

# Synthesis and copolymerization of 2-thiobenzimidazole and using their complexes in the extraction of the organosulfur compound

Asaad F. Khattab<sup>1</sup>, Ahmed A. H. Al-Kadhimi<sup>2</sup>, Farah. Kh. H. Al-Juboory<sup>3</sup>

<sup>1</sup>College of Science/ Chem. Dept., Mosul University, IRAQ

<sup>2</sup>College of Science/Chem. Dept., Tikrit University, IRAQ

<sup>3</sup>College of Science, Chem. Dept., Kirkuk University. IRAQ

---

## ABSTRACT

Monomer dithiobenzimidazole was prepared from 3,3'-diaminobenzidine. The prepared monomer was polycondensed with three types of dibromo alkanes in order to prepare three types of polydisulfides. Schiff's base was prepared from reaction of 3,3'-diaminobenzidine with salicylaldehyde. Thiobenzimidazole was prepared from the Schiff base and polymerized by two methods; polyesterification with terephthaloyl dichloride, and polycondensed with phenol-formaldehyde. All the prepared polymers were complexed with copper ion and examined as a desulfurizing reagent for light oil model. The polymers were show a reasonable efficiency of extraction.

**Keywords:** thiobenzimidazole, copolymerization, polydisulfide, copper complex, desulfurization.

---

## INTRODUCTION

The imidazole moiety has great interest in the scientific research. Their compounds are used in many fields of chemical industries like rubbers and drugs<sup>(1,2)</sup>. Imidazole functionality plays a critical role in many structures within the human body, notably as histamine and histidine<sup>(3)</sup>. Chemical modification of the imidazole functionality has led to desired covalent or physical crosslinking and the production of functional or multifunctional polymers<sup>(4)</sup>. Imidazole-based polymers readily associate with biological molecules, drugs and proteins through hydrogen-bonding<sup>(5,6)</sup>. Imidazole or benzimidazole have many active sites within their chemical structure, sites 1, 2 or 5, give the compound a special characteristic as a good chelating agent. It can be coordinated with transition metal ions through C=N group to form the very stable complexes<sup>(7,8)</sup>. In the other hand, the donor atoms like O, N and S in the benzthioimidazole structure will provide sites intended to form chelating complexes with some metal ions<sup>(9,10)</sup>. The donor sites can form unimolecular complex or poly complex as the metal atom was bonded to the nitrogen atoms of the imidazole ring<sup>(11)</sup>. Firestone et al.<sup>(12)</sup> studied the lyotropic mesophase behavior of self-assembled imidazolium ionic liquids and their polymers. The effects of alkyl chain length and introducing an acryloyl group for polymerization onto the end of the alkyl were investigated<sup>(12)</sup>. Forming the very stable complex of imidazole moiety with metal ions can be enhanced by linking the imidazole moieties by ether bridge<sup>(13)</sup>. Compounds of imidazole and their derivatives were found to be used as liquid ions<sup>(14)</sup>. The imidazole can be considered as a positive organic ion<sup>(15)</sup>, their complexes with some metal ions have high thermal stability and it can be used to remove the sulfur compounds from the petrol derivatives especially from diesel fuel<sup>(16,17,18)</sup>. Benzimidazole containing polymers received more attention for their potential application in many fields<sup>(19)</sup>. In the present work we have polymerized different compounds of imidazole and examined their complexes with copper ion to extract organosulfur compound from simulated diesel fuel sample.

## EXPERIMENTAL

### Synthetic route:

#### *A- Preparation of 6-[1'-(3',4'-diamino)]-2-thiol benzimidazole (A)<sup>(20)</sup>:*

A mixture of (0.01 mole) (2.14 g.) of 3,3-diaminobenzidine, (0.02 mole) (1.12 g.) of potassium hydroxide, (0.02 mole) (1.22 ml) of carbon disulfide, (20 ml) of 96% ethanol and (4 ml) of distilled water was refluxed for (3 hrs.), then (20 ml.) of warm water was added and acidified with (3%) acetic acid with stirring. The precipitated product was filtered and dried under 50°C, it was weighed 2.72g.

