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Original Research Article

Preparation of Polymer Nanoparticles and Doping by Some Schiff Base Compounds by using Microemulsion Systems

Mohsin E. Aldokheily, Athraa H. Mekky, Soraj A. Rahem*

Department of Chemistry, College of Science, University of Thi-Qar, Iraq

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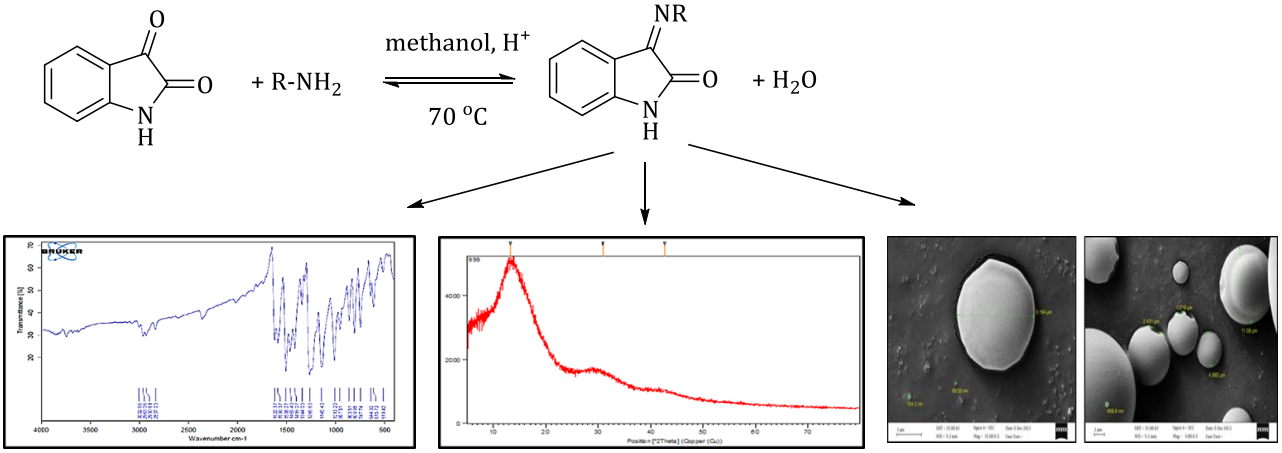
ABSTRACT

This study aims to prepare the nanoparticles of polyacrylic polymer by emulsion method using inorganic phase water and organic phase chloroforms to mixture these phases by surfactant cetyltri methyl ammonium bromide (CTABr) and doping the polymer with Schiff base compounds to improve the properties of the polymer. The Schiff base from azomethene derivatives [A_1-A_2] have been synthesized from the reaction of isatin with hydrazine once and with ethyl-4-aminobenzoate one more time, however the Schiff base A_3 has been synthesized from 3,4-Dimethoxy benzylidene with hydrazine. The structures of polymer nanoparticles were identified by using X-Ray Diffractogram (XRD) to calculate crystallite sizes (D), and study the surface forms, morphology, and diameters of polymer nanoparticles by Scanning Electron Microscope (SEM) technology. In addition, the Infrared Spectroscopy (FT-IR) was utilized to characterize the functional groups of polyacrylic nanoparticle and Schiff base syntheses. Likewise, the Hydrogen-1 nuclear magnetic resonance spectroscopic (^{1}H-NMR) and Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopic were used to determine Schiff base syntheses.

GRAPHICAL ABSTRACT



* Corresponding author: Soraj A. Rahem
✉ E-mail: sorajalirahem91@gmail.com

Introduction

Microemulsions (MEs) are defined as the metastable colloidal dispersions consisting of two immiscible liquids that are isotropic transparent (or translucent) [1]. The internal (dispersed) phase is distributed in the form of small droplets in the external (continuous) phase, i.e. they form a heterogeneous mixture of the perfect dispersed droplets [2]. To form these droplets, the shear forces are necessary, which are usually applied by shaking, stirring, or sonication with surfactant addition [3].

