

PACS numbers: 68.37.Hk, 78.30.Jw, 78.67.Bf, 81.07.Nb, 81.16.Be, 82.35.-x, 82.80.Ej

Comparative Poly2-Formyl (Pyrrole, Furan, & Thiophene): Synthesis, Characterization and Particle Size

Ahmad Al-Hamdan¹, Ahmad Al-Falah^{1,2}, and Fawaz Al-Deri¹

¹*Department of Chemistry,
Damascus University,
Damascus, Syria*

²*Faculty of Pharmacy,
Arab International University (AIU)
Damascus, Syria*

In this paper, the poly2-formyl (pyrrole, furan, & thiophene) is synthesized by acid catalysis (hydrochloric acid) in ethanolic solutions. The polymers are characterized by FTIR, EDX and SEM. PFPy is seemed as clusters of globular with size of 1325 nm and rough surface. PFFu is small nanoparticles (of about 68 nm), which clump together to form large particles with a rough, bumpy surface (like a pancreas). PFTh appears as clusters of fused spherical nanoparticles (of about 153 nm). The slow polymerization reactions give smaller particles.

У даній роботі полі2-форміл (пірол, фуран і тіофен) синтезується шляхом кислотної каталізи (соляної кислоти) в етанолових розчинах. Полімери характеризуються інфрачервоною спектроскопією на основі перетвору Фур'є, енергорозсіювальною рентгенівською аналізою та сканувальною електронною мікроскопією. Полі2-форміл пірол здається кластерами кулястої форми розміром у 1325 нм і шерсткою поверхнею. Полі2-форміл фуран — це дрібні наночастинки (близько 68 нм), які злипаються, утворюючи великі частинки з шерсткою, горбистою поверхнею (як підшлункова залоза). Полі2-форміл тіофен з'являється у вигляді скупчень зрощених сферичних наночастинок (близько 153 нм). Повільні реакції полімеризації дають більш дрібні частинки.

Key words: poly2-formyl pyrrole, polyfurfural, poly2-formyl thiophene, nanoparticles, SEM.

Ключові слова: полі2-форміл пірол, поліфурфурол, полі2-форміл тіофен, наночастинки, СЕМ.

(Received 25 November, 2021)

1. INTRODUCTION

Poly(acetylene) was a first conducting polymer, which was discovered in 1977 by Hideki Shirikawa [1]; more researchers have been interested in conducting polymers [2]. In less than one decade, most of the monomers that researchers currently used to produce conducting polymers were found [3]. Discovering of conducting polymers was a turning point in the scientific world due to their wide range of applicability [4]. Recently, conducting polymers are used in sensors [5, 6], biosensors [6], and capacitors [7], as rechargeable batteries [8], enzyme immobilization matrices [9], membranes [10], gas separation membranes [11], solar cells [12], optical displays [13], light emitting diodes [14], and electrochromic devices [15]. Heteroaromatic rings such as pyrrole, furan, thiophene and their derivatives [4, 16], polypyrrole (PPy) and its derivatives are the most widely studied conductive polymers due to the easily oxidizable monomer in aqueous solution [17], the high electrical conductivity, good electrochemical properties, and thermal stability [18]. Intrinsic properties of polypyrrole include environmental stability, good redox and conductivity behaviour [19]. Furfural was polymerized by electropolymerization [20, 21] and plasma methods [22]; it was used for fabrication of film-modified electrode [20, 22]. It is also known that doping these films with other materials, such as iodine, acid or others, modifies the electrical and optical properties [23]. Thiophene derivatives have been used to synthesis polymers with wide applications, such as solar cells and photoelectric cells [14]. Polythiophene gets important attention in research and industrial parts owing to its high environmental stability, better thermal stability and mechanical characteristics. Moreover, its interesting properties like semiconducting, electronic and optical activities along with less band gap energy [25]. Polypyrrole, polyfuran, polythiophene and their derivatives are common conducting polymers [4] and can be synthesized by chemical, electrochemical, or plasma methods [23]. 2-formyl pyrrole was polymerized by acidic catalyst (thionylchlorid) [26] and hydrochloric acid [27]. 2-formyl thiophene is polymerized by hydrochloric acid [28] and its derivative by alkyl sulfonic acid (RSO_3H) [29]. In this research, we synthesized PFPy, PFFu and PFTh by acid catalysis in alcohol as solvent, characterised by FTIR and EDX, studied its morphology by SEM, and compared their properties.