### **Polymerization of monomer (A):**

Three polymers have been prepared via the condensation of compound (A) with dibromo alkane. Polymer **PAI** was prepared as following: 0.002 mole (0.596 g.) of the compound (A) was dissolved in 15 ml of absolute ethanol and refluxed with 0.002 mole of 1,3-dibromopropane in presence of 0.08g sodium hydroxide dissolved in 8ml absolute ethanol for a period of 5hrs. The produced polymers were filtered and washed with ethanol. The weight of the resulted polymers was 0.5932g. Polymers **PAII** and **PAIII** were prepared by the same method via condensation of compound A with 1,4-dibromo butane and 1,5-dibromo pentane. The resulted weight is 0.618g and 0.623g for **PAII**, **PAIII** respectively.

### **B- Schiff Base preparation: (B):**

A solution of (0.02mole, 5.24 g) 3,3'-diaminobenzidine in (50 ml) absolute ethanol was added slowly to (0.02 mole, 2.44 g) of salicyldehyde in presence of (0.01g) para toluene sulfonic acid (PTSA). The reaction mixture was refluxed for (3 hrs.). After cooling, the precipitated Schiff Base was collected by filtration and washed with cold ethanol. The weight of product after drying was (6.7815 g). The melting point of the resultant compound was 160<sup>0</sup> C.

### **Preparation of 6- [1'-(3'-amino,4'-(p-hydroxybenzylidene))] -2-thiol benzimidazole from Schiff Base:(B1)**

A mixture of (0.008 mole, 2.92 g.) of Schiff's base (B), (0.008 mole, 0.44 g.) of potassium hydroxide, (0.008 mole, 0.49 ml) of carbon disulfide, (20 ml) of 96% ethanol and (4 ml.) of water was transferred into a 250 ml round bottom flask and heated under reflux for (3 hrs.), then (20 ml.) of warm water was added, and acidified with (3%) acetic acid with stirring. The product was filtered off and dried over night at (50<sup>0</sup>C). The weight of product after drying was (2.77 g yield 76%). The melting point of resultant compound was 245<sup>0</sup>C.

### **Preparation of Monomers (B2):**

Monomer 1,3-di-[6- [1'-(3'-amino,4'-(p-hydroxybenzylidene))] -2-thiol benzimidazole]propane (**B2-1**) was prepared as followed: 0.004 mole (1.37 g) of the compound (B1) was dissolved in (25 ml) of absolute ethanol, mixture of (0.004 mole, 0.16 g.) sodium hydroxide dissolved in (10 ml) absolute ethanol and (0.002 mole, 0.4276 g) of 1,3-dibromopropane were added. The reaction mixture was refluxed with constant stirring for (5 hrs.). The product was filtered and washed with ethanol. The weight of product after drying was (1.61 g). The melting point of resultant compound was 264<sup>0</sup> C.

The same procedure was followed for preparing monomer 1,4-di-[6- [1'-(3'-amino,4'-(p-hydroxybenzylidene))] -2-thiol benzimidazole]butane (**B2-2**) and monomer 1,5-di-[6- [1'-(3'-amino,4'-(p-hydroxybenzylidene))] -2-thiol benzimidazole]pentane (**B2-3**) by reaction of compound (B1) with 1,4-dibromobutane and 1,5-dibromopentane respectively.

### **Polyesterification of monomers (B2) with Terphthaloylchloride:**

Polymer (**PAB2-1**) was prepared by using interfacial polymerization process by adding (0.001 mole, 0.75 g) of monomer (B2-1) to (10 ml) of distilled water, few drops of sodium hydroxide solution (10%) was added until the ligand was dissolved. (0.01 mole, 2.0302 g) of freshly prepared terphthaloyl dichloride was dissolved in (10 ml) of dry benzene. The second solution was added to the first solution, and mixed by glass rod at room temperature. The resulting precipitate was filtered. The weight of product was (1.45g). Polymers (**PAB2-2** and **PAB2-3**) were prepared by the same method by polymerization of terphthaloyl chloride with monomers B2-2 and B2-3 respectively. The resulted weight of **PAB2-2** was 1.79g while **PAB2-3** was 1.73g.

### **Preparation of Phenol-formaldehyde Resins with monomers B2:**

Monomers **B2** were polymerized with phenol and formaldehyde in order to prepare polymers **PFB2-1**, **PFB2-2** and **PFB2-3**. The main method is as follows: To a mixture of (0.0003 mole) of monomer (B2), (0.003 mole, 2.041 g) of phenol, (25 ml.) of formaldehyde (37%) and (25 ml.) of ethanol (96%), sodium hydroxide solution (5%) was added to the reaction mixture to make pH=10. The reaction mixture was refluxed with constant stirring for (6 hrs.). The polymer was filtered and washed with ethanol. The weight of product after drying was (2.02 g), (2.13 g) and (2.78g) of polymers **PFB2-1**, **PFB2-2** and **PFB2-3** respectively.

