

Research Article

Base-Catalyzed Polymerization of a Substituted Methylenebicyclo[3.3.1]nonane

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Lignite humic acid on reaction with formaldehyde and aqueous alkali led to a polybicyclo[3.3.1]nonane. This was characterized spectroscopically using mass spectrometry, FT-IR, powder X-ray diffraction, TEM, and NMR studies (¹H-NMR, CP-MAS-SS-NMR) which though challenging were useful for confirming the structure of the BCN polymer. The product showed an envelope peak in its MALDI-MS spectrum, based on which \bar{M}_n , \bar{M}_w , and polydispersity index have been calculated. Based on the NMR spectrum of intermediate, the presence of the N-formyl group has been shown in it. The new polymer could be useful in agriculture in water-deficient areas. Most papers on humic acids include only broad and general information like elemental analysis (occasionally TEM, SEM, TGA, DSC, etc.). Very complicated structures have been proposed by scientists earlier. Only in very recent years, it has been recognized that these are relatively small molecules which masquerade as supramolecular structures. It is pointed out that most papers do not put down the structure of the compound and provide no concrete proof for proposing such structures. The novelty of our work is that we have characterized the precise molecular weights based on mass spectrometry and NMR spectroscopy along with a well-defined structure. This is not the case in most other publications.

1. Introduction

The use of humic acids from soil, brown coal, and city solid waste has been engaging our attention for some years now [1–5]. Humic acid isolated from lignite is used as a growth promotant in agriculture. One such example of a commercial product is Agritone 4.5 successfully used by farmers in India [6]. It is increasingly becoming clearer that humic acids are small molecules [7] which masquerade as large supramolecular structures [8, 9]. Though it has been stated that novel chemical compounds could be isolated from lignite, so far, no such compound has been isolated from it. In the meantime, we came across [10] a paper on cross-linking of humic acid using formaldehyde and alkali. This humic acid contained aromatic phenolic groups which could lead to cross-linking via methylene (-CH₂-) bridge formation. Such cross-linked

humic acids are capable of capturing both water and cations efficiently, a result which could be useful in water-deficient areas like deserts worldwide. The identification and analysis of envelope peaks in mass spectra have been used to characterize both polymers and peptides [11–15].

We carried out a similar formaldehyde-alkali reaction with lignite humic acid and isolated a new product which was lachrymatory in nature, and it is proposed that this is due to removal of the formyl group. Based on the prominent signal centered at δ 8.310 ppm in its ¹H-NMR spectrum, it has been shown to be a N-formyl derivative. This compound shows a mass spectral envelope peak pointing towards its polymeric nature. Acid hydrolysis of this led to a product, which was no longer lachrymatory in nature. Based on X-ray diffraction studies, the “monomer” is proposed to be a substituted bicyclo[3.3.1]nonane containing an exposed

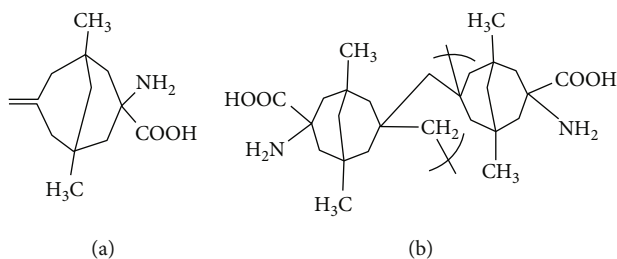


FIGURE 1: (a) Structure of the proposed monomer (3-amino-1,5-dimethyl-7-methylenebicyclo[3.3.1]nonane-3-carboxylic acid). (b) The proposed "dimeric" repeat unit of the BCN polymer.

