

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Thermal Degradation Studies of 2,2'-Dihydroxybiphenyl-Ethylenediamine-Formaldehyde Copolymer.

Sanjikumar S. Rahangdale¹, Santosh P. Chakole², Jyotsna V. Khobragade³, and W. B. Gurnule^{2*}.

¹Department of Chemistry.Jagat Arts, Commerce and IndirabenHariharbhai Patel Science College, Goregaon-441801, India.

²Post Graduate Department of Chemistry, Kaml Nehru Mahavidyalaya, Nagpur- 440024, India.

³Department of Chemistry, Gurunank Science College, Ballarpur-442701, India.

ABSTRACT

Copolymer (2,2'-BPEDF) was synthesized with molar ratio 3:1:5 of monomer 2,2'-dihydroxybiphenyl (BP), ethylenediamine (ED) and formaldehyde (F) by condensation polymerization, in acidic medium and refluxing in oil bath at 120°C for 5 h. Composition and structure of organic copolymer have been determined by elemental analysis and molecular weight determination by non-aqueous conductometric titration method. The UV-visible, FTIR and proton nuclear magnetic resonance (¹H NMR) spectra were studied to elucidate the structure. The surface features and crystalline behaviour of the copolymer was analysed by scanning electron microscope (SEM). Non isothermal thermogravimetric analysis for determination of their mode decomposition and relative thermal stability, Energy of activation, frequency factor and order of reaction have been calculated by Sharp-Wentworth (SW) and Freeman-Carroll (FC) methods. Energy of activation determined by Sharp-Wentworth and Freeman-Carroll methods are in agreement with each other. The order of reaction is found to be 0.98.

Keywords: Synthesis, Thermal, ethylenediamine, Kinetic parameter, Polycondensation, structure, composition, Thermal stability.

<https://doi.org/10.33887/rjpbcsl.2021.12.6.1>

*Corresponding author

INTRODUCTION

Investigation of warm examination includes a gathering of methods in which an actual property of substance is estimated as a component of temperature when the substance is exposed to a controlled temperature program. Thermally steady copolymers have as of late become shelter to polymer physicist because of their superior and elite utility. Since the advanced history of thermogravimetry, warm corruption of polymers and the investigation of their energy have been at the focal point of warm investigation. Numerous specialists attempted to work on the warm dependability at raised temperature by changing the monomer organization in polymer combination [1].

The warm debasement investigation of copolymer has gotten a subject of ongoing premium, being a significant property, which fundamentally chooses warm steadiness and processability. A wide assortment of thermally stable polymers have been combined and examined their thermogravimetric property and discovers numerous applications, for example, particle exchangers [2-5], semiconductors [6], high dielectric consistent for energy stockpiling capacitors [7], bundling, cements and coatings in electrical sensors, activators, impetuses and thermally stable materials [8-10]. Thermogravimetric examination of copolymer tars got from 2,4-dihydroxyacetophenone, dithiooxamide, and formaldehyde by Rahangdale et al. [11], Jinger et al. completed warm corruption of terpolymers combined from azo-n-4-bromophenyl substituted maleimide with acrylates [12, 13]. Phenolic saps are known for their wide applications in different regions due to their warm strength, simple accessibility, cost adequacy, and a portion of their incredible properties [14]. The thermal strength of terpolymers has been widely concentrated by utilizing the technique for thermogravimetric investigation (TGA) by a few creators.

Thermo insightful and dynamic investigations of terpolymer pitches got from 8-hydroxyquinoline-5-sulphonicacid/p-cresol, oxamide/melamine with formaldehyde have been detailed by Singru et al. [15-18]. 2-hydroxy, 4-metoxybezophenone, 1,5-diaminonaphthalene, formaldehyde by Das [19]. 8-hydroxyquinoline-5-sulphonicacid, catechol, and formaldehyde by Mandavgade et al. [20] has been concentrated exhaustively. Strategies for the assessment of dynamic boundaries from thermogravimetric investigations are for the most part dependent with the understanding that the Arrhenius condition is legitimate with warm and dissemination obstructions being unimportant. Different investigations on union, portrayal and thermogravimetric examination of a few new polymeric vitalities have been accounted for.

Henceforth, in the current examination, it has been arranged to contemplate the non isothermal thermo gravimetric investigation of copolymer got from 2,2'-dihydroxybiphenyl, ethlenediamine and formaldehyde which has not been accounted for so far in writing.

EXPERIMENTAL

Materials

2,2'- dihydroxybiphenyl and ethlenediamine utilized in the current examination of analyticalgrade immaculateness were bought from Sigma Aldrich Chemicals. Formaldehyde (37%) was bought from S.D. Fine Chemicals, India. Every one of the pre-owned solvents like N,N-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, acetone, and diethyl ether were obtained from Merck, India.

Synthesis of copolymer

2,2'- BPEDF copolymer was ready by condensation polymerisation of 2,2'-dihydroxybiphenyl, ethlenediamine with formaldehyde in 2M medium of hydrochloric acid in the molar proportion 3:1:5 at temperature 120°C in an oil bath with intermittent shaking, to guarantee careful blending for around 5 hrs. The earthy coloured hued resinous item was gotten. The item got was washed with hot refined water and methanol to eliminate the abundance of 2,2'-dihydroxybiphenyl, formaldehyde copolymer which may be available alongside 2,2'-BPEDF copolymer. The appropriately washed copolymer was dried, powdered and afterward separated with diethyl ether and afterward with diethyl ether. The earthy coloured shading resinous item was quickly eliminated from the cup as before long as response period was finished and afterward decontaminated. The response and recommended construction of 2,2'-BPEDF is shown in Fig. 1.

