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Electronic Supporting Information (ESI)

Rational Design, Fabrication and Characterization of Thiol-rich 3D-porous Hypercrosslink Polymer as a New Engineered Hg^{2+} Sorbent: Enhanced Selectivity and Uptake

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1. Experimental Section

1.1. General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. Products were characterized by physical data, IR, ^{1}HNMR, ^{13}CNMR and HRMS spectra. Melting points were determined on a Thermo Scientific 9200 apparatus. IR spectra were obtained on a Bomen MB:102 FT-IR spectrophotometer. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, in DMSO with tetramethylsilane as an internal standard. HRMS spectra were measured on an Agilent 5975 mass spectrometer and elemental analyses were performed on a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. The polymer morphology was examined by AFM (Nano Wizard II). The thermal stability of functionalized polymer was investigated by NETZSCH STA 409 PC/PG under a nitrogen atmosphere (rate of $N_2 \approx 1$ Lh^{-1}). The Hg concentration was determined by Inductively Coupled Plasma, Optical Emission Spectrometry (ICP-OES) analysis. Nitrogen adsorption measurements were conducted at 77 K on a Micrometrics ASAP-2020 sorption meter. The specific surface area and the pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model, respectively.

*1.2. Synthesis of calix[4]resorcinarene **1***

Calix[4]resorcinarene was prepared according to a previously reported procedure.

*1.3. Synthesis of the 3D-network polymer based on calix[4]resorcinarene **2***

The desired polymer was synthesized by adding 42 mmol of formaldehyde to 14 mmol of the prepared calix[4]resorcinarene dissolved in 40 mL NaOH solution (10%) at room temperature. The resultant mixture was heated to 90 °C and maintained at this temperature for 20 h. Next, the excess alkali was washed out of the gel formed with cold water. The gel was allowed to stand at 100 °C for 1 h. Then, the gel was transformed into the acidic form by treatment with the 0.1 M HCl solution. The resulting solid was dried at 100 °C for 10 h.

*1.4. Synthesis of novel thiol-functionalized polymer **3***

The synthesized polymer **2** obtained from the above procedure (1.0 g), 3-(trimethoxysilyl)-1-propan thiol (0.6 g, 3 mmol) were introduced into 50-mL round-bottomed flask containing 10 mL H_2O/EtOH at room temperature. The reaction mixture was heated to 90 °C and stirred at this temperature for 20 h. The desired thiol-functionalized polymer **3** was collected by filtration and washed several times with hot toluene before being dried at 100 °C.

*1.4.1. Determination of the amount of thiol functionalities grafted onto the polymer **3***

The amount of thiol functionalities grafted onto the polymer was determined by elemental analysis to be 3.4 mmol per gram of dry polymer.

1.5. Removal procedure

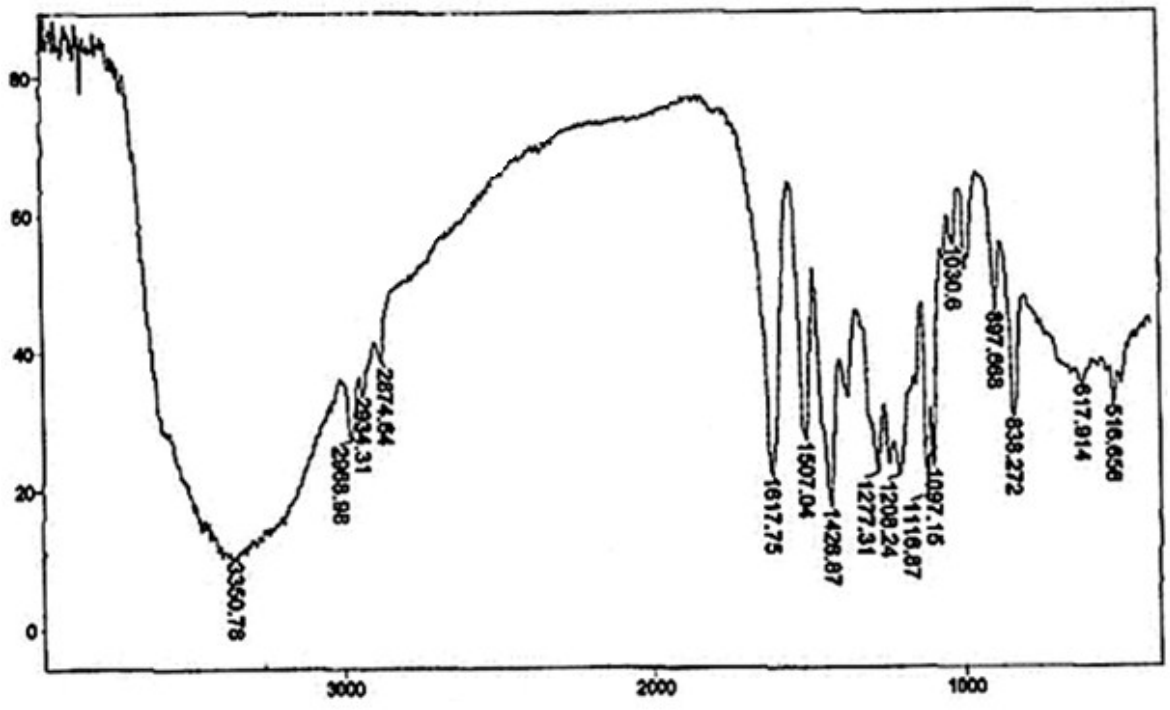
The adsorption of Hg (II) on the thiol-functionalized polymer **3** was investigated in aqueous solution using batch adsorption experiments within the pH range of 2 to 10, at 25 °C. Stock solution of Hg (II) (1000 mg/L) was prepared by dissolving required amount of a mercury salt in deionized water and diluted to get solutions of desired concentrations. The prepared sorbent (80 mg) was added to 20 ml of each Hg (II) ion solution adjusted to pH 4 using 0.1 M HNO_3 or 0.1 M NaOH solution. The solution mixture was mixed by stirring at 400 rpm for 2 min at 25 °C. The functionalized polymer was then removed by filtration and the remaining mercury in solution was determined by inductively coupled plasma optical emission spectrometry analysis (ICP-OES).

2. Characterization of calix[4]resorcinarene (1)

2,8,14,20-tetraalkylpentacyclo-[19.3.1.1.1.1]octacosa-1(25),3,5,7,(28),9,11,13 (27),15,17,19(26),21,23-dodecane-4,6,10,12,16,18,22,24-octol (***c*-methylcalix[4]resorcinarene**, $C_{32}H_{32}O_8$)