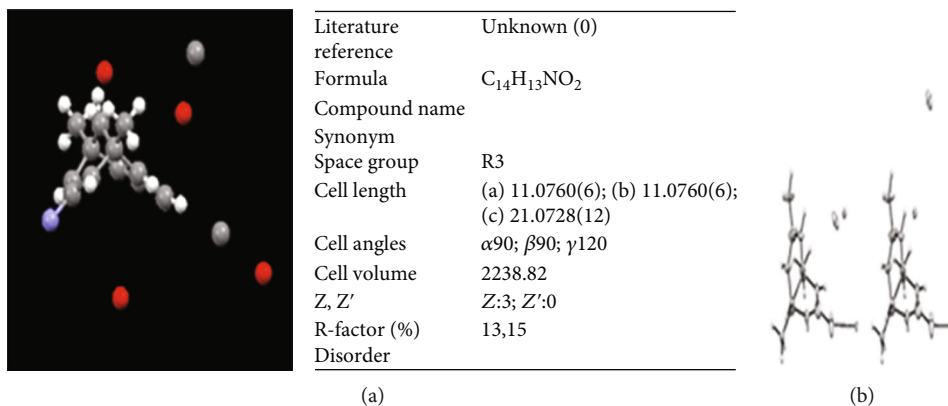


FIGURE 2: (a) X-ray diffraction study of lignite humic acid-HCHO/OH⁻ reaction product which provided evidence for the proposed monomer (poly-(3-amino-1,5-dimethyl-7-methylenebicyclo[3.3.1]nonane-3-carboxylic acid)). (b) ORTEP diagram of BCN polymer obtained from X-ray diffraction studies which again confirms the substituted bicyclo[3.3.1]nonane skeleton.

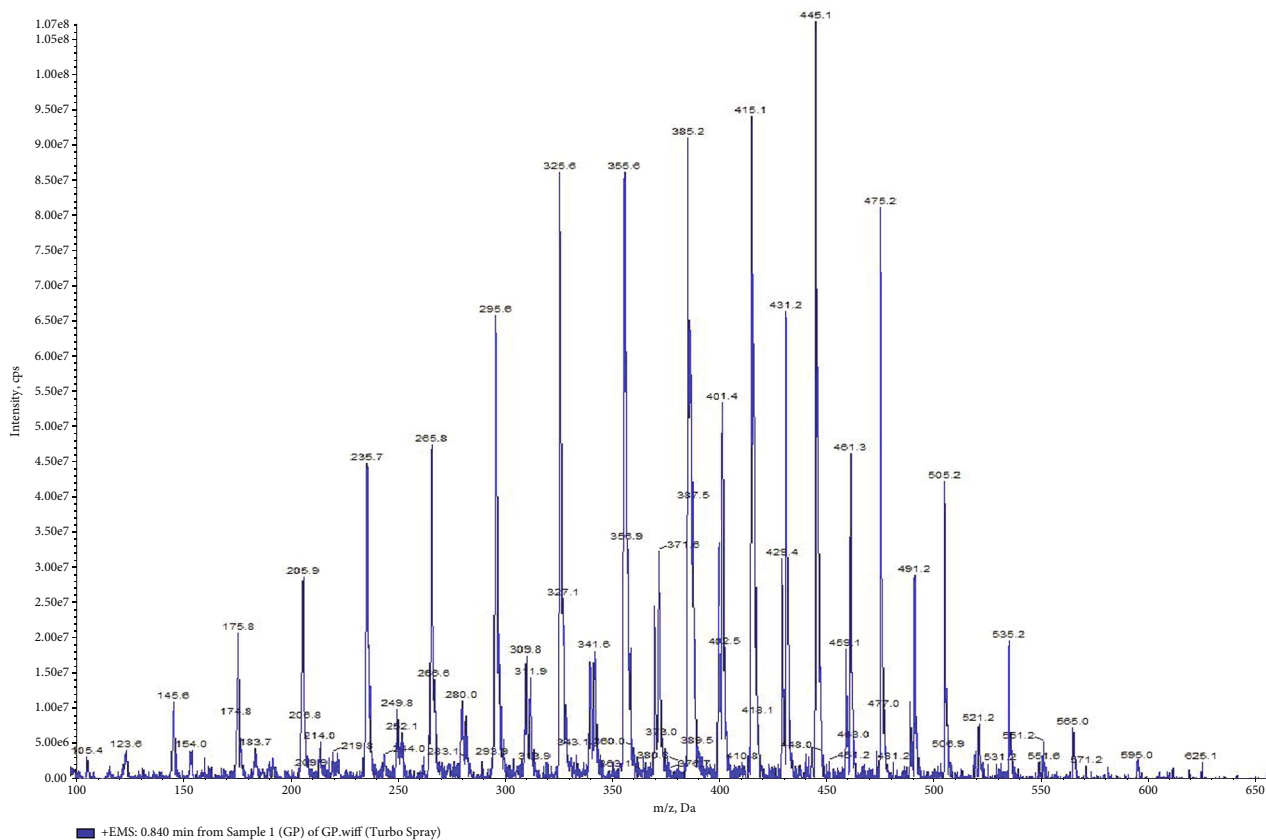


FIGURE 3: MALDI-MS spectrum showing envelope peak of BCN polymer.

