3$ 3.8		

Table 3 : Approximate CMR chemical shifts

RCH$_3$ 10-30	R$_2$CH$_2$ 25-40	R$_3$-CH 30-50
H$_3$C-O 53-75	C $\equiv$ C 75-100	C $\equiv$ N 110-125
Benzene 128.5	C = C 100-140	C = N 145 - 162
RCOOR, RCONHR,	RCOR, RCHO	
RCOOH 165-180	190-210	

SECTION - II

Q5) Attempt any four of the following :   [20]

a)   What information do you obtain from low angle scattering of X-rays in polymer analysis?

b)   How is iodine number of unsaturated polymers determined? What is its significance?

c)   Describe the TGA apparatus. What information does one obtain from a thermogravimetric analysis?

d) Explain the behavior of PTFE during TGA studies.

e) Find the interplanar spacing from the following data for the crystal obtained in a powder camera method :

λ of X rays used = 154 nm

Order of reflection = 1

Length of blackened arc on the camera = 58.88 mm

Camera radius = 57.3 mm

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

Q6) Attempt any four of the following : **[20]**

a) Using a polymer as an example, explain how thermal stability is determined.

b) Discuss the maximization method used in TGA.

c) What information is obtained from DTG? Explain your answer.

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

e) Explain refractive index and Abbe number. How are these useful in getting information about transparency, mechanical properties and moisture resistance of the polymeric materials.

f) Define glass transition temperature. Write a note on the significance of the phenomenon of glass transition temperature in polymers.

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P1013

[4028] - 401
M.Sc. (Sem. - IV)
POLYMER SCIENCE
PS - 410 : Polymer Processing
(2008 Pattern) (New)

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

   a)   With the help of a neat diagram explain the working of a reciprocating screw injection molding. Enlist the advantages over ram based injection molding.

   b)   Explain blow molding process. Enlist industrially important products prepared by this process.

   c)   What is the importance of flight angle, root diameter and pitch in designing a screw in extrusion?

   d)   Write a note on compression molding of polymers.

   e)   Explain the variation in number of rollers and their arrangement in the process of calendaring.

   f)   Describe design peculiarities of pressure forming.

Q2) Attempt <u>any four</u> of the following :   **[20]**

   a)   Explain the typical values of the crystalline melting point and glasstransition temperature for textile fibers.

   b)   How do the stress-strain properties of the typical fiber change with draw ratio? Explain your answer in detail.

c) Enumerate the design characteristics of object obtained by compression molding. Discuss advantages and disadvantages of compression molding.

d) List and explain the criteria of choosing a polymeric material for desired application.

e) What is the approximate denier of a fiber 0.02mm in diameter if the specific gravity of the polymer is 1.2?

f) Describe the versatility of extrusion as a process.

SECTION - II

Q3) Attempt <u>any four</u> of the following : **[20]**

a) Explain with examples of synthetic fibers prepared by wet spinning process.

b) Compare and contrast the properties of natural and synthetic fibers.

c) What do you mean by the term staple fiber and filament?

d) Give examples of thermoformed products. With the help of neat diagrams describe thermoforming process.

e) Write a short note on specialty fibers.

f) What is the significance of molecular weight drawing ratio and temperature in melt spinning?

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

a) Discuss importance of compounding.

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

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

d) Enlist any three synthetic elastomers. Write their structures, special properties and applications.

e) Compare and contrast reinforcing and non-reinforcing fillers. Describe the theory of reinforcement action of carbon black.

