Total No. of Questions : 4]

SEAT No. :

P452

[Total No. of Pages : 4

[4328] - 302

M.Sc. (Semester - III)

POLYMER SCIENCE

PS - 311 : Condensation Polymerization

(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 any four of the following : **[20]**

a) Write the steps and mechanism involved in step growth polymerization. Give two examples of step polymerization reaction wherein there is no formation of by-product.

b) Describe dependence of $\overline{X}_w$ and $\overline{X}_n$ on various factors in polyesterification reaction.

c) Write in detail how stoichiometric balance effects the DP in condensation polymers.

d) Write a note on multi-chain polymerization.

e) 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.

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

P.T.O.

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

a) Describe the methods for the preparation of hyperbranched polymers and dendrimers. What are the limitations ?

b) Write a note on rheology of branched polymers.

c) Write a short note on the characterization techniques employed for hyperbranched polymers and dendrimers.

d) 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.

e) A linear step polymerization is 98 % complete. Calculate $\overline{X}_n, \overline{X}_w$, and PDI.

f) Explain how cyclic oligomers are formed in step growth polymerization. Why are they formed ?

SECTION - II

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

a) Explain the following regarding the preparation of linear unsaturated polyesters

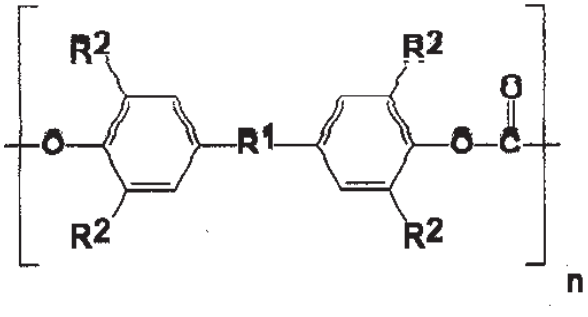
i) Phthalic anhydride is preferred to phthalic acid.

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 by-products.

iii) For the manufacture of the anhydride o-xylene is preferred to naphthalene.

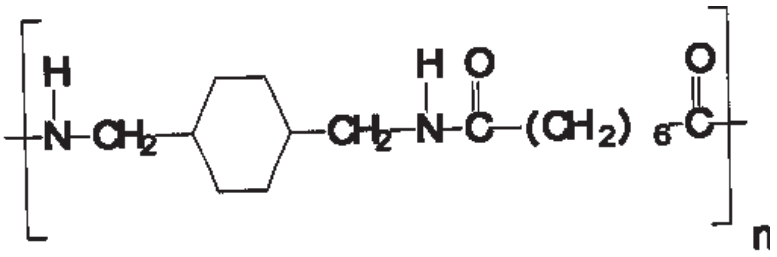
b) What is the difference between short, medium and long oil resins? What are the differences in solubility, mode of curing and nature of finishes using these three categories of resins?

c) Comment on the Tg of the polycarbonates shown below.



R^1	R^2	Tg^0 C
CH_2	H	147
$C(CH_3)_2$	H	149
$C(PH)_2$	H	121
$C(CH_3)_2$	CH_3	210
SO_2	CH_3	260

d) How is the polymer (1) prepared ? Explain why it has greater hardness, smaller elongation at break and lower water absorption than nylon 6. Why is this polymer preferred to nylon 6 where physical and electrical properties have to be maintained under humid conditions?



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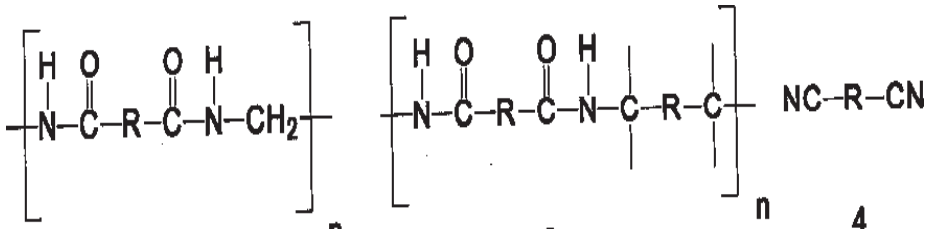
e) Explain the following regarding synthesis of polyamides

i) The use of picrylchloride in the synthesis starting from p- aminobenzoic acids;

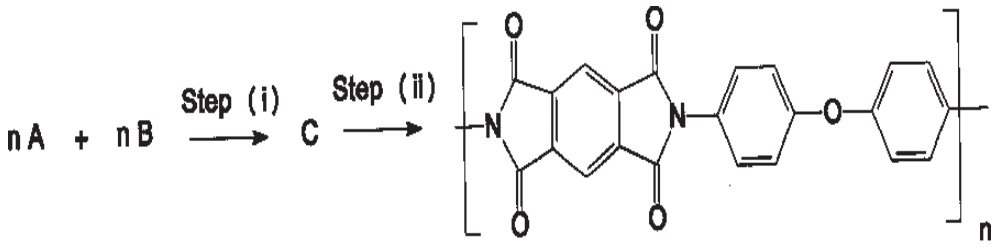
ii) The formation of nylon 2 from α- amino acids using $COC1_2$;

iii) The formation of 2 and 3 from 4.