### **Metalation the Polymers with Copper:**

(10 ml) CuCl<sub>2</sub> solution 900 (ppm) was mixed with (0.1 g.) of all prepared polymers separately in a conical flask with stirring for (24 hrs.) at room temperature. The resulting metalized polymers were filtered. The filtrate was analyzed for copper content by using Varian-AA-240FS Fast Sequential Atomic Absorption Spectroscopy, Australian.

### Extraction sulfur compound:

(10 ml.) Solution of (Dibenzothiophene in Benzene) (3083 ppm) was mixed with (0.1 g) of polymer (All polymers samples containing copper in its structure were used for desulfurization separately) in a round bottomed flask with stirring for different periods of time (4,8,12,16,20,24 hrs.) at room temperature. This step is to choose the proper contact time that gives highest sulfur removal. The resulting solution was filtered. The filtrate was analyzed for sulfur content by using Carlo Erba EA-3200 Elemental Analysis. The factors affecting on the extraction efficiency (the amount of absorbent and the temperature) were examined.

## RESULTS AND DISCUSSION

### Preparation of 6-[1'-(3',4'-diamino)]-2-thiol benzimidazole (A)

This compound was prepared according to published work<sup>(20)</sup> by refluxed the diaminobenzidine with potassium hydroxide and carbon disulfide (1:2:2 molar ratio), as shown in scheme (1). The melting point of resultant monomer was 298 °C. It was identified by infrared spectroscopy. The IR spectrum of prepared compound shows vibrations at wave number 3088 cm<sup>-1</sup> for NH-benzimidazole, while NH<sub>2</sub> group shows asymmetric and symmetric stretching vibration at 3663cm<sup>-1</sup> and 3119cm<sup>-1</sup> respectively, SH stretching vibration at 2603 cm<sup>-1</sup> C-S stretching vibration at 706 cm<sup>-1</sup> and the vibration at 1618 was belong to stretching vibration of CH=N group.<sup>(20)</sup>

### Polymerization of compound (A) with dibromoalkanes:

A set of three dibromoalkanes (1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane) were selected for condensation reaction with (A) to prepared poly disulfides (Scheme1). The IR spectra of all three polymers (PAI, PAII and PAIII) were showed a stretching vibration of aliphatic CH<sub>2</sub> at about 2951-2923 cm<sup>-1</sup>, stretching vibration of -CH=N at about 1616-1613 cm<sup>-1</sup>, C-S stretching vibration at about 663-618 cm<sup>-1</sup> and the vibration at 3420-3401 cm<sup>-1</sup> which is related to asymmetric vibration of NH<sub>2</sub> moiety. The TG curve of (PAI) shows decomposition temperature (Ti) at 490°C and final temperature (Tf) at 600°C. C.H.N.S. Elemental analysis of the prepared poly disulfides are shown in table (2).

### Preparation of Schiff Base (B):

The Schiff base under investigation was formed by the condensation of 3,3'-diaminobenzidine with salicylaldehyde (1:1 molar ratio) as shown in scheme (2). The IR (KBr/cm<sup>-1</sup>):spectrum of the prepared Schiff base shows stretching vibration of free (OH) at 3446 cm<sup>-1</sup>, asymmetric stretching vibration of (NH<sub>2</sub>) near 3388 cm<sup>-1</sup>, symmetric stretching vibration of (NH<sub>2</sub>) near 3364 cm<sup>-1</sup>, in the other hand the azomethine group show stretching vibration at 1594 cm<sup>-1</sup>. The melting point of resultant compound was 160°C.

### Preparation of 6- [1'-(3'-amino,4'-(p-hydroxybenzylidene))]2-thiol benzimidazole From Schiff Base(B1):

The formation of this compound is primarily supported by frequencies observed in its IR spectrum. The spectrum shows frequencies at 3447 cm<sup>-1</sup> for stretching vibration of free (OH), 3365 cm<sup>-1</sup> and 3114 cm<sup>-1</sup> for asymmetric and symmetric stretching vibration for NH<sub>2</sub> respectively, and important weak peak at 2610 cm<sup>-1</sup> corresponding to SH stretching vibration. The frequency at 1594cm<sup>-1</sup> is related to azomethine CH=N group while at 1277cm<sup>-1</sup> is belong to stretching vibrations of and C-N within the imidazole moiety<sup>(20)</sup>.

