

# Synthesis and characterization poly (2-formylpyrrole) (PFPy) by Acids catalysis and study of its particles size

ahmad Al-Hamdan (✉ [akhh1985@hotmail.com](mailto:akhh1985@hotmail.com))

Damascus University <https://orcid.org/0000-0003-2866-8750>

Ahmad Al-Falah

Damascus University <https://orcid.org/0000-0002-6783-6094>

Fawaz Al-Deric

Damascus University

Ibrahim Al-ghoraibi

Damascus University

---

## Research Article

**Keywords:** polymerization, acid catalysis, XRD, particles size, poly formyl pyrrole (PFPy)

**Posted Date:** September 20th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-917292/v1>

**License:**  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

## **Synthesis and characterization poly (2- formylpyrrole) (PFPy) by Acids catalysis and study of its particles size**

**Ahmad Al-Hamdan<sup>\*a</sup>, Ahmad Al-Falah<sup>b</sup>, Fawaz Al-Deri<sup>c</sup>, Ibrahim Al-ghoraibi<sup>d</sup>**

*\*.a. Corresponding Author ,PhD student in Damascus University at the Department of Chemistry, Damascus, Syria., akhh1985@hotmail.com*

*b. Professor in Damascus University at the Department of Chemistry and Faculty of Pharmacy. Arab International University (AIU). A-Falah@aiu.edu.sy, Damascus, Syria.*

*c. Professor in Damascus University at the Department of Chemistry, Damascus, Syria.*

*d. Professor in Damascus University at the Department of physics, Damascus, Syria.*

### **Abstract:**

In this paper Poly (2-formyl pyrrole) (PFPy) was synthesized using hydrochloric acid as catalysis in alcohol. PFPy is green dark very fine powder. Then the polymer forms glass substrate in the reaction mixture. The resulting polymer was characterized by (FT/IR, EDX and XPS) to determine the polymer structure. The polymer was scanned by scanning electron microscope (SEM) and its film by AFM for its morphological properties. We found the polymer consisting of spherical particles with a rough surface (average diameters of 430 nm) and they formed clusters. We proposed a method for calculated particles size depending on the crystals size (by Scherrer equation) and percentage of crystallization of polymer from XRD. The average particles size is 336.7 nm. The particles size in this method may be closer to reality because the XRD includes a large number of particles and it not optional as SEM and AFM.

**Keyword:** polymerization, acid catalysis, XRD, particles size , poly formyl pyrrole (PFPy).

---

### **1. Introduction:**

Conductive polymers were discovered in the mid of 20<sup>th</sup> century, this was a turning point in the scientific world due to their wide range of applicability[1]. Recently conducting polymers are used in sensors[2][3], biosensors[3], capacitors[4], solar cells[5] , optical displays[6], light emitting diodes[7] , as rechargeable batteries[8] , enzyme immobilization matrices[9], membranes[10], gas separation membranes[11] and electro chromic devices[12], conductive polymers war used as thin films for most of their applications. In recent years, synthesis and characterization of polymers containing hetero aromatic rings [13] such as Pyrrole, furan and thiophene [14] have been extensively studied because of their potential in advanced optoelectronic applications [13]. Polypyrrole (PPy) and its derivatives are the most widely studied conductive polymers due to the easily oxidizable monomer in aqueous solution [15], the high electrical conductivity, good electrochemical properties, thermal stability [16] and the high mechanical strength which is easily generated both chemically and electrochemically [17]. Intrinsic properties of polypyrrole include environmental

stability, good redox and conductivity behavior [18] have many applications, including batteries, electrochemical sensors and biosensors [19], conductive textiles and fabrics, drug delivery systems and mechanical actuators [20]. Polypyrrole is electrochemically driven and can be constructed in linear or bending (bilayer) actuators. [21] Poly(2-formylpyrrol) was synthesized by addition of thionylchloride to its solution in tetrachlorocarbon [22]. The 2-formylpyrrole can polymerize in acid without an oxidizing agent. Poly(2-formylpyrrole) was synthesized using acidic catalyst in alcohol. The prepared polymer was characterized by FT/IR, XPS, EDX, SEM and EIS technique.