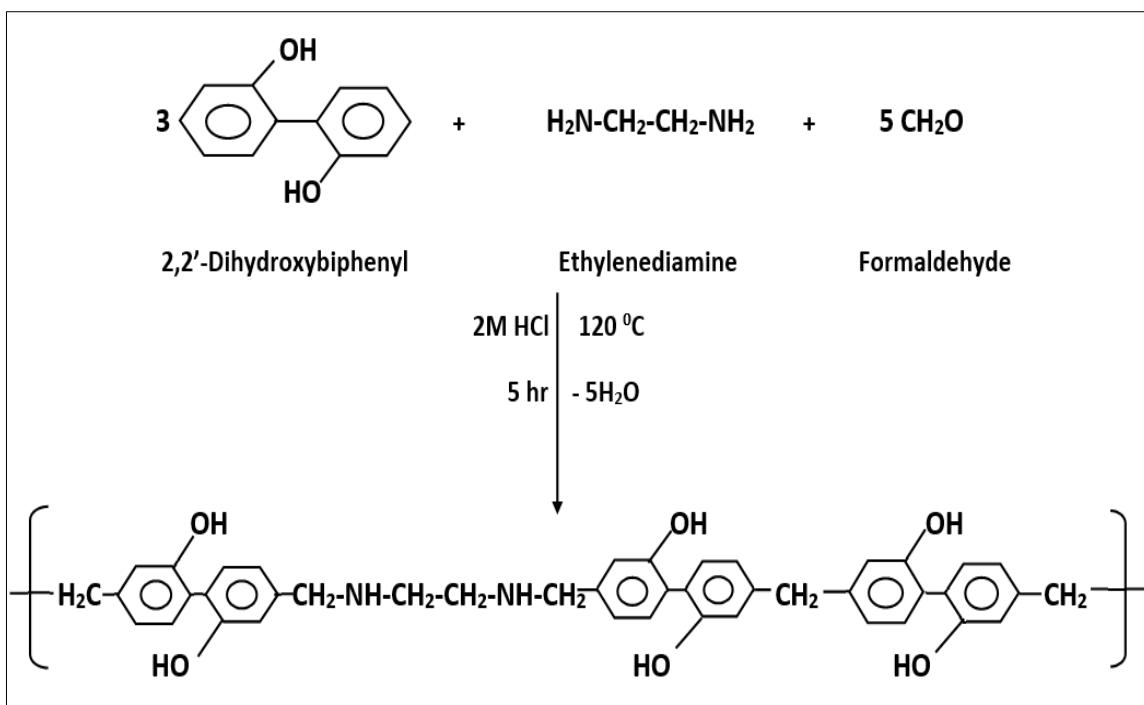


Figure 1: Synthesis of 2,2'-BPEDF Copolymer

Analytical and Physico-Chemical Studies

The basic investigation was done on Elemental Vario EL III Carlo Erba 1108 basic analyzer instrument. The electronic ingestion spectra (UV-visible) of the copolymer in DMSO was recorded on twofold bar spectrophotometer in the scope of 200-800 nm. Infrared spectra of copolymer were completed in nujol reflect on Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pellets in the scope of 4000-500 cm^{-1} . ^1H NMR range was recorded on Bruker Advance - II 400 MHz, NMR spectrophotometer utilizing DMSO-d6 as a solvent. The surface examination was performed utilizing checking electron magnifying lens at various amplifications. SEM has been filtered by a JEOL JSM-6380, a scientific checking electronic magnifying instrument. The TGA of the copolymer has been done utilizing Perkin Elmer jewel TGA/DTA analyzer. All the scientific and spectral examinations for the recently blended copolymer were done at sophisticated analytical instruments facility SAIF, Cochin University, Cochin, India.

Thermal Analysis

Warm examination strategy is related with an adjustment of weight regarding temperature. Warming is performed under stringently controlled conditions and can uncover changes in structure and other significant properties of the material being contemplated. In non-isothermal or dynamic TGA, the example is exposed to conditions expansion in temperature at straight rate. The thermogravimetric examination was acted in air with warming rate at $10^{\circ}\text{C min}^{-1}$ utilizing 5-6 mg of tests in platinum cauldron from temperature of 40°C to 750°C and thermogram is recorded for 2,2'- BPEDF With the assistance of thermogravimetric data, the warm activation energies (E_a) and order of reaction (n) determined. Additionally, the other thermodynamic boundaries suchas entropy change (ΔS), apparent entropy change (S^*) free energy change (ΔF) and frequency factor (Z) were determined.

Theoretical aspects

Thermogram was deciphered and dissected to acquire data about the rate weight reduction at various temperatures which gives data about example structure, item framed subsequent to warming. Motor boundaries still up in the air utilizing Sharp-Wentworth and Freeman-Carroll strategies as follows Sharp-Wentworth strategy Using the condition determined by Sharp and Wentworth [21],

$$\text{Log} \frac{dC}{dT} - C = \log(A/\beta) - Ea \cdot 2.303R \cdot \frac{1}{T} \dots \dots \dots \quad (1)$$

where,

dC/dT = rate of fraction of weight with change in temperature
 β = linear heating rate dT/dt .

The chart of $\log dC/dT - C$ versus $1/T$ has been plotted. The graph is a straight line with activation energy (Ea) as slope and 'A' as intercept. The straight relationship affirms that the accepted request ($n=1$) is correct.

Freeman-Carroll method

The straight line equation derived by Freeman and Carroll [22], which is in the form of $\Delta \log f_0$
 $(dW/dt) \Delta \log Wr = n - Ea \cdot 2.303R \Delta (1/T) \Delta \log Wr \dots \dots \dots \quad (2)$

where,

dW/dt = rate of change of weight with time.

$Wr = W_c - W$

W_c = Weight loss at completion of reaction.

W = Fraction of weight loss at time t .

Ea = Energy of activation. n = Order of reaction.

The plot between the terms $\Delta \log f_0 (dW/dt) \Delta \log Wr$ versus $\Delta (1/T) \Delta \log Wr$ gives a straight line. The slope, $Ea/2.303R$, gives energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), apparent entropy change (S^*) can also be calculated by further calculations.

RESULTS AND DISCUSSION

The recently blended 2,2'-BPEDFcopolymer was observed to be brown in shading. The copolymer is dissolvable in solvents, for example, dimethylformamide (DMF), Dimethylsulphoxide (DMSO), Tetrahydrofuran (THF) concentrated aq.NaOH and KOH, however insoluble in practically all natural and inorganic solvents. The 2,2'-BPEDF copolymer was analysed for the carbon, hydrogen and nitrogen content. The organization of copolymer acquired based on basic investigation information was observed to be in acceptable connection which is introduced in Table 1. Copolymer was dissected for the carbon, hydrogen and nitrogen content. The arrangement of copolymer acquired based on essential investigation information was observed to be in acceptable relationship which is introduced in Table 1.