### Preparation of Monomers (B2):

The three monomers are differ in their flexibility whereby they are differ in the length of bridge binding the imidazole moieties (propane, butane and pentane) The melting points of the resultant monomers **B2-1**, **B2-2** and **B2-3** were 264°C, 277°C and 294°C. The IR spectrum of the monomers elucidate the disappearance of SH stretching vibration. They shows stretching vibration of CH<sub>2</sub> aliphatic at about 2970-2850 cm<sup>-1</sup>, stretching vibration of C=N at 1613-1593 cm<sup>-1</sup> and stretching vibration of C-Sat 749-733cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectra of all three monomers by using DMSO as a solvent showed peaks of methylene groups at (δ=0.8-2.9 ppm), NH peaks at (δ=4.3 ppm), C-H of benzene ring at (δ=6.63-7.5 ppm), peaks of C-H benzimidazole at (δ=7.5-7.58 ppm), peaks of N=C-H of benzylidenimin at (δ=8.1-8.3 ppm) and O-H phenolic at (δ=12.8-12.9 ppm).

### Polymerization of B2 monomers:

Two routes were followed to polymerized monomers B2; first with terphthaloyl chloride through interfacial polymerization method to synthesized the polyesters, secondly with phenol and formaldehyde to prepare the more thermally stable polymers. The polyester of the three monomers of B2 were characterized by IR spectroscopy. The IR spectra of all three polymers were show stretching vibrations of(NH) at about 3425-3418 cm<sup>-1</sup>, stretching vibration of

CH<sub>2</sub> aliphatic at about 2900-2830 cm<sup>-1</sup>, stretching vibration of –CH=N at about 1689-1600 cm<sup>-1</sup> and stretching vibration of esteric C-O at 1319-1205 cm<sup>-1</sup> that can be considered a good performance for ester linkage formation. C.H.N.S. elemental analysis of prepared polymers are shown in table (1). The TG curve of (PBA2-2) shows initial decomposition temperature (Ti) at 325°C and final temperature (Tf) at 448°C. The structure of phenol-formaldehyde resins were investigated by infrared spectroscopy. The IR spectra of all three resins shows a wide peaks of (OH) stretching vibration at about 3500-3100 cm<sup>-1</sup>, stretching vibration of CH<sub>2</sub> aliphatic at about 2923-2886 cm<sup>-1</sup>, stretching vibration of –CH=N at about 1614-1610 cm<sup>-1</sup>. The TG curve of (PFB2-2) shows initial decomposition temperature (Ti) at 485°C and final temperature (Tf) at 600°C. C.H.N.S. elemental analysis of prepared phenol-formaldehyde resins are shown in table (1).

### Complex of the polymers with copper:

All the prepared chelating polymers can be complex with the copper (II) ions from aqueous solution. The Cu (II) complexes with the prepared chelating polymers were obtained by stirring the chelating polymers in aqueous solution of Cu(II) (900 ppm) at room temperature in the pH ≤ 7 by using few drops of acetic acid. These complexes are certainly formed through the thiol benzimidazole which was considered as a good chelating agent with transition metals ions<sup>(21)</sup>

Table (2) shows the number of milligrams of metal ions Cu(II) captured by 0.1g of the prepared polymers. The results demonstrated that the stoichiometry of the obtained complexes is approximately (1:1) between the metal ion and the repeating unit moiety within the polymer chain.