2 3 4

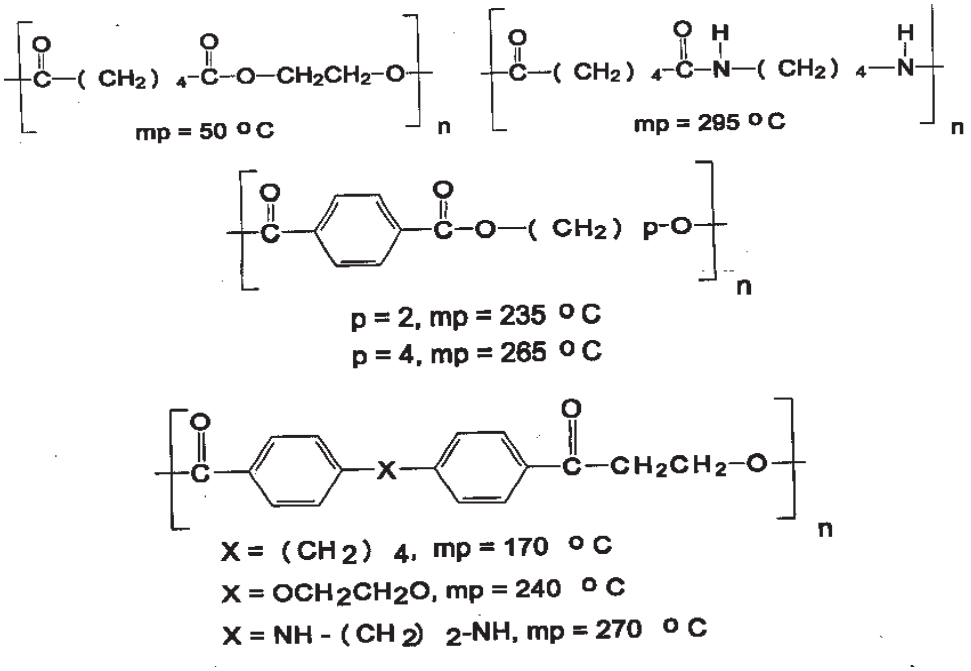
f) Give the structures of A and B in the reaction shown. How is step i) and step ii) carried out ? The formation of voids in step ii) is a problem. What causes this and how can it be avoided ?



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

a) Comment on the relation of structure and m.p. for the polymers shown below.

Indicate the structures of monomers required for each of these polymers.



b) Resol prepolymers were synthesized using sodium hydroxide and magnesium hydroxide as catalyst. The prepolymers formed were used towards Step II crosslinking reaction. Will the behaviour of the two prepolymers be different towards crosslinking ? Explain .

c) 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.

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

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

f) Compare crosslinking reactions in phenol - formaldehyde with urea - formaldehyde resins.

■■■

Total No. of Questions : 4]

SEAT No. :

P453

[Total No. of Pages : 3

[4328] - 303

M.Sc. (Semester - III)

POLYMER SCIENCE

PS - 312 : Physical Chemistry of Polymers

(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 any four of the following: **[20]**

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

b) What is the difference between primary and secondary glass transition temperature?

c) Explain what happens during quenching of polymers. Comment on the thermal and mechanical properties of melt and solution crystallized polymers.

d) Consider the following facts: nylon 6 is crystalline, poly(vinyl carbazole) is amorphous and polyvinyl alcohol is crystalline. With the help of structures explain the reasons for this.

e) What are plasticizers? Explain with suitable examples the role of plasticizers employed in polymers.

f) Explain the features of semicrystalline and amorphous polymers. With a suitable diagram explain Tg, Tm, and Tc.

P.T.O.

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

a) Arrange the polymers in order of increasing Tg:

i) Polyethylene, polystyrene and polypropylene

ii) Poly(methylacrylate) and poly(methyl methacrylate)

iii) Poly(vinyl chloride) and poly(vinylidene chloride)

iv) Poly(methyl acrylate), poly(ethylacrylate) and poly(butylacrylate).

b) Differentiate between crystalline and crystallizability. Is it possible to obtain a polymer with 100% crystallinity. Comment on its Tg, Tm and Tc.

c) What are spherulites? Comment on the mechanical properties of a rapidly crystallized polymer sample and slowly crystallized polymer sample.

d) Write a short note on HDT of polymers and its significance.

e) Explain the term degree of crystallinity. What are X_v, X_m, and X_{cal}.

f) Differentiate between plasticization and copolymerization on Tg of polymers. Give examples.

SECTION - II

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

a) What is solubility? Enlist the factors on which solubility of polymers depend.

b) Write a note on determination of solubility parameter of polymers.

c) Explain in short i) size of linear and branched polymer of identical molecular weight, and ii) solubility of crystalline and amorphous polymers.

d) Write a note on theta temperature and virial coefficients.

e) Write a short polymer electrolytes.

f) Discuss the cases of LCST > UCST and UCST > LCST.

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

a) Discuss the dissolution of crystalline and amorphous polymers.

b) Write a short note on Flory-Huggins interaction parameter.

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

d) Describe applications of radiation induced modification of polymers.

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

f) Estimate solubility parameter of poly-n-ethyl 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-ethylmethacrylate is 1.05.

■■■

Total No. of Questions : 6]

SEAT No. :

P454

[Total No. of Pages : 4

[4328] - 304

M.Sc. (Semester - III)

POLYMER SCIENCE

PS - 313 : Analytical Chemistry of Polymers

(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_9N (Mol. Wt. 95) and the polymer **B** and **C** based on the data given below. Explain your answer.

(i) Polymerization (i) Hydrolysis*

A ----------> Polymer **B** ----------> Polymer **C**

(ii) Purification (ii) Purification

* Assume there is no backbone degradation during hydrolysis

A IR: 2180,1630, 890 cm^{-1}; UV: 207 nm $\in$ ~ 6000

B Mol. Wt.: 9500; IR: 2200 cm^{-1};

C Mol. Wt.: 11,400; IR: 3300 - 2500 (broad), 1730 cm^{-1}. **[6]**

b) Deduce the structure of any two of the following. Explain the given data. **[4]**

i) $C_8H_8O_2$ IR: 3300,1680,1605,1505, 850 cm^{-1};
UV : 270 nm $\in$ ~ 12000. Gives positive iodoform test.

ii) $C_7H_6O_2$ IR: 1760, 1595,1495,760,690 cm^{-1};

iii) C_5H_8O IR: 2720 (w), 1695,1630, 800;
UV: 233 nm $\in$ ~ 8000.