## **2. Experimental:**

**2.1. Materials:** Pyrrole-2-carboxaldehyde 98% sigma, Hydrochloric acid 35.5% Sigma, sulfuric acid 98% Sigma Acetic acid, trichloro acetic acid sigma, formic acid Sigma.

## **2.2. Measurements:**

Poly(2-formylpyrrole) was characterized with FT/IR (JASCO FT/IR model M4100) spectrophotometer between 4000 and 400  $\text{cm}^{-1}$ , Surface morphologies were examined with SEM, EDX and XPS (TESCAN model MIRA3), XRD (Philips, model:PW1370 , Cu(0.154056 nm) step size 0.05 deg. ) and AFM (Nanosurf model:eseyscan2).

## **2.3. Synthesis:**

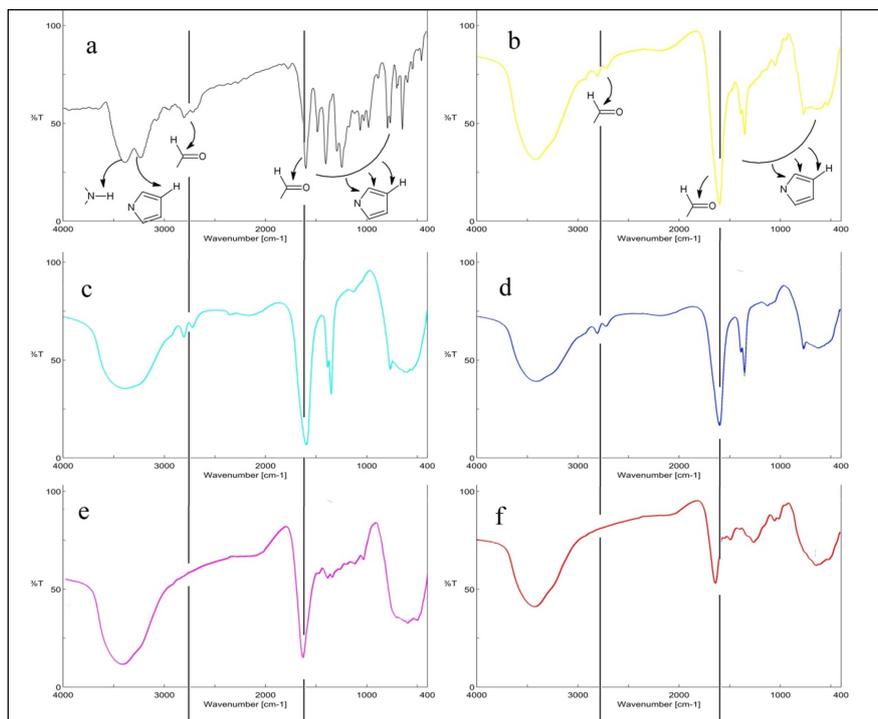
The 2-formyl Pyrrole (10mmol,0.97g) was dissolved in the alcohol (25ml) then hydrochloric acid 35.5% (10ml) was added. Mixture solution was placed at room temperature for 48 h. Color of reaction solution changed to yellow then black. Then the polymer precipitates, and forms on the walls of the reaction vessel and any substrate (e.g. glass) in the reaction mixture. Formed precipitate was collected by decantation, KOH (5%) solution was added and mixture was boiled for several minutes. The precipitate was filtered, washed with distilled water, then alcohol each one several times and dried at 105°C for 48 hours. It was kept for study later on.