### Desulfurization efficiency:

All the chelating polymers give a reasonable efficiency to extract the sulfur organic compound from stimulated sample of diesel fuel, whereby there are interaction between organosulfur compounds and copper ion on the polymer chain<sup>(22)</sup>. The effects of time, temperature and amount of used polymers on extraction efficiency were studied. The results were shown in (Tables 3,4,5). The results revealed that the chemical structure is the dominant factor effects on the extraction efficiency. It was clearly noticed that the presence of azomethine moiety within the polymer chain will increase the efficiency of extraction. In the other hand, the longer the chain separated the imidazole group (propane, butane, pentane) the higher efficiency of extraction

## REFERENCES

- [1]. K.K. Mothilal, C.Karunakaran, A.Rajendran, and R.Murugesan, J. Inorg. Biochem., 98,322-335,( 2004).
- [2]. S. Özden, D. Atabey, S. Yildiz and H. Göker, Bioorg. Med. Chem.,13, 1587- 1598, (2005).
- [3]. Bredas J. L., Poskin M. P., Delhalle J., Andre J. M. and Chonjnaki H. J., Phys. Chem., 88, 5882-7, (1984).
- [4]. Ranucci E., Spagnoli G. and Ferruti P, Macromol Rapid Comm., 20, 1-6, (1998).
- [5]. Batra D., Hay DNT, Firstone MA., Chem. Mater, 19, 4423-31, (2007).
- [6]. Tennyson AG., Kamplain JW. and Bielawski CW., The Royal Society of Chemistry, Chem. Comm., 2124-6, (2009).
- [7]. K. Isele, V. Broughton, C.J. Matthews, J. Chem. Soc. Dalton Trans.,20, 3899-3905,(2002).
- [8]. Y.L.Zhou , M.H.Zeng and S. W.Ng ., Acta Cryst., E66. m57, (2010).
- [9]. L.C. Liang, Coord. Chem. Rev. ,250, 1152-1177, (2006).
- [10]. R. Balamurugan, M. Palaniandavar, R.S. Gopalan and G.U. Kulkarni. Inorg. Chim.Acta, 357(4), 919-930, (2004).
- [11]. Claypool G. E., Holser W. T., Kaplan I.R., Sak I., Chem. Geo., 28,199-260, (1980).
- [12]. Batra D., Seifert S., Firstone MA., Macromol. Chem. Phys., 208, 1416-27,(2007).
- [13]. D. Yuan and H. V. Huynh, Molecules ,17, 2491-2517,(2012).
- [14]. C.S. Song, Catal Today, 86, 211-263,(2003).
- [15]. J.D. Holbrey, W.M. Reichert and R.D. Rogers, J. Chem. Soc. Dalton Trans., 15, 2267-2274, (2004).
- [16]. C. Huang, B. Chen, J.Zhang, Z. Liu and Y. Li, Energy and Fuel, 18 (6), 1862, (2004).
- [17]. I.V. Babich and J.A. Moulijn, Fuel, 82,607-631,(2003).
- [18]. Yosuk S., Kazuom S., Ki-Hyouk C., Yozo K. and Isao M., Fuel, 84, 903-910, (2005).
- [19]. I. J. B.Lin and Vasam, J. Orgmet.chem., (2005).
- [20]. Maw – Ling Wang, Biing-Lang Liu, Journal of Chinese Institute of Chemical Engineers, 38, 161-167(2007).Developed by Ramish Dhani, Pharma Research Library (2013).
- [21]. A. John and P. Ghosh, Dalton Trans., 39, 7183–7206,(2010).

**Table (1): Elemental analysis of the prepared polymers**

Compound	C%	H%	N%	S%
PAI measured	61.911	6.920	14.935	16.910
PAI calculated	61.54	6.89	14.72	16.85
PAII measured	62.036	7.124	14.864	16.791
PAII calculated	61.98	7.02	14.46	16.55
PAIII measured	62.479	7.263	14.430	16.426
PAIII calculated	62.40	7.15	14.20	16.25
PFB2-1 measured	73.004	8.092	9.271	5.571
PFB2-1 calculated	72.24	7.97	9.23	5.28
PFB2-2 measured	73.200	8.168	9.181	5.528
PFB2-2 calculated	72.39	8.05	9.13	5.22
PFB2-3 measured	73.521	8.451	9.109	5.486
PFB2-3 calculated	72.54	8.12	9.02	5.16
PAB2-1 measured	71.043	6.931	9.501	5.830
PAB2-1 calculated	70.14	6.82	9.48	5.43
PAB2-2 measured	71.342	7.006	9.268	5.627
PAB2-2 calculated	70.32	6.91	9.37	5.36
PAB2-3 measured	72.080	7.958	9.255	5.415
PAB2-3 calculated	70.50	7.00	9.26	5.30