Table 1: Elemental analysis and empirical formula of copolymer

Copolymer	% of C Observed (cal.)	% of H Observed (cal.)	% of N Observed (cal.)	% of O Observed (cal.)	Empirical Formula of repeated unit	Empirical Formula weight
2,2'- BPEDF	75.80 (75.88)	5.82 (5.88)	4.10 (4.12)	14.28 14.12	$C_{43}H_{40}O_6N_2$	680

The number normal sub-atomic weight (M_n) was controlled by conductometric titration in non-aqueous medium, for example, dimethylsulphoxide (DMSO) utilizing ethanolic KOH as a titrant. The explicit conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of copolymer. There are a few breaks before the total balance of all phenolic hydroxyl gatherings. The main break in the plot was the littlest break furthermore, expected that this compares to a phase in titration when a normal one phenolic hydroxyl gathering of each chain was neutralized. From the plot the first and only breaks were noted. The normal level of polymerization (\overline{DP}) and henceforth the number normal sub-atomic weight ($\overline{M_n}$) of the copolymer not really set in stone utilizing the equation. This perception is in concurrence with the pattern saw by before laborers [23]. The conductometric titration bend as displayed in Fig. 2 and the outcome is displayed in Table 2.

Total milliequivalents of base required for complete neutralization

$$\overline{(DP)} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequiv of base required for smallest interval}}$$

$$(\overline{Mn}) = (\overline{DP}) \times \text{weight of repeating unit (monomer)}$$

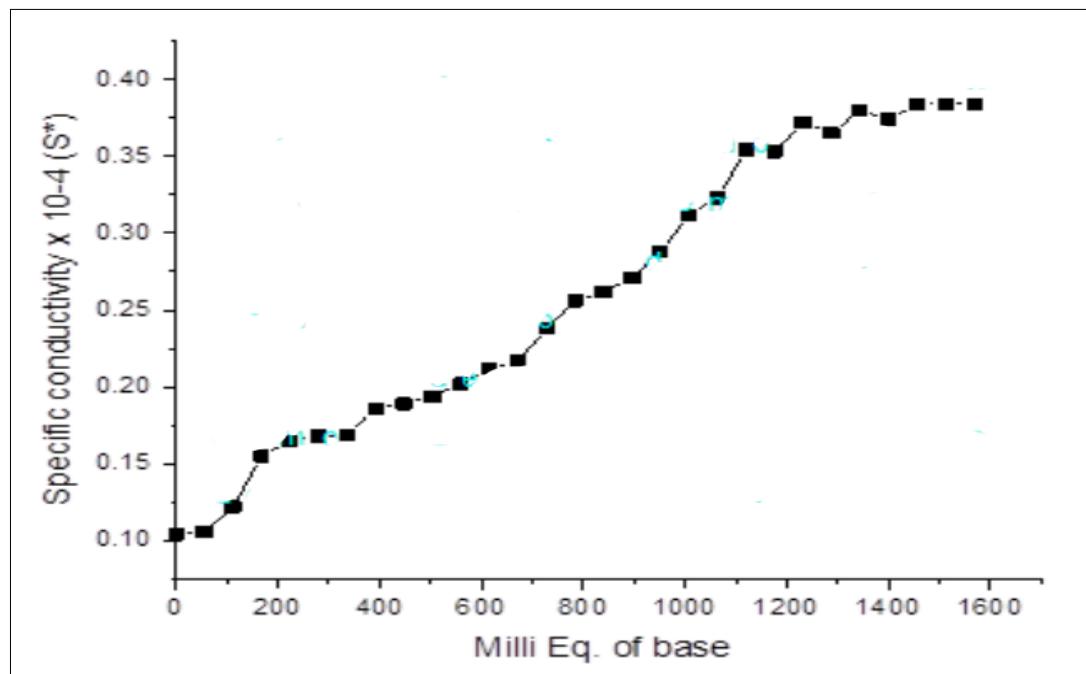


Figure 2. Conductometric titration curve of 2,2'-BPEDF Copolymer

Table 2: Molecular weight determination of 2,2'-BPEDF Copolymer

Copolymer	First stage of neutralisation Meq./100g sample	Final stage of neutralisation Meq./100g sample	Degree of polymerisation	Empirical formula weight (n)	Number average molecular mass
2,2'-BPEDF	110	1398	12.70	680	8636.00

UV-Visible Spectrum

The UV-visible spectra of 2,2'-BPEDF copolymer are displayed in Fig.3. UV-visible spectra of all the filtered gums have been recorded in unadulterated DMSO in the locale of 200 – 800 nm at a filtering pace of 100 nm min⁻¹ and at an outline speed of 5 cm min⁻¹. The scrutinized of the UV-visible spectra of copolymers should practically comparable nature. The spectra of these copolymers exhibit two retention maxima in the area 248.50 and 262.50 nm. These noticed places of the assimilation groups demonstrate the presence of hydroxy gathering, which is in formation with the sweet-smelling core. The presence of previous band (more extreme) can be represented $\pi \rightarrow \pi^*$ progress, while the later band (less extraordinary) might be expected to $n \rightarrow \pi^*$ electronic change. The presence of phenolic hydroxyl bunch (auxochromes) is liable for hyperchromic shift for example Σ_{max} higher qualities. This perception is in acceptable concurrence with the proposed generally plausible constructions of these copolymer.

