Microwave assisted synthesis and characterization of terpolymer derived from o-aminophenol, urea and formaldehyde

¹Amit M. Surjushe, ²Arun B. Patil

¹Department of Chemistry, Smt. Vatasalabai Naik Mahila Mahavidyalaya, Pusad, 445204 (M S), India. ²Department of Chemistry, Phulsingh Naik Mahavidyalaya, Pusad, 445204 (M S), India.

ABSTRACT: This paper presents the microwave assisted synthesis of a terpolymer by using the o-aminophenol, urea and formaldehyde. The o-APUF terpolymer have been synthesized from o-aminophenol (o-AP), urea (U) and formaldehyde (F) in DMF media at 132 ± 2 °C for 110 sec where as the conventional method took five hours refluxing at 126 to 128°C. The synthesized terpolymer was purified and then characterized on the basis of spectral data generated from FTIR, H¹NMR[,] C¹³NMR and SEM.

Keywords: microwave irradiation, structure, spectral analysis, o-APUF.

INTODUCTION

Tercopolymer are macromolecular entities which form an integral part of the backbone. Tercopolymers are found to be amorphous powder or crystalline resinous in nature and form special class of polymers which are widely known for their uses. Terpolymer is found very useful application as adhesive, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins.[1,2,3] Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions.[4,5]. However, the metal ion removal by chelating ion-exchange resin using batch equilibration method has gained rapid acceptance because of its wide variety of sorbent phases, high degree of selectivity, high loading capacity and enhanced hydrophilicity [6]. Ionexchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4].

MATERIAL AND METHODS: SYNTHESIS OF 0-APUF TERPOLYMER

The proportionate mixture of o-aminophenol (0.1 mol, 1.091 g) and urea (0.1 mol, 0.70 g) with formaldehyde (7.50 ml of 37 %, 0.2 mol) in a proportion of 1:1:2 in the presence of DMF medium at $130 \pm 2^{\circ}$ C for 110 Second using a microwave system. The resinous brown solid mass obtained was immediately removed from the flash as soon as the reaction period was over and then it purified.

The resinous brown product so obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of mortar and pestle. The powdered sample was washed many times with boiling water and ethanol to remove unreacted monomers. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The resulting terpolymer sample was filtered, washed several time with boiling water, dried in air, powdered and kept in vacuum over silica gel. The yield of the terpolymer was found to be 88%. The reaction is shown as follows.





Fig. 1. Reaction and Suggested Structure of Representative o-APUF terpolymer

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RESULTS AND DISCUSSION: I. 1H-NMR SPECTROSCOPY

The NMR spectra of o-APUF terpolymers were scanned in DMSO and have been shown in (Fig. 2). The NMR spectral data are incorporated in (Table 1). Proton NMR spectra of terpolymer show a weak multiplet signal (unsymmetrical pattern) 7.80 to 7.90 (δ) ppm is due to the aromatic protons. The weak multiply signals in the range at 6.62 – 6.76 (δ) ppm is due to the amido –CH₂-NH-CO linkage. A signal at 3.66 – 4.12 (δ) ppm is due to methylene proton of (Ar – CH₂ – N) moiety. The signal appeared in the range of 8.28 – 8.34 (δ) ppm can be assigned to proton of phenolic -OH. A week signal appeared in the range of 1.2507-1.2526 (δ) ppm is due to the presence of Ar-NH₂ group. In the region of 2.16 – 2.69 (δ) ppm is due to methelenic bridges of Ar – CH₂ – Ar linkage[14].

Cl	nemical shift (ð) ppm of copoly	Nature of proton	Expected	
o-APUF-I	o-APUF-II	o-APUF-III	o-APUF-IV	assigned	Values
7.9	7.8	7.89	7.88	Aromatic proton (unsymm. Pattern)	6.5-8.5
6.62	6.64	6.76	6.76	Amido proton of – CH2-NH-CO linkage	6-7
3.66	3.89	3.99	4.12	Mathelene proton of Ar-CH2-N moiety	3-5.5
8.28	8.34	8.31	8.34	Proton of Ar-OH (phenolic-OH)	7.5-8.5
1.2507	1.2526	1.2505	1.2513	Amine Ar-NH ₂	1.1-3.5
2.16	2.49	2.54	2.69	Methelene proton of Ar-CH2-Ar	1.5-5.5
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Table 11H NMR Spectral Data of o-APUF Terpolymer

Fig. 2. ¹H NMR Spectra of o-APUF Terpolymer

55 5.0 4.5

Chemical Shift 6 (ppm)