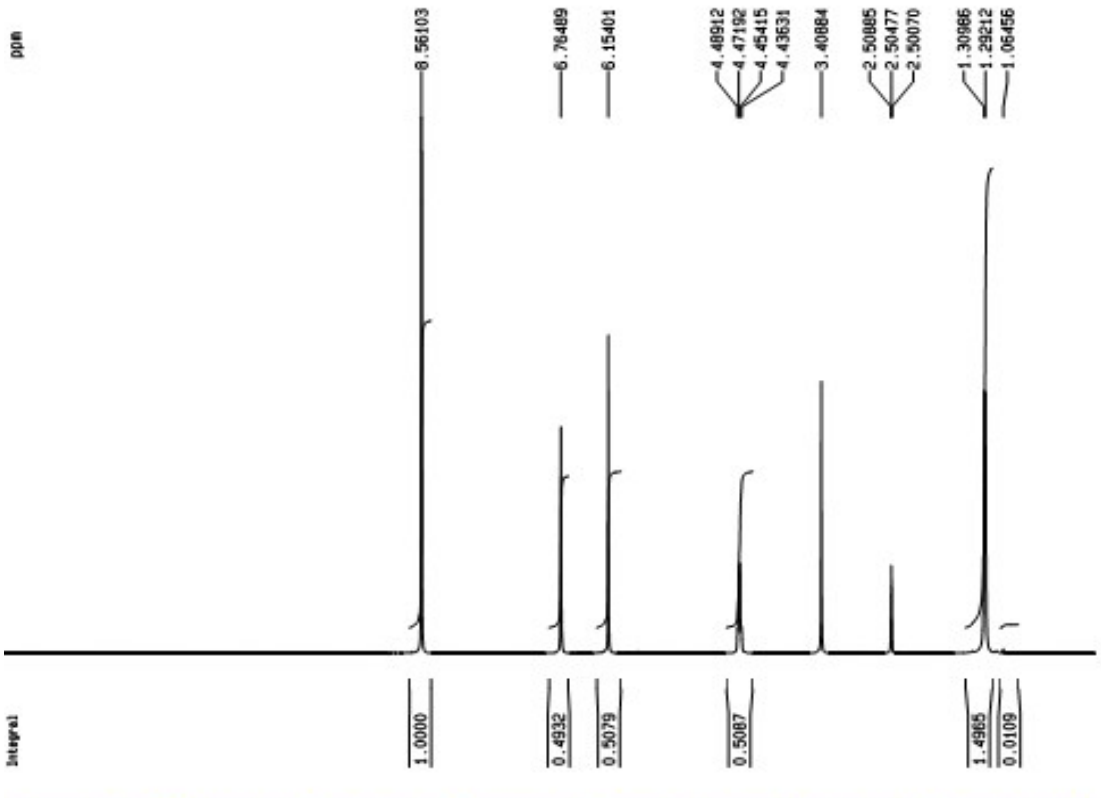
Yield 60%; white powder, m.p.: > 360˚C; IR (KBr): ν = 3000-3500 (OH) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =1.29-1.30 (d, 12H, CH_3),4.43-4.49 (q, 4H, H-5), 6.15 (s, 4H, H-1), 6.76 (s, 4H, H-4), 8.56 (s, 8H, OH) ppm;^{13}CNMR (100MHz, DMSO-d_6): δ = 22.0 (CH_3), 29.0 (C-5), 102.5 (C-3), 123.5 (C-1), 125.7 (C-2), 152.3 (C-4) ppm.

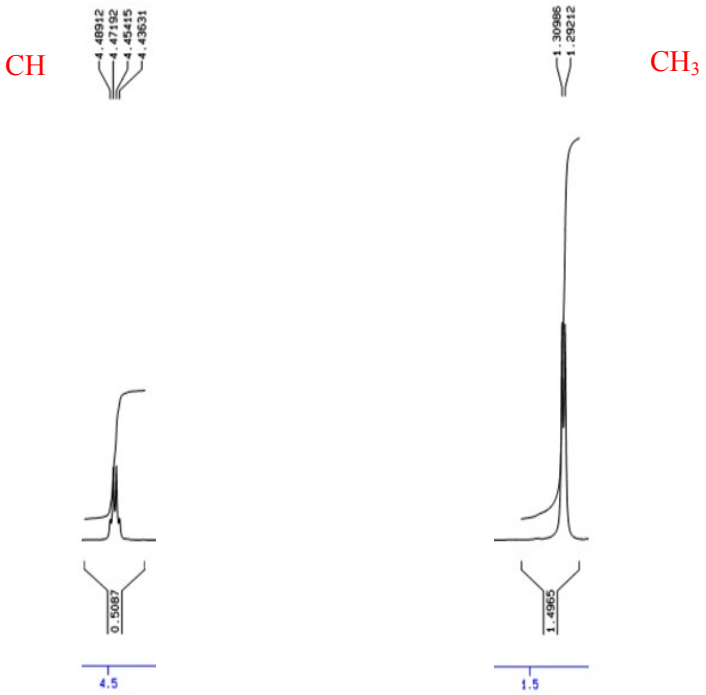
2.1. IR Spectra



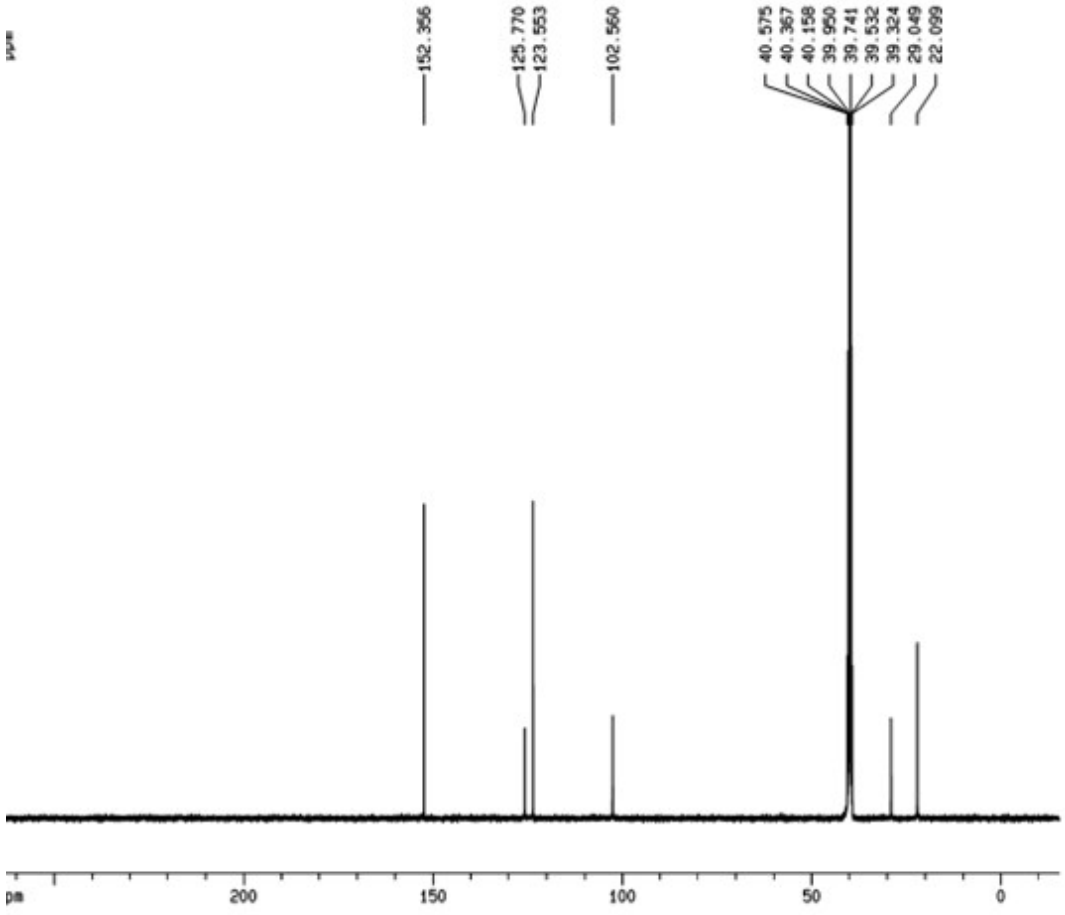
2.2.