Microemulsions are a special kind of emulsions which are of high significance due to the thermodynamic stability, the simplicity of manufacture, and high-solubility capacity for both lipophilic and hydrophilic compounds [4]. They are able to solubilize insoluble materials as polymers. [5] The term "polymer nano-composite" has evolved to refer to a multicomponent system in which the major constituent is a polymer or a blend thereof and the minor constituent has at least one dimension below 100 nm [6]. This study focused on the acrylic polymers nanoparticle properties and applications after doping with Schiff base compounds to improve the absorbing properties of the polymer.

The chemistry of Schiff base species has been initially of notable importance. Schiff bases also known as imine or azomethine [7]. They are organic compounds reactions between the substances containing amino groups (NH_2, NH_2OH, $NH_2–NH_2$, etc.) with carbonyl groups (aldehydes or some ketones) which in honor of the German chemist, Hugo Schiff, are called the Schiff base reactions [8]. The electrophilic carbon atoms of aldehydes and ketones can be the targets of nucleophilic attack by amines. The final result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond, and the general formula is $R_1R_2C=NR_3$, in which R is an organic side chain [9]. The Schiff bases are widely used for industrial purposes and also exhibit a broad range of biological activities [10].

Materials and Methods

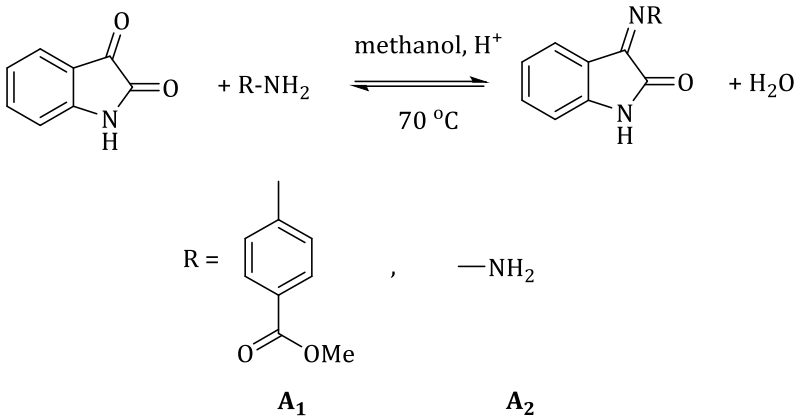
Chemicals and Instrument

The primary substances and solvents in this study were purchased from BDH and Sigma Aldrich companies, which were used without further purification. The melting point was measured using a melting point apparatus and it was uncorrected. The Infrared spectroscopy (FT-IR) spectra were recorded by potassium bromide KBr disk on "Perkin Elme, tensor 27 Bruker" in the range of (400-4000) cm^{-1} in the College of Science, University of Thi-Qar. Hydrogen-1 nuclear magnetic resonance (^{1}H-NMR) and Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on "a Bruker –DRX system Al 400 MHz spectrometer" solvent d_6-DMSO by the internal standard Tetrimethyl silane (TMS) in Higher School of Chemistry/Sharif and Tehran Universities, Iran. The X-Ray Diffractogram (XRD) crystalline structure for any material can be recognized by studying the phase of (XRD) for that material, XRD Instrument, and Generator Settings 40 mA, 40 kV, Anode Material (Cu), Panalytical Company- MODEL X' Pert Pro, Iran. The Scanning Electron Microscope SEM type of the electron microscope captures the images of a sample by its scanning with a high-energy beam of the electron to produce signals which contain information about the sample's surface morphology, composition, etc. the FESEM instrument was ZEISS MODEL SIGMA VP, Iran.

Preparation methods

Synthesis of A_1, A_2

Isatin 10 mmol (1.47 g) in 15 mL methanol was added to 0.1 mL of the glacial acetic acid, and 10 mmol (30 mmol) of ethyl-4-aminobenzoate, or hydrazine, respectively. The reaction mixture was refluxed for 24 hours, and then the solid product was filtered, dried, and recrystallized from ethanol to give **A_1** and **A_2**, respectively [11].