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

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P1014

[4028] - 402
M.Sc. (Sem. - IV)
POLYMER SCIENCE
PS - 411 : Rheology and Mechanical Properties of Polymers
(2008 Pattern) (New)

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

a) Explain the following terms :

   i)   Weissenberg effect.   ii) Bingham plastic.

   iii) Deborah number.   iv) Zero shear viscosity and

   v)   Shear thinning.

b) Describe Hook's equation and Newton's equation.

c) Write a note on the kinetic theory of rubber elasticity.

d) Explain Kelvin-Voigt model in parallel. Which phenomenon is explainable using this model? What are the limitations of this model?

e) Describe theory of visco-elasticity for amorphous polymeric materials. Can it be extended to crystalline polymeric materials? Explain.

f) Explain how the parameters such as :

   i)   molecular entanglement

   ii) crystallinity, and

   iii) molecular weight effect viscoelastic properties of polymers.

Q2) Attempt <u>any four</u> of the following :   **[20]**

a) Describe the process of creep and stress relaxation in polymers.

b) Describe the effect of branching and stereo-regularity of polymers on rheological properties.

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c) Write an account on the rheological properties of polymeric melt. Explain its behavior like a solid and a fluid.

d) Explain the importance of time-temperature superposition.

e) Draw and explain stress-strain curve for the following polymeric materials :
   i) hard and brittle.   ii) hard and strong
   iii) hard and tough   iv) soft and weak and
   v) soft and tough

f) Explain the relevance of die swell and shark skin effect to the rheological behavior.

SECTION - II

Q3) Attempt <u>any four</u> of the following :   **[20]**

a) Write a brief account on the classification of adhesives.

b) What are the different methods of applying an adhesive onto the substrate?

c) What are the different tests to control the quality of adhesives during manufacturing?

d) What is the difference between paint and varnish?

e) Discuss tinting resistance of white pigment and tinting power of dye pigment.

f) Enlist the equipments used for the production of paints. Explain the working of ball mill.

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

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

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

c) Describe different methods of applying an adhesive on to the substrate.

d) Suggest polymeric materials for packaging of special electronic gadgets. Give reasons.

e) Discuss the hiding power or covering power of pigments used in surface coating.

f) Describe the different techniques used for testing of paints and varnishes.

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P1015

[4028] - 403
M.Sc. (Sem. - IV)
POLYMER SCIENCE
PS - 404 : Special Topics
(2008 Pattern) (New)

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

  a) Polymers are the most suitable materials for biomedical applications. Discuss.

  b) Suggest polymers for (i) bone replacement, (ii) dental application, and (iii) blood substitutes.

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

  d) Write a note on applications of controlled release of drugs.

  e) Write and explain Fick's law or Ferry's law.

  f) Discuss the applications of polymeric membranes in pollution control.

Q2) Attempt <u>any four</u> of the following :   **[20]**

  a) What are electroactive polymers? Discuss the mechanism of conduction in inherently conducting polymers.

  b) What are piezo electric and pyroelectric polymers? Explain their applications.

  c) Discuss various applications of polymers filled with conducting fillers.

  d) Discuss the applications of polymers in nano technology.

e)   What are liquid crystalline polymers? How is liquid crystallinity detected?

f)   What are functional polymers? Enlist applications of functional polymers.

SECTION - II

Q3) Attempt <u>any four</u> of the following :   **[20]**

a)   Enlist the principles of Green Chemistry. Give two examples of reactions where there is avoidance of waste generation.

b)   What are polymer gels? Give examples and applications of polymer gels.

c)   What are biodegradable polymers? Give examples and applications of biodegradable polymers.

d)   Explain how recycling of post consumer polymer is carried out. Enlist the types of plastic containers that should not be recycled.

e)   What are polymer blends? Describe role of compatibilisers in blending.

f)   What are water soluble polymers? Give examples and applications of water soluble polymers.

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

a)   Write and describe two examples chemical reactions carried out under green conditions.

b)   Write and describe the synthesis of two polymer gels and list their uses.

c)   Write a note on polymer nanocomposites in medicine.

d)   Enlist the accepted mechanisms of biodegradation. Explain essential features of biodegradation.

e)   What factors in a polymer hamper recycling? With suitable equations, explain how poly(ethylene terephthalate) is recycled. Give a few useful products obtained from recycled poly(ethylene terephthalate).

f)   With reference to polymer blends, what are LCST and UCST?