TABLE 1: Calculation for \bar{M}_n and \bar{M}_w of the new BCN polymer.

M_i	x_i	$M_i x_i$	$\frac{M_i x_i}{31217.2}$	$\frac{M_i x_i}{31217.2 M_i}$
123.6	0.5	61.8	0.001	0.1236
145.6	1.2	174.72	0.005	0.728
175.8	2.1	369.18	0.011	1.9338
205.9	2.8	574	0.018	3.7062
235.7	4.6	1081	0.034	8.0138
265.8	4.7	1245.5	0.039	10.3662
295.6	6.5	1917.5	0.061	18.0316
325.6	8.8	2860	0.091	29.6296
355.6	8.8	3124	0.1	35.56
385.2	9.3	3675.3	0.117	45.0684
415.1	9.5	3943.4	0.126	52.3026
445.2	10	4450	0.142	63.2042
475.2	8.3	3942.5	0.126	59.8752
505.2	4	2020.8	0.064	32.3328
535.2	2	1070	0.034	18.1968
565	1	565	0.018	10.17
595	0.3	178.5	0.005	2.975
625.1	0.2	125	0.004	2.5
	84.6	31217.2		394.7178

$$\bar{M}_n = 31217.2$$

$$\bar{M}_w = 33393.1259$$

$$PD = \frac{33393.1259}{31217.2000} = 1.06$$

$$\text{Charge} = 14.83$$

$$\text{Degree of dispersity} = \frac{31217.2}{445.1} = 70$$

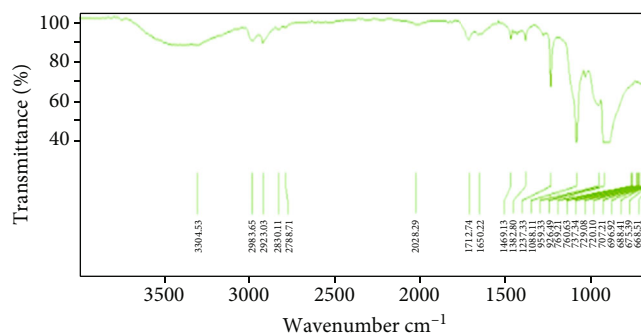
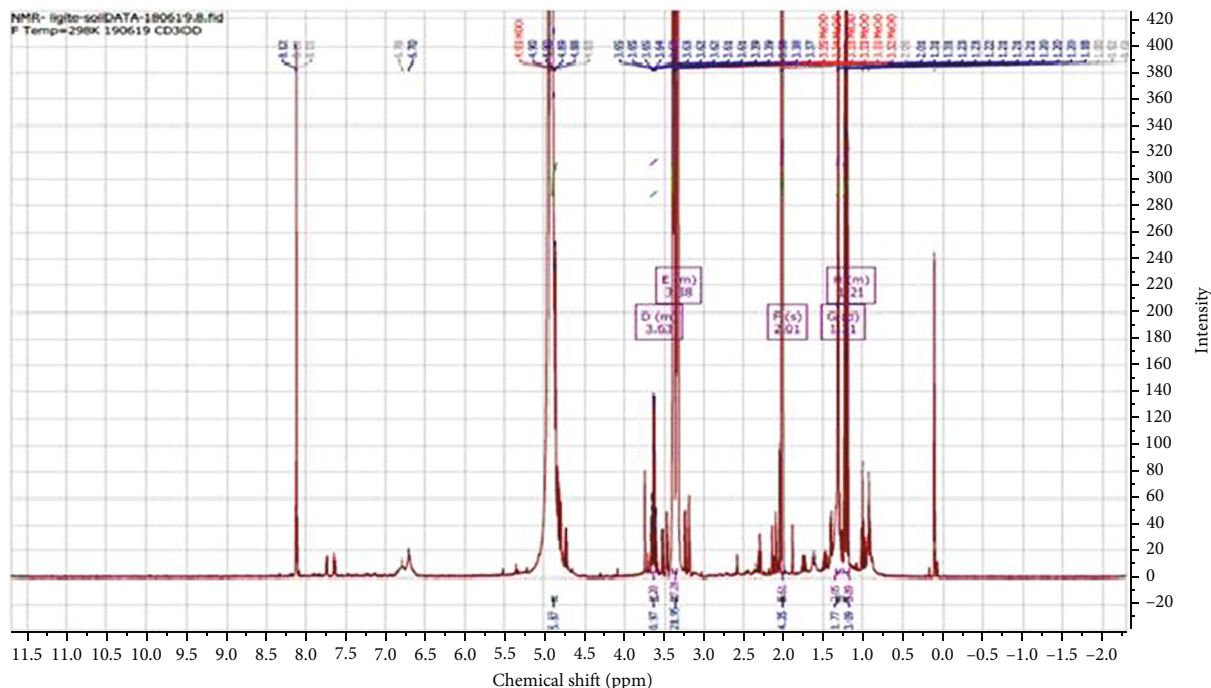