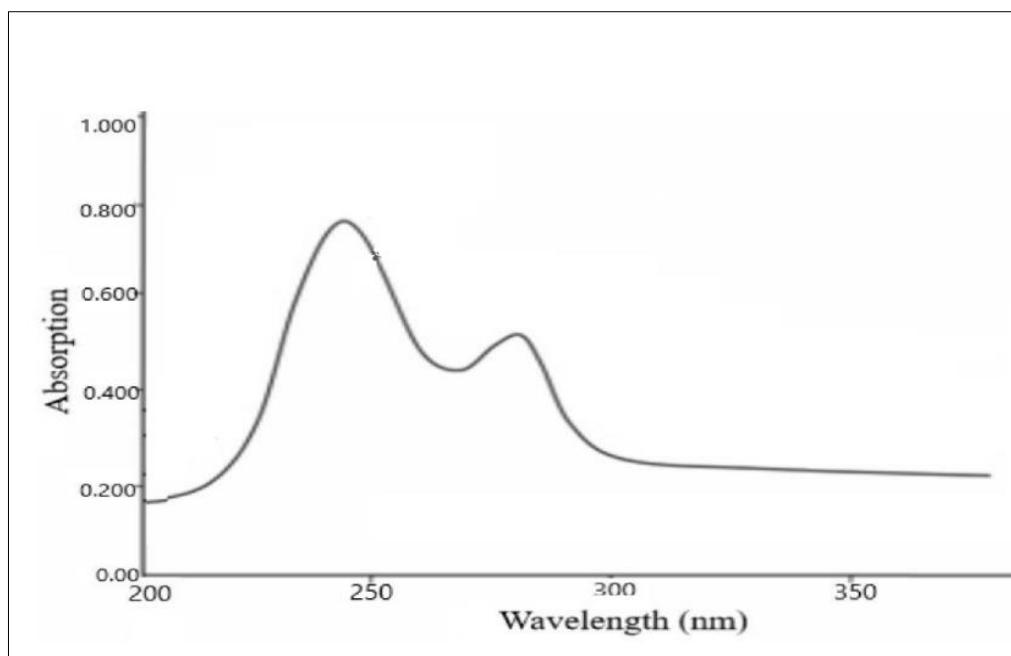


Figure 3: UV- Visible spectra curve of 2,2'- BPEDF-II Copolymer

FT-IR Spectrum

The IR range of copolymer is displayed in Fig.4. A broad absorption band appeared in the region 3400-3415 cm^{-1} may be assigned to the stretching vibrations of phenolic (-OH) groups exhibiting intramolecularhydrogen bonding [24-25]. The band, at 3060-3061 cm^{-1} indicate the presence of >NH stretching [26-30]. The band at 1434-1436 cm^{-1} may beascribed to aromatic skeletal ring. The band at 1380-1381 cm^{-1} indicate the presenceof methylene (-CH₂) bridge. The band around 1259-1260 cm^{-1} may be due to -C-Nstretching. The 2,4,2',4' substitution of aromatic benzene ring recognized by the medium / weak absorption bands appeared at 756-758, 815-817, 929-960 and 1093-1099 cm^{-1} respectively.

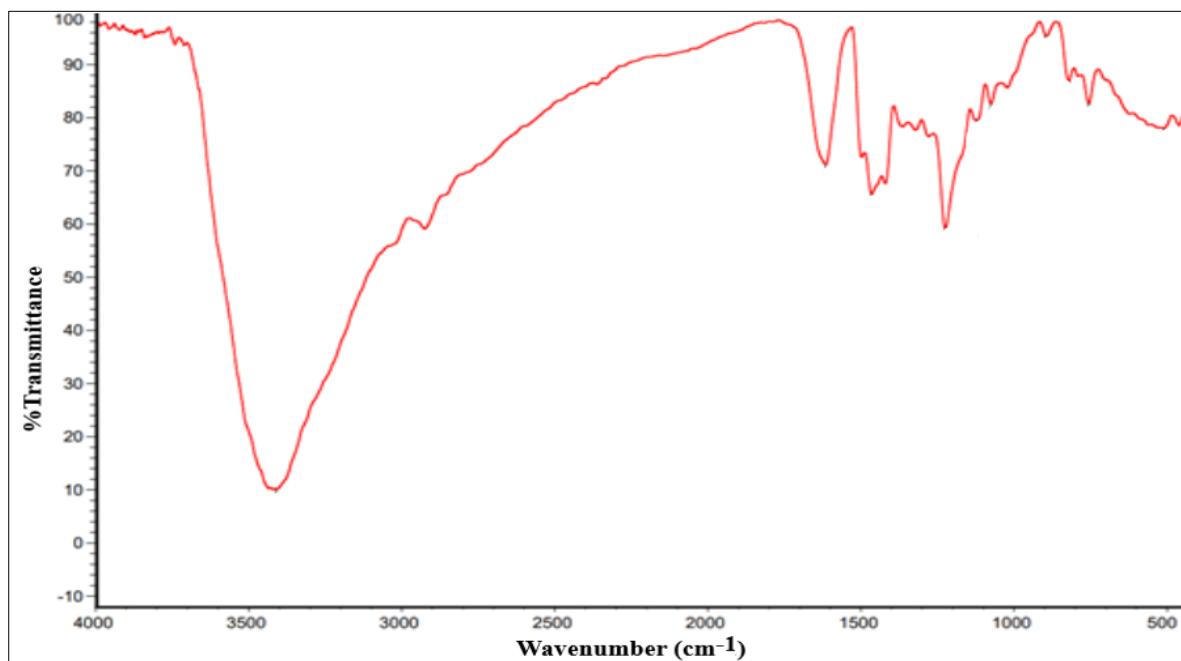


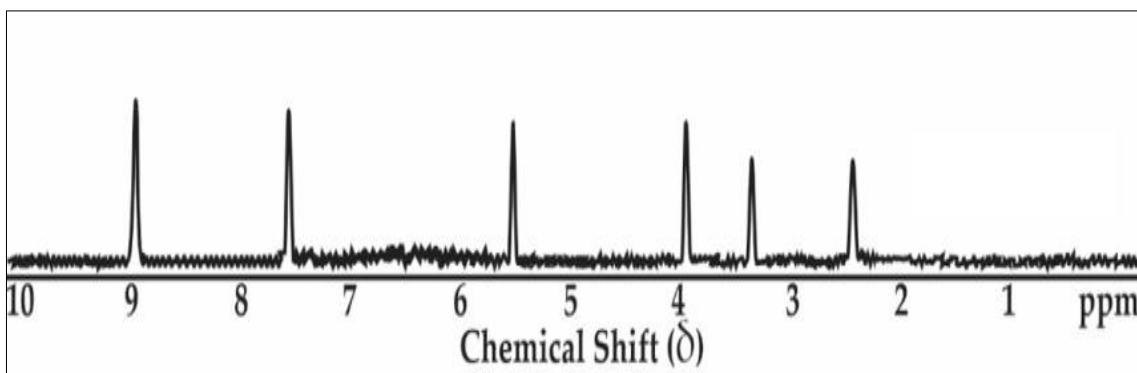
Figure 4: Infrared spectra of 2,2'-BPEDF Copolymer