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P1184

[4028]-34

M.Sc.

POLYMER SCIENCE

PS - 313 : Polymer Chains and Their Characteristics

(Old Syllabus)

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 cohesive energy density and solubility parameter. Enlisting the variables influencing solubility parameter, explain its industrial significance.

   b) What are virial coefficients? Explain Flory Theta temperature, a good solvent and a poor solvent.

   c) Write short notes on colligative properties with respect to the molecular weights of polymers.

   d) Explain Flory-Huggins theory and the assumptions on which it is based.

   e) What is LCST and UCST? Explain with suitable examples.

   f) Explain in short :
      i) Size of linear and branched polymer of identical molecular weight, and
      ii) Solubility of crystalline and amorphous polymers.

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

   a) Discuss the dissolution of crystalline and amorphous polymers.

   b) What is hydrodynamic volume and excluded volume? What is the origin of excluded volume?

   c) Relate Flory Huggins interaction parameter with cohesive energy density.

d) How does high energy radiation bring out chemical changes in polymers? How does it affect the properties of polymers?

e) Predict the effect of high energy radiation on polystyrene, PVC, and PMMA.

f) Estimate the solubility parameter of isosorbide diester.
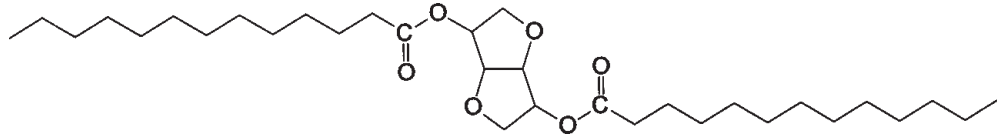
Use the following data :

Group	$F_{Free\ volume}$
(CH_2)	280
$H\text{-}C\equiv$	140
$(\text{-}CH_3)$	420
$(\text{-}COO\text{-})$	511

ρ (density) $= 1.51$ g/cm^3

SECTION - II

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

a) Explain the following :
   i) Weissenberg effect,
   ii) Bingham plastic,
   iii) Plasticity,
   iv) Elasticity, and
   v) Viscosity.

b) Write and explain Hook's equation and Newton's equation for polymeric materials.

c) Explain Voigt model. Which phenomenon is explainable using this model? What are the limitations of the model?

d) Explain the term visco-elasticity relevant to polymeric materials.

e) Explain how the parameters such as :
   i) molecular entanglement,
   ii) crystallinity, and
   iii) molecular weight affect visco-elastic properties for polymers.

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

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

   a) Explain power law model.

   b) Draw and explain stress strain curve for the following polymeric materials:
       i)   Hard and brittle,
       ii)   Hard and strong,
       iii) Hard and tough,
       iv)   Soft and weak, and
       v)   Soft and tough.

   c) Describe cone and plate viscometer. Explain its scope and limitation in the study of rheological behaviour of polymeric melt.

   d) Describe the effect of molecular weight, molecular weight distribution on viscosity and zero shear viscosity.

   e) What are storage and loss moduli? Describe with respect to polymeric materials.

   f) Explain the relevance of die swell and shark skin effect to the rheological behaviour.

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P1185

[4028]-41

M.Sc.

POLYMER SCIENCE

PS - 410 : Analysis and Testing of Polymers

(Old Syllabus)

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 the following :

    a)   Determine the structures of the monomer **A**, the copolymer **B** and the derived polymer **C**. Determine the ratio of the two monomers in **B** from the data given below. Explain your answer.   **[4]**
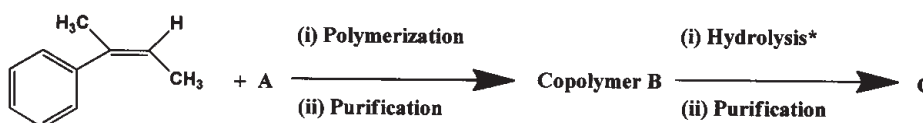

    * Assume no backbone degradation during hydrolysis.