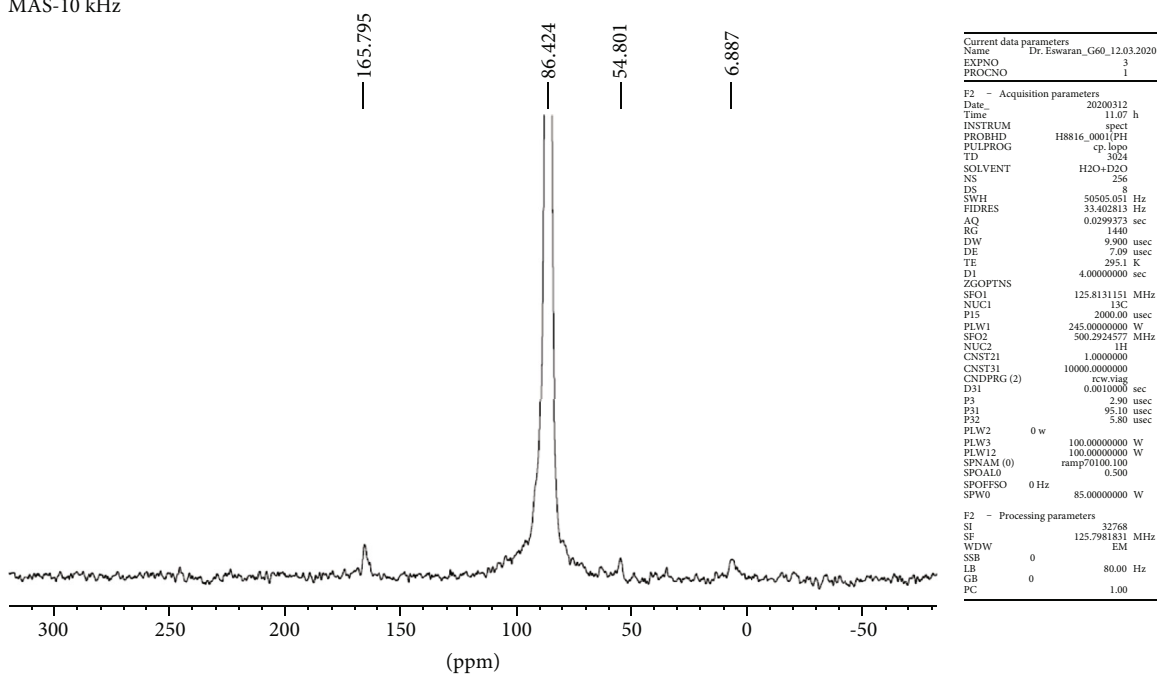
FIGURE 4: FT-IR spectrum of the BCN polymer.

exocyclic double bond. This new compound is not aromatic in nature but is a bridged alicyclic compound, not known in chemical literature before. Thus, cross-linking via formation of methylene ($-\text{CH}_2-$) bridge observed in aromatic phenols cannot occur in our case. It is proposed that, instead, a base-catalyzed olefin polymerization happens in our case leading to the formation of the substituted polybicyclo[3.3.1]nonane. The envelope peak of the poly-(3-amino-1,5-dimethyl-7-methylenebicyclo[3.3.1]nonane-3-carboxylic acid) is centered at m/z 445.1 a. m. u. and attributed to the

“dimeric” repeat unit $(223.16 \times 2 - 1\text{H}) = 445.1$ a. m. u. (% error: 0.04%). Further, \bar{M}_w , \bar{M}_n , and polydispersity index have also been calculated. Computationally, a supramolecular structure with a cavity has been generated [16, 17]. Based on the NMR evidence, it is proposed that this cavity traps formaldehyde $-\text{OH}^-$ $[\text{OHCH}_2\text{O}^-]$ making it lachrymatory. On treatment with dilute HCl, the product was no longer lachrymatory. The latter could be important in agriculture for retention of cations and water, in water-deficient soils, especially in deserts [18–20].

