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Research Article

SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC POLYESTERS WITH DIFFERENT OXADIAZOLE MOIETIES

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ABSTRACT

Heterocyclic compounds are widely used in life sciences and technology. They find their application in drug industry also. Hence we focused our attention in synthesizing new heterocyclic monomers and aromatic polymers containing substituted oxadiazole ring by polycondensation reaction. The synthesized monomers and the polymers were characterized by the FT-IR spectroscopy, the crystalline nature by XRD, thermal stability by TGA analysis and their solubility was also investigated. These polymers exhibited excellent thermal stability and crystalline nature which shows a good potential for their wide application as multipurpose functional material. It is believed that the application of these polymers will be continually developed in future.

Keywords: Heterocyclic Monomer, Polymer, Oxadiazole, FT-IR analysis, XRD, TGA

1. INTRODUCTION

Polymer is a class of materials which all of us use in our day to day life. They are the main constituents in our food, clothes, human bodies etc. Hence it is important for every chemist to understand its importance, properties and applications [1]. The word polymer is derived from a Greek word *poly* means many and *mers* means parts. In other words polymers are giant molecules of higher molecular weight, called macromolecules, which are building up together by the linkage of smaller molecules, called monomers. The essential feature of a monomer is polyfunctionality, the capacity to form chemical bonds to at least two other monomer molecules [2]. The reaction by which the monomers can combine to form a polymer is known as polymerization. Polymerization in current terminology is classified as step growth and chain growth polymerization [3].

This paper highlights the synthesis of new aromatic polyesters with heterocylic ring in their backbone, formed by polycondensation reaction between the mixtures of diols and diacid. The properties of the polyesters include high tensile strength, abrasion, resistance, and resilience which make them very important in the manufacture of clothing and carpets. Application of polyesters are that they can be used in industries because of excellent properties and also used in making films for they are of good balance between mechanical strength and barrier properties against oxygen, smells and oils [4]. Oxadiazoles are a class of heterocyclic aromatic chemical compound of the azole family; with the molecular formula $C_2H_2N_2O$ [5]. In the present work, new polyesters containing oxadiazole, heterocyclic ring, as a preparatory compound have been synthesized and characterized successfully.

2. MATERIAL AND METHODS

The materials used for the synthesis of Monomer and polymers are Semicarbazide hydrochloride, Sodium acetate, Cinnamaldehyde, Benzaldehyde, P-hydroxy benzaldehyde, Furfuraldehyde and solvents. All the above chemicals are of Analar grade and purchased at Sigma Aldrich and used without any further purification.

2.1. Synthesis of monomers

2.1.1. Synthesis of Monomer (M1, M2, M3)

Synthesis of Monomer consists of three stages:

2.1.1.1. Stage 1 - Synthesis of Semicarbazone

A 0.2 mole of Semicarbazide Hydrochloride and sodium acetate were taken in a beaker and were dissolved in water. The solution was added to 0.2 mole of aromatic aldehyde and constantly stirred well for 20 minutes. The solution was kept in a water bath for 20 minutes to accelerate the reaction. The obtained solution was added to the ice cold water, filtered and dried.

2.1.1.2. Stage 2 - Synthesis of 1-Oxa-3,4 Diazole

The 10g of Cinnamaldehyde Semicarbazone obtained from stage 1 was dissolved in a glacial acetic acid and then 10g of sodium acetate was dissolved in glacial acetic acid separately. Both the solutions were mixed slowly for about an hour and kept undisturbed for 20 minutes. To the solution, bromine in acetic acid was slowly added and stirred till the brown colour faded. Obtained solution was poured into the ice cold water. The solid obtained was filtered and dried.

2.1.1.3. Stage 3 - Synthesis of Monomer

The crude product obtained from the stage 2 (5g) was dissolved in ethanol followed by 5g of Para-hydroxy benzaldehyde and refluxed on a hot plate using magnetic stirrer for 30 minutes. Then it was poured into ice cold water, filtered, dried and washed.