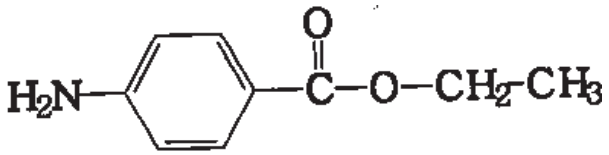
P.T.O.

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

a) Identify the seven isomers of cyclic ketones ($C_6H_{10}O$) from the proton NMR data given below, giving reasons.

Isomer **A** has only two singlets in 3 : 2 ratio while isomer **B** contains 6H, singlet and two other triplets each of 2H. Isomer **C** has three sets of signals and no methyl group. Isomer **D** and **E** each have only one methyl which is a triplet. Of these **D** can be resolved into enantiomers but **E** cannot. Isomer **F** and **G** both have only one methyl (3H). In both of these the methyl is a doublet. The methyl group of **F** is at a lower field than that of **G.**

b) Make a neat sketch of the proton NMR of the possible polymer raw material **1.** Consider chemical shifts, multiplicity, integration, coupling constants, intensity of the lines within a multiplet and comparative intensity of different lines of different multiplets.



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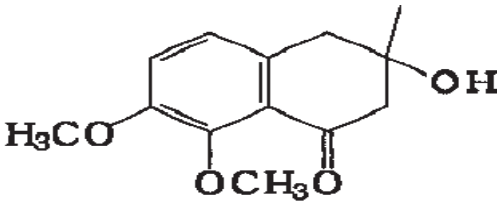
Q3) Attempt any two of the following: **[12]**

a) Identify six isomers of olefins with the formula C_6H_{12} based on the CMR data. Isomer **A** has only two signals while **B** has only three signals.

Isomer **C** and **D** both only have four signals. Isomer **C** has q (2C), t (2C), t, s while **D** has q (3C), s, d, t. Isomers **E** and **F** both have five signals. The pattern in E is q (2C), t, d, t,d while **F** has q (2C), q, d, d, d. Note the signals underlined correspond to those above 100 ppm.

b) Assign the signals seen in the CMR spectrum of 2, giving reasons.

29.2, 37.7*, 54.1*, 55.9, 56.3, 70.8 (w), 110.5, 116, 122 (w), 131.5 (w), 154.0 (w), 157.7 (w), 196.0 (w). * These signals are triplets in off resonance.



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c) Deduce the structure of a compound $C_9H_{10}O_2$ from the CMR signals given below. Assign the signals. Explain your answer.

22, 67,128.2, 128.3 (st), 128.6 (st), 137, 172

DEPT 1: 22,128.2,128.3,128.6 all up; 67 down; 137,172 both absent.

DEPT 2: 128.2,128.3,128.6 all up.

Q4) Deduce the structure of a compound $C_6H_{10}O$ from the spectral data. Assign the CMR and ^{1}H-NMR signals. Explain your answer. **[8]**

UV: 235 nm $\epsilon \sim 9100$; IR: 1695,1620, 805 cm^{-1}.

CMR: 21, 28, 32,124,156,198

DEPT 1: 21, 28, 32,124 all up; 156 and 198 both absent.

DEPT 2: 124 up

^{1}H-NMR: 1.74 (d, J = 2.75 Hz, 12 mm); 1.98 (d, J = 2.55 Hz), 2.02 (s, integration with 1.98, 24 mm) ; 5.96 (narrow multiplet , 4 mm).

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

O-H 3600 (free)	NH 3300	≡ C-H 3300
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	- C(=O)-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

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, RCONHR , 165-180 RCOOH	RCOR, RCHO,190-210	

SECTION - II

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

a) Compare the absorption and fluorescence techniques of X-ray analysis in the detection of impurities in polymers.

b) Write a note on the x-ray diffraction pattern for polyethylene. How is the repeat distance along a polymer chain be estimated ?

c) Write a note on the significance of dichroic ratio and infrared dichroism and information obtainable from dichroism of absorption bands?

d) Write a note on the factors affecting the accuracy of thermogravimetric measurement for polymer structure analysis.

e) Sketch and explain the X ray diffraction pattern for oriented and unoriented poly oxymethylene. Define and explain birefringence.

f) Discuss Freeman Carroll method to determine kinetic parameters of polymer degradation by use of TGA.

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

a) Explain the powder camera method used to study X ray diffraction pattern of polymers.

b) Discuss the importance of preliminary tests for identification of a polymeric sample.

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

d) Explain principle of TEM analysis for polymer characterization.

e) Citing suitable examples, discuss the factors affecting TGA curves.

f) Draw and explain DTA curve showing Tg = 65°C, Tm = 210°C and degradation above 340°C.

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Total No. of Questions : 4]

SEAT No. :

P455

[Total No. of Pages : 2

[4328] - 401
M.Sc. (Semester - IV)
POLYMER SCIENCE
PS - 404 : Special Topics
(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 any four of the following: **[20]**

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

b) Explain the difficulties in recycling PVC?

c) Describe the different polymer recycling processes? Write a note on "green" recycling of beverage bottles.

d) Discuss the role of protecting groups in the synthesis of functional polymers by anionic polymerization.

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

f) Suggest polymers for artificial heart, artificial skin and kidney. Justify your choice.

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

a) What are essential features of biodegradation? Describe the accepted mechanisms of biodegradation.

P.T.O.

b) Enlist the factors that accelerate biodegradation. What are the methods to study the degradation of polymers?

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

d) Describe applications of polymeric materials filled with conducting fillers. What are the property requirements of conducting filler?

e) Explain why polyacrylamide and xanthan gum are used in oil recovery.

f) Discuss polymeric nanocomposites and enlist their applications.

SECTION - II

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

a) Write a note on Fick's law or Ferry's Laws and explain the various terms.

b) Discuss mechanism of reverse osmosis employing polymer membranes.

c) Describe ultrafiltration , microfiltration and nanofiltration using polymeric membranes.

d) Describe the term "liquid crystallinity". Compare and contrast lyotropic and thermotropic polymers.

e) Describe different factors affecting liquid crystallinity in polymers.

f) Discuss the factors on which the viscosity of water soluble polymers depends.

