ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Effect of Annealing on Spectral, Magnetic and Antimicrobial Properties of Terpolymer Nd (III) Metal Chelate.

Kiran Meghwal[a], Narendra Pal Singh Chauhan[b], Nirmala Kumari Jangid[c], and Pinki Bala Punjabi*[,a].

[a]Department of Chemistry, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India.
[b]Department of Chemistry, B. N. P. G. College, BN University , Udaipur-313001, Rajasthan, India
[c]Department of Chemistry, Banasthali University, Tonk, Rajasthan, India

ABSTRACT

The terpolymer was prepared by solution condensation polymerization technique in acidic medium. Nd (III) metal chelate was synthesized by using terpolymer resin of 2-amino-5-chloro benzophenone, salicylic acid and formaldehyde. The metal complex was annealed at three different temperatures i.e. 373, 473 and 573 K. The spectral study was done by FTIR spectroscopy. DC magnetization study was also done to measure parameters like saturation magnetization, coercivity and retentivity. The thermal annealing leads to increase in coercivity with decrease in saturation magnetization. The average molecular weight and the polydispersity index for the terpolymer were calculated by gel permeation chromatography (GPC). Elemental analysis was done to measure the percentage of carbon, hydrogen, nitrogen and metal in the terpolymer and Nd(III) metal chelate. Examination of antimicrobial activity against gram positive, gram negative and fungal strains clearly shows that with increase in thermal annealing temperature the activity increases which may be due to the increase in isotropic nature of metal chelate leading to greater conjugation of π-electrons.
Keywords: Terpolymer; metal complex; Magnetic parameter.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

The terpolymers are used in high performance elastomers with excellent high temperature, oil and chemical resistance. Terpolymer resin is used in ion exchange process to recover certain metal ions from waste solutions and for the purpose of waste water solution and removal of iron from boiler water. It is used in energy storage capacitors as high dielectric constant terpolymer. Chauhan et al. prepared terpolymer resins by polycondensation of vanillin (V) and chloro/bromo-substituted acetophenone (CA/BA) with furfural (FU) in the presence of 1M HCl in 1:1:2 molar proportions. Both terpolymer resins have shown excellent antimicrobial activity as compared to the standard ciprofloxacin and amphotericin-B drugs [1]. Chauhan also prepared a terpolymer poly (vanillin-co-furfural-co-4-methylacetophenone) by polycondensation technique in the presence of an acid catalyst. The structure of terpolymer has been elucidated on the basis of various physico-chemical techniques [2]. A monomer, *p*-chloroacetophenone oxime (CAO), has been synthesized from *p*-chloroacetophenone and hydroxylamine hydrochloride and its copolymer resin *p*-chloroacetophenone oxime-formaldehyde (CAO-F) has been synthesized from *p*-chloroacetophenone oxime (CAO) and formaldehyde in 1:2 M proportion. A terpolymer resin *p*-chloroacetophenone oxime-formaldehyde benzoic acid (CAO-F-BA) has also been synthesized by condensation of *p*-chloroacetophenone oxime (CAO), benzoic acid (BA), and formaldehyde (F) in 1:1:2 M proportion in the presence of hydrochloric acid. All the synthesized resins have shown reasonably good antimicrobial activities as compared to standard drugs [3]. The polymer metal complex is a metal complex containing a polymer ligand presenting a remarkably specific structure in which central metal ions are surrounded by an enormous polymer chain [4]. Based on this polymeric ligand, the polymer metal complex shows interesting and important characteristics, especially catalytic activities which are different from the corresponding ordinary metal complexes of low molecular weight [5]. The biochemical applications of these types of polychelates have further motivated the researchers for the synthesis of new coordination polymers. Aminobenzophenones are a new class of biologically active compounds. A great variety of aminobenzophenones and their derivatives have been synthesized. These compounds showed different types of biological activity such as antitumoral and anticonvulsive activities and activity against the hepatitis C RNA virus [6,7]. Some aminobenzophenones showed high activity against a panel of human cancer cell lines including multi drug resistant ones [8,9]. It has been also shown that aminobenzophenones with an amino group in the ortho position of the benzophenone ring show interesting biological activity [10]. Extremely high thermal stability and high char yield of phthalocyanine polymer annealing at higher temperatures makes it an attractive source of carbon which have a widely potential application for preparing electromagnetic (EM) wave absorption materials and highly conducting polymer [11]. The effect of annealing on structural changes in liquid crystalline copolyester based on 6-hydroxy-2-napthanoic acid–*p*-hydroxybenzoic acid–terephthalic acid-4,4-biphenyldiol copolymer was investigated by Yoon et al [12].