Table 1: Structures of Monomers (M1, M2, M3)

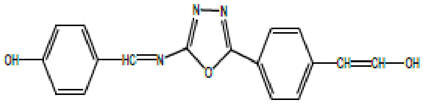
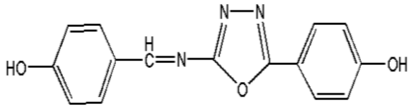
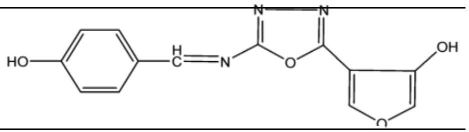
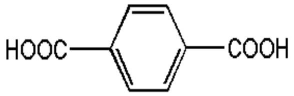
Symbols of Monomers	Aromatic Aldehyde used	Structure
M1	Cinnamaldehyde	
M2	Benzaldehyde	
M3	Furfuraldehyde	
Commercially Available Monomer **(M)**	-	

Fig. 1: P1

Fig. 2: P2

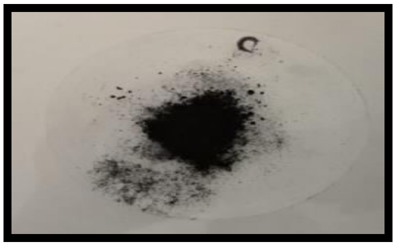


Fig. 3: P3

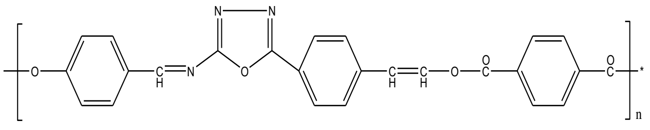
2.2. Synthesis of polymers

The synthesized monomers were made to react with commercially available monomer (M) to get polymers.

Equimolar quantity of Monomer (M1, M2, and M3) and M (Terephthalic acid) were dissolved in N-Methyl-2-pyrrolidone separately. The reacting solutions (M1+M, M2+M, M3+M) were thoroughly mixed separately in a round bottom flask. To this mixture, 0.5-1 ml of Pyridine was added, followed by a pinch of p-Toluene sulfonic acid and refluxed on an oil bath for about an hour at a temperature of 110-120 °C. After an hour, one spatula of calcium chloride and 4 ml of Dichlorophenylphosphite were added and refluxed for another one hour. Then the viscous liquid was poured into the ice cold water. The solid obtained was filtered and dried.

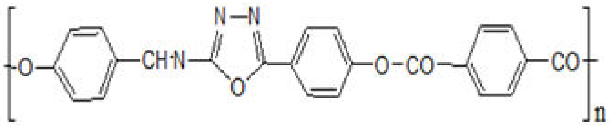
2.3. Structure of polymers

2.3.1. Polymer (P1)

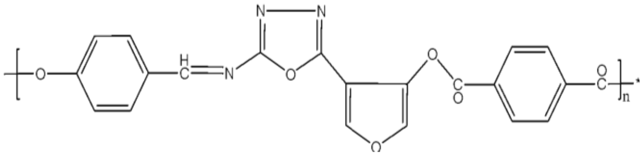


(Polyester)

2.3.2. Polymer (P2)



2.3.3. Polymer (P3)



3. RESULTS AND DISSCUSION

3.1. Solubility test

Solubility of the newly synthesized polymers (P1, P2, P3) containing Oxadiazole ring was tested at room temperature in various solvents such as DMF, DMSO, NMP, Water, Conc. HCl, 10% NaOH and Alcohol. The polymers were either partially soluble or insoluble. The solvent resistivity of the aromatic polymers is due to the rigid rod-like structure. The presence of Oxadiazole groups as the polymer backbone makes it difficult to dissolve in common aprotic solvents. The chemical stability of the polymers makes a suitable adsorbent for industrial effluents.