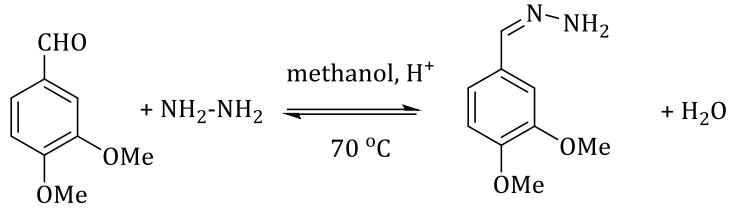


A1 **A2**

Scheme 1: Synthesis of A_1, A_2

Synthesis of A_3

3,4-Dimethoxy benzylidene (10 mmol,1.66 g) in 15 mL methanol was added to 0.1 mL of the glacial acetic acid, (10 mmol, 3200 mg) of hydrazine, and then the reaction mixture was refluxed for 12 hours. The solid product was filtered, dried, and recrystallized from ethanol to give A_3.



Scheme 2: Synthesis of A_3

Preparation of Polymer Nanoparticales

The emulsion diffusion method was used to prepare polymer nanoparticles. First, chloroform (50 mL) and DI water (150 mL) were mixed by stirrer for 24 hours. Then, the mixture solvent was separated by a separator funnel to obtain the chloroform-saturated water and water-saturated chloroform, as well. The chloroform-saturated water was used to dissolve PCL 1.00 g and 0.03 g from the compounds of Schiff base synthesis, as indicated in Table 1. Next, the water-saturated chloroform was used to dissolve the surfactant CTABr 1.00 g. This organic phase was mixed and was kept with chloroform-saturated aqueous phase at 10-20 °C temperature. Then after, the stirrer (500) rpm was used for 1 h before being emulsified with an ultrasonic probe for 15 min. DI water (200 mL) was added to the reaction; while the moderate stirring was kept for 1 h. Finally, the chloroform and a part of water were removed using rotary evaporator under reducing pressure [12].

Results and Discussion

Analysis of Schiff base (A_1- A_3)

Ethyl 4-{[(3*Z*)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]amino}benzoate A_1: Orange crystal, mp=230-233, Yield: 51% .

FT-IR (KBr, cm^{-1}): 3187 (stretching of NH amide), 2985, 2906 (stretching of C-$H_{aromatic}$), 2906 (stretching of C-$H_{aliftic}$), 1751 (C=O_{ester}), 1655 (stretching of C=O_{amide}), 1600 (stretching of C=N_{imine}), 1336 (C-O), and 1352(C-N), as depicted in Figure S1 and Table 2.

^{1}H-NMR (400 MHz, DMSO-d6) (δ ppm): 11.04 (s, 1H, NH), 8.06- 6.29 (m, 8H, aromatic protons) 4.31(q, 2H, O$\underline{CH_2}CH_3$), 1.33 (t, 3H, $OCH_2\underline{CH_3}$), and 2.5 of solvent (DMSO-d_6), as demonstrated in Figure S2 and Table 3.

^{13}C-NMR (101 MHz, DMSO-d_6) (δ ppm) at 165.37 (C=O ester), 163.22 (C=O amide), 155.13 (C=N), 154.88- 111.69 (C=C aromatic), 60.74 O-$\underline{CH_2}CH_3$, 14.26 $CH_2\underline{CH_3}$, and 39.52 DMSO-d_6, as presented in Figure S3 and Table 4.

(3*Z*)-1*H*-indole-2,3-dione 3-hydrazone A_2: Yellow crystal, mp=168-170, Yield: 48%

FT-IR (KBr, cm^{-1}): 3358, 3180 (stretching of NH_2), 3157 (stretching of NH_{amide}), 2957 (stretching of C-$H_{aromatic}$), 1686 (stretching of C=O_{amide}), and 1657 (stretching of C=N_{imine}), as indicated in Figure S4 and Table 2.

