[103] SEAT No.________ No of Printed Pages: 04

SARDAR PATEL UNIVERSITY

M.Sc. (Industrial Polymer Chemistry), Semester – IV, Examination

Mon sday, 18th March, 2019

PS04CIPC21 - Spectroscopy of Polymers-II

Time: 02:00 – 05:00 PM **Maximum Marks – 70**

Q.1 Select the correct answer from the choices given below for each of the following question **[08]**

(a) Which of the following ions appears at non-integral m/z values?
(i) Molecular ions only (ii) Fragment ions only
(iii) Fragment ions and metastable ions (iv) Metastable ions only

(b) Which of the following molecule will show two peaks at higher m/z values with intensity ratio 1:1/3 in mass spectrometry?
(i) Bromobenzene (ii) Chlorobenzene (iii) Benzene (iv) Acetylene

(c) Which of the following is the characteristic vibrations for C-H bending of alkyne?
(i) 2230 cm^{-1} (ii) 900 cm^{-1} (iii) 650 cm^{-1} (iv) 1650 cm^{-1}

(d) Which of the following band is a symmetry forbidden electronic transition?
(i) $\sigma\rightarrow\sigma^*$ (ii) $\pi\rightarrow\pi^*$ (iii) $n\rightarrow\pi^*$ (iv) All the above

(e) Which of the following peak is observed for DMSO-d_6 residual solvent in the ^{1}H-NMR spectrum?
(i) 7.15 (ii) 2.49 (iii) 1.5 (iv) 7.26

(f) How many types of protons are present in the 1,2-dichloropropane?
(i) 2 (ii) 3 (iii) 4 (iv) 6

(g) How many signal will be observed in the ^{13}C-NMR spectrum of anthracene?
(i) 2 (ii) 4 (iii) 7 (iv) 12

(h) Which of the following 2D-spectroscopy is useful to study ^3J or ^4J ^{1}H-^{13}C couplings?
(i) HMBC (ii) COSY (iii) HMQC (iv) INADEQUATE

Q.2 Answer ANY SEVEN. **[14]**

(a) Why the UV-visible spectra of 2,2'-dimethyl biphenyl is similar to o-xylene?

(b) How the presence of amine group at para position affect the IR spectra of nitrobenzene?

(c) What are different relaxation processes in NMR spectroscopy?

(d) How axial and equatorial isomers of cyclohexanol can be distinguished by ^{1}H-NMR spectroscopy?

(e) How different anomers of glucose can be distinguished by ^{1}H-NMR spectroscopy?

(f) How primary, secondary, tertiary and quaternary carbons can be distinguished by DEPT techniques?

(g) Why ^{13}C-NMR spectra are more difficult to record than ^{1}H-NMR spectra?

(h) What is metastable ions?

(i) How many signals are expected in the mass spectrum of toluene? Assign the structure of fragments for each m/z value.

Q.3(a) Answer the followings. **[06]**

(i) Discuss different types of molecular vibrations observed when a molecule is irradiated by IR radiation.

(ii) Discuss different characteristic electronic transition in UV spectroscopy.

(P.T.O.)

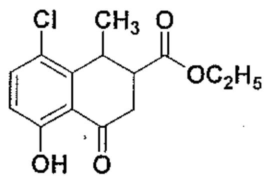
(b) Answer the followings. **[06]**

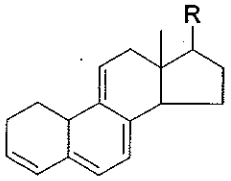
(i) Write a note on coupled interaction and Fermi resonance in IR spectroscopy with suitable examples.

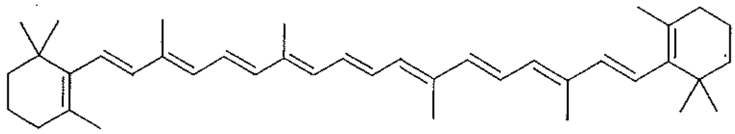
(ii) Explain different factors affecting the position of carbonyl group frequency in IR spectra of esters and lactones.

OR

(b) Calculate λ_{max} for the following compound. **[06]**







Q.4(a) Answer the followings. **[06]**

(i) Explain principle of NMR spectroscopy.

(ii) Write a note on chemical shift.

(b) Explain different method for simplification of complex NMR spectra. **[06]**

OR

(b) Discuss Nuclear Overhauser Effect by suitable example. **[06]**

Q.5(a) Answer the followings. **[06]**

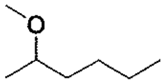
(i) What are the differences between HETCOR, HMQC and HMBC correlation spectroscopy?

(ii) How o, m, p-cresol can be distinguished by ^{13}C-NMR spectroscopy?

(b) Answer the followings. **[06]**

(i) Sketch ^{1}H-^{1}H COSY of ipsenol by taking approximate δ values.