In this work, we have synthesized a terpolymer using 2-amino-5-chloro benzophenone with salicylic acid and formaldehyde through solution condensation polymerization technique in acidic medium. The synthesized terpolymer was further subjected for incorporation of metal ion using Nd (III) metal ion resulting in the formation of polymer metal complex which was further annealed at three different temperatures. The as-prepared terpolymer, metal complex and the annealed samples of metal complex were analysed by various characterization techniques. The spectral property was examined by FTIR spectroscopy. The magnetic parameters were obtained by using Vibrating Sample magnetometry. The antimicrobial activities of all the samples were also compared using broth dilution method.

EXPERIMENTAL

Materials

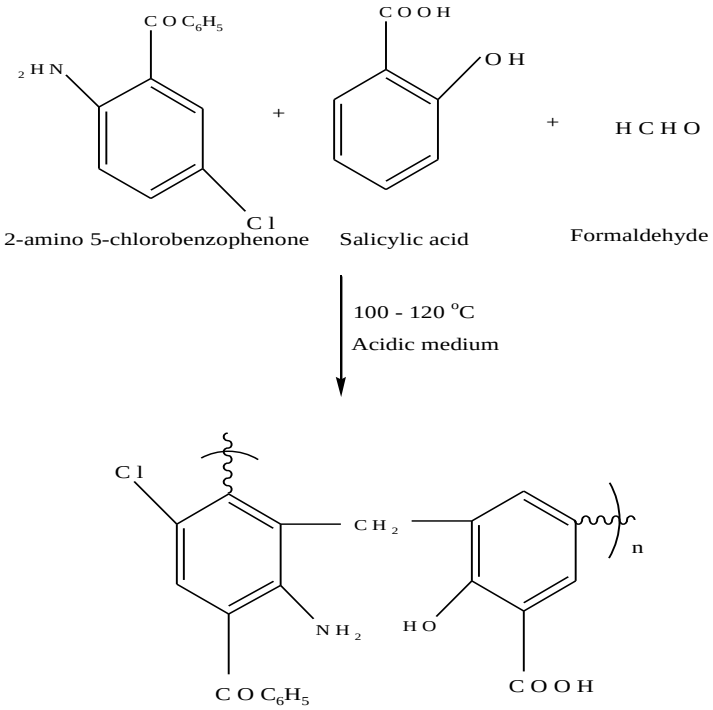
2-amino-5-chloro benzophenone (Sigma Aldrich), salicylic acid (CDH), formaldehyde (Rankem 37-41%), glacial acetic acid (Rankem), neodymium (III) nitrate hexahydrate $Nd(NO_3)_3.6H_2O$ (Alfa Aesar). Solvents such as acetone (Merck), dimethylformamide (sd fine chem. Ltd.) and ethanol were purified by standard procedures before use.

ISSN: 0975-8585

Synthesis

Synthesis of terpolymer ligand

Terpolymer was synthesized through solution condensation polymerization technique in acidic medium as shown in **Scheme 1**. 2-Amino 5-chlorobenzophenone (2 mol) was dissolved in glacial acetic acid in round bottom flask and salicylic acid (2 mol) dissolved in 15 mL of glacial acetic acid was slowly added into it. Then formaldehyde (10 mL) was added dropwise into the reaction mixture. It is then refluxed at 100-120 °C for 10-12 hours. The progress of the reaction was monitored by thin layer chromatography (TLC). After the reaction time is over, it was allowed to cool. A red coloured terpolymer resin obtained was separated and washed several times with warm water, and ethanol to remove the unreacted monomers. The resin was air dried and powdered well**.**