FIGURE 5: ^1H -NMR spectrum of the BCN polymer.

G60
13C CP
MAS-10 kHz

FIGURE 6: ^{13}C -CP-MAS-SS-NMR spectrum of the BCN polymer.

2. Experimental

2.1. Materials and Methods. All the reagents and solvents were purchased from Sigma-Aldrich (greater than 99.9% purity). FT-IR studies were performed using Bruker Tensor 27 FT-IR with diamond ATR cell in methanol solution. Ini-

tial ^1H -NMR studies were done in the International Centre for Genetic Engineering and Biotechnology (ICGEB, New Delhi) and the Translational Health Science and Technology Institute, Faridabad (THSTI, Faridabad). ^1H -NMR, 2D-NMR, temperature-dependent NMR, and solid-state NMR spectra were recorded using Bruker 500 MHz NMR

instrument in D₂O solution in Tata Institute of Fundamental Research (TIFR), Hyderabad. Mass spectrum of this compound was recorded in THSTI, Faridabad, and MALDI-MS spectrum was recorded in the Regional Center for Biotechnology (RCB, Faridabad) in methanol solution. Transmission electron microscopy (TEM) was also recorded using the G2 30-U twin microscope in methanol solution and mica-coated ITO grid. Single-crystal X-ray diffraction was recorded using Bruker Smart Apex II Ultra with sample characterizing temperature range of 80 K–500 K for crystal structure determination and electron density mapping. The specifications are as follows: rotating anode; molybdenum source; collimator diameter, 0.5 mm; maximum operating power, 45 kV 80 mA; detector, CCD detector (Apex II) with a fixed distance of 58.2 mm; and 3-axis goniometer with fixed Kappa axis. Powder X-ray diffraction was recorded using Bruker D8 Advance with sealed tube anode, copper source, maximum operating power of 40 kV 40 mA, and detector (LYNXEYE (1D)). Both single-crystal X-ray diffraction and powder X-ray diffraction were recorded at X-ray facility in Indian Institute of Science (IISc), Bengaluru.

2.2. Synthesis of Polybicyclo[3.3.1]nonane. 500 mg of lignite humic acid and 50 mL of 1 M NaOH solution were poured into a 250 mL of round bottom flask. The mixture 70 mL of 37% formaldehyde was added. It was then refluxed with stirring at 60°C for 2.5 h. In the next step, solution was allowed to cool down at room temperature and then filtered.

The filtrate was acidified with hydrochloric acid (HCl) followed by ethyl acetate extraction. The ethyl acetate fraction was kept in the refrigerator with anhydrous sodium sulphate overnight. Following filtration, the filtrate was subjected to the Buchi evaporation to obtain the colorless, water-soluble polybicyclo[3.3.1]nonane (yield 280 mg).

3. Results and Discussion

The proposed structures of the “monomeric” and the “dimeric” repeat unit are shown in (Figure 1).

This is based on the most intense peak observed at m/z 445.1 in the MALDI-MS spectrum.

Single-crystal X-ray diffraction analysis reveals that the molecular formula of the proposed monomer is C₁₃H₂₁NO₂ and the systematic name is 3-amino-1,5-dimethyl-7-methylenebicyclo[3.3.1]nonane-3-carboxylic acid with the molecular weight of m/z 223.1512 a. m. u. (Figure 2).

The molecule can exist in the double chair, chair-boat, and double boat conformations which could interconvert fairly rapidly due to low energy barriers between the different conformers.

3.1. Mass Spectral Studies on the BCN Polymer. The MALDI-MS spectrum of BCN polymer dissolved in methanolic solution shows the envelope peak centered at m/z 445.1 a. m. u. (Figure 3). This peak represents the “dimer” of 3-amino-1,5-dimethyl-7-methylenebicyclo[3.3.1]nonane-3-carboxylic acid (error percentage being 0.04% ($2 \times 223.1512 = 446.3024 - 1H = 445.2924$ a. m. u.)). [21].