[1]HNMR Spectra

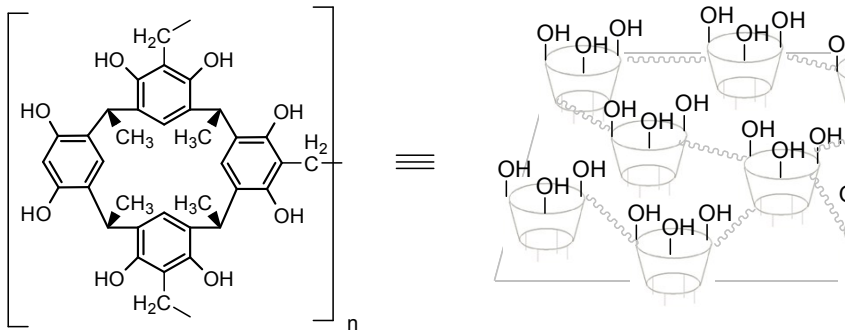




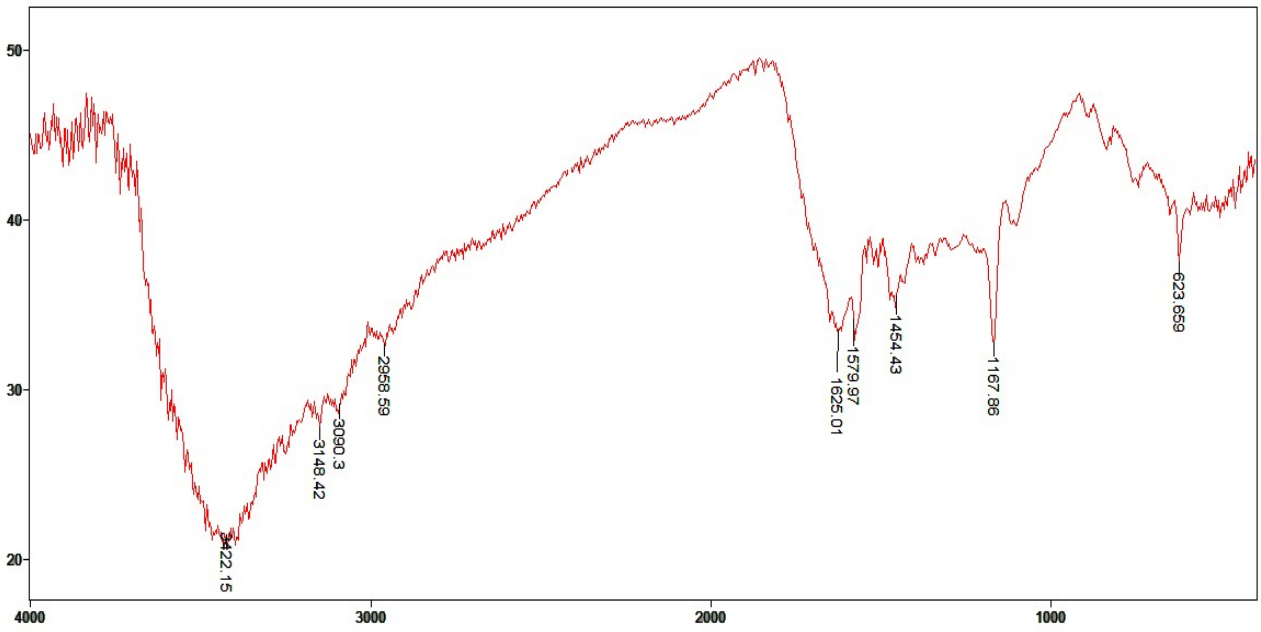
2.3. *^{13}CNMR Spectra*



3. Characterization of 3D-network polymer (2)

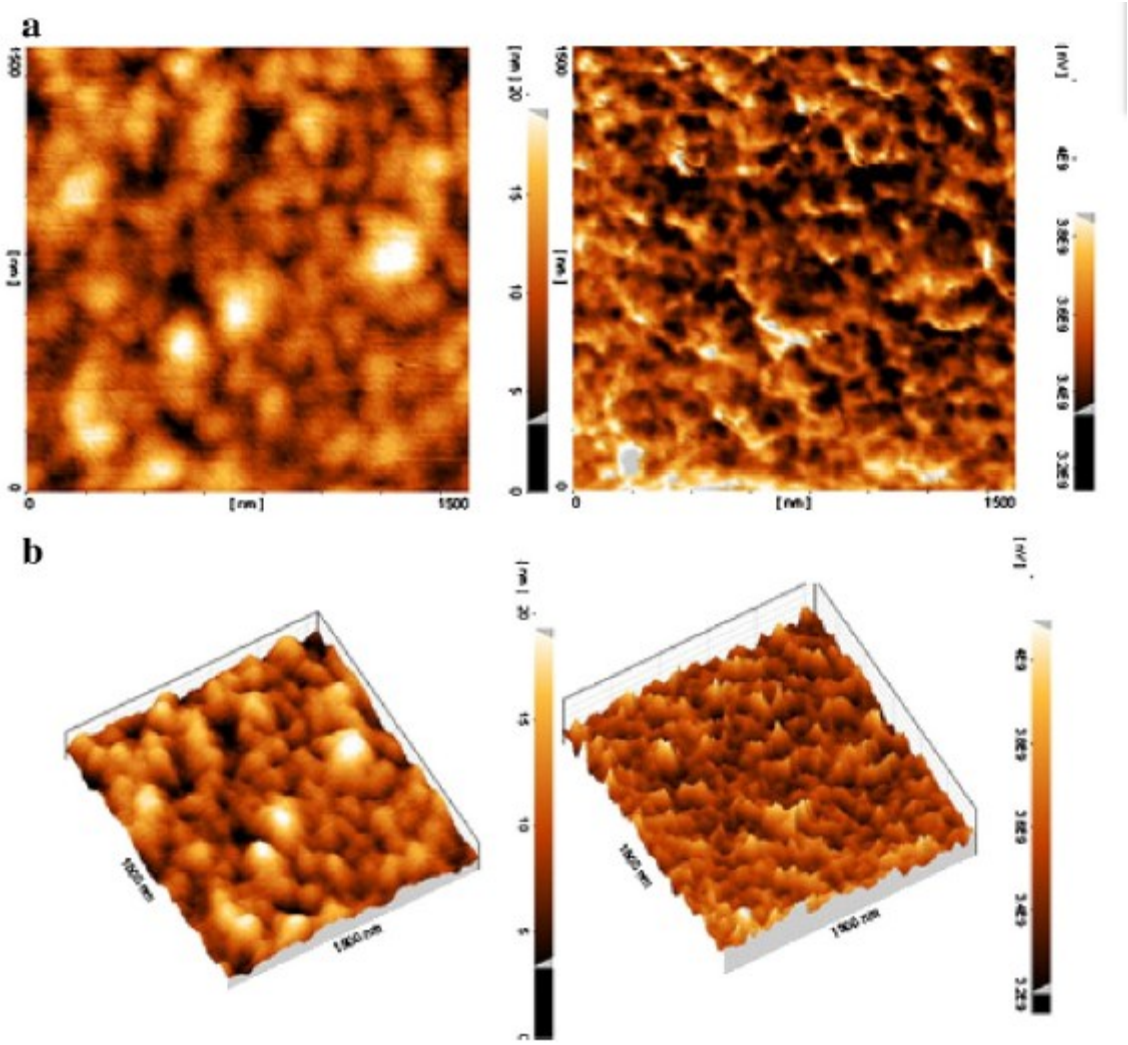


3.1. IR Spectra

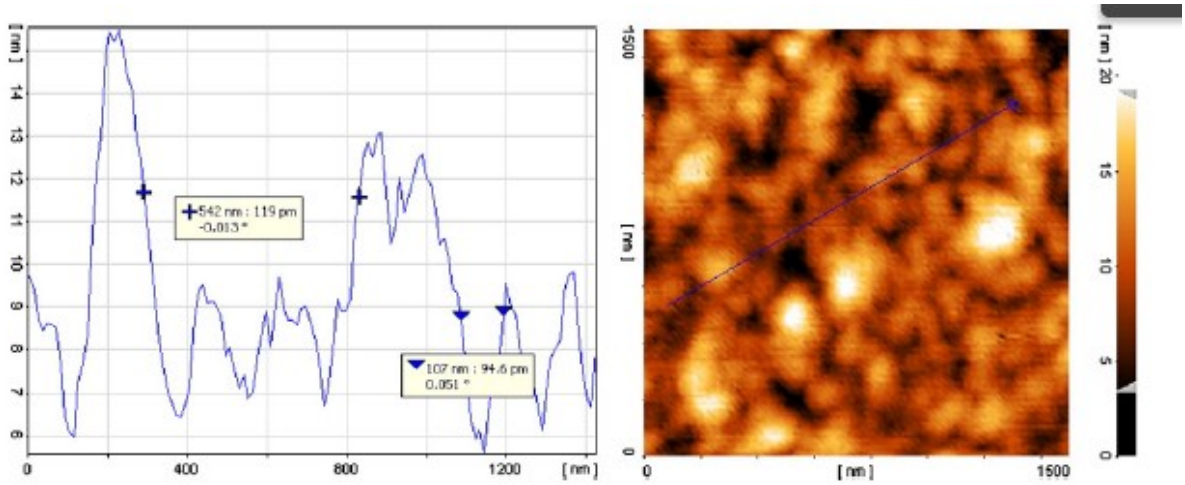


IR Spectra of 3D-network polymer **2**

3.2. AFM images



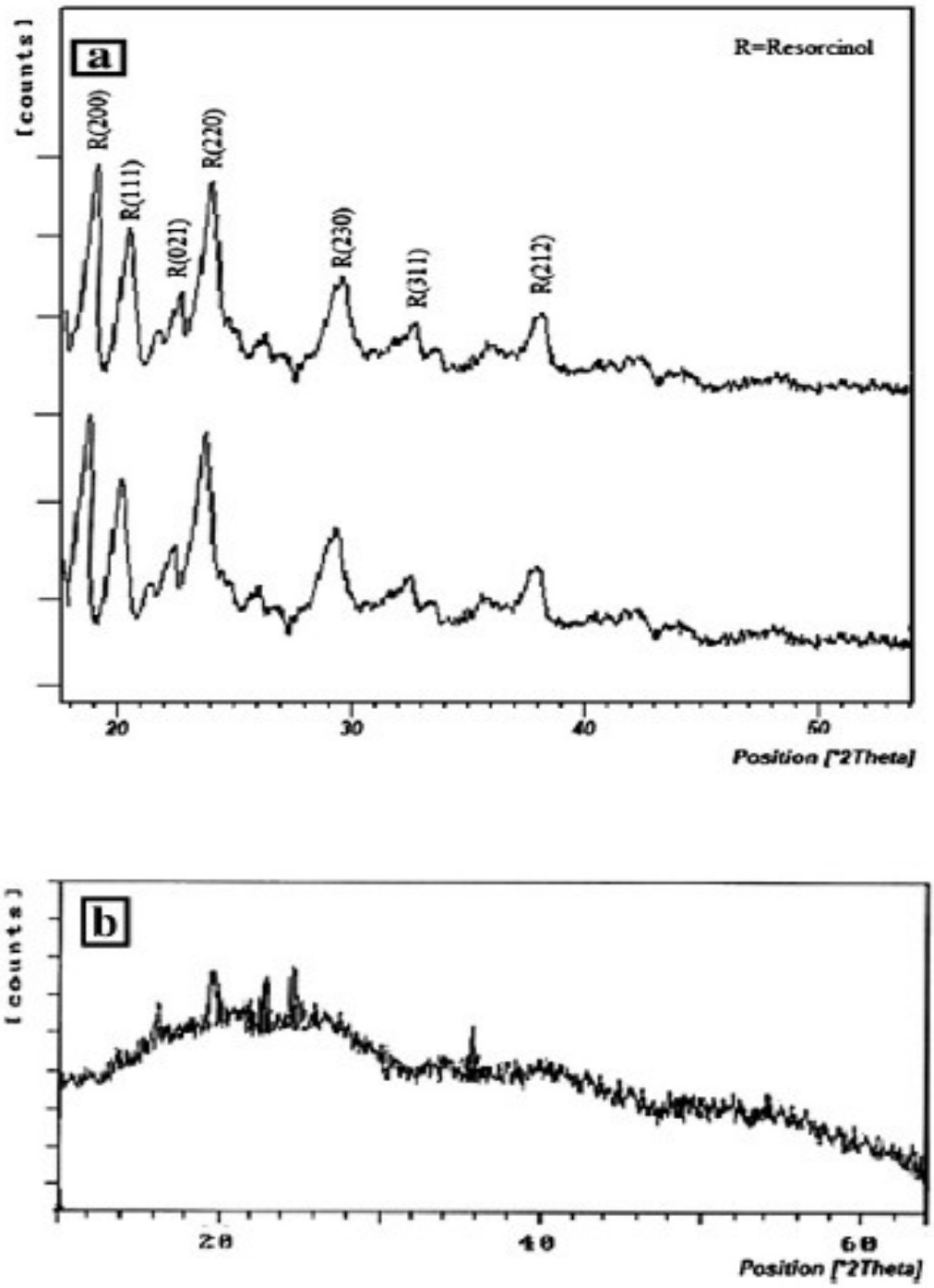
(a) AFM images (1 μ× 1 μ) of network polymer and (b) AFM surface plot of network polymer.



Section analyses of network polymer.

3.3. X-ray diffraction

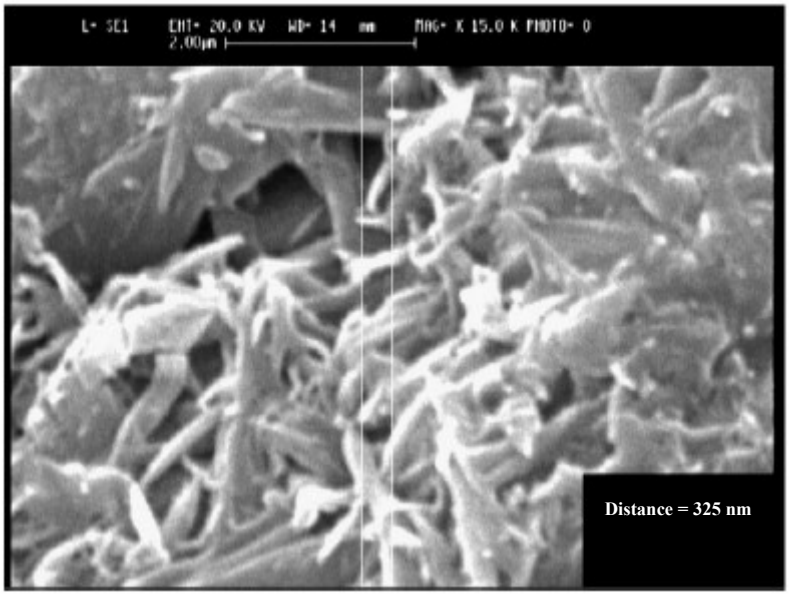
The XRD patterns of the prepared network polymer and calix[4]resorcinarene are depicted. It seems that to the intense and sharp diffraction peaks of calix[4]resorcinarene, it exhibited a high degree of crystallinity and this may be attributed to the hydrogen bonding between the resorcinarene units (a). As it can be seen in this figure, most of the peaks in the XRD patterns of the methylcalix[4]resorcinarene samples can be completely indexed with resorcinol in the standard card (JCPDS No. 00-038-1969). It can be observed that when the calix[4]resorcinarene is incorporated into a polymer system crystalline peaks are still exhibited but the intensity of the peaks decreases and a broad spectrum appears. In other words, the amorphous nature of the polymer increases and almost the fine disrupts crystals of the calix[4]resorcinarene were existed (b). Some distinct peaks were observed for the network polymer which indicated that the network polymer molecules have the semi crystalline nature but broad spectrum shows that its composition consists predominantly of an amorphous phase.