(ii) Calculate chemical shift values for C atoms of following compound.

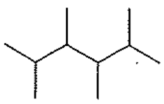


OR

(b) Answer the followings. **[06]**

(i) Sketch ^{13}C-^{1}H HETCOR and ^{1}H-^{1}H COSY of butanoic acid by taking approximate δ values.

(ii) Calculate chemical shift values for C atoms of following compound.



Q.6(a) Write a note on FAB and ESI techniques used in mass spectrometry. **[06]**

(b) Answer the followings. **[06]**

(i) Discuss the principle and derive the governing equation of mass spectrometry.

(ii) Explain Mclafferty rearrangement observed in mass spectrometry.

OR

(b) Answer the followings. **[06]**

(i) Discuss the general rules for predicting prominent peaks in EI-Mass spectra.

(ii) Determine the formula of fragment from the following mass spectrometry data.
m/z(abundance): 69(100), 70(1.1), 71

TABLE 4.12 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm). Carbon Atom of Substituents in parts per million from TMS^a

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	9.3	0.7	−0.1	−2.9	21.3
CH_2CH_3	15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	9.1	−2.4	0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C_6H_5	12.1	−1.8	−0.1	−1.6	
CH_2OH	13.3	−0.8	−0.6	−0.4	64.5
$CH_2O(C{=}O)CH_3$	7.7	−0.0	−0.0	−0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	26.6	−12.7	1.6	−7.3	
OCH_3	31.4	−14.4	1.0	−7.7	54.1
OC_6H_5	29.0	−9.4	1.6	−5.3	
$O(C{=}O)CH_3$	22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
$(C{=}O)H$	8.2	1.2	0.6	5.8	192
$(C{=}O)CH_3$	7.8	−0.4	−0.4	2.8	24.6 (CH_3), 195.7 (C=O)
$(C{=}O)C_6H_5$	9.1	1.5	−0.2	3.8	196.4 (C=O)
$(C{=}O)F_3$	−5.6	1.8	0.7	6.7	
$(C{=}O)OH$	2.9	1.3	0.4	4.3	168
$(C{=}O)OCH_3$	2.0	1.2	−0.1	4.8	51.0 (CH_3), 166.8 (C=O)
$(C{=}O)Cl$	4.6	2.9	0.6	7.0	168.5
$(C{=}O)NH_2$	5.0	−1.2	0.0	3.4	
$C{\equiv}N$	−16	3.6	0.6	4.3	119.5
NH_2	19.2	−12.4	1.3	−9.5	
$N(CH_3)_2$	22.4	−15.7	0.8	−11.8	40.3

(P.T.O)

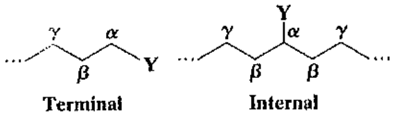
Table 5.1 The ^{13}C Shift Parameters in Some Linear and Branched Hydrocarbons

^{13}C Atoms	Shift (ppm) (*A*)
α	+9.1
β	+9.4
γ	−2.5
δ	+0.3
1° (3°)[a]	−1.1
1° (4°)[a]	−3.4
2° (3°)[a]	−2.5
2° (4°)	−7.2
3° (2°)	−3.7
3° (3°)	−9.5
4° (1°)	−1.5

Table 5.2 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

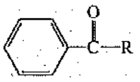
Compound	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

Table 5.3 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a] (+ left, − right)



	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+ 9	+ 6	+10	+ 8	−2
$CH{=}CH_2$	+20		+ 6		−0.5
$C{\equiv}CH$	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+ 3	+ 2	−2
COO^-	+25	+20	+ 5	+ 3	−2
COOR	+20	+17	+ 3	+ 2	−2
COCl	+33	+28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3^+	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3^+	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

TABLE 7.12
EMPIRICAL RULES FOR BENZOYL DERIVATIVES

Parent chromophore: 		
R = alkyl or ring residue		246
R = H		250
R = OH or Oalkyl		230
Increment for each substituent:		
—Alkyl or ring residue	*o, m*	3
	p	10
—OH, —OCH_3, or —Oalkyl	*o, m*	7
	p	25
—O^-	*o*	11
	m	20
	p	78
—Cl	*o, m*	0
	p	10
—Br	*o, m*	2
	p	15
—NH_2	*o, m*	13
	p	58
—$NHCOCH_3$	*o, m*	20
	p	45
—$NHCH_3$	*p*	73
—$N(CH_3)_2$	*o, m*	20
	p	85

Base value for homo-annular diene	253nm
Base value for hetero-annular diene	214nm
Increment for:	
• Double bond extending conjugation • Alkyl substituent or ring residue • Exocyclic double bond	+30nm +5nm +5nm
Polar groups (auxochrome): -OAc -OR -SR -Cl , -Br -NR_2	 +0nm +6nm +30nm +5nm +60nm

—x—