2. EXPERIMENTAL

2.1. Materials and Measurements

2-formyl pyrrole 98% sigma, 2-formyl thiophene 98% sigma, furfural

98% sigma, hydrochloric acid 35.5% sigma, methanol 98% sigma polymers were characterized with FTIR (JASCO FT/IR model M4100) spectrophotometer between 4000 and 400 cm^{-1} . Surface morphologies were examined with SEM, EDX (TESCAN model MIRA3).

2.2. Synthesis

The monomer (10 mmole) was dissolved in the alcohol (25 ml); then, hydrochloric acid 35.5% (5 ml) was added. Mixture solution was placed at room temperature for 24 h. The precipitate was filtered, washed with distilled water and 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

Polymers were characterized by using infrared spectroscopy FTIR. The structure of polymer was confirmed with disappearance of the aldehyde group in polymer. Figure 1 shows FTIR spectra of polymers. In Figure 1, *a*, FTIR spectra of PFPy are observed at 3484 cm^{-1} due to the N-H vibration in pyrrole ring (the peak at 3484 cm^{-1} is wide may be due to bound or imprisoned water). The peaks at 1500–700 cm^{-1} vibration bands are due to the C-H out of plane vibrations, and C=C and C-C stretches of the pyrrole rings are. The C=N and C-N stretches of the pyrrole rings (C=N caused by electron

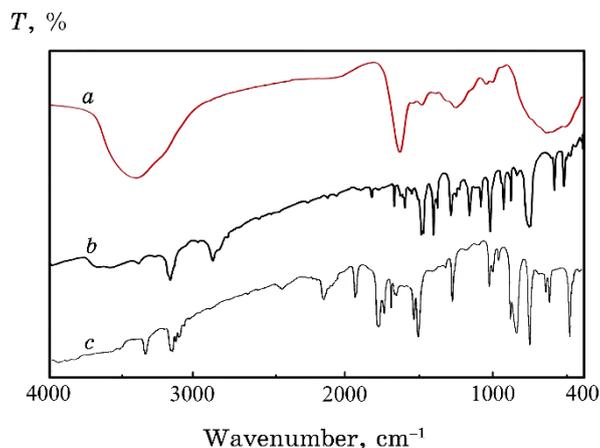


Fig. 1. FTIR spectrum of: *a*) poly(2-formyl)pyrrole; *b*) polyfurfural; *c*) poly(2-formyl)thiophene.

resonance and tautomerism in the ring) are at 1620 and 1270 cm^{-1} . In Figure 1, *b*, FTIR spectra of polyfurfural are observed at 3130 cm^{-1} due to aromatic C–H; peaks about 2845, 2812 cm^{-1} are attributed to the C–H aldehyde. The peaks between 1500 cm^{-1} to 1000 cm^{-1} were due to C=C in furan ring and C–H out of plane. Figure 1, *c* shows FTIR spectrum for polythiophene observed at 3110 cm^{-1} (C–H aromatic), 2825 cm^{-1} (C–H aliphatic), and the peaks between 1500 cm^{-1} to 1000 cm^{-1} (C=C thiophene ring and C–H out of plane).