Table 3: FT-IR Data of 2,2'-BPEDF Copolymer

Observed band frequencies (cm ⁻¹)	Assignment	Expected band frequencies (cm ⁻¹)
3415(b)	-OH phenolic Intermolecular hydrogen bonding	3400-3200
3061(m)	-NH, stretching	3000-3400
1434(sh,m)	Aromatic ring(substituted)	1600-1450
1380(sh,m)	-CH ₂ methylene bridge	1390-1270
1259(m)	C-N stretching	1200-1500
599(m)	2, 4, 2', 4' substitution in aromatic ring	550-600
829(m)	Ring substitution	800-840

Proton NMR Spectrum

¹H NMR spectra of 2,2'- BPEDF copolymer is introduced in Fig. 5 and NMR spectral information is displayed in table 3. The singlet got in the locale 2.39 (δ) ppm might be because of the methylene proton of Ar - CH₂ - Ar connect. The powerless various signs (unsymmetrical example) in the locale of 6.50 (δ) ppm might be credited to sweet-smelling proton (Ar-H). The signs in the reach at 8.89 (δ) ppm might be because of phenolic hydroxyl protons. The much down field substance shift for phenolic - OH obviously demonstrates the intramolecular hydrogen holding of - OH bunch. The sign showed up in the area at 5.51 (δ) ppm is because of the proton of - NH connect. The sign showed up in the district at 3.80 (δ) ppm is because of the methylene proton of Ar - CH₂ connect. The methyl protons of the -CH₂ moiety might be recognized by the serious top at 3.30(δ) ppm.

**Figure 5: ¹H NMR Spectra of 2,2'-BPEDF Copolymer**

Surface Morphology (SEM)

Fig. 6 addresses the filtering electron micrographs of 2,2'- BPEDF copolymer tar. The photos of 2,2'-BPEDF copolymer display wipe like construction got from the conglomeration of little granules. At lower amplification the gum shows spherulites in which the gems are masterminded more modest in surface region with all the more firmly stuffed constructions. This shows the glasslike idea of the copolymer tar and this property shows the low particle trade limit with regards to higher hydrated size metal particle. At various amplification the pitches show more nebulous person with less shut stuffed surface having profound pits. Amorphous character with less shut pressed surface having profound pits. The amorphous character demonstrates that tar in this way has higher trade for metal particles. The morphology in this manner distinguished by SEM as glasslike just as undefined or change among translucent and nebulous, showing pretty much good particle trade limit. The polymerization response continues by presenting indistinct character in the copolymer test [31].

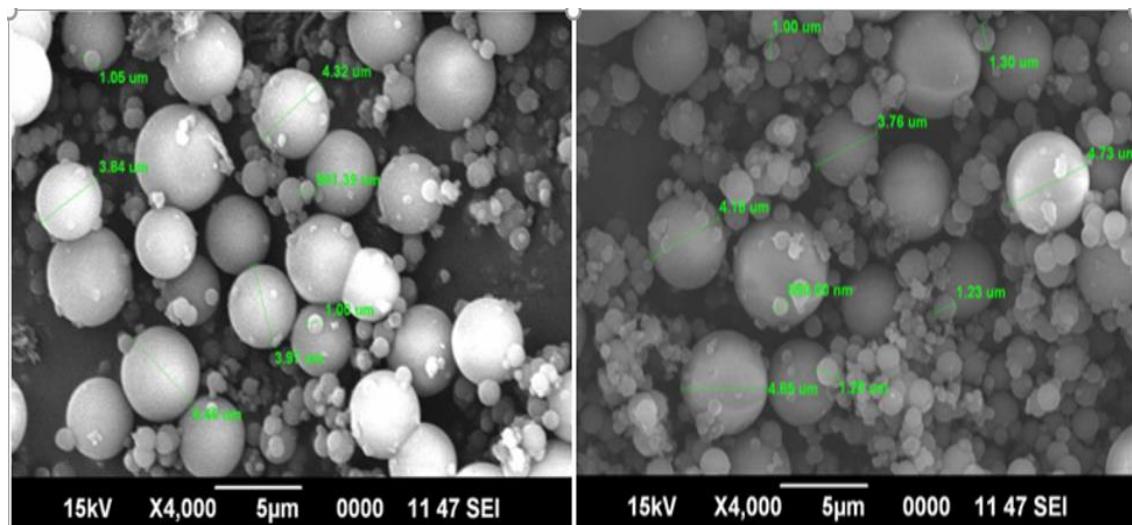


Figure 6: Scanning Electron Microscopy of 2,2'-BPEDF Copolymer

Thermal Analysis

2,2'-BPEDF copolymer was exposed to thermogravimetric examination and the information was utilized to survey the debasement design. Warm debasement conduct of blended copolymer has been fused in Table 4.and deterioration design is displayed in Fig.7in temperature range from 40 to 750°C. Decomposition example of copolymer thermogram shows four decay steps in which the deficiency of water atom (4.27% expected and 4.02% determined) has been seen up to 150°C. initial step decay step begins from 178 to 290°C which addresses the debasement of phenolic - OH bunches appended to fragrant core (27.49% anticipated also, 27.96% determined). The Second decay step begins from 290 to 580°C, comparing to 82.12% mass loss of fragrant core against determined 82.31%. The third deterioration step begins from 290 to 580°C which compares to loss of side chain of ethylenediamine. In fourth stage 540-724°C complete ethylenediamine moiety (98.33% expected and 100% determined). Consequently, no residue may be assigned after complete degradation.