    A: C_5H_7N; IR: 2150, 1625, 960 cm^{-1}. UV: 212 nm $\varepsilon \sim 10000$.

    B: Mol. Wt. 11160; IR: 2200, 1605, 1495, 765, 695 cm^{-1}.

    C: Mol. Wt. 11920; IR: 3300 to 2500 broad, 1720, 1605, 1495, 765, 695 cm^{-1}.

    b)   Draw structures of six olefinic esters with the formula $C_4H_6O_2$. Indicate, giving approximate values, how each of these can be differentiated from their IR spectra.   **[8]**

Q2)   Answer **any one** of the following :   **[10]**

    a)   The hydroxy acid 1 could be used as a monomer for the preparation of polyesters. Make a neat sketch of its ^{1}H-NMR. Consider chemical shift, multiplicity, coupling constants, intensity of lines within a multiplet and

intensity of lines in different multiplets. Assume integration for one hydrogen as 16 mm, and coupling of A and B equal to that of A and C and no coupling of A with OH.

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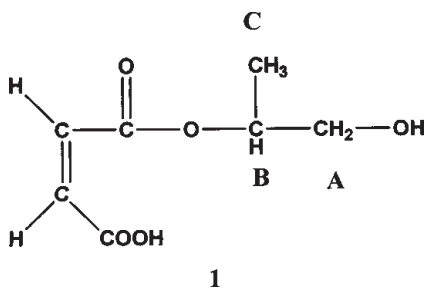
b) Identify the compounds given below which in ^{1}H-NMR show all peaks as singlets

   i) C_3H_6O only one peak,

   ii) $C_2H_4Cl_2$ only one peak,

   iii) C_3H_9N only one peak,

   iv) C_5H_{12} only one peak,

   v) $C_3H_8O_2$ only two peaks,

   vi) $C_5H_{10}O$ only two peaks,

   vii) $C_8H_6O_2$ only two peaks.

Q3) Answer **any two** of the following :   **[12]**

a) Identify the seven isomers of carbonyl compounds, all with the formula $C_5H_{10}O$ from their CMR spectral data given below. Isomer A, B, C all show singlets in 190 to 200 region whereas D, E, F and G all show doublets (in off resonance) in this region. Isomers A and D each show three signals in PND spectrum while isomers B and E each show four signals. Isomer C, F, and G all show five signals each. Isomer F is the only one which shows one doublet (in off resonance) in the region 0 to 50 ppm.

b) Identify the three pyridine derivatives all with the formula C_6H_7N from the CMR data given below :

   i)   18 (q), 122 (d, st*), 145 (s), 149 (d, st*)   st* = strong

   ii)   23 (q), 121 (d), 123 (d), 127 (d), 149 (d), 157 (s)

   iii) 18 (q), 122 (d), 133 (s), 136 (d), 147 (d), 150 (d)

c) Identify the two compounds both with formula $C_6H_{11}NO$ from their CMR data. Assign the signals.

   i)   Amide - 22 (t), 29 (t), 31 (t), 36 (t), 42 (t), 180 (s)

   ii)   Oxime - 24 (t), 25 (t), 25.2 (t), 27 (t), 32 (t), 161 (s)

Q4) Deduce the structure of an important polymer raw material C_3H_6O from its spectral data. Comment on the chemical shifts in ^1H and ^{13}C-NMR. Explain the couplings seen in ^1H-NMR. Explain your answer.