XRD pattern a) calix[4]resorcinarene (**1**) and b) polymer (**2**)

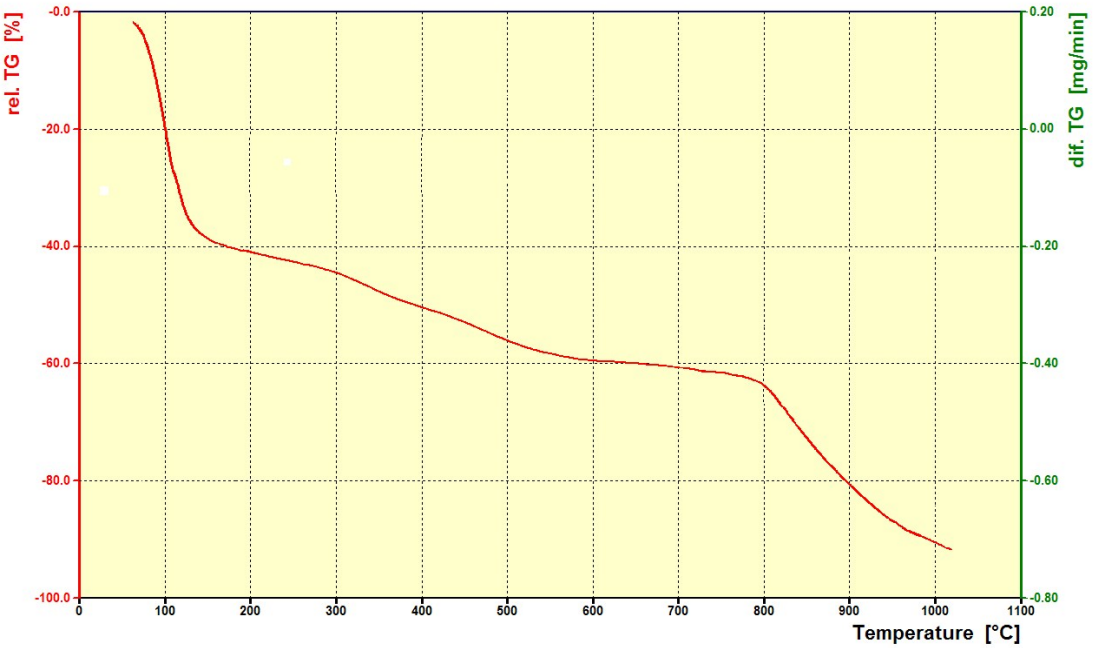
3.4. SEM image

In this image, one can observe that more porous structure with meshwork was obtained for network polymer. SEM confirmed that the average size of pores network polymer is in agreement with the AFM data.