^{1}H-NMR (400 MHz, DMSO-d_6) (δ ppm): i99 10.70, 10.52 (s, 2H, NH_2), 9.59 (s, 1H, NH of isatin), 7.36-6.84 (m, 4H for isatin ring), and 2.5 DMSO-d_6**,** as depicted in Figure S5 and Table 3.

^{13}C-NMR (101 MHz, DMSO-d_6) (δ ppm): 162.78(C=O), 138.64 (C=N), 127.06-109.99, (H-aromatic carbon), and 39.52 DMSO-d6, as indicated in Figure S6 and Table 4.

3,4-dimethoxybenzaldehyde hydrazone A_3: Yellow crystal, mp=290-292, Yield: 82%.

FT-IR (KBr, cm^{-1}): 3079 (stretching of NH_{amide}), 3002, 2962 (stretching of NH_{amine}), 3079 (stretching of C-$H_{aromatic}$), 3002 (stretching of C-$H_{aliftic}$), 1623 (stretching of C=O_{amide}), 1598 (stretching of C=N_{Imine}), 1344 (C-O), and 1313 (C-N), as illustrated in Figure S7 and Table 2.

^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 8.64 (s, 1H, proton of imine), 7.49-7.38 (m, 3H, aromatic protons), 7.08 (s, 1H, NH_2), 7.06 (s, 1H, NH_2), 3.82 (s, 3H, OCH_3), 3.35 (s, 3SH, OCH_3) and 2.5 DMSO-d_6, as presented in Figure 8 and Table 3.

^{13}C-NMR (101 MHz, DMSO-d_6) (δ ppm) at 160.87, (C=N), 151.60-108.96, (C=C aromatic), 55.66, 55.42 (2O-$\underline{CH_3}$), and 39.52 (DMSO-d_6), as depicted in Figure S9 and Table 4.

Analysis of characterization of Polymer Nanoparticle

Analysis of Infrared Spectroscopy FT-IR

The FT-IR spectra of polymer polyacrylic in Figure S10 depicted bands at 2963, 2930, and 2837cm^{-1} which were assigned to C–$H_{aliphatic}$. On the other hand, the band at 1622 cm^{-1} was owed to the stretching vibration of C=O ester.

In Figure S11, the FT-IR of $\mathbf{S_1}$ of the polymer doping with compound $\mathbf{A_1}$ demonstrated the absorption band at 3017 cm^{-1} which was designated to the stretching vibration of C-$H_{aromatic}$. The band at 2946, 2918, and 2849 cm^{-1} refers to C–H aliphatic and 1590 cm^{-1} to the C=C group. The absorption band at 1730 and 1621 cm^{-1} refers to C=O_{ester}, C=O_{amid}, and 1640 to C=N; while the bands at 1274 and 1243 cm^{-1} referred to C-N and C-O [13].

While in Figure S12, the FT-IR spectra of $\mathbf{S_2}$ exhibited the following absorption bands at 3014 cm^{-1} C-$H_{aromatic}$. The band at 2918 and 2849 cm^{-1} refers to the stretching vibration of C–H polymer. The absorption band at 1733 and 1690 cm^{-1} causes by stretching vibration of C=O_{ester}, C=O_{amid}, and 1550 to C=N; while bands at 1272 and 1194 cm^{-1} refer to C-N and C-O. In addition, the band at 1436 cm^{-1} refers to N-N.

On the other hand, FT-IR of $\mathbf{S_3}$ in Figure S13 indicated the absorption bands at 3012 cm^{-1} as being attributed to C-$H_{aromatic}$, and likewise the band at 1570 cm^{-1} refers to =C–H group. The band at 2849 cm^{-1} was due to the stretching vibration of -C–H. Besides, the bands at 1730 and 1242 cm^{-1} to C=O_{ester} and C-O groups, respectively. In addition, the stretching at 1630 cm^{-1} of C=N, 1391 cm^{-1} of N-N, and 1270 cm^{-1} of C-N was presented in Table 5.