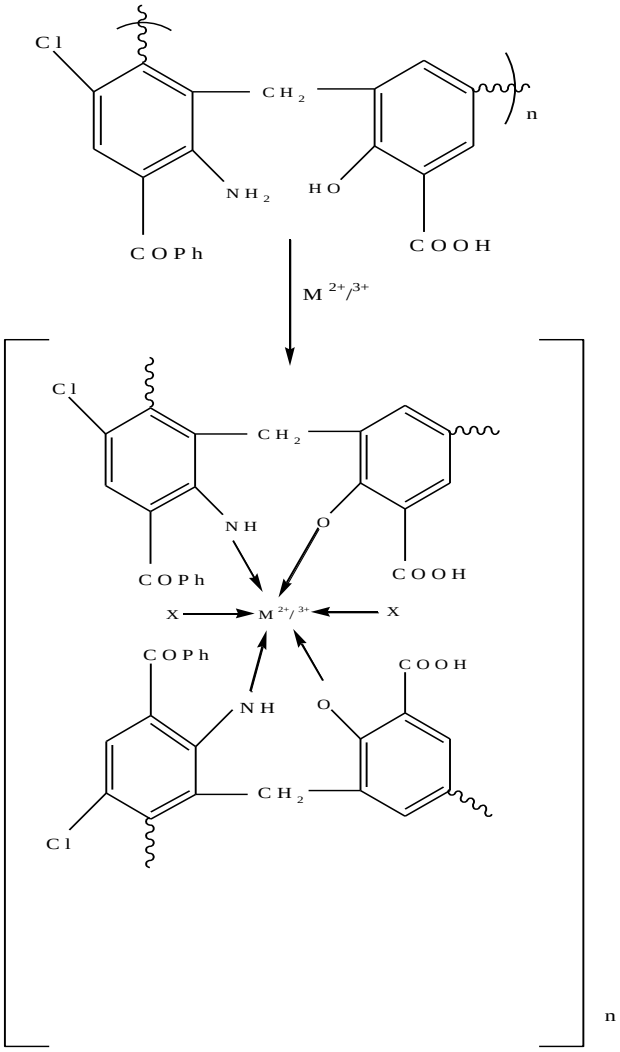


Scheme 1. Synthesis of terpolymer ligand

Preparation of Polymer metal complex

The polymer metal complex of Nd(III) was synthesized using as-prepared terpolymer as ligand. The terpolymer ligand (0.1 mol) was dissolved in acetone and the metal nitrate (0.05 mol) of Nd(III) was dissolved in acetone separately and filtered off. The resultant solutions were mixed together with constant stirring and refluxed for 8 h at 90-110 °C. The product was then filtered off and washed with ethanol to remove the impurities if present any. The polychelate obtained was air dried, powdered and subjected to analysis. The reaction scheme for the preparation of the polychelate is shown in Scheme 2.

ISSN: 0975-8585



Scheme 2. Synthesis of polymer metal complex

CHARACTERIZATION

The average molecular weight and its polydispersity index were determined with gel permeation chromatography (GPC) analysis by Turbo matrix–40, Perkin Elmer. A Perkin Elmer Spectrum-RX-IFTIR spectrophotometer was used to obtain the IR spectra between 4000 to 250 cm^{-1}. The samples were prepared in pellet form using spectroscopic grade KBr. DC magnetization measurements were done using a Lake Shore 7304 vibrating sample magnetometer (VSM) at room temperature.

RESULT AND DISCUSSION

Molecular weight measurement

The number $\bar{M}_n$ and weight $\bar{M}_w$ average molecular weights were found to be 81 and 461, respectively. The average molecular weight ($\bar{M}_z$) of the terpolymer was found to be 1553. The polydispersity index ($\bar{M}_w/\bar{M}_n$) for the terpolymer was found to be 5.677, which clearly indicate the broad molecular weight distribution in the polymer. The starting molecular weight of the sample is 8909.7 and End molecular weight is 4.0. The single peak in Figure 1 of gel permeation chromatograph clearly shows that complete polymerization of terpolymer ligand has taken place.