**Table (2): Milligrams of uptake copper ions by 0.1 gram of polymer**

polymer	AI	AII	AIII	PFB2-1	PFB2-2	PFB2-3	PAB2-1	PAB2-2	PAPB2-3
Cu(II)/ mg	8.02	8.09	8.07	8.13	8.16	8.17	7.95	8.03	8.08

**Table (3):- Milligrams of extracted sulfur by(0.1) g of different polymers at different times**

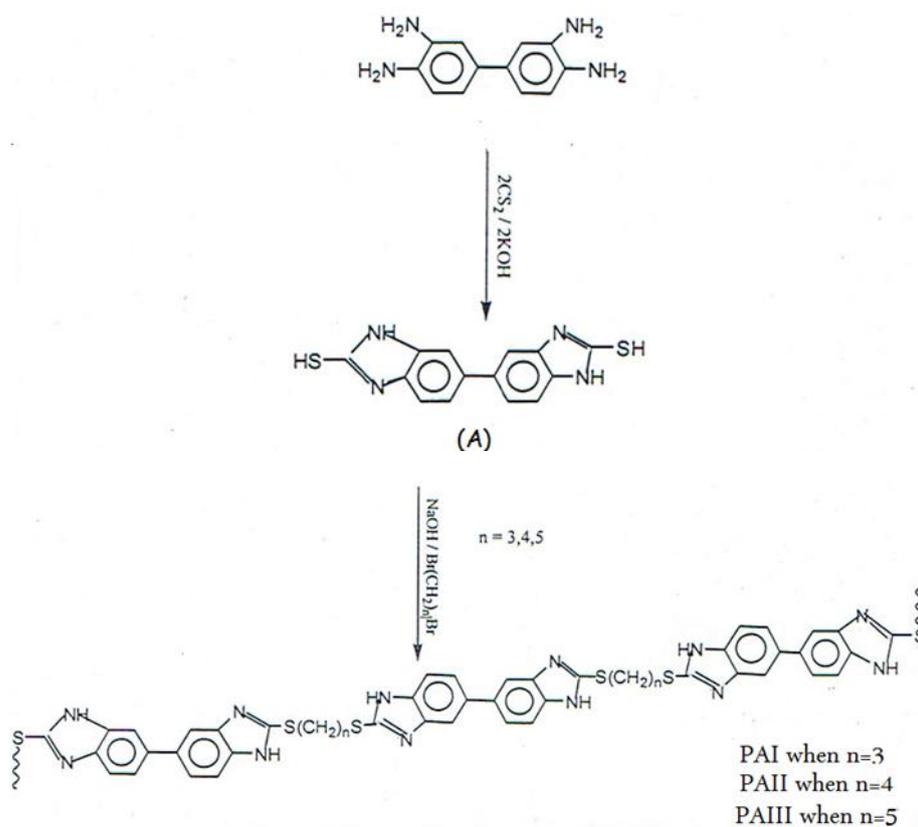
Polymer	4(hr.)	8hr	12hr	16hr	20hr	24hr
PAI	0.74	1.62	3.89	6.01	7.60	7.60
PAII	0.79	1.66	4.30	6.04	7.67	7.67
PAIII	0.88	2.20	4.61	6.42	7.70	7.70
PFB2-1	1.68	2.80	6.64	9.49	10.82	10.90
PFB2-2	1.82	3.00	6.85	9.73	10.97	11.00
PFB2-3	1.85	3.04	7.54	9.81	10.99	11.01
PAB2-1	6.5	1.58	3.64	5.72	7.69	7.48
PAB2-2	8.7	2.12	4.15	6.78	7.82	7.83
PAB2-3	8.2	1.61	3.81	5.94	7.61	7.64

