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SYNTHESIS AND NMR ANALYSIS OF COPOLYESTERS

SAYEEDA SULTANA*, S. GUNA SEKARAN and T. VENKATA RAMAN

Department of Chemistry, St. Peter's University, CHENNAI (T. N.) INDIA

ABSTRACT

Copolyesters contain more than one type of diol and diacid. In the present work, copolyesters based on succinoyl chloride with aliphatic and aromatic diols were synthesized by solution polycondensation method. The vibrational band assignment has been made for some of the specific modes of vibration observed from FTIR spectra. From the chemical shift values of ^{1}H NMR spectra, the repeating structural units present in copolyesters were assigned.

Key words : Copolyesters, FT-IR spectra, ^{1}H NMR spectra

INTRODUCTION

Polymer spectroscopy deals with the application of wide range of spectroscopic methods to study polymers. Infrared spectroscopy is useful both; for micro structural studies and for determination of major structural units in polymers. Much of literature[1, 2] were reported about the utility of IR spectra for the characterisation of polymers. Nuclear magnetic resonance spectroscopy is a powerful technique for polymer characterization. Many examples can be cited from the early literature including those attributed by Bovey[3]. Slomin and Urman[4] have used NMR spectroscopy to determine the composition and structure of copolyesters. In the present work, copolyesters were synthesized by the condensation of diol and diacid chlorides following the procedure given by Polk et al [5-7] and characterised by spectroscopic techniques.

EXPERIMENTAL

Synthesis of poly[oxy – (2, 3-butylene) –oxy-succinoyl – co-oxy – (1, 4- naphthyl) – oxy- succinoyl] (PBNS)

A 500 mL three necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer and reflux condenser with guard tube was charged with1 mole

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[*] Author for correspondence

of 1, 4 -dihydroxy naphthalene, 2 moles of 2, 3-butane diol, , 3 moles of succinoyl chloride and 250 mL of 1, 2-dichlorobenzene. The mixture was heated to reflux for 25-30 hrs at 140-160 ºC in nitrogen atmosphere with constant stirring and cooled to get pure dull black copolyester. The yield was 65-70 %.

Synthesis of poly [oxy– (diethylene) –oxy- succinoyl – co-oxy –(1, 4 -naphthyl) – oxy- succinoyl] (PDNS)

In the same experimental set up as above, a mixture of 1 mole of 1, 4-dihydroxy naphthalene, 2 moles of diethylene glycol, 3 moles of succinoyl chloride and 250 mL of 1, 2-dichlorobenzene was heated to reflux for 25-30 hrs at 140-160 ºC to get PDNS.

RESULTS AND DISCUSSION

FTIR Spectral analysis

The IR spectra of copolyesters were recorded using Perkin-Elmer spectrophotometer in the frequency region 4000-500cm^{-1}. KBr pellet technique was employed for recording the IR spectra of copolyesters. The vibrational frequencies assigned for the copolyesters PBNS and PDNS are summarized in Tables 1 and 2.

Table 1 : IR Spectrum and vibrational band assignment of PBNS

Frequency (cm^{-1})		Vibrational band assignment
IR	Intensity	
3600	w	Free –OH group
3057	m	Aromatic C-H asymmetric stretching
3011	m	Aromatic C-H symmetric stretching
2961	m	Aliphatic C-H asymmetric stretching
2890	m	Aliphatic C-H symmetric stretching
1698	vs	>C=O stretching of ester group
1623	w	C⎓C stretching of aromatic homocyclic compound

Cont…

Frequency (cm^{-1})		Vibrational band assignment
IR	**Intensity**	
1525	w	Aromatic C⎓C stretching
1279	m	C-H inplane deformation of naphthalene with 2 adjacent H atoms
1106	w	C-O stretching of ester
1061	w	Aromatic C-H inplane deformation

vs- very strong, vw – very week, s – strong, w – week, m-medium

Table 2 : IR Spectrum and vibrational band assignment of PDNS

Frequency (cm^{-1})		Vibrational Band Assignment
IR	**Intensity**	
3600	vw	Free –OH group
3060	m	Aromatic C-H asymmetric stretching
3006	m	Aromatic C-H symmetric stretching
2931	m	Aliphatic C-H asymmetric stretching
2895	m	Aliphatic C-H symmetric stretching
1709	vs	>C=O stretching of ester group
1575	vw	C⎓C stretching vibration of aromatic homocyclic compd.

vs- very strong, vw – very week, s – strong, w – week, m-medium

NMR Spectral analysis

The proton NMR spectra of copolyesters contain characteristic absorptions in aliphatic and aromatic regions. The results obtained are discussed as follows –

Aliphatic protons

Aliphatic protons, in the absence of any deshielding effects caused by neighbouring groups or atoms are usually the most highly shielded of all the common organic types. A methylene group of ethylene oxides absorb near 2.3 δ, which is at considerably higher field than ordinary CH_2–O groups (near 3.6 δ). The absorption due to –CH_2–O group of aliphatic diols is observed near 3.8 δ in the ^1H NMR spectra of copolyester PDNS. The methine group of 2, 3-butyl moiety has absorption at δ 3 ppm in the copolyester PBNS. The succinoyl group (two CH_2 groups) in the copolyesters PBNS and PDNS is confirmed by the absorptions in the region 2-2.7 δ.

Aromatic protons

Aromatic protons of substituted benzene generally absorb in the range 6.5 -8.5 δ. Electron- withdrawing groups shift the absorption to lower field and electron-donating groups shift the absorption to higher field because of the local diamagnetic shielding effect. The presence of aromatic moieties in the repeating unit of copolyesters is confirmed by the absorption in the region 6.3-8.5 δ.

In the present investigation, a detailed work is done on the analysis of vibrational bands and chemical shifts to confirm the structure of repeating units of the synthesized copolyesters.

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