IR : No significant peak above 1500 cm^{-1}

CMR: 13.1, 47.3, 47.6

DEPT 1: 13.1, 47.6 up, 47.3 down; DEPT 2: 47.6 up

^1H-NMR: 1.32 (d, J = 6 Hz, 15 mm); 2.42 (dd, J = 2.5 and 3.5 Hz, 5 mm); 2.72 (dd, J = 3 and 3.5 Hz, 5 mm); 2.98 (ddq, J = 2.5, 3 and 6Hz, 5 mm).**[6]**

Table 1 : Some characteristic IR data in cm^{-1}; Values are approximate.

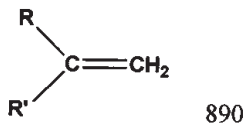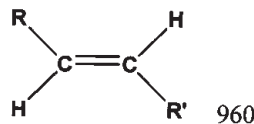| OH - 3600 (free)	NH - 3300	$\equiv$C–H 3300
C$\equiv$N 2250	C$\equiv$C 2200	C = C 1620
Vinyl ester 1760	Saturated ester 1740	Saturated ketone 1720
Saturated amide 1650	890	960

Table 2 : Approximate chemical shifts (δ values).

CH$_3$–C 0.9	C = C–CH$_3$ 1.6	O = C–CH$_3$ 2.0
R–OCH$_3$ 3.3	O = C–OCH$_3$ 3.8	H$_2$C = C 4.6
C = C–H 5.1	HC = C–CO 6.3	C = CH–CO 5.7
Ph-OCH$_3$ 3.8		

Table 3 : Approximate CMR chemical shifts

RCH$_3$ 10 – 30	R$_2$CH$_2$ 25 – 40	R$_3$–CH 30 – 50
H$_3$C–O 53 – 75	C $\equiv$ C 75 – 100	C $\equiv$ N 110 – 125
Benzene 128.5	C = C 100 – 140	C = N 145 – 162
RCOOR, RCONHR, RCOOH 165 – 180	RCOR, RCHO 190 – 210	

SECTION - II

Q5) Attempt **any four** of the following : **[20]**

a) Write a note on dichroism and birefringence and its use in characterization of polymers.

b) With the help of a neatly labeled diagram explain scanning electron microscope. Mention important applications.

c) Define acid number in the analysis of polymers. Describe the method for the analysis of acetyl number of polymers.

d) How is iodine number of unsaturated polymers measured? What is its significance?

e) How are density, refractive index and color tests important in testing and analysis of polymers?

f) Write a short note on semiconductor detector used in X-ray analysis.

Q6) Attempt **any four** of the following : **[20]**

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

b) Describe the different detectors used for detecting X-rays.

c) Find the interplanar spacing from the following data for the crystal obtained in a powder camera method:

λ rays used = 154 nm
Order of reflection = 1
Length of blackened arc on the camera = 58.88 mm
Camera radius = 57.3 mm

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

e) Write a short note on significance of refractive index and Abbe number.

f) Explain the different transitions obtained when a semicrystalline polymer is heated in DSC.

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P1186

[4028]-42
M.Sc.
POLYMER SCIENCE
PS - 411 : Structure and Properties of Bulk Polymers
(Old Syllabus)

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) Enlist the differences between crystallinity and crystallizability. Is it possible to obtain 100% crystalline and 100% amorphous polymers? Explain.

   b) With the help of structures explain the cis-, trans and 1, 2-vinyl configuration of butadiene units in polybutadiene molecule. Which one is most crystalline and why?

   c) What is the effect of molecular weight on glass transition temperature?

   d) Explain Schatzki crankshaft model. With the help of examples explain your answer.

   e) Explain what happens to polymers upon quenching. Comment on the Tg and Tm of samples before and after quenching.

   f) Define first order and second order transition in polymers. What is secondary glass transition? How does secondary glass transition exhibit itself?

Q2) Attempt <u>any four</u> of the following :   **[20]**

   a) Do poly (methylmethacrylate) and syndiotactic poly (methylmethacrylate) exhibit glass transition temperature? Justify your answer.

   b) Show with suitable examples the effect of restricting groups on glass transition of polymers.

   c) Write a note on the growth and structure of spherulites in crystalline polymers and the arrangement of molecules in the spherulites.