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

a) Describe the principles of Green Chemistry and their relevance to polymers.

b) Describe the attributes of green solvents in organic synthesis.

c) Write a note on chemical modification of polymers to obtain functional polymers.

d) Describe various applications of nanomaterials using polymer matrix.

e) What are hydrogels? How are they classified? Enlist their applications.

f) What do you understand by LCST and UCT in polymer blends?

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Total No. of Questions : 4]

SEAT No. :

P456

[Total No. of Pages : 2

[4328] - 402
M.Sc. (Semester-IV)
POLYMER SCIENCE
PS - 410:Polymer processing
(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 any four of the following: **[20]**

a) Bring out the advantages of reciprocating screw injection molding over ram based injection molding.

b) Describe the significance of flight angle, root diameter and pitch in designing a screw in extrusion.

c) Write a short note on RIM and RRIM.

d) Describe the different roller arrangement in a calendering process.

e) Describe the defects and their causes in injection molding.

f) What are the defects that occur in transfer molding? Suggest measures to overcome them.

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

a) What are the sources of variation in thickness in the product formed by thermoforming?

P.T.O.

b) Explain the need and role of different additives for polymers. Explain the role of plasticizers giving examples.

c) Describe the different Zones in the barrel of an extruder. Explain the variation in the screw in each zone.

d) With the help of a neat diagram explain co-rotating twin screw extruder.

e) Describe the preparation of any one synthetic fiber. Give three examples of synthetic fibers.

f) Write a short note on preparation and application of non - woven fiber.

SECTION - II

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

a) Define (i) continuous filament, (ii) staple fiber, (iii) Denier, (iv) tenacity, and (v) crimp. Explain the terms with suitable examples.

b) Compare the processes of wet spinning and dry spinning. Give examples.

c) What fiber properties are important in textile uses?

d) Write short note on fiber-after treatment.

e) Draw and explain stress-strain curve for silk like and wool like fibers.

f) Describe preparation and applications of non woven fibers.

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

a) Enlist the property changes achieved by vulcanization.

b) Explain master batching. Give instances where master batching is practiced in Industry.

c) Define and explain the terms moisture content and moisture regain of fiber.

d) Explain the importance of molecular weight ratio and temperature in melt spinning.

e) Discuss the criteria for selecting a polymeric process for obtaining polymeric object.

f) Describe sorching of rubber. Explain the conditions leading to sorching.

■■■

Total No. of Questions : 4]

SEAT No. :

P457

[Total No. of Pages : 2

[4328] - 403

M.Sc. (Semester - IV)

POLYMER SCIENCE

PS - 411: Rheology and Mechanical Properties of Polymers

(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 any four of the following: **[20]**

a) Explain the terms : i) Bingham plastic, ii) Weissenberg effect, iii) Zero- shear viscosity, iv) Deborah number, and v) Shear thickening.

b) Explain relaxation and retardation in polymeric materials.

c) Write a note on dynamic mechanical model for testing polymeric materials.

d) With the help of neat diagrams, describe i) hard and brittle, ii) hard and strong, iii) hard and tough, iv) soft and weak, v) soft and tough polymers.

e) Write a short note on power law model.

f) Explain the usefulness of shear thinning in processing.

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

a) What is the role of branching and stereoregularity of polymers on the rheological properties?

b) What is storage modulus with respect to polymers?

c) Describe cone and plate viscometer. What is its scope and limitation in the study of rheology of polymers?

P.T.O.

d) Explain stress strain behaviour of i) strong and soft, and ii) strong and brittle polymeric materials.

e) Write a note on the process of creep and stress relaxation.

f) Write a note on relevance of viscoelastic properties for polymers.

SECTION - II

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

a) Write a short note on mechanism of adhesion of a substrate to metal, wood and paper surface.

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

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

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

e) What is the difference between paint and varnish?

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

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

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

b) What techniques are used for testing of paints and varnishes?

c) Discuss the significance of polylactic acid as a packaging material in various commercial applications.

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

e) Discuss the property requirements of polymers for packaging of food, fruit and vegetables.

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

■■■

Total No. of Questions : 6] **SEAT No. :**

P448 **[Total No. of Pages : 4**

[4328] - 41

M.Sc.

POLYMER SCIENCE

PS - 410 : Analysis & Testing of Polymers

(2004 Pattern)

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.***

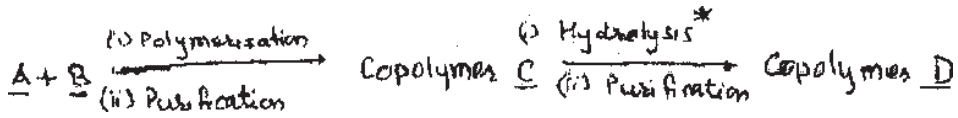
SECTION - I

Q1) a) Deduce the structures of the monomers A and B and that of copolymers C and D from the data given below. Infer the ratio of A to B in the copolymer C. Explain your answer. **[7]**

Monomer A ($C_{10}H_{12}$) : IR - 1635, 1595,1505, 965, 760 UV 245 nm. $\varepsilon > 8000$
Monomer B (C_4H_5N) : IR 2180, 1630, 895, UV 212 nm $\varepsilon > 8000$

Copolymer C mol wt 9460, IR 2210 cm^{-1}

Copolymer D mol wt 9640, IR 3300 to 2500 broad 1725 cm^{-1}



* Assume no backbone degradation.

b) Answer any one of the following. **[3]**

i) Deduce the structure of a compound with molecular formula $C_5H_{10}O$ which gives positive iodoform test and shows IR bands at 3300, 1635, 985 and 915 cm^{-1}, Assign the IR bands and explain your reasoning.