3.2. FT-IR spectral behavior of monomers and polymers

3.2.1. FT-IR Spectral Study of Monomer (M1)

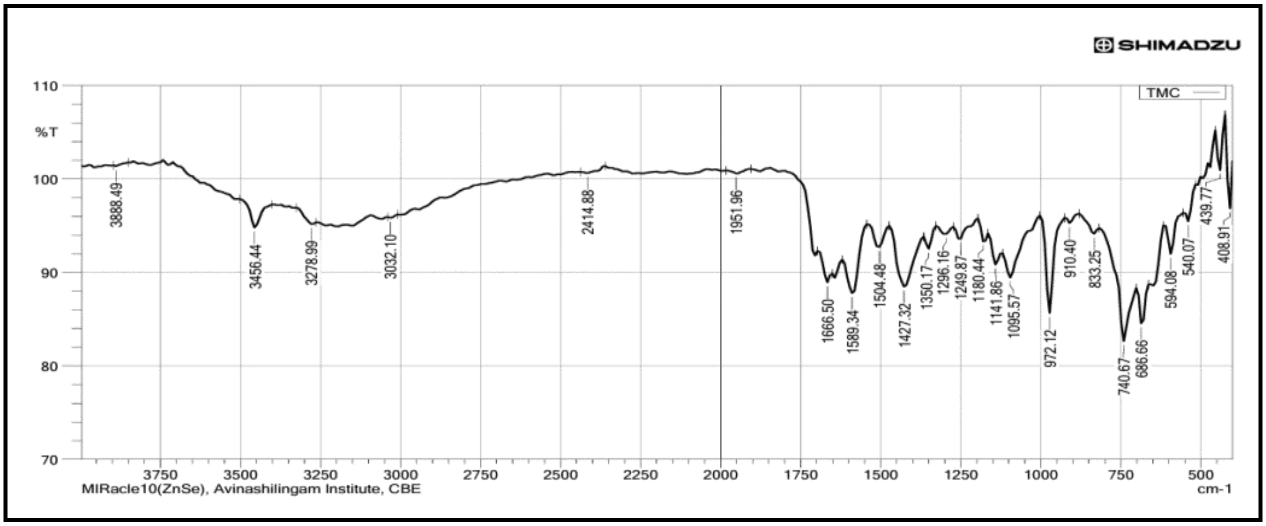


Fig. 4: FT-IR spectrum of monomer M1

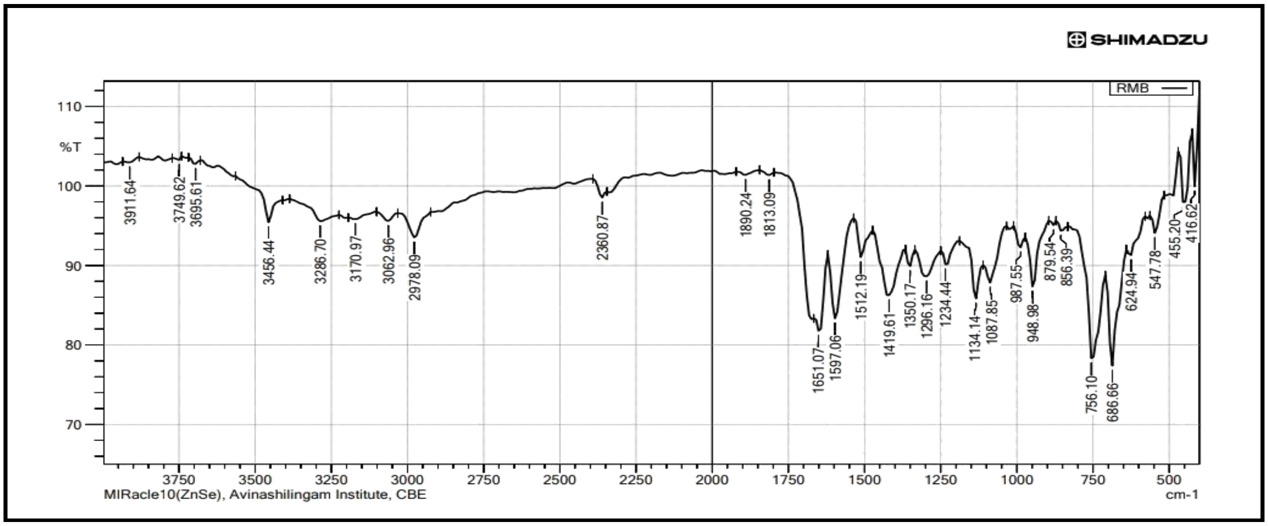


Fig. 5: FT-IR spectrum of monomer M2

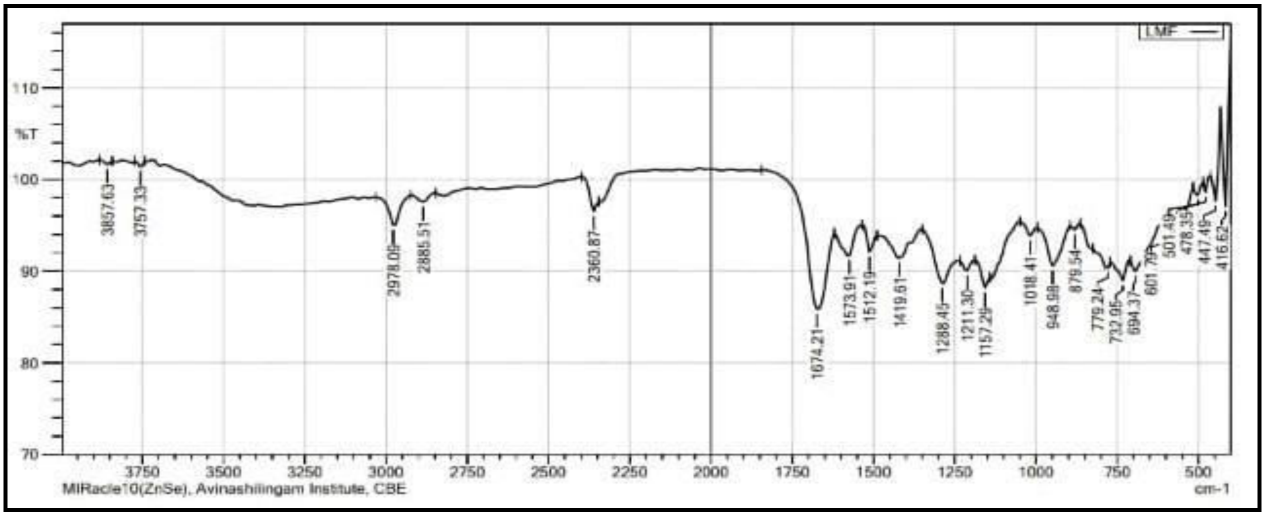


Fig. 6: FT-IR spectrum of monomer M3

Table 2: FT-IR values of Monomers

Monomers	Functional Group	Frequency (cm^{-1})
M1	terminal -OH	3456.44
	Imine –CH-	3032.10
	-C=N-	1504.48
	-C-O-C-	1141.86
	-N-N-	1095.57
M2	terminal -OH	3456.44
	Imine –CH-	3062.96
	-C=N-	1512.19
	-C-O-C-	1134.14
	-N-N-	1087.85
M3	terminal -OH	3757.33
	Imine –CH-	2978.09
	-C=N-	1512.19
	-C-O-C-	1157.29
	-N-N-	1018.41