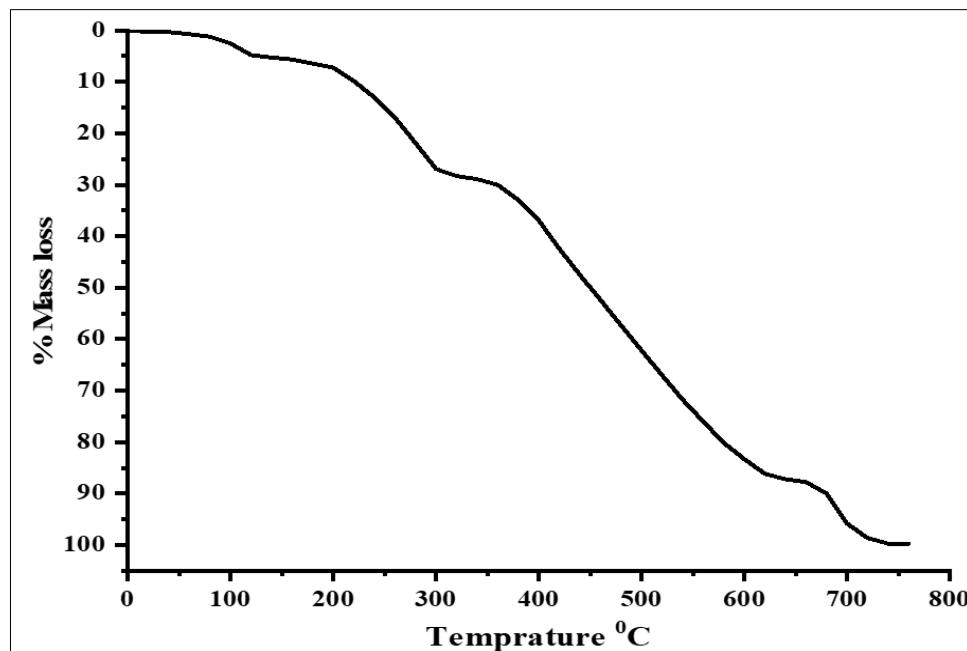


Figure 7: Decomposition pattern of 2,2'-BPEDF copolymer

Kinetics of Thermal Decomposition by the, Sharp and Wentworth, and Freeman-Carroll Methods

The noticed thermal dependability of 2,2'-BPEDF copolymer copolymer might be expected to the more grounded intermolecular hydrogen holding present in polymer which might be credited due to the presence of water of crystallization bringing about the protection from higher temperature. By applying the thermogravimetric information to four thermal corruption dynamic strategies, that is, the Sharp and Wentworth, and Freeman-Carroll strategies, it shows four unique debasement steps relating to loss of particular gatherings. The thermoanalytical information still up in the air for various stages as given in Table 4. This motor examination ought to be a beginning stage to get the valuable data on the conduct of test.

Table 4: Kinetic Parameters of 2,2'-BPEDF copolymer

Copolymer 2,2'-BPEDF						
Activation energy		Half Decomposition Temperature (T°C)	Entropy change ΔS (J)	Free energy change ΔF (kJ)	Frequency factor Z (S⁻¹)	Apparent entropy change (S*)
F.C.	S.W.					Order of reaction (n)
17.47	17.96	298	-153.24	35.26	568.36	-24.94
						1.02

To acquire the relative warm solidness of terpolymer 2,2'-BPEDF, the strategies depicted by Sharp and Wentworth, and Freeman-Carroll were embraced. From the outcomes, it is inferred that the upsides of motor boundaries show great concurrence with one another in Sharp furthermore, Wentworth and Freeman-Carroll's strategies as displayed in Table 4. Genuinely equivalent aftereffects of motor boundaries, in particular entropy change(ΔS), energy of actuation (E_a),order of reaction (n), frequency factor (z), obvious entropy (S^*)are got for every corruption step got by Sharp and Wentworth and Freeman-Carroll strategies are in great concurrence with one another with slight varieties between the outcomes; it is that the upsides of active boundaries rely uponactive strategies utilized just as corrupting species at a specific advance. All out estimations acquired from various dynamic strategies showed that the mathematical worth of active boundaries relies upon the numerical models used to investigate the exploratory information and level of corruption. By utilizing the previously mentioned procedures, varieties in the outcomes are gotten which addresses adaptability and incredible utility of warm corruption of numerical energy conditions in thermogravimetry. Nonetheless, it is hard to reach any one of a kind inference in regards to the deterioration instrument. From the thermogravimetric examination, dynamic plots of the copolymer have been displayed in Figures 8,9 and 10.