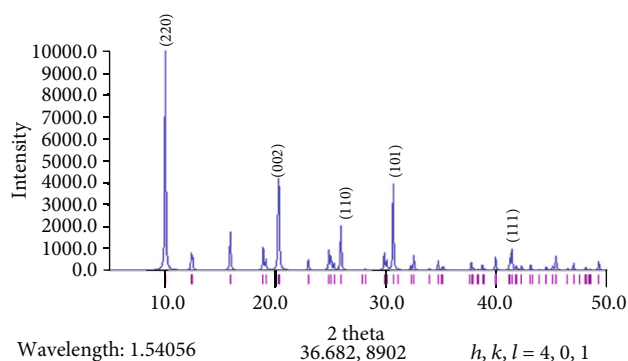


FIGURE 7: Powder X-ray spectrum of BCN polymer.

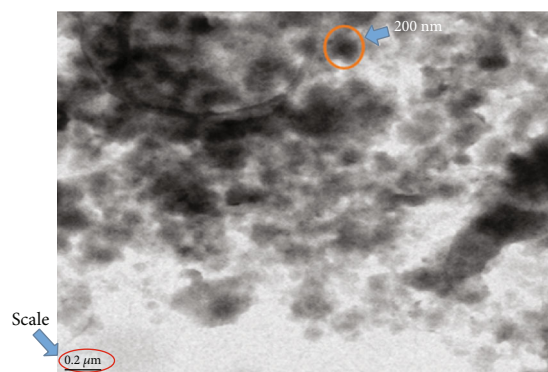


FIGURE 8: TEM image of the BCN polymer.

The periodic pattern of loss of m/z 30 a. m. u. (N-formylated intermediate) and 14 a. m. u. (N) has been observed which confirms its formation.

3.2. Analysis of the Envelope Peak and Determination of \bar{M}_n and \bar{M}_w . The envelope peak obtained from MALDI-MS spectrum and its analysis shows the polymeric nature of the material. Based on the above, the number average molecular weight (\bar{M}_n) and weight average molecular weight (\bar{M}_w) and degree of dispersity have been calculated (Table 1). The formulas used are given below.

$$\bar{M}_n = \sum M_i x_i,$$

$$\bar{M}_w = \frac{\sum M_i x_i M_i}{\sum M_i x_i}, \quad (1)$$

$$PD = \frac{\bar{M}_w}{\bar{M}_n}.$$

The charge of the polymer is calculated to be 14.83. Charge = (445.1/loss between any two consecutive peaks in mass spectrum).

The above calculation shows its polymeric nature and confirms that the total number of monomeric units involved is 140.

3.3. FT-IR Spectral Studies. The FT-IR spectral studies show the peaks of native lignite humic acid at 1040, 1530, 1544,

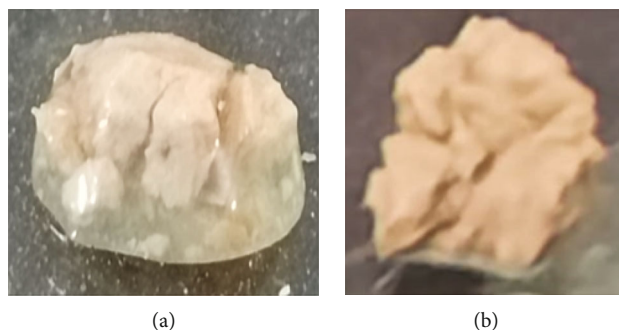


FIGURE 9: (a) Swollen BCN polymer after addition of water. (b) Image after 25 minutes at room temperature.

1620, and 1700 (C=O stretching); 2850, 2920, and 3400 (O-H stretching); and 3690 cm^{-1} (O-H stretching) absorption bands previously [22]. The FT-IR spectrum of BCN polymer is shown in (Figure 4).

The methanolic solution of BCN polymer provides the absorption band at 1088.11 (C-O stretching); 1237.93, 1382.80, and 1469.13 (C-H bending); and 2028.29, 2788.71, 2830.11, 2923.03, and 2983.85 cm^{-1} (C-H stretching). The peaks obtained at 1650.22 (N-H), 1712.74 (COOH), and 3304.83 cm^{-1} (O-H stretching) confirm the presence of $-\text{NH}_2$, $-\text{COOH}$, and $-\text{OH}$ functional groups in this polymer, respectively.