3.2.2. FT-IR Spectral Study of Polymers (P1-P3)

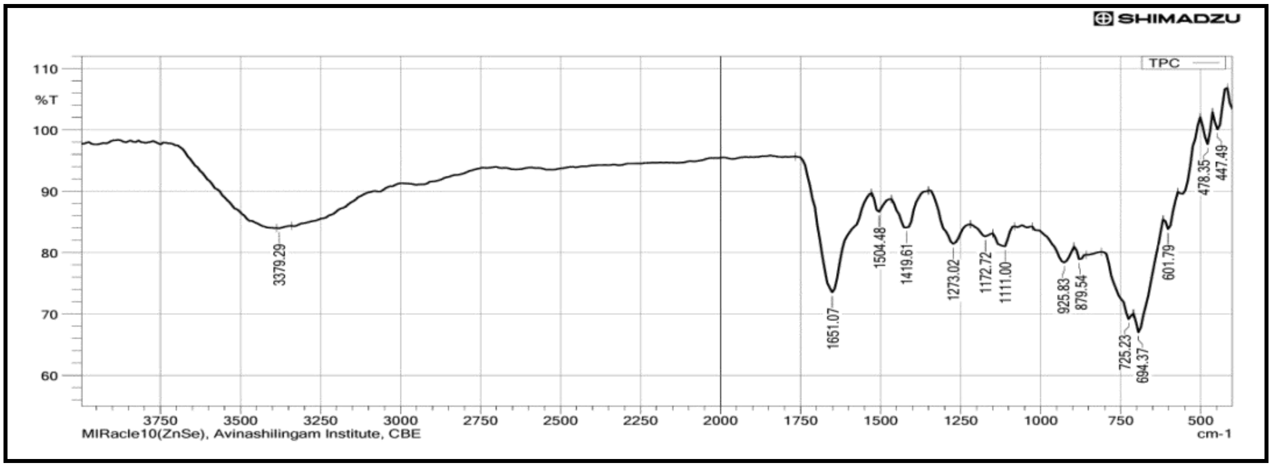


Fig. 7: FT-IR spectrum of the polymer P1

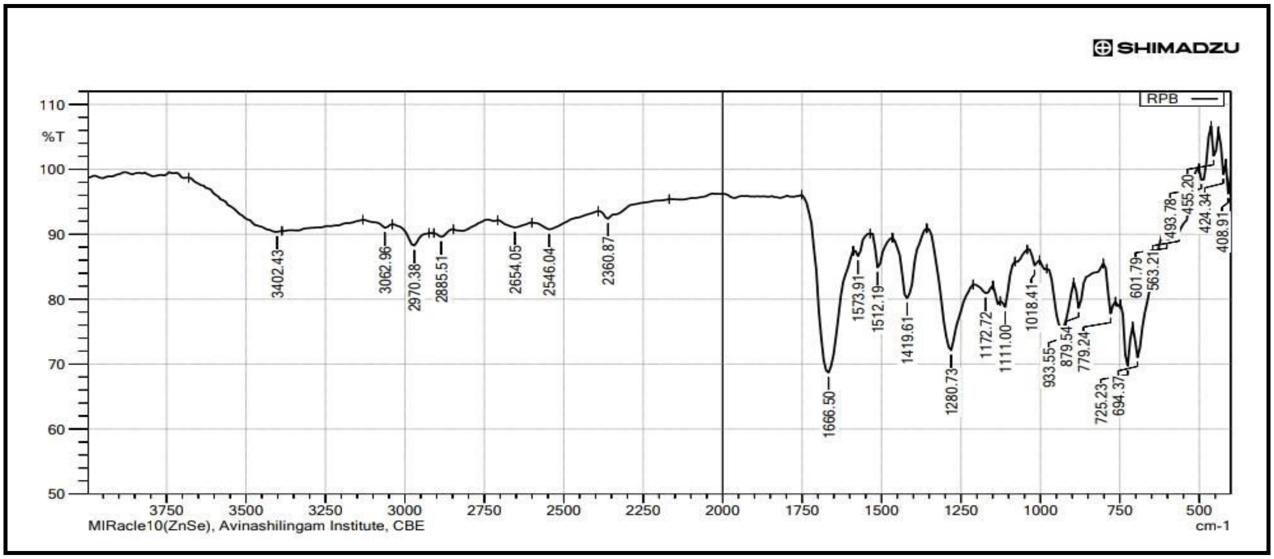


Fig. 8: FT-IR spectrum of the polymer P2

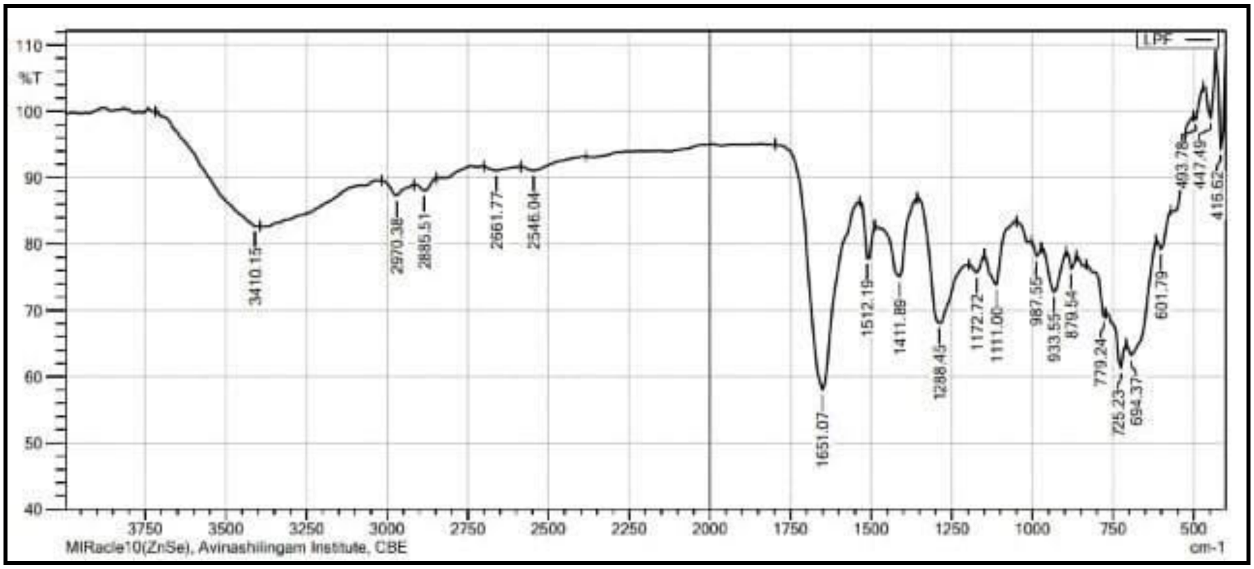


Fig. 9: FT-IR spectrum of the polymer P3

Table 3: FT-IR values of Polymers

Polymers	Functional groups	Frequency (cm^{-1})
P1	Ester	1651.07
	-C=N-	1504.48
	-C-O-C-	1111.00
P2	Ester	1666.50
	-C=N-	1512.19
	-C-O-C-	1111.00
P3	Ester	1657.07
	-C=N-	1512.16
	-C-O-C-	1111.00

On comparing, the FT-IR absorption peak values of monomers and their respective polymers the formation of ester linkage and the presence of oxadiazole moiety in the polymer backbone has been confirmed.

3.3. Xrd spectral study of polymers

The polymers synthesized are subjected to XRD analysis. The percentage crystallinity (% χ_c) is calculated from the intensities of XRD peaks by using the formula:

$$\%\chi_c = (I_C/I_C+I_A) \times 100$$

The XRD study on the polymer reveals the % crystallinity of the polymer. This indicates that the polymer in the solid state that have considerable amount of orderly structure that is crystalline structure. P2 polymer shows higher order of crystalline nature. But polymer P3 which has furfuraldehyde substitution has more of amorphous nature.

