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Sardar Patel University

M.Sc.(Industrial Polymer Chemistry) Sem-III

PS03CIPC21: Spectroscopy of Polymers

Day & Date: Friday, 1st January 2021

Time: 10:00 a.m. to 12:00 noon

Max. Marks: 70

Q-1 (A) Answer the following **Multiple Choice Questions**. All questions are compulsory [08]

- 1) The valence skeleton vibration at $1,153\text{ cm}^{-1}$ in the IR spectrum of polypropylene corresponds to the...
 - a. Isotactic configuration
 - b. Syndiotactic configuration
 - c. Atactic configuration
 - d. Mixture of atactic and syndiotactic configurations
- 2) The measurement in the stereoregularity in the polymers by the assignment of an IR frequency to a particular isomer may be established by....
 - a. Correlation with the isomers of low-molecular-weight analogs
 - b. Assignments based on normal coordinate analysis
 - c. Comparison of absorbance with calculated values from other physical techniques such as NMR spectroscopy
 - d. All the above
- 3) Which of the following is an auxochrome?
 - a. Chlorine
 - b. Carbonyl
 - c. Ethylenic
 - d. Nitro
- 4) Which of the following statement is TRUE about UV-visible spectroscopy?
 - a. It refers to the part of the electromagnetic spectrum between the cosmic and γ -ray wave region.
 - b. Electronic transitions take place by absorption of UV-visible radiation by a molecule
 - c. Change in only rotational energy level takes place only by absorption of UV-visible radiation by a molecule
 - d. The spectrum consists of discrete lines.
- 5) How many signals does the furfuraldehyde molecule have in the ^1H NMR spectra?
 - a. 2
 - b. 3
 - c. 4
 - d. 5
- 6) Which of the following method is used for obtaining sharp line solid-state NMR?
 - a. Incoherent averaging
 - b. Dipolar decoupling
 - c. Dipolar interactions
 - d. Quadrupolar interactions
- 7) The chemical shift value of CDCl_3 in ^{13}C -NMR spectra is obtained at...

a. 77.0 δ ppm b. 67.0 δ ppm c. 39.7 δ ppm d. 118.3 δ ppm

- 8) Which of the following is an example of HOMO-correlation spectroscopy?
a. HMBC b. HMQC c. INADEQUATE d. ^{13}C - ^1H -COSY

Q-1 (B) Answer the following as directed. All questions are compulsory [16]

- 1) Which band in CO_2 is IR inactive?
- 2) Write the characteristic group frequency of the nitro functional group.
- 3) What is the amide-II band?
- 4) What is the effect of H-bonding to the $-\text{OH}$ stretching vibration of cyclohexanol?
- 5) What is Beer's law?
- 6) Give examples of chromophoric groups.
- 7) Define the hyperchromic effect.
- 8) Why cis-stilbene absorbs at 280 nm ($\epsilon = 13,500$) but trans-stilbene absorbs at 295 nm ($\epsilon = 27,000$)?
- 9) Give two examples of NMR inactive nuclei.
- 10) How many signals are obtained in the ^1H -NMR spectrum of 1,2-dichloropropane?
- 11) Which is the internal reference used for the sample scanned in D_2O in NMR?
- 12) Assign Pople notation for nitropropane.
- 13) What is the difference between HMQC and HMBC?
- 14) What is the function of Fourier Transform in NMR?
- 15) Give the multiplicity and position of $\text{DMSO}-d_6$ solvent in ^{13}C -NMR spectra.
- 16) What information can be gained by DEPT-135?

Q-2 Attempt any Seven from the following [14]

- 1) How ring strain affects the carbonyl stretching in cyclic ketone?
- 2) What are bending vibrations in IR spectroscopy?
- 3) How B-band differs in the UV-visible spectra of pyridine and benzene?
- 4) Give a comparison of K-band and B-band of benzene.
- 5) What are the relaxation processes in NMR?
- 6) Give brief about chemical shift equivalence by rapid rotation in the ^1H -NMR spectra of cyclohexane.
- 7) How anomeric structures of D-glucose can be differentiated by NMR spectroscopy?
- 8) What are the differences between HMQC and HETCOR?
- 9) Why ^{13}C -NMR spectra are more difficult to record compare to ^1H -NMR spectra?