X-Ray Diffractogram Techniques (XRD)

The X-ray diffractogram (XRD) analysis has been performed to study the structure and crystallite size for the polymer doping by Schiff bass synthesis in which the crystallite sizes are determined by Scherrer formula [14]:

$$D = \frac{K\,\lambda}{\beta\ COS\theta}$$

Where K=0.89 is the shape factor, (λ) is the wavelength of irradiation (Cu Kα = 0.154056 nm), β is (FWHM), and θ is XRD diffractogram angle, as indicated in Table 6.

According to the diffractogram of the pure acrylic polymer containing peaks at 2Θ=13.2, its crystal size was 3.956 nm and a weak peak at 2Θ=30.9 and 2Θ=42.7 had 1.165, 2.110 nm crystal sizes, respectively which are depicted in Figure S14.

The XRD diffractogram is demonstrated in Figure S15 of the sample $\mathbf{S_1}$, in which the highest peak at 2Θ=21.467 has height about 7360, and it has a peak at 2Θ= 20.47 and its crystal sizes were about 39.229nm and 25.762nm, respectively. The second high peak at 2Θ=24.513 has height about 2331, and a peak at 2Θ= 24.01 has crystal sizes about 36.516nm and 34.935nm, respectively which probably they return the density of peaks to

the factional groups from A_1 in addition to the peaks of polymer nanoparticles [15].

The XRD diffractogram of sample **S_2**is presented in Figure S16 which indicates the highest peak at 2Θ=21.459 has height about 4990 and the crystal sizes 33.343nm, as well. It has a peak at 2Θ= 20.96 and its crystal size is 19.986nm. The second high peak at 2Θ=24.51 have high about 1319, the crystal size about 29.790 nm, and also it has a peak at 2Θ= 24.00 by its crystal sizes as 40.176 nm which perhaps they return peaks to factional groups for A_2 in addition to the peaks of polymer nanoparticles [15].

As depicted in Figure S7, the obtained XRD diffractogram patterns of **S_3** have two high peaks which reach to 5330, the first at 2θ = 21.450 that peaks at 2θ =20.53 and the second peak which is smaller, reaches to 1628 at 2θ =24.49 and it peaks at 2θ =23.96. The crystal size of the former sets at 26.944, 20.944, 28.726, and 40.176 nm, respectively. According to the literature, the shape of the first and the most intense peak reflects the ordered packing of the polymer chain [16].

Scanning Electron Microscope of Polymer Nanoparticle

SEM is considered as one of the most important techniques and it is used in investigating the knowledge of morphology for the surface. It was studied for polymer acrylic, as depicted in Figure S18, which has a spherical shape and the diameters as 3.164, 4.980, and 11.09 μm, respectively.

As presented in Figure S19, the morphological analysis of **S_1** appears as a white area having a rough surface. Moreover, the analysis indicates that nano dimensions in image with its size as 100 nm were about 65.13, 17.76, 83.63, 134.8, 183.1, and 205.5 nm, while the image with 1μm size was about 81.88, 96.76, 169.7, 223.3, 644.4 nm and 1.004 μm.

In Figure S20, the SEM images for **S_2** demonstrate the roughness of surface and the growth of some particles. The image with its size as 100 nm, the nano dimensions were about 35.36, 73.73, 122.7, and 227.8 nm, but the image with it size as 200 nm has the nano dimensions about 52.10, 66.99, 145.2, 179.9, and 186.9 nm.

As depicted in Figure S12, the SEM images for sample **S_3** show the surface morphology exhibiting in a rough surface. It has nano-size areas as 26.05, 48.38, 53.38, 94.54, and 135.7 nm with its voulume as 100 nm, on the other hand in the above-mentioned Figure, the volume 1 μm has sizes as 89.32, 96.76, 163.8, 254.1, 583.9 nm, and 1.167 μm.