3.2. EDX Analysis

For the determination of relative composition of elements of the polymer formation, an elemental analysis was performed using EDX technique. Table shows EDX results for polymer surface. The poly(2-formyl) pyrrole contains carbon 70%, nitrogen 13.5% and oxygen 19%. The ratio N/C is about 19.3% (one nitrogen atom for five carbon atoms). The polyfurfural contains carbon 66.0%, oxygen 11.2% and chlorine 12.6%. The ratio O/C is about 30% (more one oxygen atom for five carbon atoms). The poly(2-formyl) thiophene contains carbon 63.0%, sulphur 11.2%, chlorine 12.6% and oxygen 11.2%. The ratio S/C is about 21.1% (one oxygen atom for five carbon atoms), and the ratio S/Cl is about one (one sulphur atom for one chlorine atom). High percentage of oxygen is due to adsorbed or trapped water in the polymer structure.

When comparing their EDX (Table), PFFu and PFTh have a high percentage of chlorine due to the electrically bonding of the chloride ion to the ionized ring. This is not observed in PFPy because the nitrogen is trivalent. This ionization contributes to a partial loss of the aromatic character of the compound and makes the reaction slow.

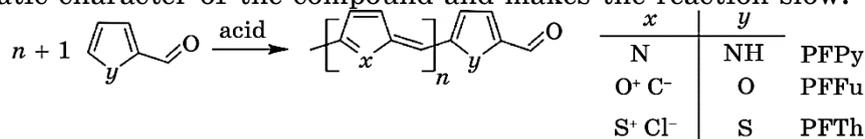


TABLE. EDX results for polymer surface.

Element	PFPy		PFFu		PFTh	
	wt. %	atomic, %	wt. %	atomic, %	wt. %	atomic, %
C	64.8	70.4	50.0	66.4	41.9	63.0
N	14.5	13.5	—	—	—	—
O	19.0	15.5	20.4	20.3	9.9	11.2
S	—	—	—	—	23.4	13.2
Cl	1.7	0.6	29.6	13.3	24.8	12.6

3.3. SEM

Figure 2, *a, b* shows the SEM image for PFPy. They appear as clusters of large spherical nanoparticles. The particles in the cluster have rough surface and average size of about 1325 nm. PFFu was shown in Fig. 2, *c, d*. This polymer consists of small particles (nanoparticles of 68 nm), which clump together to form large particles with a rough, bumpy surface (like a pancreas). Figure 2, *e, f* shows the SEM image of PFTh. This polymer appears as clusters of fused spherical nanoparticles (about 153 nm).

Precipitation of polymers is during a three-stage process. Nucleation is the phase, in which part of the polymer is transiting to a solid state (perhaps, one chain). This nucleus grows by regular bonding to other chains of the polymer (during the second stage) to form a small crystalline particle. At the final stage, the polymeric chains accumulate randomly to form the macroparticle. At this point, the particles may fuse and form clusters. Huge clusters agglomerate to form complex particles. The particle size depends on the rate of a chemical reaction: the faster rate, the larger particle size.