3.4. NMR Spectral Studies of the BCN Polymer

3.4.1. ^1H -NMR Spectral Studies. ^1H -NMR spectral studies showed the formation of the N-formyl derivative. Peaks are centered at δ 8.310 (s, H) for N formyl group (NHCHO), 2.21-2.30 (m, 2 H) for CH_2 , 1.99-2.11 (m, 2 H) for CH_2 , 1.70-1.83 (m, 2 H) for CH_2 , 1.56-1.67 (m, 2 H) for CH_2 , 1.12-1.40 (m, 2 H) for CH_2 , and 0.77-0.86 (m, 3 H) for CH_3 group (Figure 5). The detailed spectra are shown in SI-1 to SI-2.

3.5. CP-MAS Solid-State NMR Spectral Studies on the BCN Polymer. FT-IR spectrum and the alkali solubility of the compound indicated the presence of the carboxylic acid groups. However, ^1H -NMR solution studies could not provide evidence for the presence of the carboxylic acid group [23]. Hence, we undertook ^{13}C -CP-MAS-SS-NMR studies using Bruker 500 MHz instrument at 8 kHz for BCN polymer, shown in (Figure 6).

This study provided evidence for the presence of carboxylic acid at 165.795, CH_2OH at 86.424, OCH_2 signal at 54.801, and the methyl group peak at 18.292 ppm. Solid-state NMR studies thus confirmed the new compound being a carboxylic acid.

3.6. Powder X-Ray Diffraction Studies. Powder X-ray studies are generally used for characterizing crystallinity of materials and determining dimensions of unit cell. The spectrum has intense and sharp peaks. It contains a good proportion of highly disordered materials as shown in (Figure 7).

The peaks at 2θ values shows the plane (220), (002), (110), (101), and (111) and points towards crystalline graphite-like structure. The neighboring planes (002), (110), and (220) indicate the random lattice structure of

the crystalline material. The three peaks (110), (002), and (220) show the saturated structure of the material [24, 25].

3.7. Transmission Electron Microscopy Studies. Transmission electron microscopy (TEM) has been extensively used by researchers as characterization tool for better understanding morphology at atomic scale (Figure 8).

The 3D morphology of BCN polymer has been shown to be polycrystalline in nature [26]. The size of an aggregate is 200 nm at $0.2\text{ }\mu\text{m}$ scale.

Preliminary water retention studies of BCN polymer were carried out by the addition of 4-5 drops of water to 44 mg of BCN polymer (Figure 9). Observation reveals that the polymer swelled and the weight increased up to 90 mg.

Based on the above experiment, 104% increment of weight in BCN polymer on addition of water has been observed. After leaving it to dry for 30 minutes at room temperature, it weighed 66 mg indicating water retention up to 50% [27]. Further water retention studies using DOSY-NMR experiments are planned.

4. Conclusion

A new substituted methylenebicyclo[3.3.1]nonane (BCN) polymer has been prepared from lignite humic acid by base-catalyzed process. Spectroscopic studies like mass spectrometry, FT-IR, powder X-ray diffraction, and TEM and NMR studies (^1H -NMR, CP-MAS-SS-NMR) though challenging were useful for confirming the structure of the BCN polymer. Most useful was the analysis of envelope peak observed in its mass spectrum at m/z 445.1 which helped us to calculate its \bar{M}_n , \bar{M}_w , polydispersity index (PD), degree of dispersity, and charge on polymer. The new polymer could be used in water-deficient areas.

Data Availability

The data used to support the findings of this study have been deposited in the figshare repository (doi:10.6084/m9.figshare.22682530).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

SI-1: $^1\text{H-NMR}$ spectrum in the region δ 2.0-11.5 ppm, which provides concrete evidence for the aliphatic/alicyclic nature of the compound. Since this $^1\text{H-NMR}$ spectrum was recorded in D_2O , the protons of NH_2 and COOH get exchanged by deuterium and hence not observed in this spectrum. SI-2: expanded $^1\text{H-NMR}$ spectrum in the region δ 1.44–2.04 ppm where signals for different $-\text{CH}_2-$ and $-\text{CH}_3$ groups are observed. Detailed $^1\text{H-NMR}$ assignments are included in the text of the manuscript. Scheme 1: schematic for synthesis of BCN polymer. (*Supplementary materials*)

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