## **3. Results and Discussion:**

### **3.1. FTIR Analysis:**

FT/IR spectrum of solid content of the reaction was recorded after 2,7,15,30 min and 48 h (polymer). **Fig. 1** shows FT/IR spectrum for monomer and solid content of the reaction at several reaction times. For monomer (**Fig. 1-a**), the peak at 3441 $\text{cm}^{-1}$  was related to N-H in pyrrole rings, absorption bands at 3230  $\text{cm}^{-1}$  was due to aromatic C-H, peaks about 2757  $\text{cm}^{-1}$  is attributed to C-H aldehyde, peak at 1667  $\text{cm}^{-1}$  were related to C=O aldehyde and the peaks between 1500 $\text{cm}^{-1}$  to 1000  $\text{cm}^{-1}$  were due to C=C in pyrrole ring and C-H out of plane. Solid content of the reaction after 2,7,15 and 30 min (**Fig. 1 b, c, d and e** respectively) have wide peak at 3512  $\text{cm}^{-1}$  which was due to humidity. Most peaks were shifted as a result of polymerization. The peak at 3441  $\text{cm}^{-1}$  for monomer is masque by the peak at 3512  $\text{cm}^{-1}$  because water confinement within the polymer structure. Also, the peak at 1667  $\text{cm}^{-1}$  in monomer spectra become weaker and was shifted to 1671  $\text{cm}^{-1}$ , 1675  $\text{cm}^{-1}$ , 1678  $\text{cm}^{-1}$ , 1680  $\text{cm}^{-1}$ , 1685  $\text{cm}^{-1}$  for 2,7,15, 30min and polymer respectively. This shows that

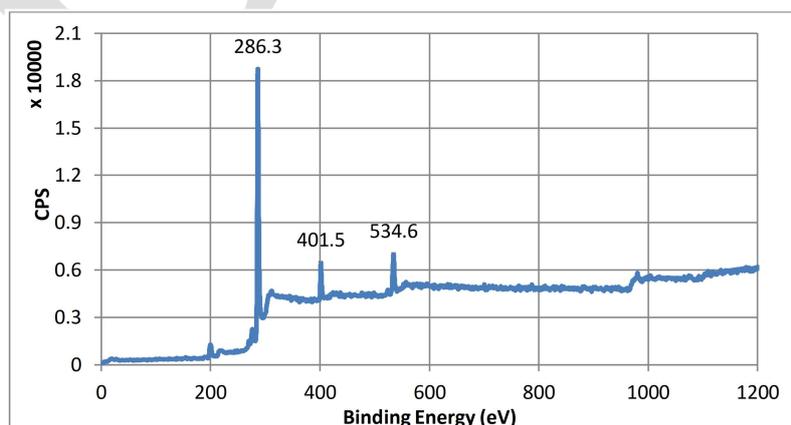
polymerization reaction happened on aldehyde group. Peaks in the fingerprint region after polymerization were become weaker and less intense.



**Fig. 1:** FT/IR spectrum a-monomer, b- solid content of the reaction after 2min, c- after 7min d- after 15min e- after 30min f- polymer.

### 3.2. XPS Analysis:

X-ray photoelectron spectroscopy (XPS) is an excellent technique for analyzing the top 5-10 nm of a surface. **Fig. 2** shows the X-ray photoelectron spectroscopy for polymer (PFPy). XPS spectra had three peaks at 534.6, 401.5 and 286.3 eV were due to O 1s, N 1s and C 1s respectively. This shows the polymer make up carbon, oxygen and nitrogen.



**Fig. 2** X-ray photoelectron spectroscopy for (PFPy).

**Fig. 3** shows the analysis of C 1s peak. From **Fig. 3** carbon atoms in polymer were three kinds C=C-H (286.45) 56.57%, C-N (287.3) 37.72%, C=O (289.6) 5.7%. This result corresponds to number of atoms in the formula.