ISSN: 0975-8585

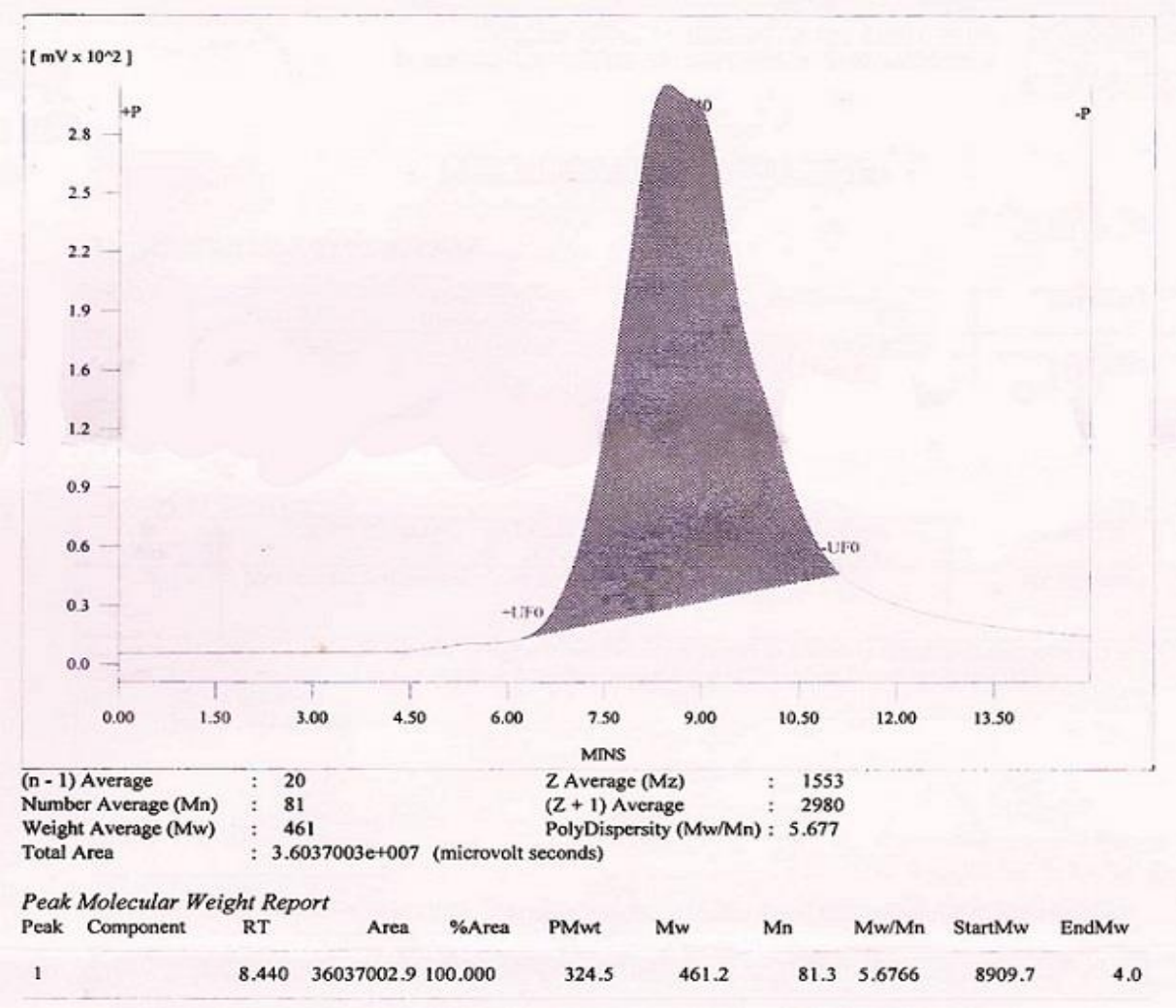


Figure 1. Gel Permeation chromatography

Elemental analysis

Table 1. Elemental analysis of terpolymer and metal complex

Compound abbreviation	Elements				
	Carbon	Hydrogen	Nitrogen	Oxygen	Metal
Terpolymer	59.53	5.34	4.42	25.38	-
Metal complex	40.24	4.12	2.79	23.85	20.65

Fourier transform Infrared spectral studies

The FTIR spectrum of terpolymer shows a broad band at 3401 cm^{-1} which may be assigned to $–NH_2$ stretching and the band at 3009 cm^{-1} is assigned to –COOH present in aromatic ring which is involved in intramolecular hydrogen bonding. The strong band at 1609 cm^{-1} is attritubed to the –NH bending vibrations. A weak band appearing in the region 2920 cm^{-1} is assigned to $–CH_2$ linkage present in the terpolymer. The band at 1667 cm^{-1} is attributed to –C=O stretching vibrations of Ar-COOH. The band at 1458 cm^{-1} is assigned to –CH bending and at 1359 cm^{-1} to C-N stretching. The out of plane bending due to –NH shows a band at 803 cm^{-1} The C-Cl vibrations appear at 750 cm^{-1} and C-Cl deformation appear at 445 cm^{-1} , the shift to lower frequency is due to greater electronegativity of chlorine atom as compare to carbon atom.