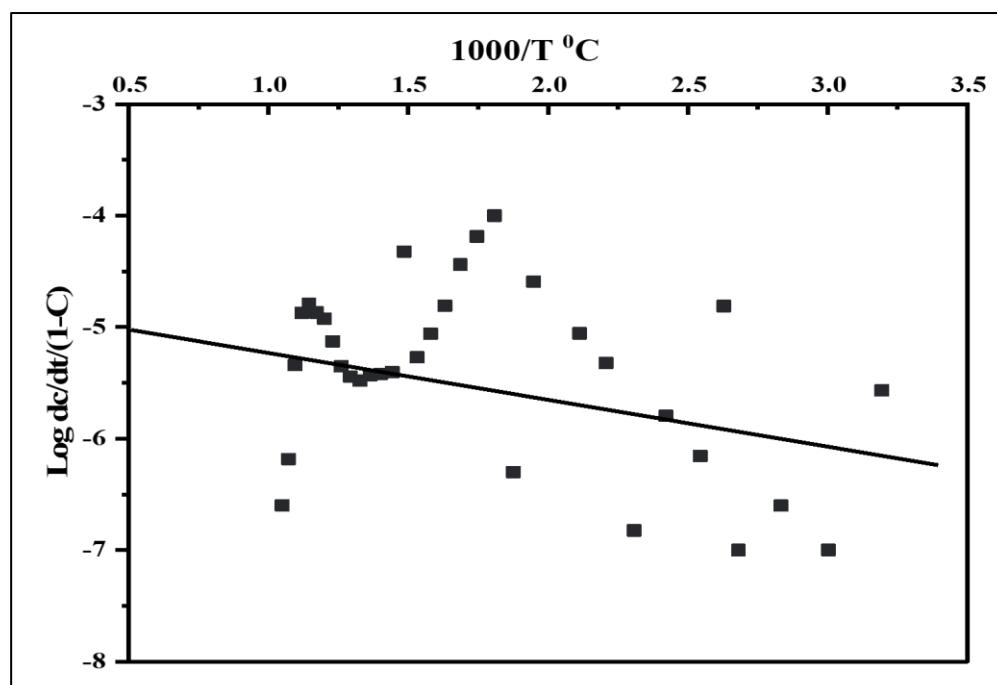


Figure 8: Sharp and Wentworth's plot of 2,2'-BPEDF copolymer

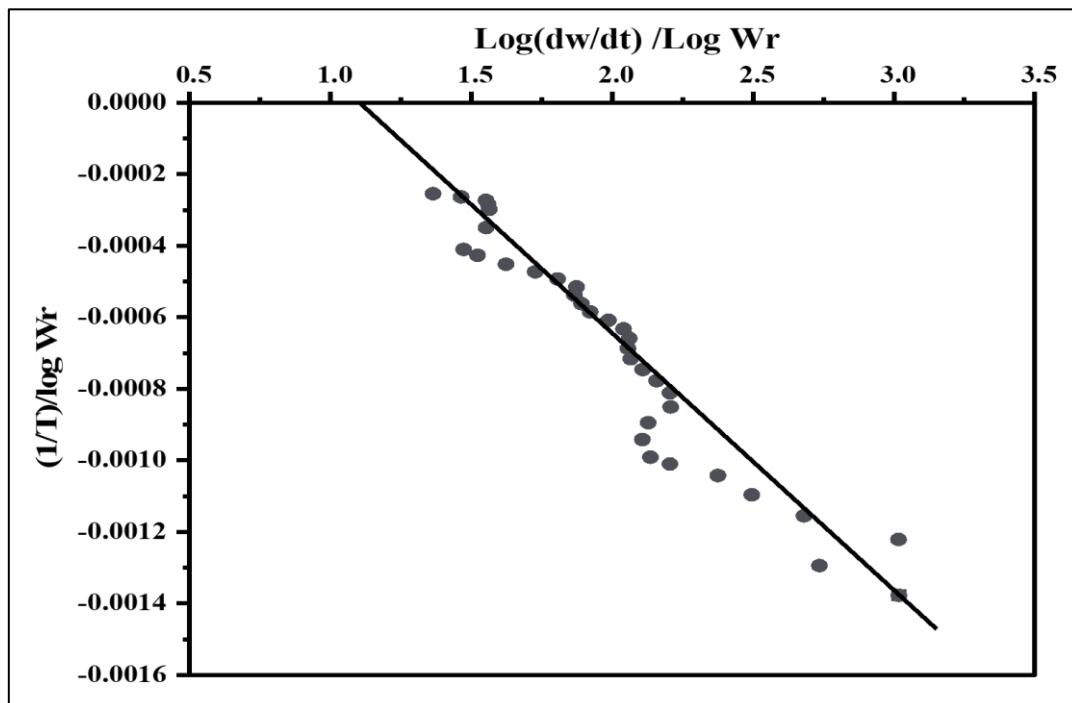


Figure 9: Freeman-Carroll's plot of 2,2'-BPEDF copolymer for order of reaction.

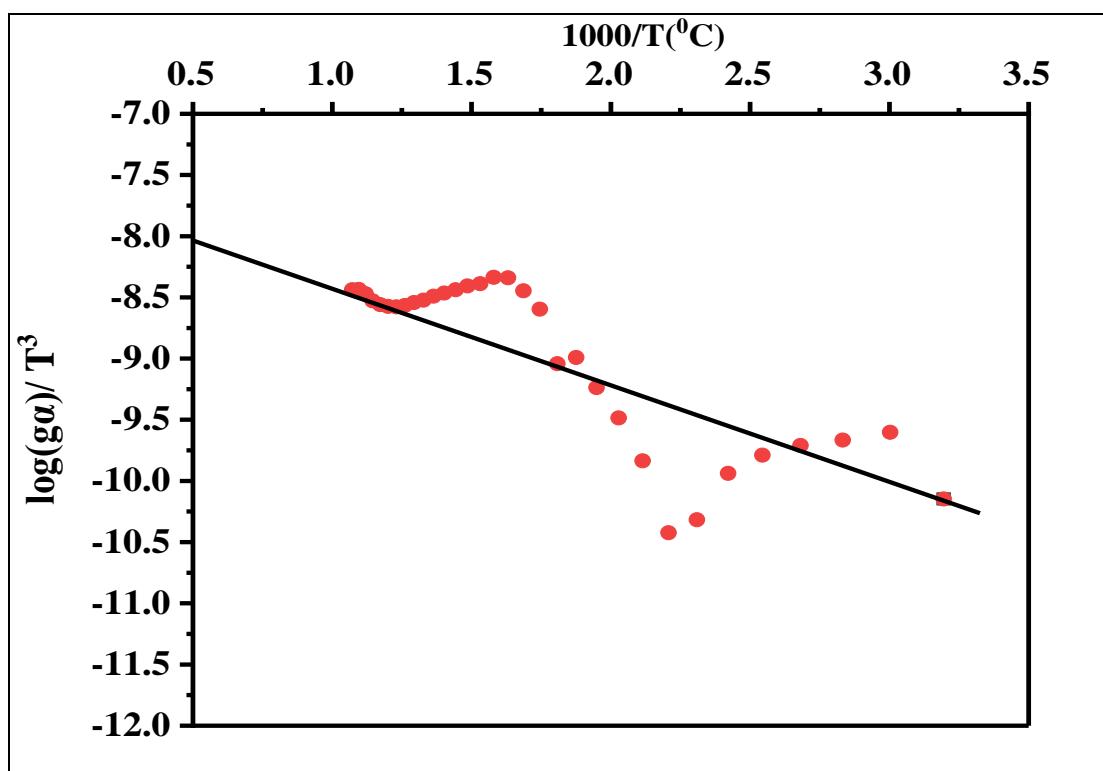


Figure 10: Freeman-Carroll's plot of 2,2'-BPEDF copolymer for activation energy.