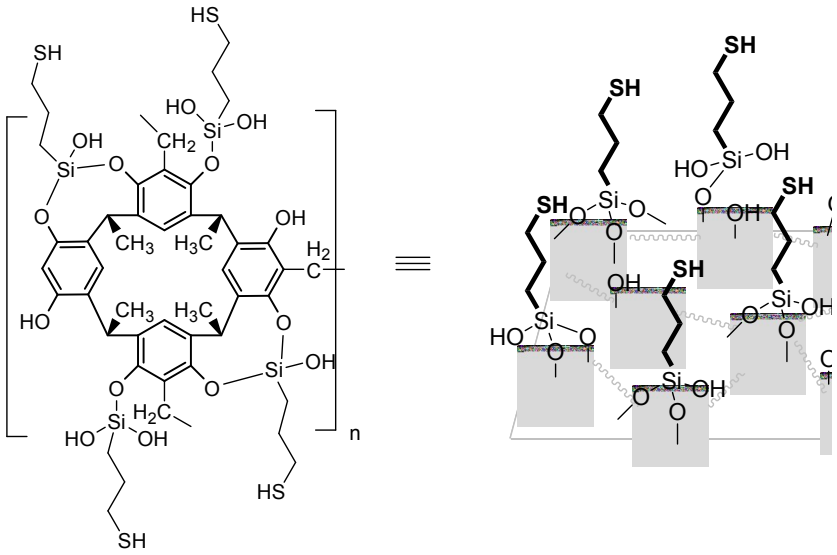
SEM image of 3D-network polymer **2**

3.5. TGA curve

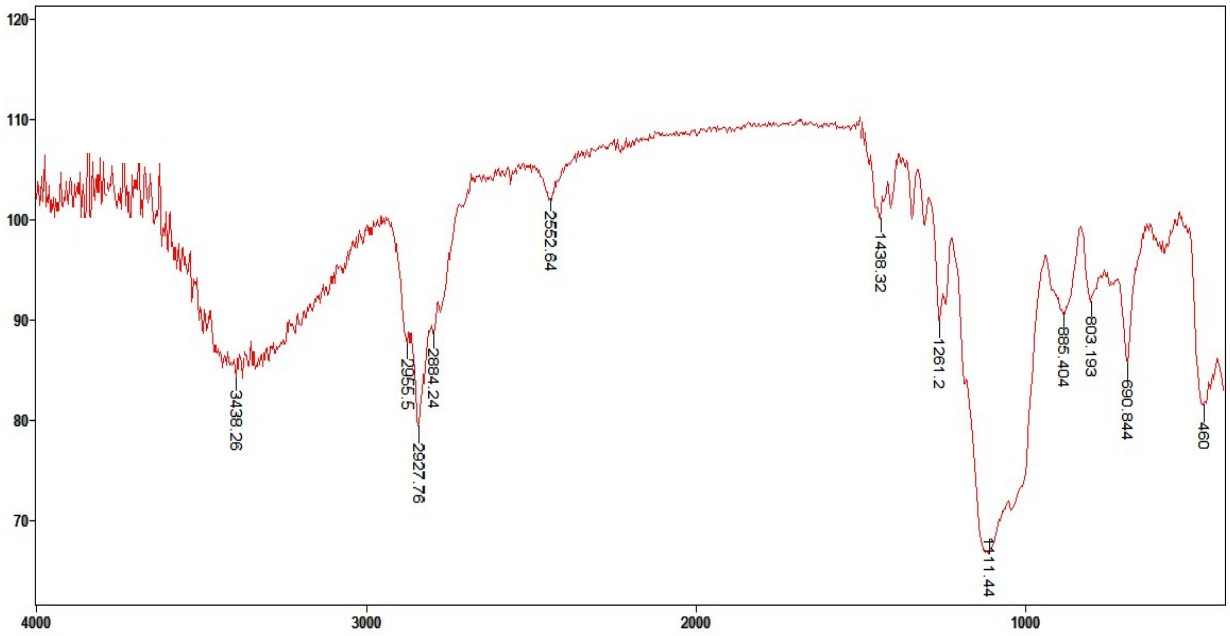


TGA curve of 3D-network polymer **3**

4. Characterization of novel thiol functionalized 3D-network polymer (3)

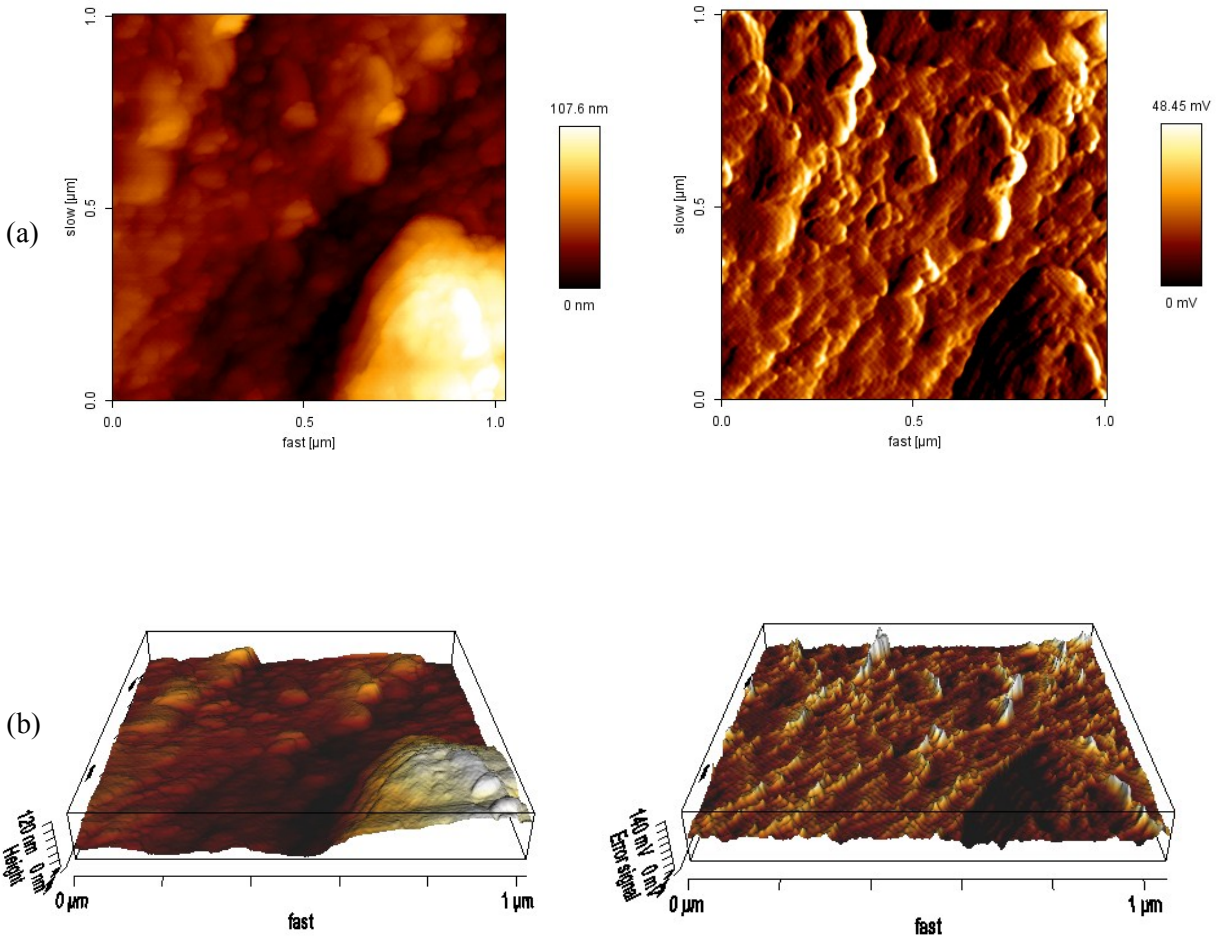


4.1. IR Spectra



IR Spectra of thiol functionalized polymer **3**

4.2. AFM images



AFM images (1.0 µm × 1.0 µm) of thiol functionalized polymer **3**, (a) 2D and (b) 3D height and phase plots