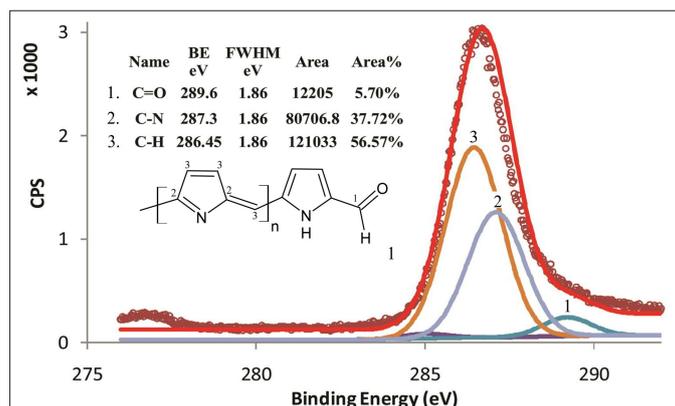


Fig. 3 (C 1s) spectra with typical peaks

### 3.3. EDX Analysis:

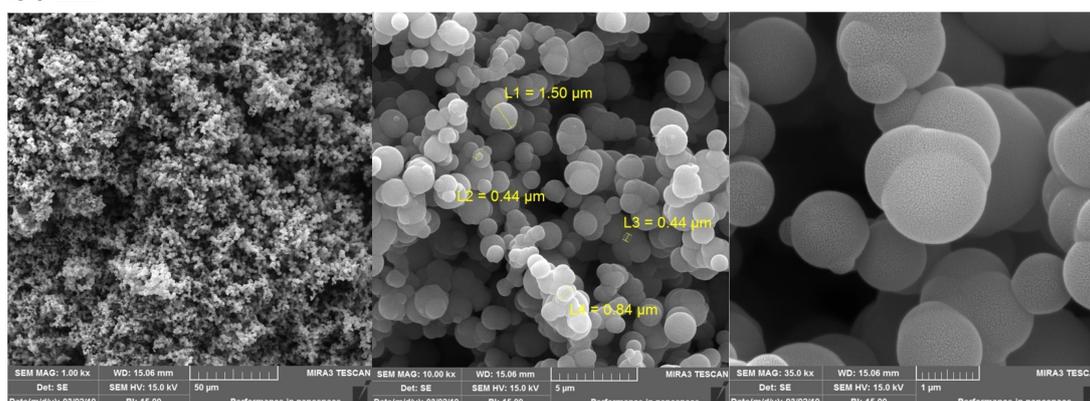
EDX is used to determinate the relative composition of the elements on a surface. **Table1** shows EDX analysis for three areas of polymer surface. The table showed disproportionate relative composition due to the inaccuracy of the EDX analysis. The polymer contains carbon 70.42%, nitrogen 13.48% and oxygen 15.02%. The rate N/C is about 19.1% (one nitrogen atom for five carbon atoms) this was accorded with polymer structure. The oxygen rate was more than expected because of the water confinement within the polymer structure.

Table 1: EDX analysis for Three areas of polymer surface.

Ele/C	area 3		area 2		area 1		Element
	Atomic %	Wt%	Atomic %	Wt%	Atomic %	Wt%	
100.0%	70.4	64.8	74.6	68.5	66.2	61.2	C
19.1%	13.5	14.5	8.8	9.4	18.2	19.6	N
22.0%	15.5	19.0	15.4	18.8	15.6	19.2	O
0.9%	0.6	1.7	1.2	3.3	0.0	0.0	Cl
	100.0	100.0	100.0	100.0	100.0	100.0	Total

### 3.3. Scanning electron microscope (SEM):

The morphology of poly (2-formylpyrrole) particles was studied using scanning electron microscope. **Fig. 4** shows the photo of the scanning electron microscopy (SEM). The polymer consists of spherical nanoparticles which were merged together to be cluster. The particles in the cluster have rough surface and average size about 438 nm.