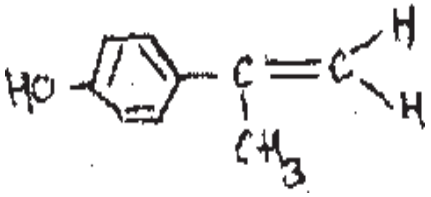
ii) Explain the IR frequencies given below:

RCOC1 1780; RCOOR' 1735; $RCOCH_3$ 1715; $R'CONR_2$ 1660 cm^{-1}

P.T.O.

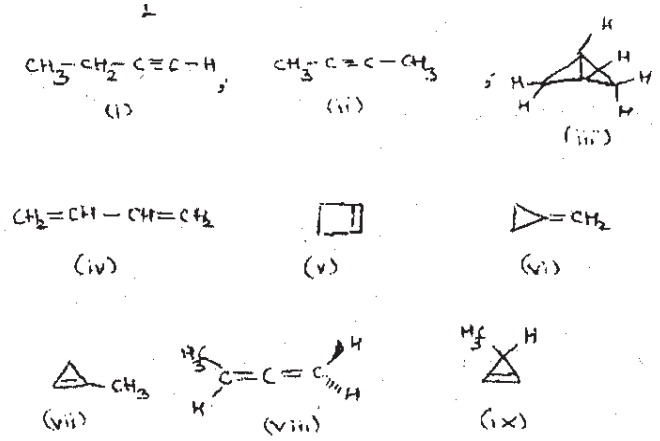
Q2) Answer any two of the following. **[10]**

a) In the presence of alkali at temperatures above 150°C, bisphenol A decomposes into 1. Make a neat sketch of the ^1H NMR of 1. Consider chemical shift, multiplicity, coupling constants, intensity of lines within a multiplet and intensity of lines of different multipliets.



b) The nine isomers of C_4H_6 are shown below. Identify these from their ^1H - NMR behaviour.

A shows only one line; B and C show two sets of signals in a 2:1 ratio, B shows major signal at ~ 1.5 δ ppm whereas in C this signal is at ~ 2.2 δ ppm, Isomers D to I all show three sets of signals . D has no signal upfield of 4.5, D and F has no signal downfield of 4.5, E has a signal fro at ~ 1.0 (t, 3H). G, H and I show 1,2 and 3 hydrogens respectively in the region downfield of 4.0.



c) Identify the compounds given below in which all peaks are singlets in ^1H NMR i) C_3H_3C1only two peaks ii) C_3H_9N only one peak iii) C_5H_{12} only one peak iv) $C_4H_{10}O$ only two peaks v) $C_5H_{10}O$ only two peaks.

Q3) a) Identify nine isomers (neglecting stereoisomers) of $C_6H_{14}O_2$ all containing two OCH_3 groups from the CMR data given below. Explain your answer. **[9]**

Isomers A and B both show only three signals, each signal corresponds to two carbons, A shows q, t, t while B has q,q,d. Isomers C and D both show only four signals. In C these are q(st), q, t(st), d while D has q(st) q (st), d, d.

Isomer E, F, G each show only five signals E has q (st), q,q,t, s; F has q(st), q q, t, s, while G shows q (st), q, t, t, d.

Note that the most downfield carbon of D is at ~ 100

Isomer H and I both show six signals as q, q, q, t, t, d. In H the ^{1}H-NMR shows one methyl (t, ~0.9) while I shows one methyl (d, ~1.2) in CMR q, t, d, s indicates multiplicity in off resonance; st is strong.

b) Answer any one of the following . **[4]**

i) Identify the two compounds from the CMR data, comment on the chemical shifts of each compound and the difference in chemical shift of the two compounds.

C_4H_4N – 25.7 (t), 47.1 (t); $C_5H_{11}N$ – 24.6 (t), 48.6 (q, 56.7) (t)

ii) Deduce the structure of a compound $C_8H_8O_3$ from its CMR spectrum. Assign the signals

52.3, 112.9, 117.4, 119.4, 130.4, 135.9, 162.4, 170.9

DEPT - 1: 52..3, 117.9, 119.4, 130.4, 135.9 all up; 112.9, 162.4,170.4 absent

DEPT - 2: 117.9, 119.4, 130.4, 135.9 all up

Q4) Deduce the structure of an important polymer raw material (C_3H_6O) from its spectral data. Assign the spectral data. Comment on the chemical shifts in ^{1}H and ^{13}C NMR. Explain the coupling seen in ^{1} H-NMR. **[7]**

IR-no significant peak above 1500 cm^{-1}

CMR: 13.1 (q), 47.3 (t), 47.6

^{1}H -NMR: 1.32 (d, J= 6 Hz, 15mm); 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 (dd q, J = 2.5, 3 and 6Hz, 5 mm)

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

O-H	3600 (free),	N-H	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

$R\text{-}CH_3$	10-30,	R_2CH_2	25-40,	$R_3\text{-}CH$	30-50,
$H_3C\text{-}O$	53-75,	$C \equiv C$	75-100,	$C \equiv N$	110-125,
Benzene	128.5,	C=C	100-140,	C=N	145-162,
RCOOR, $RCOCH_2$/RCOOH		165-180		RCOR/RCHO	190-210,

SECTION - II

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

a) Sketch and explain the X ray diffraction pattern for oriented and unoriented polyoxymethylene. Define and explain birefringence.

b) What are the dielectric properties of polymers? Discuss one method for determination of dielectric constant of polymer.

c) Why it is relevant to analyse for elements in polymers?

d) What are the difficulties encountered in identifying polymers? Explain how burning test and solubility of polymer are useful?

e) Discuss X ray diffraction method for determination of crystallinity of polymer.

f) Explain in detail principle of SEM analysis of polymers.

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

a) Discuss the principle and the applications of thermogravimetric analysis for the study of polymers.

b) How DTA and DSC techniques could be used to supplement the information obtained from TGA of polymer? Explain with examples.

c) Draw a typical DSC curve for a polymer having Tg 65 degrees, Tm 265 degrees, and decomposition temperature of 320 degree centigrade. Comment on the endo / exo transitions.

d) Differentiate between dynamic and isothermal TG analysis.

e) How will you determine the kinetic parameters from the thermogravimetric curve of a polymer?

f) Describe the determination of crystallinity in polymers using DSC.