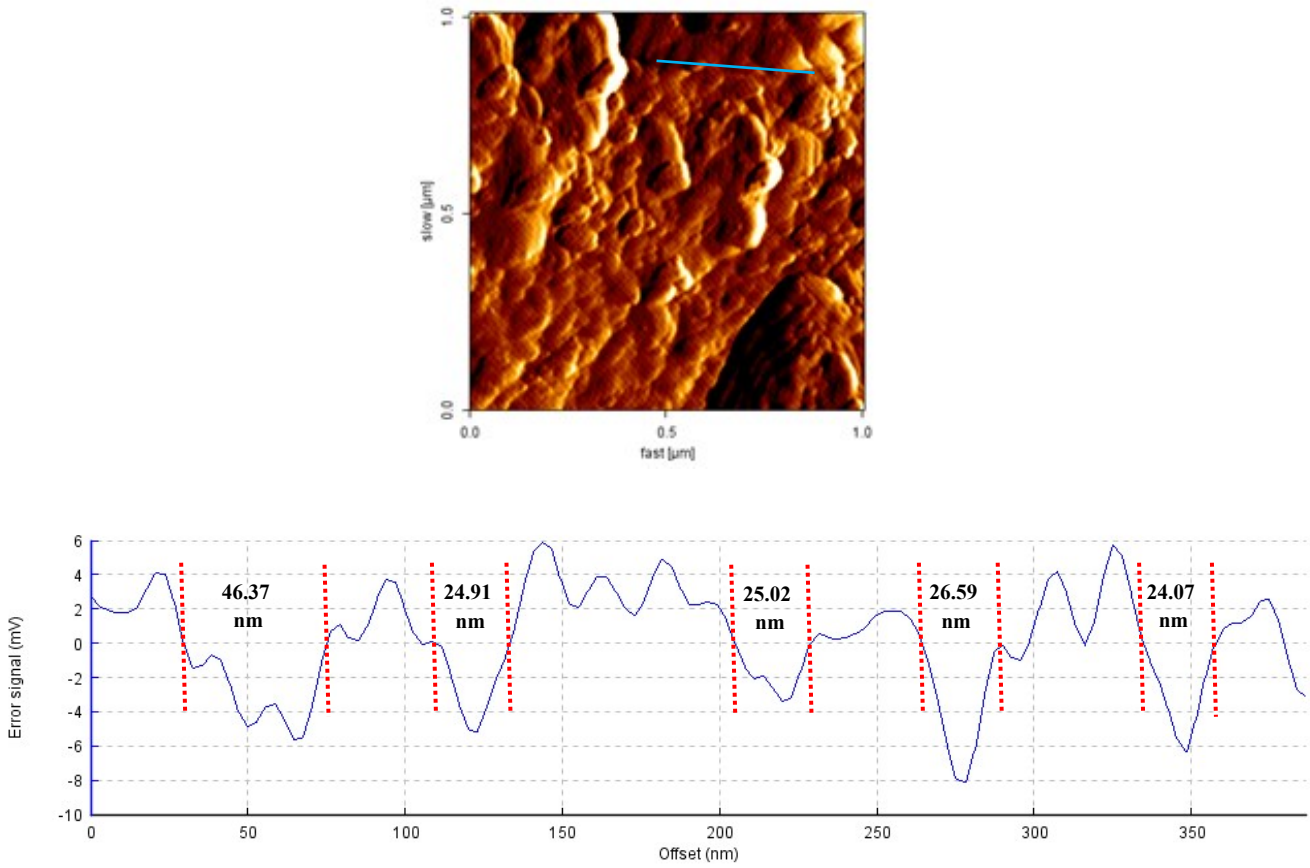
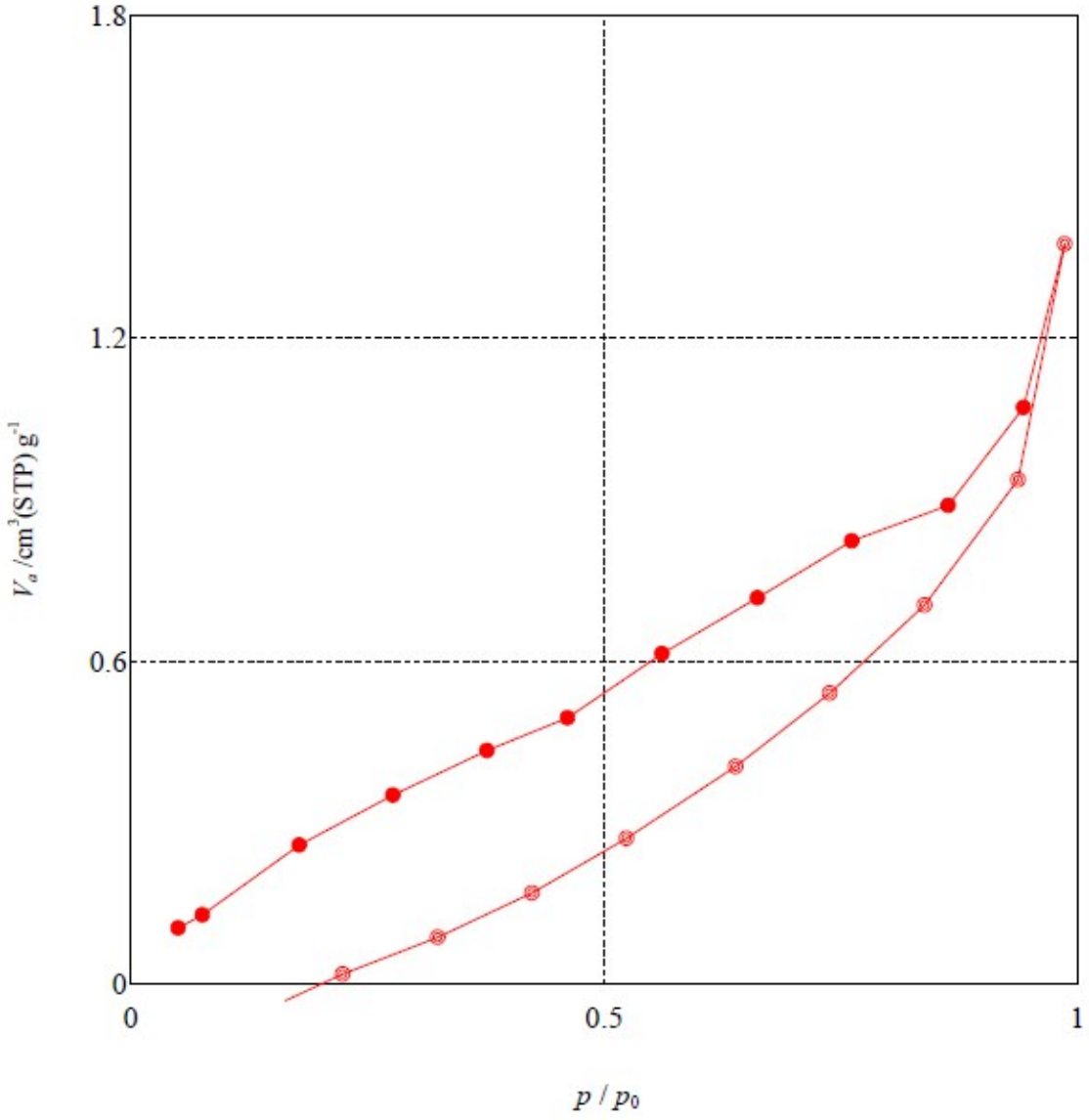


Image profile (the analysis of the height along a linear path) of thiol functionalized polymer **3**

4.3. BET analysis

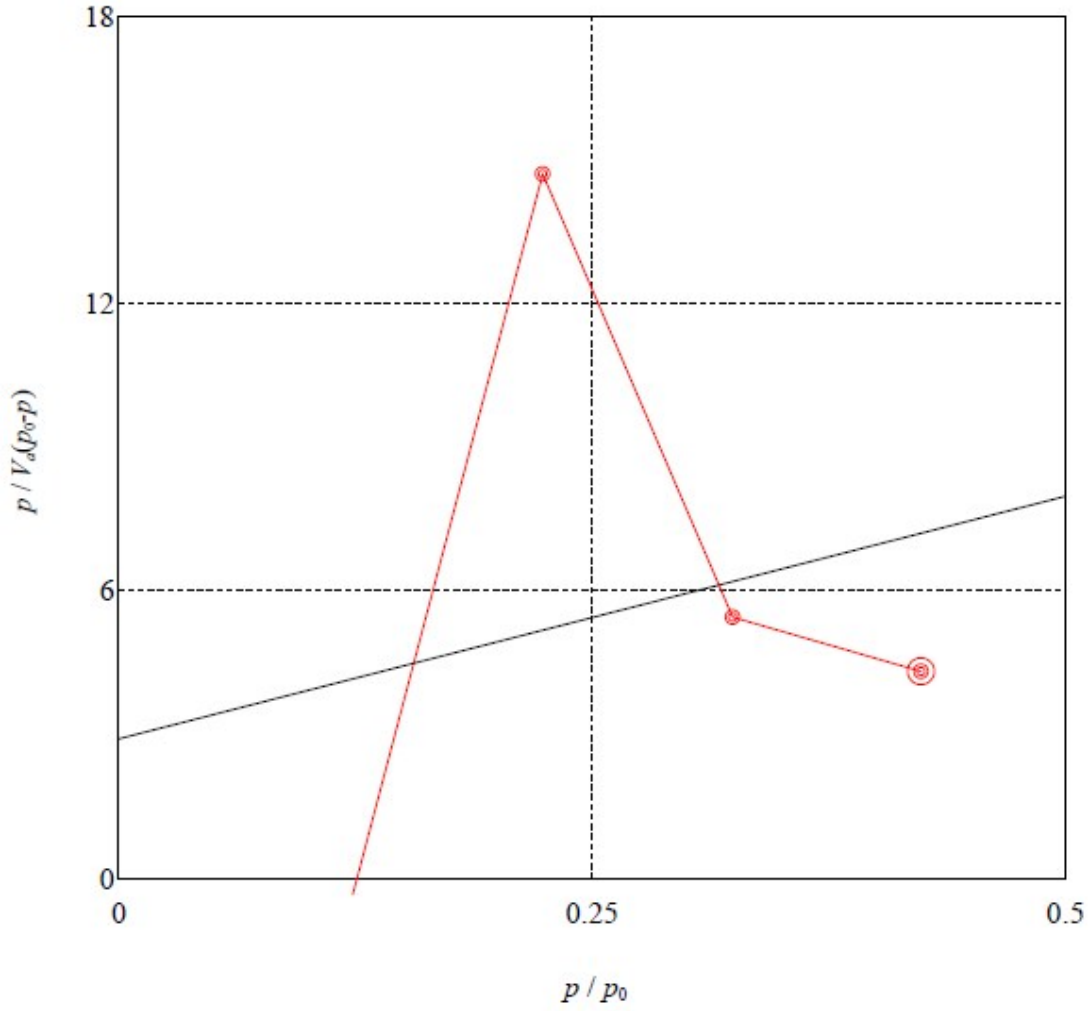


Adsorption / desorption isotherm

Adsorbate N2

Adsorption temperature 77 [K]