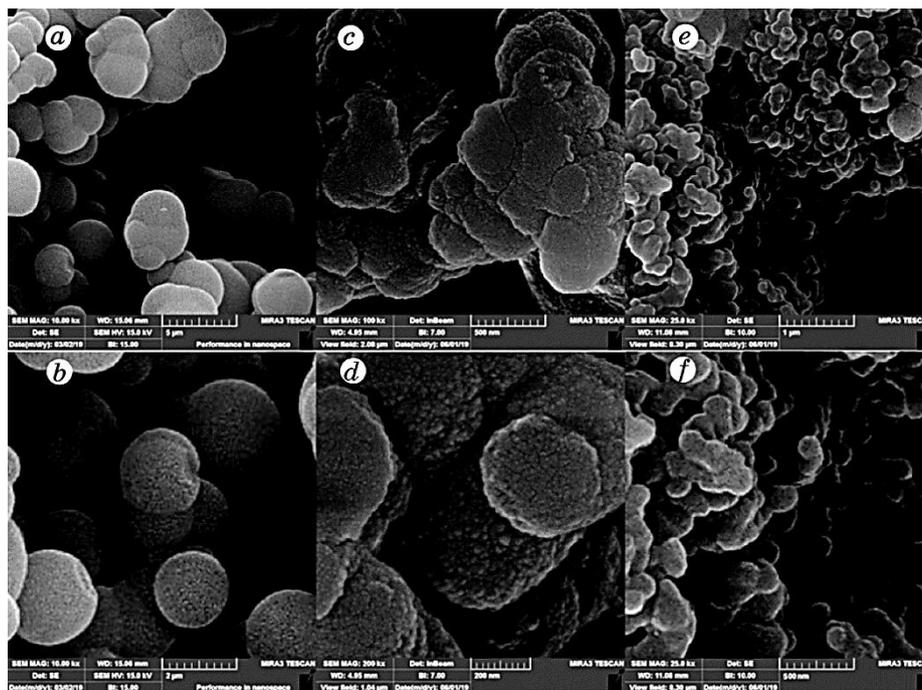


Fig. 2. Image of the scanning electron microscopy (SEM) of polymers powder.

The polymerization reaction (in the studied polymers) takes place through electrophilic addition [29, 30], and its rate is related to the nucleophilicity of the ring. The pyrrole ring in (2-formyl) pyrrole is effective due to the high basicity of nitrogen, which makes its reaction easy and fast, and its particle size is huge. While furfural and 2-formyl thiophene are less effective, so it reacts slowly and gives smaller particles. In general, furan is weakly aromatic and reacts more slowly than thiophene, making its particles smaller.

4. CONCLUSIONS

The particle size and morphology of polymers prepared from 2-formyl heterocyclic aromatic rings are related to the type of monomer. Poly(2-formyl) pyrrole particles are spherical of 1.3 μm with a rough surface, while PFFu particles are of about 68 nm and fuse with each other to form masses with a rough surface. PFTTh nanoparticles, which are of about 153 nm, form clusters. Slow polymerization reactions give smaller particles.

5. HIGHLIGHTS

Three conjugated polymers from heteropentacyclic aromatic aldehydes were synthesized by hydrochloric acid.

Polymer particle size was evaluated by the scanning electron microscopy images and compared. Particle size is related to the potency of the aromatic ring.

ACKNOWLEDGEMENT

The authors feel great thanks and gratitude to Dr. Hassan Kalawi, Ms. Marwa Al-Kheder and Ms. Mirna Jabbour.

REFERENCES

1. H. Shirakawa, *Current Applied Physics*, **1**, Nos. 4–5: 281 (2001); doi:10.1016/s1567-1739(01)00052-9
2. C. S. Park, C. Lee, and O. S. Kwon, *Polymers*, **8**, No. 7: 249 (2016); doi:10.3390/polym8070249
3. N. K, and C. S. Rout, *RSC Advances*, **11**, No. 10: 5659 (2021); doi:10.1039/d0ra07800j
4. R. Kumar, S. Singh, and B. C. Yadav, *IARJSET*, **2**, No. 11: 2394 (2015).
5. S. C. Hernandez, *Inter. Science*, **19**, Iss. 19–20: 2125 (2007).
6. Y. P. Zhang, S. H. Lee, K. R. Reddy, A. I. Gopalan, and K. P. Lee, *Journal of Applied Polymer Science*, **104**, No. 4: 2743 (2007); doi:10.1002/app.25938