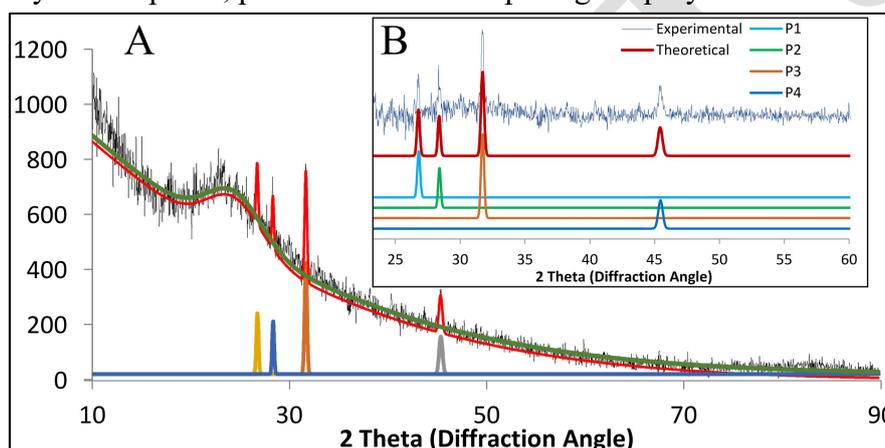
**Fig. 4** the photo of the scanning electron microscope (SEM) for polymer.

### 3.4. X-Ray Diffraction (XRD):

The crystal structures of PFPy were characterized by XRD analysis. **Fig 7-a** shows the XRD pattern of PFPy. The broad peaks Below the baseline are mainly due to the scattering from PFPy chains at the interplanar spacing and indicate a typical form of amorphous polymer [23]. To determine the crystalline percentage  $P_{cry}\%$ , it is essential to deconvolute the XRD spectra of the samples to find the area of the amorphous and crystalline peaks [24]. The  $P_{cry}\%$  was calculated using Equation [25] [26].

$$P_{cry}\% = \frac{A_{cry}}{A_{cry}+A_{Amo}} \times 100 \quad \text{Eq. 1}$$

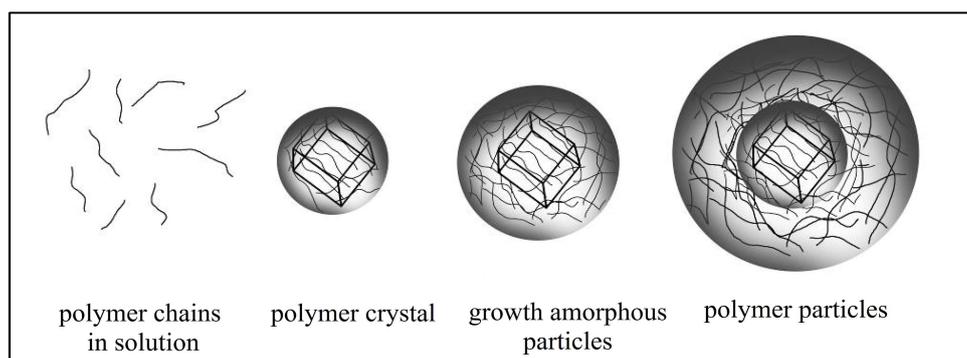
where  $A_{cry}$  and  $A_{Amo}$  are the areas of crystalline peaks and the area of amorphous, respectively [26] the crystalline percentage  $P_{cry}\%$  was about 1.46%. **Fig 7-b** shows the XRD pattern of PFPy for crystalline part. If we check the main peaks of the XRD patterns carefully, the peaks situate at 26.81, 28.42, 31.75 and 45.45° giving d spacing of 0.333, 0.314, 0.282 and 0.199 nm, respectively. [27] **Table 3** shows the percentage areas of crystalline peaks, particles size and d spacing for polymer from XRD pattern.



**Fig. 5** the X-Ray Diffraction (XRD) for polymer

**Table 2** percentage areas of crystalline peaks and its parameters.

Peak No.	2 theta °	A%	FMW (rad)	particles size (nm)	d spacing (nm)
P1	26.81	0.30%	0.00240	58.61	0.333
P2	28.42	0.24%	0.00204	69.49	0.314
P3	31.75	0.62%	0.00347	41.05	0.282
P4	45.45	0.30%	0.00290	51.28	0.199