■■■

Total No. of Questions : 4]

SEAT No. :

P449

[Total No. of Pages : 2

[4328] - 42

M.Sc. (Semester-IV)

POLYMER SCIENCE

PS - 411: Structure and Properties of Bulk Polymers

(2004 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 tables / Calculators is allowed.***

SECTION - I

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

a) Atactic polystyrene shows a transition, designated Tl,l at about l60 degree C. How is it different from the Tg? Name some other polymers in which similar transition is found to occur.

b) What is Schotzki crankshaft transition? Give examples of polymers which display this type of transition.

c) What structural parameters influence the melting point of a polymer?

d) Write notes on i) Internal plasticization, ii) external plasticization.

e) Discuss the various factors which affect the crystallisability of polymers with suitable examples.

f) Describe a method to determine the degree of crystallinity in semicrystalline polymer.

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

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

P.T.O.

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

c) What is the effect of crystallization temperature on the fold length.

d) Write notes on i) spherullites, ii) cold drawing.

e) What is Tg? Explain with a suitable diagram the dilatometric method for the determination of Tg in polymers.

f) Explain the effect of molecular weight of polymer on Tg of polymer.

SECTION - II

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

a) What are traditional ways of joining materials? What are their disadvantages?

b) Write an account of naturally occurring polymers used as adhesives.

c) Describe selection criteria for material to be used as adhesive.

d) Describe the adhesive used in the field of furniture. Justify the selection.

e) What are different adhesives used in leather industry?

f) The importance of particle size and shape in selecting pigment for paint formulation.

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

a) Discuss importance of barrier properties of surface coatings, with special emphasis on oxidation and protection from atmospheric moisture and corrosive gases.

b) Enlist different components used in paint formulation. Comment on purpose of each component.

c) Suggest polymeric materials for 'three layer pack'. Give the function of each layer.

d) Discuss the property requirements for polymer to act as packing material.

e) Discuss importance of ecofriendly packaging polymeric materials.

f) Describe the preparation of BOPP. Write its importance as packaging material.

■■■

Total No. of Questions : 4]

SEAT No. :

P450

[Total No. of Pages : 3

[4328] - 43

M.Sc. (Semester - IV)

POLYMER SCIENCE

PS - 404 : Special Topics in Polymer Science

(2004 Pattern)

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 table / Calculator is allowed.***

SECTION - I

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

a) Describe the method of polymeric waste management to generate energy. Comment on the pollution during energy generation.

b) Discuss economic aspects of polymer recycling.

c) Addition polymers are generally not susceptible to biodegradation. Why?

d) Discuss the influence of polarity, aromaticity, crystallinity and crosslinking on the biodegradability of polymers.

e) Compare the strategies of obtaining functional polymers by 'spacer arm' technique, and chemical modification route.

f) Describe different applications of functional polymers in material science.

P.T.O.

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

a) Write a brief note on classification of LCPs.

b) Discuss influence of kinks, substitution and aromaticity on liquid crystallinity of polymers. Elaborate the answer with suitable examples.

c) What are experimental methods of studying polymeric blends and their miscibility?

d) Explain factors influencing miscibility of polymeric blends. What is the effect of melt blending, emulsion blending and solution blending on miscibility of the polymeric blend thus obtained.

e) Explain influence of limiting oxygen index, bond dissociation energy and crystallinity on inherent thermal stability of polymers.

f) What are the difficulties in processing thermally stable polymers such as polyimides? How are these difficulties overcome?

SECTION - II

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

a) Why polymeric materials are of importance in biomedical applications?

b) Suggest the polymers for blood veins and arteries, sutures and adhesives to treat deep wounds.

c) What is the selection criteria for engineering applications of plastics?

d) Discuss preparation and important applications of polyether ether ketones as engineering plastics.

e) What are polymeric membranes? Discuss mechanism of separation of suspended and dissolved low molecular weight substances in liquids using polymeric membranes.

f) Discuss applications of polymeric membranes in gas separations.

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

a) Discuss importance of polymeric materials for various controlled release applications.

b) What are solitons and polarons? How this concept is used for explaining conduction mechanism in inherently conducting polymers.

c) Discuss applications of inherently conducting polymers.

d) Discuss use of polymeric materials in the development of engineering composites.

e) Write importance of epoxy resins in composites.

f) Write a note on Fick's law and Ferry's law in separation process.

■■■

Total No. of Questions : 4]

SEAT No. :

P736

[Total No. of Pages : 2

[4328]-31
M.Sc.
POLYMER SCIENCE
PS - 310 : Kinetics and Mechanism of Polymerization Processes
(2004 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 any four of the following : **[20]**

a) With a suitable example, discuss the importance of stoichiometric ratio of the reactants in step growth polymerization.

b) With a suitable example discuss the effect of by - product removal on the molecular weight built up of the polymer formed in step growth polymerization.

c) 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.

d) Bring out the differences between chain growth and step growth polymerizations.

e) Discuss the role of monofunctional and trifunctional monomers in step growth polymerization? How will it affect gel point?

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

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

a) Write in detail the cationic mechanism of addition polymerization.

b) Explain the mechanism of anionic polymerization.

c) Define chain transfer agents? What is the role of a CTA on the rate expression and molecular weights obtained in a chain transfer agent.

d) Discuss the role of retarders in radical polymerization process.

e) Enlist assumptions made for deriving rate expression for typical polyesterification reaction. Describe its suitability based on experimental evidences.

f) Describe the effect of temperature and pressure on chain polymerization.

P.T.O.