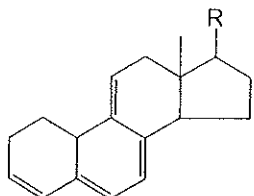
Q-3 Answer the following. [08]

- A) Write a note on characteristic group frequencies in the IR spectra of poly(methyl methacrylate) and polyvinyl alcohol. [06]
- B) What are the factors affecting the theoretical number of IR bands? [02]

OR

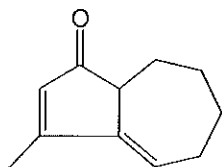
- Q-3 *Answer the following.* [08]
A) Write a note on applications of vibrational spectroscopy in polymer chemistry. [06]
B) Give brief about characteristic group frequencies in the IR spectra of poly(acrylonitrile). [02]

- Q-4 *Answer the following.* [08]
A) Write a note on electronic transition in UV-visible spectroscopy. [05]
B) Calculate the λ_{max} value of the following molecule. [03]



OR

- Q-4 *Answer the following.* [08]
A) How solvent polarity affects the UV-visible spectra of conjugated diene and α,β -unsaturated carbonyl compounds? [05]
B) Calculate the λ_{max} value of the following molecule. [03]



- Q-5 *Answer the following.* [08]
A) How tacticity of poly(methyl methacrylate) can be distinguished by NMR? [06]
B) Why the $^1\text{H-NMR}$ spectrum of DMSO shows separate signals for two methyl groups at room temperature? [02]

OR

- Q-5 *Answer the following.* [08]
A) Explain different methods for simplification of complex NMR spectra. [06]
B) What information can be gained by $^1\text{H-NMR}$ of polymers with small line width signals? [02]

- Q-6 *Answer the following.* [08]
A) Sketch $^1\text{H-}^1\text{H}$ COSY of *m*-dinitrobenzene by taking approximate δ values. [04]
B) Calculate chemical shift values for C atoms of *o*-chloroaniline. [04]

OR

- Q-6 *Answer the following.* [08]
A) Sketch $^{13}\text{C-}^1\text{H}$ HETCOR spectra of butanoic acid by taking approximate δ values. [04]
B) Calculate chemical shift values for C atoms of 2,2-dimethyl butane. [04]

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Table 5.1 The ¹³C 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°) ^a	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5

Table 5.2 The ¹³C 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 (+ l.f., - right)

Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+ 9	+ 6	+10	+ 8	-2
CH=CH ₂	+20		+ 6		-0.5
C≡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	+36	+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 ₂ ⁻	+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	<i>a, m</i>	3
	<i>p</i>	10
-OH, -OCH ₃ , or -Oalkyl	<i>a, m</i>	7
	<i>p</i>	25
-O ⁻	<i>a</i>	11
	<i>m</i>	20
-Cl	<i>p</i>	78
	<i>a, m</i>	0
-Br	<i>p</i>	10
	<i>a, m</i>	2
-NH ₂	<i>p</i>	15
	<i>a, m</i>	13
-NHCOCH ₃	<i>p</i>	58
	<i>a, m</i>	20
-NHCH ₃	<i>p</i>	45
	<i>a, m</i>	73
-N(CH ₃) ₂	<i>a, m</i>	20
	<i>p</i>	85

TABLE 7.7 EMPIRICAL RULES FOR ENONES

Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	<i>α</i>	10
	<i>β</i>	12
	<i>γ</i> and higher	18
Polar groupings:		
-OH	<i>α</i>	35
	<i>β</i>	30
	<i>δ</i>	50
-OCOCH ₃	<i>α, β, δ</i>	6
-OCH ₃	<i>α</i>	35
	<i>β</i>	30
	<i>γ</i>	17
	<i>δ</i>	31
-Cl	<i>α</i>	15
	<i>β</i>	12
-Br	<i>α</i>	25
	<i>β</i>	30
	<i>δ</i>	95
Exocyclic double bond		5
Homocyclic diene component		39

Empirical rules for diene

Base value for homo-annular diene	253nm
Base value for hetero-annular diene	214nm
Increment for:	
• Double bond extending conjugation	+30nm
• Alkyl substituent or ring residue	+5nm
• Exocyclic double bond	+5nm
Polar groups (auxochrome):	
-OAc	+0nm
-OR	+6nm
-SR	+30nm
-Cl, -Br	+5nm
-NR2	+60nm

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	21.5
CH ₂ CH 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≡CH	5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	12.1	-1.8	-0.1	1.6	
CH ₂ OH	13.3	0.8	0.6	-0.4	64.5
CH ₂ O(C=O)CH ₃	7.7	-0.0	-0.0	-0.0	20.7 (CH ₂), 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 ₆ H 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 ₆ H 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≡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