**Fig. 6** growth of polymer particles on its crystal.

The polymer particles are formed during the deposition of the polymer from the solution, in the beginning, crystals are formed of several polymer chains, then particles are randomly gathered to configure particles (**Fig. 6**). In the polymer particle, percentage of the crystals can be given by:

$$P_{cry}\% = \frac{m_{cry}}{m_{tot}} \times 100 \quad \text{Eq. 2}$$

The density of polymer is same for crystal and amorphous part, Eq.2 can be written as follows:

$$P_{cry}\% = \frac{V_{cry}}{V_{tot}} \times 100 = \frac{r_{cry}^3}{r_{tot}^3} \times 100 \quad \text{Eq. 3}$$

For  $i$  crystal its diameter is  $D_i$  and percentage  $P_i\%$  Eq.2 can be written as follows:

$$P_{cry}\% = \frac{\left(\frac{\sum_1^n (P_i\% \times D_i)}{2 \times P_{cry}\%}\right)^3}{r_{tot}^3} \times 100 \quad \text{Eq. 4}$$

$$r_{tot}^3 = \frac{\left(\frac{\sum_1^n (P_i\% \times D_i)}{2 \times P_{cry}\%}\right)^3}{P_{cry}\%} \times 100 \quad \text{Eq. 5}$$

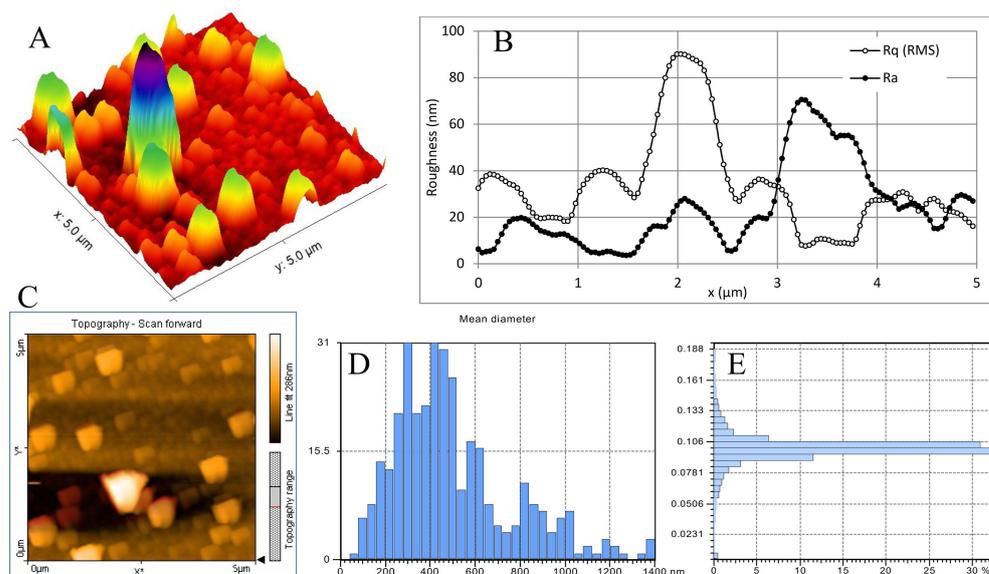
If  $D_r$  is average diameter of polymer particles Eq.2 can be written as follows:

$$D_r = \sqrt[3]{\frac{\left(\frac{\sum_1^n (P_i\% \times D_i)}{P_{cry}\%}\right)^3}{P_{cry}\%}} \times 100 \quad \text{Eq. 6}$$

The percentage of the crystals can be determined from XRD. By crystalline peaks parameters from **table 4**, the particles size can calculate by the **Eq. 6**. The average particles size is 336.7 nm. The particles size in this method may be closer to reality because the XRD includes a large number of particles and it not optional as SEM and AFM.