ISSN: 0975-8585

In the FTIR spectra of metal complex, broad band in the region 3400 cm^{-1} appears which may be due to the coordination of metal ion with lone pair of nitrogen atom present in 2-amino-5 chloro benzophenone. The band in the region of 750- 740 cm^{-1} are assigned to metal-oxygen bonding and the weak bands in the 500 cm^{-1} range are assigned to metal-nitrogen bonding in metal complex.

When the metal complex is annealed at different temperatures, there are notably some changes in the IR absorption bands, the changes at 373 K are less pronounced as compare to changes take place at 473 K and 573 K. These changes in IR absorption were due to the degradation or cross-linking of the polymer metal complex. The degradation can be evidenced by the resultant weight loss.

Effect of annealing on magnetic property of metal complex

The Nd (III) metal complex was annealed at three different temperatures i.e. 373 K, 473 K and 573 K. DC magnetization using a VSM technique has been used to study the magnetic property of as-prepared and annealed samples. The magnetization (M) has been measured as a function of the field (H) applied in the plane of the surface of the samples. The annealed samples show isotropic magnetic nature as compare to as-prepared sample which shows anisotropic behaviour. The parameters obtained are tabulated in table 1. The coercivity (H_c), remanence (M_r) and squareness (M_r/M_s) increases with annealing temperature with decrease in saturation magnetization (M_s). The increase in magnetic parameters may be attributed to the increase in conjugation and π-electron delocalization in the ring.

Table 2. Magnetic parameters

S.No.	Sample	Saturation magnetization (M_s) emu g^{-1}	Coercivity (H_c) G	Retentivity (M_r) emu g^{-1}	Squareness (M_r/M_s)
1	As-prepared	4.21	75.01	86.64	20.58
2	373 K	3.80	98.53	94.31	24.82
3	473 K	1.32	110.25	37.38	28.32
4	573 K	0.56	125.69	19.46	34.75

EFFECT OF ANNEALING ON ANTIMICROBIAL STUDY

The antimicrobial activity of terpolymer, terpolymer Nd (III) metal complex and three annealed samples of metal complex were studied in different concentrations against four pathogenic bacterial strains two gram positive ((*S. aureus* MTCC 96 and *S. pyogenus* MTCC 442), two gram negative ((*E. coli* MTCC 443*, P. aeurginosa* MTCC 441) and three fungal strains (*C. albicans* MTCC 227*, A. niger* MTCC 282 and *A. clavatus* MTCC 1323). Antibacterial and antifungal activities were assessed in terms of Minimum Inhibitory Concentration (MIC). Minimum inhibitory concentration is the lowest level of anti-biotic in a culture media that will prevent its growth while zone of inhibition is the area around an anti-biotic disc that has no bacterial growth. To find MIC bacteria were grown in decreasing amounts of anti-biotic, and a concentration of anti-biotic was found out at which the bacteria grow in, the dilution right before that is the MIC. The results of antibacterial activity (Table 3, Figure 2) and antifungal activity (Table 4, Figure 3) of terpolymer, terpolymer Nd (III) metal complex and three annealed sample of metal complex shown in above mentioned tables and figures.

Table 3. Antibacterial Activity

Minimum Inhibition Concentration (MIC) Microgram μgL^{-1}					
S.No.	Compound	*E. coli* MTCC 443	*P. aeruginosa* MTCC 441	*S. aureus* MTCC 96	*S. pyogenus* MTCC 442
1	Terpolymer	500	250	125	125
2	Terpolymer-Nd	125	200	100	200
3	373 K	100	150	**62.5**	100
4	473 K	100	100	**50**	**62.5**
5	573 K	100	100	**50**	**25**
6	Gentamycin	0.05	1	0.25	0.5
7	Amphicillin	100	100	250	100