**Table(4):Extracted sulfur(mg) from dibenzothiophene solution by (0.1)mg polymer at different temperatures**

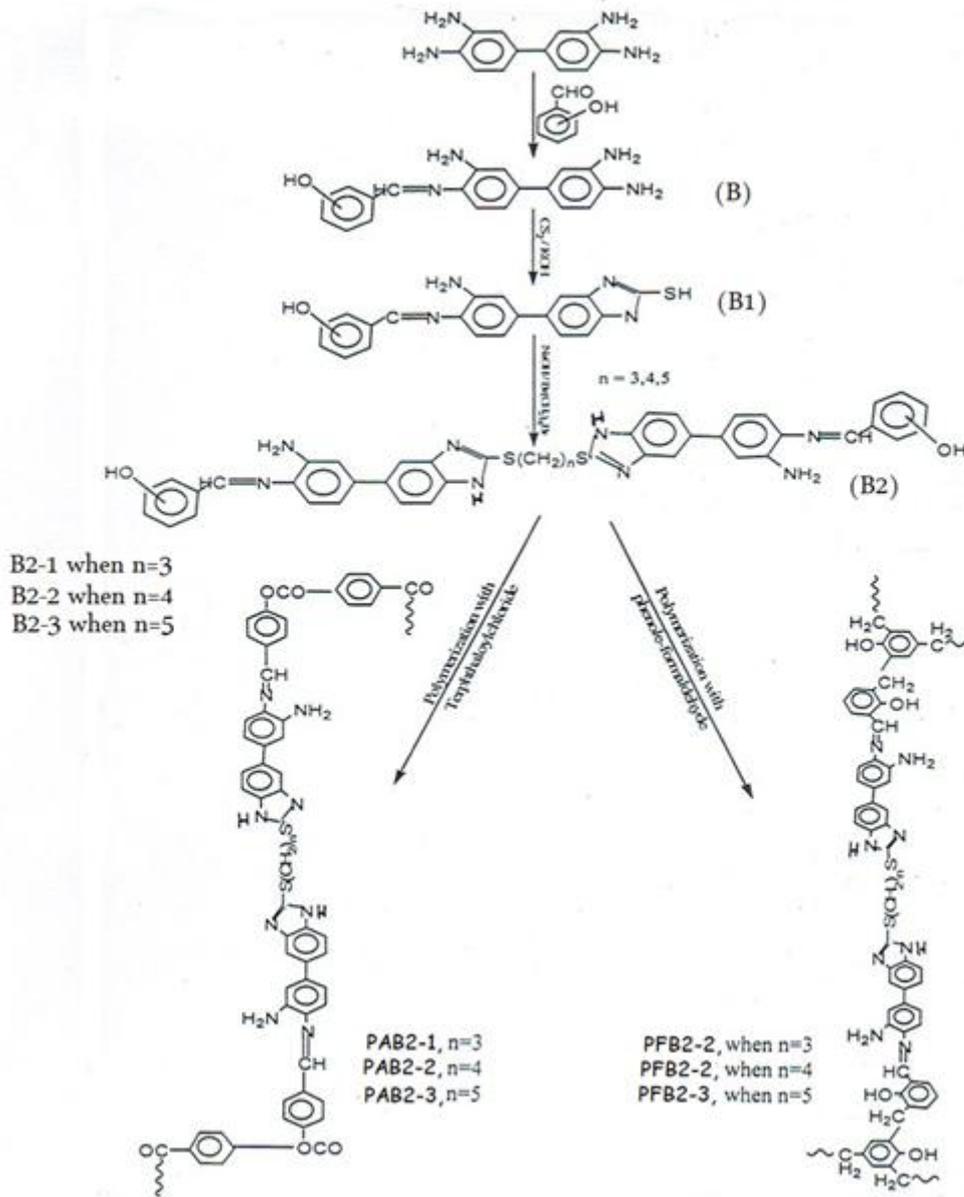
Polymer	25 °C	35 °C	50 °C
PAI	7.60	8.46	9.71
PAII	7.69	9.07	11.40
PAIII	7.71	9.15	11.49
PFB2-1	10.84	11.60	12.04
PFB2-2	11.00	11.82	12.91
PFB2-3	11.01	11.95	13.48
PAB2-1	7.48	9.34	10.89
PAB2-2	7.83	9.68	11.72
PAB2-3	7.64	9.61	11.44

**Table (5): Extracted sulfur (mg) from dibenzothioophene by using different amounts of polymers at (50 °C) (Time of treatment 20hrs)**

polymer	0.1g	0.2g	0.3g
PAI	9.71	13.91	15.82
PAII	11.40	14.92	15.93
PAIII	11.49	15.16	16.88
PFB2-1	12,04	14.87	16.45
PFB2-2	12,91	15.62	16.66
PFB2-3	13.48	15.87	17.19
PAB2-1	10.89	13.40	14.81
PAB2-2	11.72	15.37	16.97
PAB2-3	11.44	15.21	16.89



**Scheme (1): Preparation of monomer (A) and its polymers**



Scheme (2): Preparation of monomers (B) and related polymers