### 3.5. Atomic force microscopy (AFM) analysis:

Atomic force microscopy (AFM) is an excellent tool to study morphology and texture of diverse surfaces [28] and employed as a powerful technique to statistical study and analysis the morphology of polymer thin films surfaces with parameters such as roughness ( $R_a$ ) root mean square (RMS), kurtosis (Ku), skewness (Sk) and mean diameter [29]. Atomic force microscopy (AFM) scans of  $5 \mu\text{m} \times 5 \mu\text{m}$  areas of polymer film with thickness 280 nm. **Fig 7** shows 3D image, Roughness, Topography, Mean diameter and elevation distribution of polymer film. **fig 7-B** shows the polymer film roughness and RMS, statistical analysis of AFM data shows the surface parameter ( $R_a = 2.63 \text{ nm}$ ,  $\text{RMS} = 23 \text{ nm}$ ,  $R_v = 2 \text{ nm}$ ,  $R_p = 34 \text{ nm}$ ,  $R_{\text{max}} = 37 \text{ nm}$ ,  $\text{Ssk}(\text{RMS}) = 1.98$  and  $\text{Ku} = 5.49$ ), when polymer formed and precipitated the active pointes in surface of substrate absorb polymer chains. They accumulate on surface and grow to join together, and form a rough layer which seems as joined balls. In **fig 7-d** shows mean diameter of polymer particles in Film where average size about 420 nm, that corresponds to what the SEM images show in this work.



**Fig. 6** A) 3D image B) Roughness, C) Topography, D) Mean diameter and E) elevation distribution of thin film of polymer

#### 4. Conclusions:

A novel polymer was synthesized by a simple and easy method by adding concentrated hydrochloric acid to the monomer solution in alcohol. The polymer was characterized by FT/IR, EDX, XRD and XPS to confirm its structure. The polymer was scanned by scanning electron microscope (SEM) and its film by AFM for its morphological properties. The polymer particles have a rough surface and its diameters were less than 1000 nm and the average diameter about 430 nm (in the synthesis conditions). In XRD, the crystalline percentage  $P_{\text{cry}}\%$  was about 1.46% and The average particles size is 336.7 nm.

#### 5. Highlights

- A novel polymer was synthesized and characterized by a simple and easy method.
- New method was proposed for calculating polymer particles size based on their crystallization and crystals size from XRD data.
- Determine particles size by SEM and AFM and compare them with XRD

#### 6. Compliance with Ethical standards:

Funding: this study was funded by Al-Furat University and Damascus university.

Conflict of interest: Authors declares that they have no conflict of interest.

#### 8. References:

- [1] R. Kumar , S. Singh and B.C. Yadav, IARJSET, **2**,Iss 11: 2394, (2015);
- [2] S.C. Hernandez , Inter Science, **19**, Iss 19-20: 2125 (2007);
- [3] Y.P. Zhang , S.H. Lee, K. R. Reddy, A. I. Gopalan, & K.P. Lee, Journal of Applied Polymer Science, **104**, Iss 4: 2743 (2007); doi:10.1002/app.25938.
- [4] A., Rudge, J. Davey, I. Raistrick, S. Gottesfeld, & J. P. Ferraris, Journal of Power Sources, **47**, Iss 1-2: 89 (1994); Doi:10.1016/0378-7753(94)80053-7.