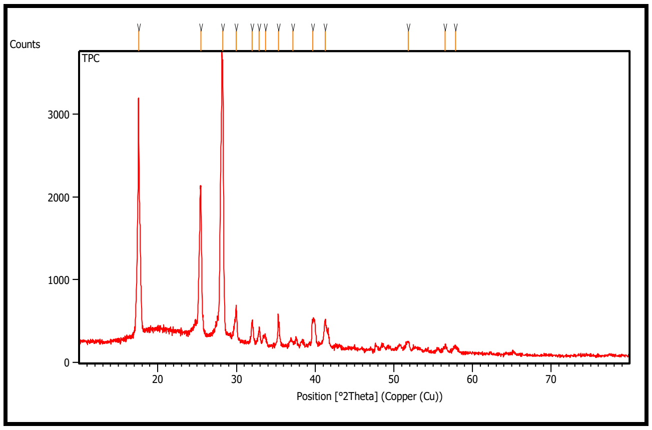


Fig. 10: XRD of P1

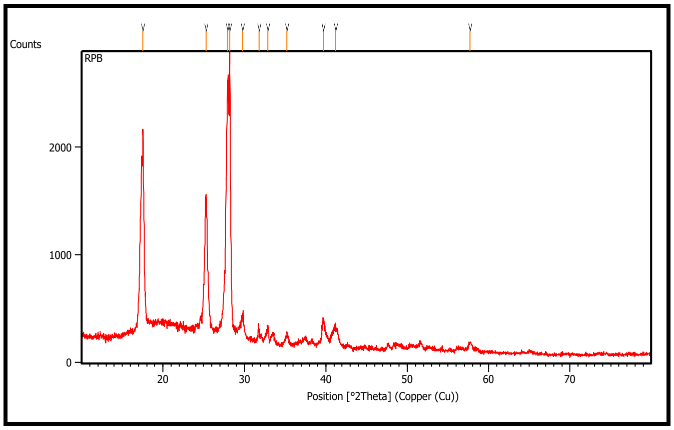


Fig. 11: XRD of P2

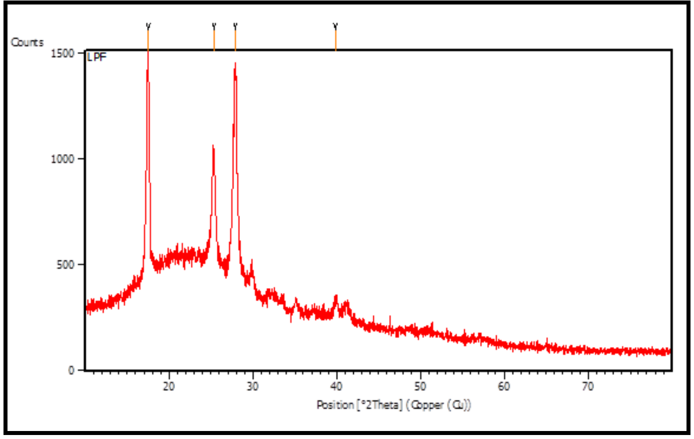


Fig. 12: XRD of P3

Table 4: Crystallinity of Polymers

Polymers	% Crystallinity
P1	77.89
P2	89.0
P3	40.6

P2 polymer shows higher order of crystalline nature. But polymer P3 which has furfuraldehyde substitution has more of amorphous nature.

3.4. Thermal Stability of The Polymers

3.4.1. Thermal Stability of Polymer (P1)

Initial weight loss *i.e.* 68.3% weight loss shown at 380°C may be accounted for the loss of weight of moisture and occluded solvent or non-solvent. It is clearly seen from the thermogram that the polyester is thermally stable. The high thermal stability of this polymer is due to the presence of the heterocyclic and aromatic rings present in the polymer back bone. The azomethine as well as oxadiazole groups in the polymer chain contributed to the very high thermal stability of the polymer.

3.4.2. Thermal Stability of the Polymer (P2)

Initial weight loss *i.e.* 41.4% weight loss at 310ºC may be accounted for the loss of weight of moisture and occluded solvent or non-solvent. It is clearly seen from the thermogram that the polyester is thermally stable. The high thermal stability of this polymer is due to the presence of the heterocyclic and aromatic rings present in the polymer back bone. The final charring takes place around 600ºC. The azomethine and oxadiazole groups in the polymer chain also as contributed to the very high thermal stability of the polymer.