Sample weight	0.1530	[g]
Saturated vapor pressure	90.168	[kPa]

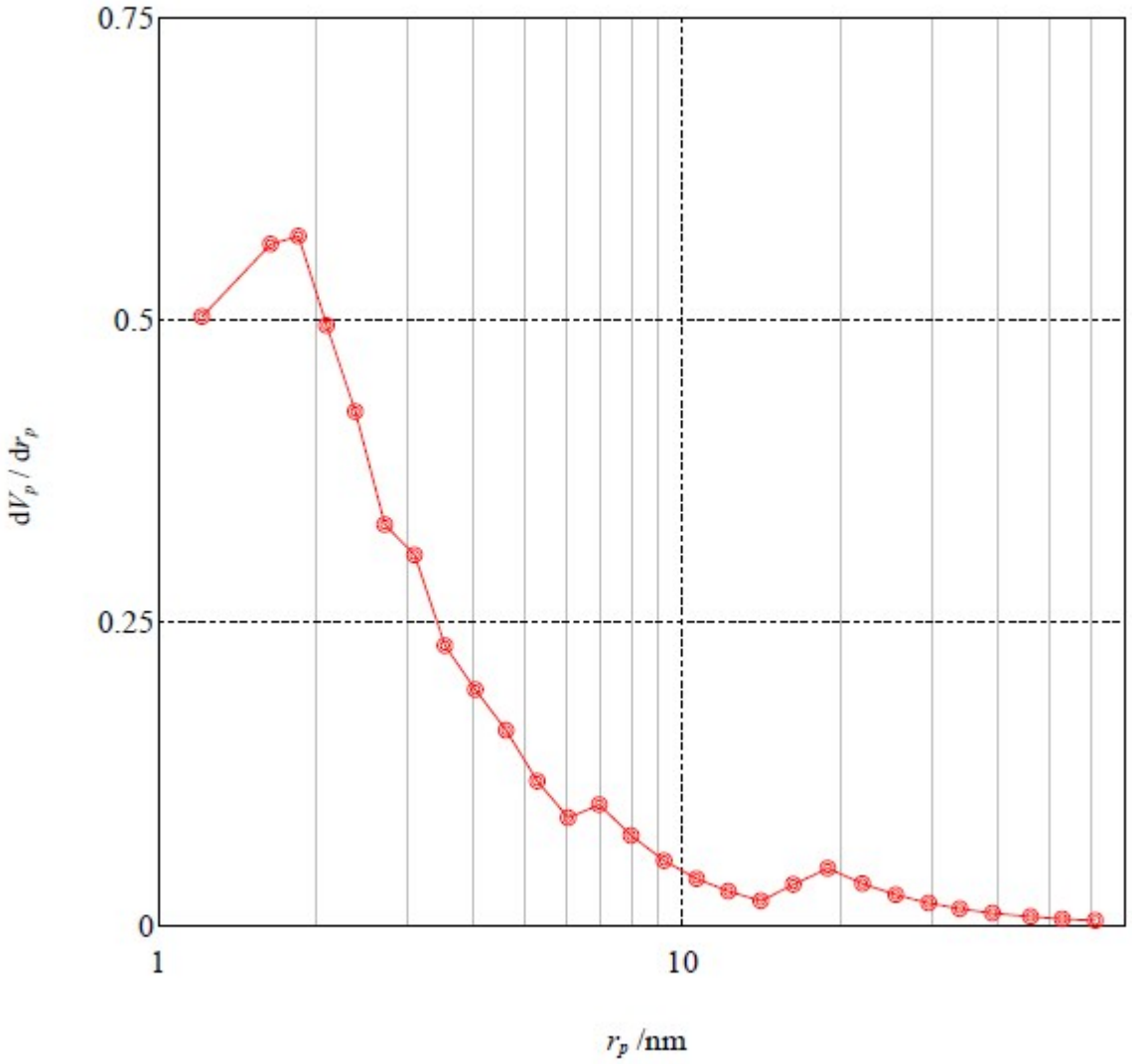


BET-Plot

Adsorbate N2

Adsorption temperature 77 [K]

V_m	7.6653E-02	[cm^3(STP) g^{-1}]	$a_{s,BET}$	3.3363E-01	[m^2 g^{-1}]
C	4.4780		Total pore volume (p/p_0=0.987)	2.1268E-03	[cm^3 g^{-1}]
Mean pore diameter	25.499	[nm]			



BJH-Plot

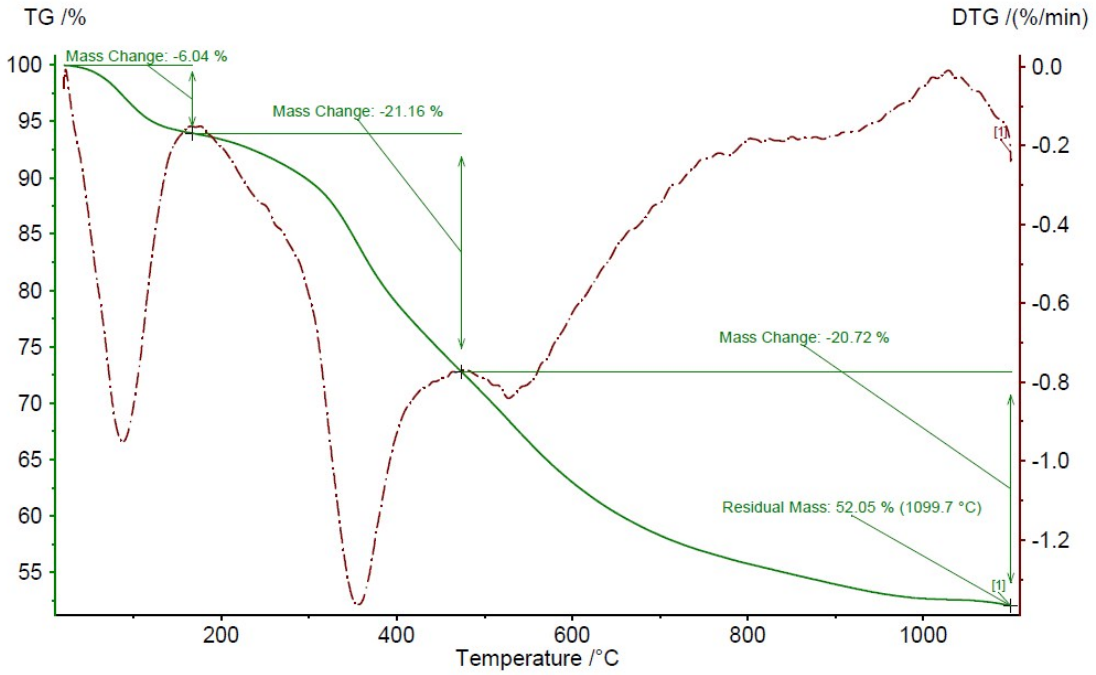
Adsorption branch

Adsorbate N2

Adsorption temperature 77 [K]

V_p	2.7050E-03	[$cm^3\ g^{-1}$]	$r_{p,peak}(Area)$	1.85	[nm]
a_p	1.5804	[$m^2\ g^{-1}$]			

4.4. TGA and DTG curves



TGA and DTG profile of thiol functionalized polymer **3**