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d) Define heat capacity. Explain the construction and method of suitable instrument to determine glass transition temperature.

e) Write a suitable expression for the estimation of glass transition temperature of copolymers.

f) Write a short note on theories of glass transition temperature.

SECTION - II

Q3) Attempt <u>any four</u> of the following : **[20]**

a) What is the difference between adhesion and cohesion? Write a note on the mechanism of adhesion of a substrate to metal, wood and paper surface.

b) Write and explain the differences between varnishes and paints. Give commercial examples of paints and varnishes.

c) What is tinting and tint resistance? Explain tinting resistance of white pigment and tinting power of dye pigment.

d) Write a note on the classification of adhesives.

e) How does one test the adhesives during their manufacture? What are the quality control tests?

f) What are the salient features to be considered before adhesive application on a surface?

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

a) How is pigment to binder ratio important in the preparation of a paint formulation?

b) Why is polylactic acid preferred as a packaging material in several commercial applications?

c) In what polymeric material are electronic gadgets normally packed and why?

d) Write a note on the equipments used in the paint industry. Explain the working of any one equipment.

e) Suggest packaging material for
   i) Milk and dairy products.
   ii) Confectionary items.
   iii) Agrochemicals.
   iv) Printed circuit boards, and
   v) Glass wares.

f) Write a note on oil bound paints, enamel paints and powder coating.

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P1187

[4028]-43

M.Sc.

POLYMER SCIENCE

PS - 404 : Special Topics in Polymer Science

(Old Syllabus)

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

a) Discuss the hurdles in recycling polymers after their use.

b) Describe the classification/codes for polymers with respect to recycling.

c) Describe the different criteria for assessing biodegradability of polymers.

d) What are the peculiarities for biological degradation of small molecules that are not met with in biodegradation of polymers?

e) What are functional polymers? Describe application of functional polymers in organic synthesis.

f) Explain the formation of functional polymers by chemical modification route. Are these reaction different from reactions of low molecular weight compounds.

Q2) Attempt <u>any four</u> of the following :   **[20]**

a) Explain the different phases in a liquid crystalline polymer. Discuss the structure property relationship in liquid crystalline polymers.

b) Describe synergistic blends and miscible blends? Describe the experimental tools to differentiate them.

c) Enlist and explain the different methods of increasing thermal stability of polymers.

d) Describe with equations the addition and the condensation route for the preparation of polyimides.

e) Discuss the various methods to obtain polymeric material with predictable properties. What are the advantages and limitations of blending polymers to obtain the desired properties.

f) Define thermally stable polymers, flame retardant polymers and polymers with high HDT. Discuss the resulting properties.

SECTION - II

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

a) Compare suitability of polymers with other materials for biomedical applications.

b) What polymers find applications in

   i) Bone replacement.
   ii) Dental applications and
   iii) Blood substitute.

c) Discuss the applications of polymeric membranes in pollution control.

d) How is nylon as an engineering plastic prepared? What are its important applications?

e) Describe the chemistry and technology of PPS or polysulfone.

f) Differentiate commodity, engineering and specialty plastics. Explain with suitable examples, how HDT and UL rating are important in selecting engineering plastics for

   i) Moisture resistance applications,
   ii) Fire retardant applications and
   iii) Impact resistance and glass replacement applications.

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

a) What is controlled release of drugs? Give two examples of controlled release drugs. With suitable examples describe the various mechanisms to controlled release.

b) Describe the role of general purpose resins in composites.

c) Write a note on the selection criterion for the selection of various engineering plastics for different applications.

d) Discuss the mechanism of gas separation using polymeric membranes.

e) Write a note on electrical conduction in intrinsically conducting polymers and their applications.

f) Enlist and discuss polymeric composites in aerospace and automotive industries.

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