ISSN: 0975-8585

8	Chloramphenicol	50	50	50	50
9	Ciprofloxacin	25	25	50	50
10	Norfloxacin	10	10	10	10

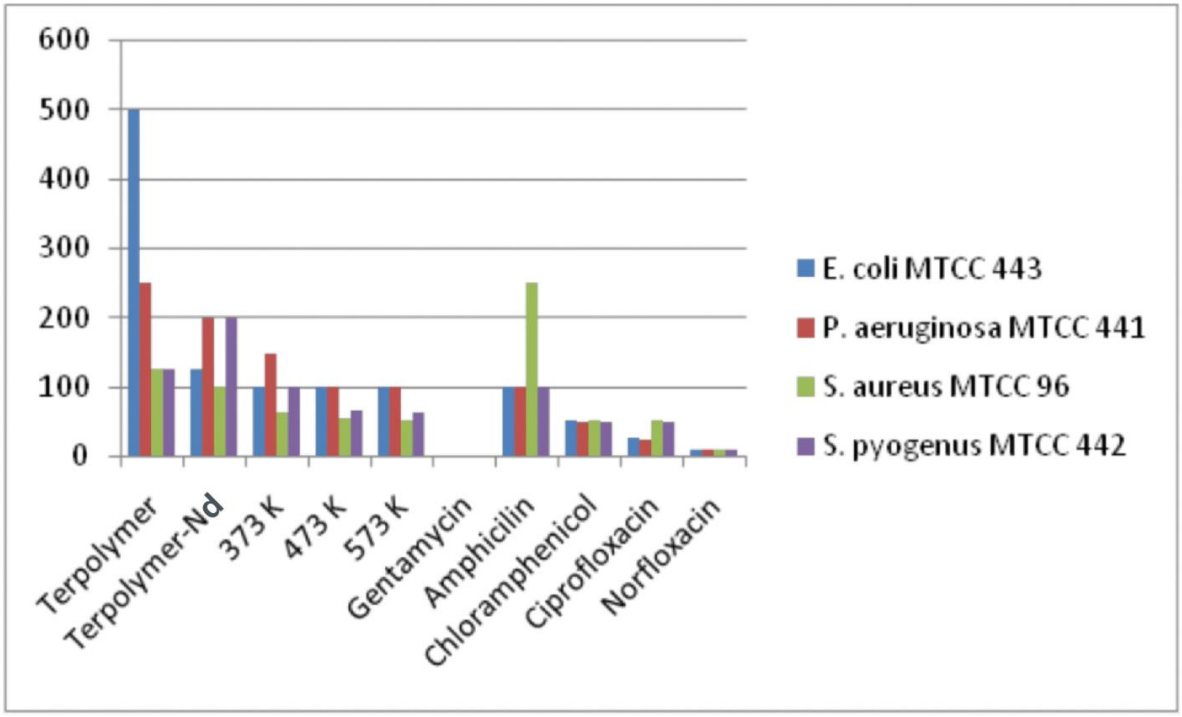


Figure 2. Graph showing antibacterial activity

Figure 2. Graph showing antibacterial activity

Table 4: Antifungal activity

Minimum Inhibition Concentration (MIC) μgL^{-1}				
S. No.	**Samples**	***C. albicans* MTCC 227**	***A. niger* MTCC 282**	***A. clavatus* MTCC 1323**
1	Terpolymer	500	250	250
2	Terpolymer-Nd	250	100	100
3	373 K	**100**	**100**	**100**
4	473 K	200	**100**	**100**
5	573 K	**100**	**100**	**100**
7	Nystatin	100	100	100
8	Greseofulvin	500	100	100