By utilizing the previously mentioned strategies, slight varieties are gotten in the middle of Sharp what's more, Wentworth and Freeman-Carroll strategy which are observed to be in acceptable concurrence with each other. According to the perspective of compound energy, 2,2'-BPEDF copolymer is thermally steady. Low upsides of recurrence factor uncovered that deterioration response of copolymer might be moderate also, no other conceivable explanation can be given. Be that as it may, in Freeman-

Carroll, and Sharp and Wentworth's plots, everything focuses didn't fall on straight line, which demonstrates that the disintegration of terpolymer isn't complying with first request of response impeccably [32-33].

CONCLUSIONS

Synthesized copolymer (2,2'-BPEDF) has been affirmed which is upheld by the outcomes got by essential investigation and phantom information. From the natural examination, UV noticeable, IR, and ¹H-NMR ghostly investigations, the proposed design of the integrated copolymer is affirmed. The upsides of dynamic boundary acquired from the Sharp and Wentworth what's more, Freeman-Carroll techniques are in acceptable concurrence with one another. Thermogram of copolymer gum shows four corruption steps and ethylenediamine particle nearly debases totally up to 750°C. From the outcomes got, the upsides of active boundaries are altogether controlled by the degree of debasement and estimation techniques used to break down the test data. In TGA the energy of initiation assessed from the Sharp-Wentworth and Freeman-Carroll techniques are observed to be almost equivalent and the dynamic boundaries obtained from Freeman Carroll technique are found to comparable, showing the normal reaction mode. Be that as it may, it is hard to draw any interesting end with respect to the decomposition system. Low upsides of crash recurrence factor (Z) may be concluded that the deterioration response of 2,2'- dihydroxybiphenyl, ethylenediamine what's more, formaldehyde copolymer can be delegated 'moderate response'. The deterioration response was begun at higher temperature, demonstrating a copolymer 2,2'-BPEDF is thermally steady at higher temperature.

ACKNOWLEDGMENTS

The author wish to communicate their true gratitude to Principal, Kamla Nehru Mahavidyalaya, Nagpur, India for collaboration and for giving important research center offices what's more, to the Director, STIC Analysis Cochin for did otherworldly examination and warm investigation.

REFERENCES

- [1] Gurnule W B, Rathod Y U. Curr Appl Polym Sci 2020;4: 1 - 8.
- [2] Azarudeen RS, Ahmad MAR, Burkanudeen AR. Desalination 2011;268(1-3): 90 – 96.
- [3] Gurnule WB, Bisen VR. Int J TrenInnov Comp Commu 2015;3(20):86 – 93.
- [4] Singru RN, Zade AB, Gurnule WB. J Appl Polym Sci 2008; 109(2): 859-868.
- [5] Ahamed MR, Azarudeen R, Karunakaran M, Karikalan T, Burkanudeen A. Int J Chem Env Engg 2010; 1(1):7-12.
- [6] Burkanudeen AR, Ahamed MAR, Azarudeen RS, Begum MS, Gurnule WB. ArabianJ Chem 2016;9: 296-305.
- [7] Velmurgan G, Ahmed KR, Azarudeen RS. Iranian Polym J 215;24(3):222 – 242.
- [8] Mane VD, Wahane NJ, Gurnule WB. JApplPolym Sci. 2009; (111) 6, 3039–3049.
- [9] Azarudeen RS, Ahamed MAR, Thirumarimurugcm M, Prabu N, Jeyakumar D. PolymAdv Technol 2016;27(2): 235 - 244.
- [10] Ahamed MAR, Balasubrarnanian N, Azarudeen RS, Thirurnarirnurugan M. Separation Sci Technol 2018;53(3): 513 – 526.
- [11] Rahangdale SS, Zade AB, Gurnule WB. Ultra Science 2007; 19:213–218.
- [12] Srivastava SC, Haque MA, Paliwal LJ. Materials Today Proceeding 2017;4(4): 691-699.
- [13] Zalloum RM, Mubarak SM. J Appl Polym Sci 2008; 109:3180-3184.
- [14] Chauhan NPS. J Ther Anal Cal 2012; 110 (3):1377-1388.
- [15] Singru RN, Zade AB, Gurnule WB. J Appl Polm Sci 2008; 109(2):859-868.
- [16] Yeole MM, Shrivastava S, Gurnule WB. Der Pharma Chemica 2015; 7(5):124-129.
- [17] Gurnule WB, Makde CS, Ahmed M. J Env Res Develop 2013; 7(3):1183-1192.
- [18] Gharbi S, Khiari J, Jamoussi B. JChemEng Process Technol 2014; 5(4):1-7.
- [19] Das NC, Gurnule WB. Int J Curr Engg Sci Res 2019; 6 (1):1414-1425.
- [20] Mandavgade SK, Dontulwar JR, Gurnule WB. Der Pharma Chemica. 2012; 4(4):1695-1703.
- [21] Sharp JB, Wentworth SA. Anal Chem 1969; 41(14): 2060-2062.
- [22] Freeman ES, Carroll BJ. Phys Chem 1958; 62 (4): 394-397.
- [23] Ahmad N, Alam M, Al-Otaibi MAN. J.Thermal Anal Calorim 2015;119(2):1381-1391.
- [24] Ahamed MAR, Azarudeen RS, Prabhu N, Burkanudeen AR. Sepr Sci Tech 2015;50(13): 1925 – 1939.

- [25] Bawankar SV, Kukade SD. Int J Res Biosci Agri Tech 2015;2: 292-300.
- [26] Gurnule WB, Bisen VR. Int J Res Biosci Agri Tech 2017;2(5): 472-477.
- [27] Maskey S, Burhate P, Rahangdale P. Int J Res Eng App Sci 2015;5(12): 39-47.
- [28] Hamouz OC, EstatieSA, MK, Morsy MA, Saleh TA. 2017;70: 345-351.
- [29] Dutta S, Das AK. J Appl Polym Sci 2007;103: 2281.
- [30] Raj JA, Vedhi C, Burkanudeen A, Arumugam P, Manisankar P. Ionic 2010;16:171-175.
- [31] Patel MM, Kapadia MA, Patel GP, Joshi JD. Iranian Polym J 2007; 16(62):113-122.
- [32] Mane S, Ponrathnam S, Chavan N. Des. Monomers Polym 2015; 18:723-733.
- [33] Zalloum RM, Mubarak SM. J Appl Polym Sci 2008; 109:3180-3184.