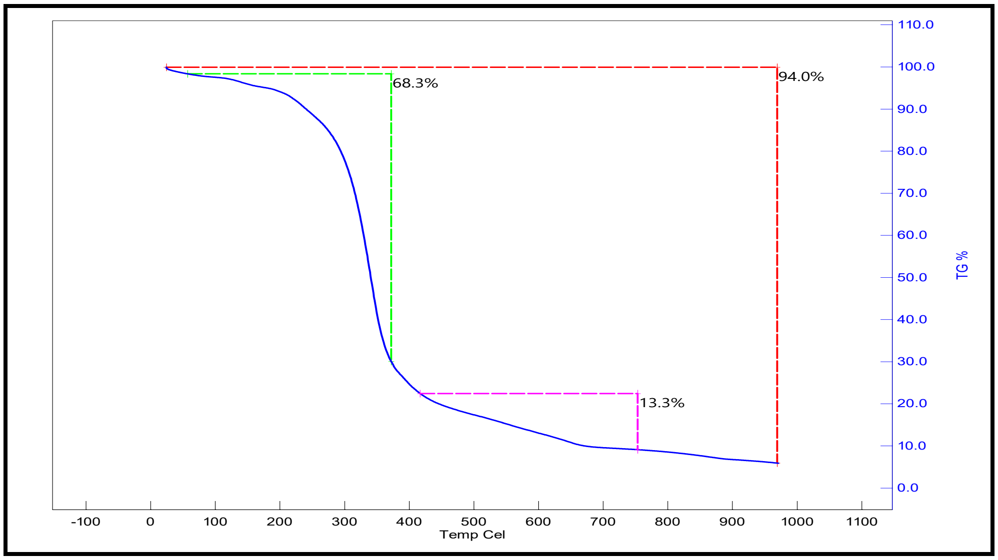


Fig. 13: TGA Curve of Polymer P1

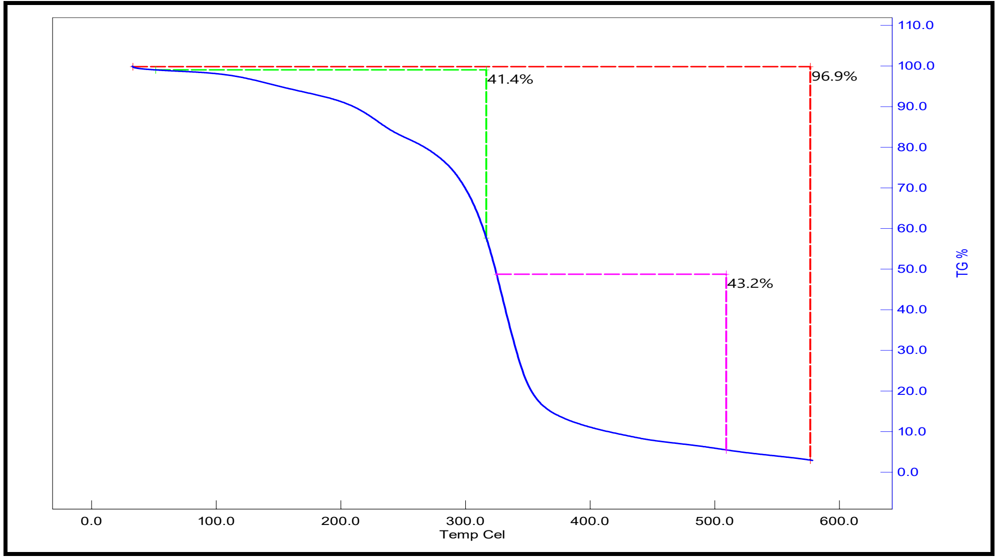


Fig. 14: TGA Curve of Polymer P2

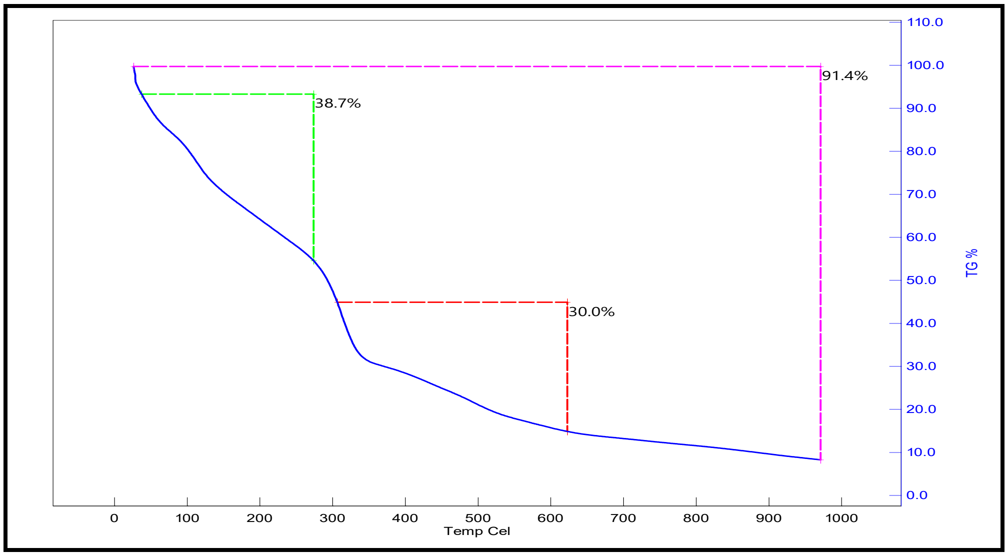


Fig.15: TGA Curve of Polymer P3

3.4.3. Thermal stability of the polymer (P3)

Initial weight loss *i.e.* 30.0% weight loss 290°C may be accounted for the loss of weight of moisture and occluded solvent or non-solvent. It is clearly seen from the thermogram that the polyester is thermally stable. The high thermal stability of this polymer is due to the presence of the heterocyclic and aromatic rings present in the polymer back bone. The azomethine as well as oxadiazole as pendant groups in the polymer chain also contributed to the thermal stability of the polymer.

4. CONCLUSION

The new monomers (M1, M2 and M3) and polymers (P1, P2 and P3) were synthesized successfully by polycondensation method. The structure of the synthesized monomers and polymers were confirmed by the FT-IR analysis and reveals the presence of assorted functional groups in the compounds. The Crystalline nature of the polymers was investigated by the XRD analysis, % crystallinity of the polymers were calculated and reveals the soaring crystalline nature of the compound. The Thermal stability of the polymers was studied using the TGA technique and the newly synthesized polymers showed good thermal stability. This study was focused on the synthesis and characterization. In future studies, these polymers can be used as corrosion inhibitors and as an adsorbent for the removal of heavy metal ion from industrial effluent waste water.

5. ACKNOWLEDGEMENTS

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