SECTION - II

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

a) Write a short note on living radical polymerization.

b) Discuss ring opening polymerization.

c) Discuss the role of solvents in cationic and anionic polymerizations.

d) Describe the structure of Ziegler - Natta catalyst used in co-ordination polymerization of olefins. Write the mechanism of polymerization of olefins when Zieger - Natta catalyst is used.

e) Explain in detail , the role of ion pairs on cationic and anionic polymerization.

f) Write a note on how to increase the rate of radical polymerization by a factor of two.

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

a) Write a note on the advantages of "Q and e" scheme in copolymerization. Enlist the limitations.

b) Vinyl cinnamate forms copolymer very easily with vinyl acetate. It does not form copolymer readily with acrylic acid. Explain this phenomenon. Write the structure of the copolymer formed when vinyl acetate reacts with acrylic acid.

c) Discuss graphical method of determining reactivity ratio in binary copolymerization. Enlist the limitations.

d) For estimating reactivity ratios, most of the methods require very low conversions in the copolymerization reactions. Why? Justify the answer with suitable examples.

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) Write a note on alternate copolymer formation tendency in certain monomer pairs.

♦♦♦♦

Total No. of Questions : 4]

SEAT No. :

P737

[Total No. of Pages : 4

[4328]-32
M.Sc.
POLYMER SCIENCE
PS - 311 : Synthesis, Structural Aspects, Properties and Applications of Polymers
(2004 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 any four of the following : **[20]**

a) Write the structure of lignin. What are the different types of bonds joining chains? What happens when pulp is sulfated? How is lignin removed? Why is the process called sulfate pulping?

b) In the process of making cellulose nitrate, explain the following.

i) Dried cellulose is stirred with an acid mixture containing HNO_3 (25%), H_2SO_4 (55%) and water (20%) at 30-40°C for 20-60 minutes.

ii) The product is then centrifuged and dropped in drowning tank.

iii) Washed with water.

iv) Product is boiled with water for several hours.

v) Then treated with NaOCl and washed with water.

c) With respect to polyurethanes, please comment and explain the following :

i) Reactions of polyols with diisocyanates are more widely used than reactions of diols with polyisocyanates.

ii) Hydroxyl terminated polyethers are preferred to hydroxyl terminated polyesters.

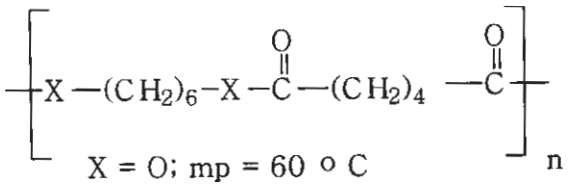
iii) The structural differences when diols or polyols react with diisocyanates.

P.T.O.

d) Explain the following regarding nylon 6.

i) Nylon 6,6 and nylon 6 are used as fibers, nylon 6,10 and nylon 11 are used as surgical sutures and brushes;

ii) Melting points are given below.

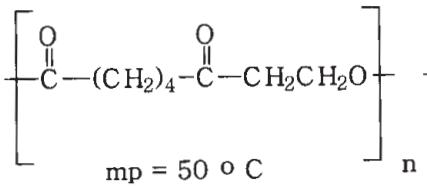


X = O; mp = 60 °C

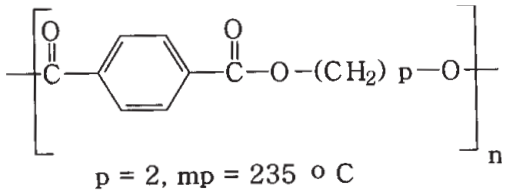
X = NH; mp = 265 °C

X = NCH_3; mp = 166 °C

e) Is there a relation between the structure and m.p. for the polymers shown below? Please write the structures of monomers required for each of these polymers.

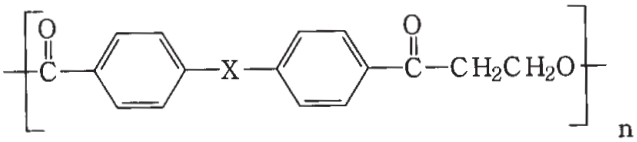


mp = 50 °C



p = 2, mp = 235 °C

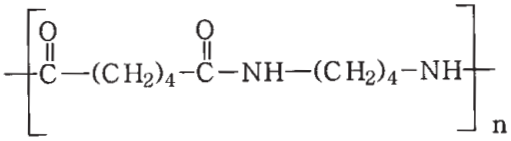
p = 4, mp = 265 °C



X = $(CH_2)_4$, mp = 170 °C

X = OCH_2CH_2O; mp = 240 °C

X = NH-$(CH_2)_2$-NH, mp = 270 °C



mp = 295 °C

f) Explain the following regarding aromatic polyamides.

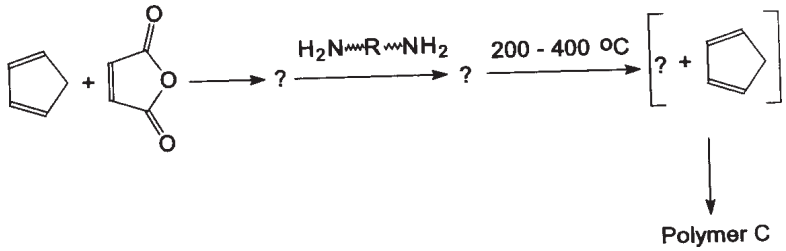
i) These have not gained commercial importance of aliphatic polyamides mainly because of production and processing difficulties.

ii) How are these polymers prepared by interfacial polymerization?

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

a) How are the aromatic polyamides Nomex and Kevlar prepared? What are their advantages? Where are these used? What are their drawbacks?

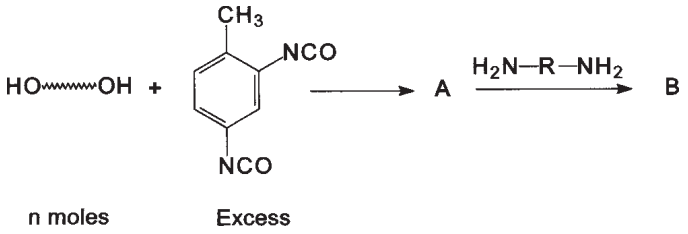
b) Complete the reactions shown below. The polymer C obtained is called PMR explain.