ISSN: 0975-8585

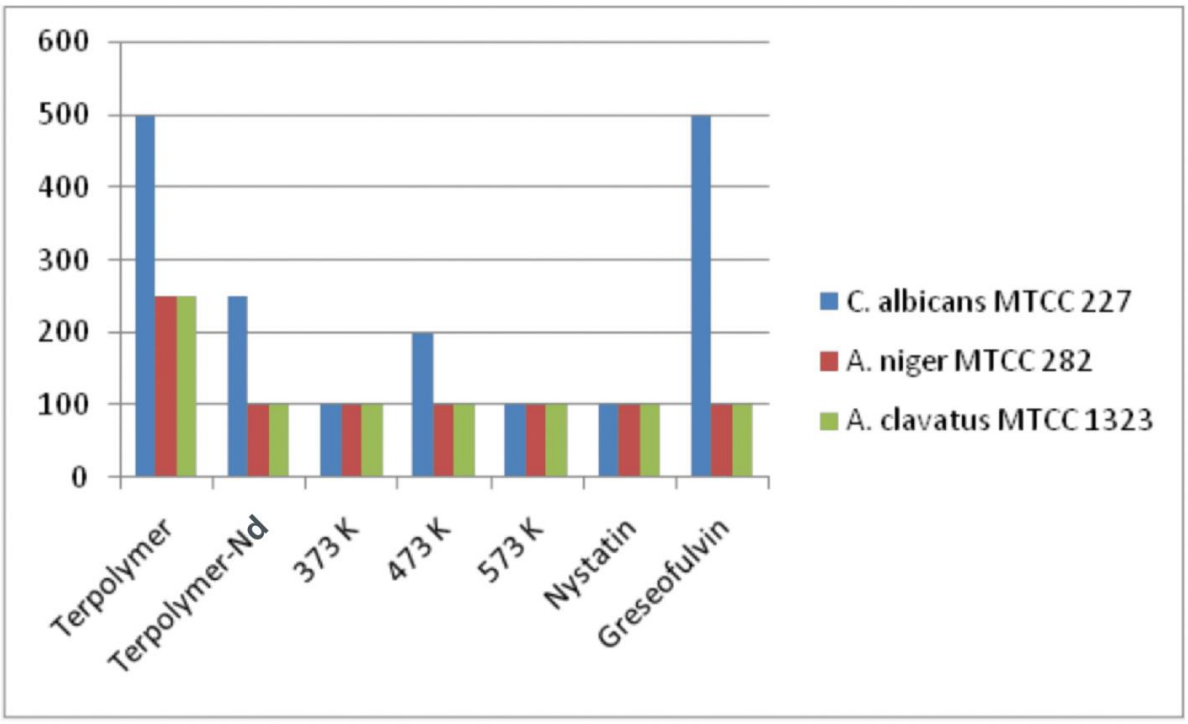


Figure 3. Graph showing antifungal activity

Figure 3. Graph showing antifungal activity

Nd (III) terpolymer metal complex and its annealed samples show good antimicrobial activity as compare to terpolymer alone. The reason may be due to increase in conjugation and delocalization of π electron in ring with increase in annealing temperature. Due to this reason annealed samples show good antimicrobial activity as compare to terpolymer alone.

CONCLUSION

Nd(III) metal chelate was successfully synthesized using 2-amino 5-chloro benzophenone and salicylic acid and the effect of annealing temperature on structure and antimicrobial properties were investigated. The magnetic parameters show that there is decrease in saturation magnetization with increase in temperature. The annealed samples shows good antimicrobial activity compared to metal complex and terpolymer.

ACKNOWLEDGEMENTS

One of the authors (Kiran Meghwal) is thankful to University Grant Commission, New Delhi for providing financial assistance in the form of SRF (Grant No.F.2(UGC/JRF/Sc) Gen/MLSU/2015/644, Dated:15.04.2015). Thanks are also due to Prof. Suresh C. Ameta for critical and valuable suggestions.

REFERENCES

[1] Chauhan NPS, Kataria P, Chaudhary J, Ameta SC. Int J Polym Mat 2012; 61: 57-71.
[2] Chauhan NPS. Des Monomers Polym, 2012; 15: 587-600.
[3] Chauhan NPS, Ameta R, Ameta SC. J Appl Polym Sci 2011; 122: 573-585.
[4] Murray RW, Ewing AG, Durst RA. Anal chem 1987; 59: 379A-390A.
[5] Miller LL, Van de Mark MR. J Am chem soc 1978; 100: 3223-3224.
[6] Doss S, Baghos V, Abdelhamid A, Halim MM. Molecules 2000; 6: 816-825.
[7] Wyss D, Arasappan A, Senior M, Wang YS, Beyer B, Njoroge G, McCoy M. J Med Chem 2004; 47: 2486-2498.

[8] Mahendra M, Doreswamy B, Sudha B, Khanum S, Shashikanth S, Sridhar M, Prasad J. Anal Sci 2003; 19: X57-X58.
[9] Hsing-Pang H, Jing-Ping L, Ying-Ting L, Neeraj M, Jang-Yang C, Yung-Ning Y, Shuenn-Shing C, Uan-Kang T, Chun-Wei C, Tung-Wei C, Chi-Hung L, Ying-Ying C, Chiung-Chiu W. Bioorg Med Chem Lett 2003; 13: 101-105.
[10] Jing-Ping L, Chun-Wei C, Jeng-Shin S, Yung-Ning Y, Ching-Fang Y, Huan-Yi T, Yu-Kang L, Yi-Ling C, Chung-Ming C, Hsing-Pang H. J Med Chem 2002; 45: 2556-2562.
[11] Wang Z, Jia K, Liu X. J Polym Res 2016; 23: 48-55.
[12] Yoon DY, Ando Y, Park OO, Karis TE, Dawson D, Huang T. Polym Prep 1996; 37: 81.