Table 1: Polymer polyacrylic doping with different Schiff base syntheses

S	S_1	S_2	S_3
Polymer	Polymer +A_1	Polymer +A_2	Polymer +A_3

Table 2: FT-IR absorption bands of (A_1 – A_3)

No.	A_1	A_2	A_3
N-H	3187	3357	3079
H-N-H	----	3180-3157	3002- 2962
C-H Aro.	2985-2906	2957	2929
C-H Alif.	2872	----	2839
N-C=O	1655 \ O-C=O 1751	1686	1598
C=N	1600	1657	1623
C=C Aro.	1498-1463	1604-1551	1579-1508
C-N	1369	1336	1362
C-O	1336	1352	1346

Table 3: ^{1}H-NMR of (A_1 – A_3)

No.	A_1	A_2	A_3
-NH_2	----	10.70, 10.52	7.08, 7.06
-NH	11.04	9.59	---
C-H Aro.	8.06- 6.29	7.36-6.84	7.49-7.38
N=C-H	---	----	8.64
C-H Alif	4.31 O$\underline{CH_2}$, 1.33 $\underline{CH_3}$	----	3.82, 3.35

Table 4: ^{13}C-NMR of (A_1 – A_3)

No.	A_1	A_2	A_3
O-C=O	165.37	----	----
N-C=O	163.22	162.78	----
N=C	155.13	138.64	160.87
C=C Aro.	154.88- 111.69	127.06-109.99	151.60-108.96
O-CH	60.74	----	55.66, 55.42
C-H Alif	14.26	----	----

Table 5: FT-IR absorption bands of (S – S_4)

No.	N-H	C-H Aro.	=C-H	C-H Alif.	C=O ester	C=O amid	C=N	C=C	C-N	C-O
S	---	---	3002-2963	2930-2837	1622	----	---	1590-1508	1344	---
S_1	3400	3017	2946	2918-2849	1730	1162	1604	1590	1247	1243
S_2	3400	3014	2918	2849	1733	1690	1590	1482	1272 N-N 1467	1194
S_3	3400	3012	2919	2849	1730	----	1620	1482	1273 N-N 1467	1242 C-O_{ether}1270

Table 6: XRD data for prepared polymer and polymer nanoparticles doping with some Schiff base compounds

No.	2θ	High	FWHM	Crystal Size (D)
S	13.2	592	2	3.956
	30.9	139	7	1.165
	42.7	70	4	2.110
S_1	5.38	831	0.17	46.319
	6.85	875	0.27	29.163
	20.47	1177	0.31	25.762
	21.467	7360	0.204	39.224
	23.67	683	0.19	42.290
	24.01	1268	0.23	34.935
	24.01	2331	0.22	36.561
S_2	5.30	557	0.21	37.496
	6.78	606	0.4	19.685
	20.96	937	0.4	19.986
	21.459	4990	0.24	33.343
	24.00	969	0.24	40.176
	24.51	1319	0.27	29.790
S_3	6.83	912	0.38	20.721
	17.07	518	0.4	19.884
	20.53	750	0.39	20.98
	21.450	5330	0.297	26.944
	24.49	1628	0.28	28.726
	25.70	506	0.34	23.730

Conclusion

The results of the study confirmed the characterization of the polymer polyacrylic nanoparticles which were prepared by emulsion method in nano sizes. Then after, the crystallite sizes of the sample were calculated using the Scherrer formula which was in the range of up to the nano sizes as 17-50 nm. The particle size was considered based on the SEM surface morphology of nanoparticles. With high-resolution images of the sample, these images gave the irregular and

angular shapes with different particle sizes and different diameters in the range of 20-600 nm.

This research reported the study of a series of Schiff base syntheses from Isatin with different aromatic amines for two Schiff base preparations A_1, A_2 and A_3 synthesis from 3,4-dimethoxy benzylidene with Hydrazine. The physical characterization using spectroscopic techniques was employed in the elucidation of the structures of the synthesized derivatives which indicated the analysis through spectrum IR, ^{1}H- NMR, and ^{13}C-NMR to the structures of these compounds.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

ORCID:

Soraj A. Rahem

https://www.orcid.org/0000-0002-9287-915X

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