II. ¹³C NMR SPECTROSCOPY

13C NMR spectra of o-APUF terpolymers are presented in Fig. 3. The 13C NMR spectra of o-APUF terpolymers peak are assigned with reference to the literature values. The 13C NMR spectra show the corresponding peaks at 122.14, 128.71, 129.49, 132.88 and 154.94 ppm with respect to C_1 - C_6 of aromaticring of the benzophenone. The peak appeared at 163.11 ppm of may be corresponding to carbonyl group of biuret moiety. The peak appeared at 67.56 ppm may be due to the presence of –C-OH group in aromatic benzophenone group. The peaks appeared at 40.27 ppm may assigned to the –CH2 – bridge in terpolymer. The medium peak appeared at 116.33 ppm may be confirmed the presence of –C-NH group of terpolymer. The 13C NMR spectrum clearly established the linear structure of the terpolymer synthesized from o-aminophenol-urea-formaldehyde.



Fig. 3. ¹³C NMR Spectra of o-APUF-I Terpolymer

III. INFRA-RED SPECTROSCOPY

The recorded FTIR spectra of o-APUF terpolymer is shown in (Fig. 4) and the important IR bands along with their assignments have appeared in the spectrum is tabulated in (Table 2). The spectrum shows a very broad absorption band at 3252-3403 cm⁻¹ may due to the the stretching vibrations of phenolic hydroxyl (Ar-OH) involved in intramolecular hydrogen bonding between –OH, >CO and >NH group of amide/imides [15]. The 1,2,3,5 tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium absorption bands appeared at 559-583 cm⁻¹, 1086-1100 cm⁻¹ respectively. The weak band at 2812-2887 cm⁻¹ may be due to stretching vibration of >NH (amide/imides). The band at 1527-1535 cm⁻¹ may be due to bending vibration of –NH in secondary amide. The bands at 1442-1447 cm⁻¹ indicate the (-C-H bending) and –CH₂ bending of CH₂ group. The band obtained at 1288-1356 cm⁻¹ suggests the presence of methylene (–CH₂) bridge. The sharp and strong band at 1624 – 1654 cm⁻¹ may be due to the bending vibration of >C=O group of urea moiety.





	Observed band	frequencies (cm		Expected band	
o-APUF-I	o-APUF-II	o-APUF-III	o-APUF-IV	Assignment	frequencies (cm- 1)
3398(b)	3403(b)	3392 (b)	3252(b)	-OH phenolic intermolecular hydrogen bonding	3500-3200
2812(w)	2887(w)	2822(w)	2842(w)	>NH stretching (Amide/Imides)	2800-2900
1629 (st,sh)	1630 (st,sh)	1624 (st,sh)	1654(st,sh)	(Carbonyl Stretching vib.)	1630-1680
1535(m)	1537 (m)	1527 (m)	1528 (m)	NH bending vibration of secondary amide	1510-1550
1447 (m)	1444 (m)	1442(m)	1443 (m)	(-C-H bending) of CH ₂ group	1445-1485
1355(sh,m)	1288 (sh,m)	1310(sh,m)	1356(sh,m)	-CH ₂ methylene bridge	1250-1340
559 (m)	583(m)	562 (m)	594 (m)	1,2,3,5 substitution	550-600
1100 (m)	1086(m)	1094 (m)	1089 (m)	in aromatic ring	1050

Table 2IR frequencies of o-APUF Terpolymer

sh=sharp, b=broad, st= strong, m= medium, w=weak

IV. SCANNING ELECTRON MICROSCOPY (SEM)



(a)



Fig. 5. SEM Micrographs of o-APUF Terpolymer

The scanning electron morphology of the o-APUF terpolymer sample was investigated by different magnification 1000X and 5000X, which are shown in Fig. 5 (a) and (b) respectively. The terpolymer appeared to be brown in colour. The SEM morphology of o-APUF terpolymer exbitits spherulites and fringed model. The spherules are typical polycrystalline formation having as good as smooth surface. In the present case the spherulites are complex polycrystalline nature of o-APUF terpolymer. The morphology of terpolymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. The morphology shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The terpolymer exhibits characters that are more amorphous with closed packed surface having deep pits. Thus, by SEM micrographs morphology study of o-APUF terpolymer shows a transition between amorphous and crystalline state. However, the o-APUF terpolymers show a more amorphous structure rather than crystalline, hence o-APUF terpolymer exhibits higher metal ion exchange characteristic.

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