7. A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, and J. P. Ferraris, *Journal of Power Sources*, **47**, Nos. 1–2: 89 (1994); doi:10.1016/0378-7753(94)80053-7
8. L. Duan, J. Lu, W. Liu, P. Huang, W. Wang, and Z. Liu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **414**, No. 1: 98 (2012); doi:10.1016/j.colsurfa.2012.08.033
9. G. Bayramoğlu, M. Karakışla, B. Altıntaş, A. Metin, M. Saçak, and M. Y. 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**, No. 9: 12 (2018).
11. X. Ding, F. Tan, H. Zhao, M. Hua, M. Wang, Q. Xin, and Y. Zhang, *Journal of Membrane Science*, **1**, No. 1: 53 (2019); doi:10.1016/j.memsci.2018.10.033
12. J. C. Zhang, X. Zheng, M. Chen, X. Y. Yang, and W. L. Cao, *Express Polymer Letters*, **5**, No. 5: 401 (2011); doi:10.3144/expresspolymlett.2011.39
13. F. Roussel, R. Chan-Yu-King, and J. M. Buisine, *Eur. Phys. J. E*, **11**: 293 (2003); <https://doi.org/10.1140/epje/i2002-10158-1>
14. T. Kasa and F. Gebrewold, *Advances in Physics Theories and Applications*, **62**, Iss 1: 28 (2017).
15. G. H. Shim and S. H. Foulger, *Photonics and Nanostructures — Fundamentals and Applications*, **10**, No. 4: 440 (2012), doi:10.1016/j.photonics.2011.12.001
16. B. X. Valderrama-García, E. Rodríguez-Alba, E. G. Morales-Espinoza, K. M. Chane-Ching, and E. Rivera, *Molecules*, **21**, No. 172: 1 (2016); doi:10.3390/molecules21020172
17. A. Reza, *E-Journal of Chemistry*, **3**, No. 4: 186 (2006).
18. W. L. Yuan, X. Yang, L. He, Y. Xue, S. Qin, and G. H. Tao, *Frontiers in Chemistry*, **6**, No. 1: 1 (2018); doi:10.3389/fchem.2018.00059
19. R. Ansari, *E-Journal of Chemistry*, **3**, No. 4: 186 (2006); doi:10.1155/2006/860413
20. Y. Fu, Y. Lin, T. Chen, and L. Wang, *Journal of Electroanalytical Chemistry*, **687**, No. 1: 25 (2012); doi:10.1016/j.jelechem.2012.09.040
21. T. Wei, X. Huang, Q. Zeng, and L. Wang, *Journal of Electroanalytical Chemistry*, **743**, No. 1: 105 (2015); doi:10.1016/j.jelechem.2015.02.031
22. C. J. Mathai, M. Anantharaman, S. Venkitachalam, and S. Jayalekshmi, *Thin Solid Films*, **416**, Nos. 1–2: 10 (2002); doi:10.1016/s0040-6090(02)00700-9
23. S. Saravanan, C. Joseph Mathai, M. R. Anantharaman, S. Venkatachalam, D. K. Avasthi, and F. Singh, *Synthetic Metals*, **155**, No. 2: 311 (2005); doi:10.1016/j.synthmet.2005.09.006
24. M. R. Raj, S. Anandan, R. V. Solomon, P. Venuvanalingam, S. S. K. Iyer, and M. Ashokkumar, *Journal of Photochemistry and Photobiology A: Chemistry*, **262**, No. 15: 34 (2013); doi:10.1016/j.jphotochem.2013.04.013
25. M. Ramesan and K. Suhailath, *Micro and Nano Fibrillar Composites (MFCs and NFCs) from Polymer Blends*. Woodhead Publishing Series in Composites Science and Engineering (2017), p. 301–326; <https://doi.org/10.1016/B978-0-08-101991-7.00013-3>
26. H. Braunling and R. Becker, *U.S.A. Patent Number: US5004560A*.

27. A. Al-Hamdan, A. Al-Falah, F. Al-Deri, and I. Al-Ghoraibi, *Nanosistemi, Nanomateriali, Nanotehnologii*, **20**, Iss. 1: 195 (2022); https://www.imp.kiev.ua/nanosys/media/pdf/2022/1/nano_vol20_iss1_p0195p0205_2022.pdf
28. A. Al-Hamdan, A. Al-Falah, and F. Al-Deri, *Kuwait Journal of Science*, **48**, No. 3: 1 (2021); doi:10.48129/kjs.v48i3.9624
29. M. B. Zaman and D. F. Perepichka, *The Royal Society of Chemistry*, **33**, No. 1: 4187 (2005); doi:10.1039/B506138E
30. A. Al-Hamdan, A. Al-Falah, F. Al-Deri, and M. Al-Kheder, *Polym. Sci. Ser. B*, **63**, No. 3: 191 (2021); doi:10.1134/S1560090421030015