- [5] J. C. Zhang, X. Zheng, M. Chen, X. Y. Yang, & W. L. Cao, *Express Polymer Letters*, **5**, Iss 5: 401 (2011); doi:10.3144/expresspolymlett.2011.39.
- [6] A. Mirsakiyeva , **PhD thesis** :KTH Royal Institute of Technology,Stockholm, Sweden. 2017.
- [7] T. Kasa and F. Gebrewold, *Advances in Physics Theories and Applications*, **62**, Iss 2017: 28 (2017).
- [8] L. Duan, J. Lu, W. Liu, P. Huang, , W. Wang, & Z. Liu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **414**, Iss 2012: 98 (2012); doi:10.1016/j.colsurfa.2012.08.033.
- [9] G. Bayramoğlu, M. Karakışla, B. Altıntaş, U. Metin, M. Saçak & M. Arıca, *Process Biochemistry*, **44**, Iss 8: 880 (2009); doi:10.1016/j.procbio.2009.04.011
- [10] H. Gherras, A. Yahiaoui, A. Hachemaoui, A. Belfeda, A. Dehbi and A.I. Mourad, *Journal of Semiconductors*, **39**, Iss 10: 102001 (2018);
- [11] X. Ding, F. Tan, H. Zhao, M. Hua, M.Wang, Q.Xin, and Y. Zhang, *Journal of Membrane Science*, **570-571**, Iss 1: 53 (2019); doi:10.1016/j.memsci.2018.10.033.
- [12] G. H. Shim, & S. H. Foulger, *Photonics and Nanostructures - Fundamentals and Applications*, **10**, Iss 4: 440 (2012); doi:10.1016/j.photonics.2011.12.001
- [13] B.X. Valderrama, E.Rodríguez, E.G. Morales, K.M. Chane, and E. Rivera, *Molecules*, **21**, Iss 172: 1 (2016); Doi:10.3390/molecules21020172
- [14] R. Kumar , S. Singh and B.C. Yadav, *international advanced research journal in science, engineering and technology*, **2**, Iss 11: 110 (2015); Doi: 10.17148/IARJSET.2015.21123
- [15] D. Ateh, H. Navsaria & P. Vadgama, *Journal of The Royal Society Interface*, **3**, Iss 11: 741 (2016); doi:10.1098/rsif.2006.0141
- [16] W. Yuan, X. Yang, L. He, Y. Xue, S. Qin, & G.Tao, *Frontiers in Chemistry*, **6**, Iss 1: 1 (2018); doi:10.3389/fchem.2018.00059.
- [17] Le, T.-H., Kim, Y., and Yoon, H., *Polymers*, **9**, Iss 12: 150 (2017); doi:10.3390/polym9040150.
- [18] R. Ansari, *E-J. of Chem.*, **3**, Iss 4: 186(2006); doi:10.1155/2006/860413
- [19] Y. Shao, J.Wang, H. Wu, J. Liu, I. A.Aksay, & Y. Lin, *A Review. Electroanalysis*, **22**, Iss 10: 1027 (2010); doi:10.1002/elan.200900571.
- [20] Reynaerts, D., Peirs, J., & H. Van Brussel, *Sensors and Actuators A: Physical*, **61**, Iss 1-3: 455 (1997); Doi:10.1016/s0924-4247(97)80305-6.
- [21] J. D. Larson, C. V. Fengel, N. P. Bradshaw, I. S. Romero, J. M. Leger, & Murphy, A. R., *Materials Chemistry and Physics*, **186**, Iss 15: 67 (2017); doi:10.1016/j.matchemphys.2016.10.030.
- [22] H. Braunling and R. Becker, Patent: **P. No:** US5004560A, U.S.A (1991);
- [23] X.-Y. Hu, J. Ouyang, G. Liu, M. Gao, L. Song, J. Zang, & W. Chen, *Polymers*, **10**, Iss 8: 882 (2018); doi:10.3390/polym10080882.
- [24] S. B. Aziz, *Advances in Materials Science and Engineering*, **2016**, Iss 1: 1 (2016); doi:10.1155/2016/2527013.

- [25] A.S. Marf, R. M. Abdullah, & S.B. Aziz, *Membranes*, **10**, Iss 4: 71 (2020); doi:10.3390/membranes10040071.
- [26] B. Aziz, S. Marf, A. Dannoun, E. M. Brza, & R. M. Abdullah, *Polymers*, **12**, Iss 10. 2184 (2020). doi:10.3390/polym12102184.
- [27] C. He, C. Yang, & Y. Li, *Synthetic Metals*, **139**, Iss 2: 539 (2003); doi:10.1016/s0379-6779(03)00360-6.
- [28] B. Kumar, T. Rao, *Digest Journal of Nanomaterials and Biostructures*, **7**, Iss 4: 1881 (2012).
- [29] J. Arjomandi, D. Raoufi, & F. Ghamari, *The Journal of Physical Chemistry C*, **120**, Iss 32: 18055 (2016); doi:10.1021/acs.jpcc.6b04913.

Draft