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) 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?

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) The composition of four typical hydroxyl terminated polyesters are given below. Based on these indicate the structural change and use of the resulting polyurethanes for each of the compositions. Comment on the molar proportion of the components in the composition. Explain your answer.

Composition (i) Adipic acid (AA) 1.0; ethylene glycol 0.75, propylene glycol 0.35;

Composition (ii) AA 1.5, sebacic acid 1.5, diethylene glycol DEG 3.25, glycerine (Gl) 0.5;

Composition (iii) AA 3.0, 1,3 butanediol 3.0, Glycerine 1.0;

Composition (iv) AA 3.0, DEG 2.0, trimethylol propane 3.0.

SECTION - II

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

a) Describe a method for controlling the molecular weight of epoxy prepolymers. Is it necessary to control the molecular weight of the prepolymer?

b) Write a note on resol polymers. How does the ratio of phenol to formaldehyde affect the properties of the polymer formed?

c) Discuss briefly the preparation and chemical modifications of melamine formaldehyde resin. Write its important applications.

d) What is the role of aliphatic and aromatic polyamines in the curing of epoxy resins? What are the differences in the adhesive properties of these adhesives?

e) Compare and contrast the crosslinking reactions in phenol - formaldehyde and urea - formaldehyde resins.

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

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

a) Give a synthetic method for the preparation of
   i) acrylonitrile,
   ii) methyl methacrylate,
   iii) styrene, and
   iv) vinyl chloride

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

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

d) Write a short note on Ziegler - Natta Catalyzed manufacture of polyethylene.

e) Explain briefly the formation of stereoregular polypropylenes in the polymerization of propylene. Explain the role of tacticity on the properties of polypropylenes.

♦♦♦♦

Total No. of Questions : 4]

SEAT No. :

P738

[Total No. of Pages : 2

[4328]-33
M.Sc.
POLYMER SCIENCE
PS - 312 : Polymer Processing
(2004 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 any four of the following : **[20]**

a) Write a note on the role of a compounder in rubber industry.

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

c) Discuss the mechanism of vulcanization. Enlist the resulting properties.

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

e) Describe the stress - strain behaviour exhibited by

   i) unvulcanized rubber,

   ii) vulcanized rubber and

   iii) vulcanized rubber with filler.

f) Write a short note on Branbury mixing.

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

a) Enlist the different methods of spinning synthetic fibers. Describe any one method in details.

b) Enlist the merits and demerits of compression molding over other processes to get a similar product.

c) Discuss the following : Denier, tenacity, moisture content, and crimp.

d) Describe preparation and applications of non woven fiber.

e) Describe

   i) dye take up,

   ii) mercerization of finished fiber.

f) Define and explain scouring and lubrication.

P.T.O.

SECTION - II

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

a) Citing examples, describe the role and action of UV stabilizers in polymers.

b) Write design characteristics of object obtained by compression molding. Discuss advantages and disadvantages of compression molding.

c) Explain the need of twin screw in extrusion. Describe its advantages over single screw extrusion.

d) Explain in brief, the principal behind the processes of injection molding, reaction injection molding, reinforced reaction injection molding.

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

f) Extrusion process is a versatile process. Explain.

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

a) Discuss the advantages of reciprocation screw injection molding over ram based injection molding process.

b) With the help of neat diagrams, explain blow molding process.

c) What is pultrusion? Give important applications.

d) Discuss effect of variation in number of rollers and their arrangement in the process of calendering.

e) Describe any one process of obtaining an object with large internal hollow space.

f) Write a short note on thermoforming.

♦♦♦♦

Total No. of Questions : 4]

SEAT No. :

P739

[Total No. of Pages : 2

[4328]-34
M.Sc.
POLYMER SCIENCE
PS - 313 : Polymer Chains and their Characterisation
(2004 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 any four of the following : **[20]**

a) Define solubility. Enlist the factors on which solubility of a polymer depends.

b) Write a note on determination of solubility parameter of polymers.

c) Discuss

i) size of linear and branched polymer of identical molecular weight and

ii) solubility of crystalline and amorphous polymers.

d) Discuss theta temperature and virial coefficients.

e) Write a note on LCST and UCST. Where is this useful?

f) Explain Flory - Huggins theory and enlist the assumptions.

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

a) Define hydrodynamic volume and excluded volume. What is the origin of excluded volume?

b) Write a note on the random flight probability model to depict a polymer in motion.

c) Write a note on non - ideal polymer solutions.

d) Discuss radiation induced polymerization in

i) removal of monomer,

ii) polymer modification, and

iii) grafting.

e) Write a note on radiation curing of polymers. Enlist their industrial applications.

P.T.O.

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.

SECTION - II

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

a) Explain the terms :
   i) Shear thickening,
   ii) Elongational flow,
   iii) Weissenberg effect,
   iv) Bingham plastic,
   v) Viscosity.

b) Explain Voigt model. What phenomenon is explained by this model.

c) Explain the process of creep and stress relaxation.

d) Discuss the rheological properties of a solid and that of polymer melt.

e) With neat diagrams discuss :
   i) hard and brittle,
   ii) hard and strong,
   iii) soft and weak, and
   iv) soft and tough polymeric materials.

f) Write a note on Hook's equation and Newton's equation for polymeric materials.

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

a) Discuss the power law model.

b) Discuss cone and plate viscometer. What is the scope and limitation in the study of rheological behaviour of polymer melt?

c) Write a note on storage and loss modulus with respect to polymeric materials.

d) Write a note on die swell and shark skin in polymer rheology.

e) Explain the principle of time - temperature super position.

f) What is the effect of molecular weight and molecular weight distribution on viscosity and zero shear viscosity.

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