



Scholars Research Library

Der Pharma Chemica, 2012, 4(4):1397-1403  
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X  
CODEN (USA):  
PCHHAX

## Preparative Method of Novel Phthalocyanines from 3- Nitro Phthalic Anhydride, Cobalt salt and Urea with Chloromethylpolyestylene as a Heterogenous, Reusable and Efficient Catalyst

Mohammad Ali Zolfigol<sup>2</sup>, Ali Reza Pourali<sup>1</sup>, Sami Sajjadifar<sup>3,4</sup> and Shohreh Farahmand<sup>1,2,4</sup>

<sup>1</sup>Faculty of Chemistry, Bu-Ali Sina University, Hamedan, P.O. Box 6517838683, Iran

<sup>2</sup>School of Chemistry, Damghan University, Damghan, Iran

<sup>3</sup>Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran

<sup>4</sup>Department of Chemistry, Payame Noor University, Tehran, P.O. Box 19395-4697, Iran

### ABSTRACT

3-Nitrophthalic anhydride was reacted with urea and cobalt salt in nitrobenzene under  $N_2$  at  $185^\circ C$  and cobalt-tetraaminophthalocyanine (CoTNP) was produced. Cobalt-tetraaminophthalocyanine (CoTAP) was produced by reduction of CoTNP caused by Sodium borohydride under  $N_2(g)$ . CoTAP and chloromethylpolystyrene was refluxed in nitrobenzene or DMF at  $180^\circ C$  for 12h. The mixture was cooled down to reach the room temperature and then solvent removed and the resulting precipitate was washed with water to remove excess CoTAP, and dried it to get a light green solid (CoTAP-linked-polymer).

**Keywords** Phthalocyanines, Cobalttetraaminophthalocyanine, CoTAP, Phthalocyanines linked polymer.

### INTRODUCTION

Phthalocyanines are of interest not only as model compounds for the biologically important porphyrins but also because the intensely colored metal complexes are of commercial importance as dyes and pigments [1], the copper derivatives being an important blue pigment [2]. Almost 100 years of research on phthalocyanines and related compounds have produced an abundance of data on the synthesis and photo physical properties of miscellaneous derivatives of these compounds. Today literally thousands of diverse phthalocyanines have been reported in the chemical literature. Typically, temperatures around  $200^\circ C$  and reaction times of hours are needed [3]. Since the synthesis of phthalocyanines [4] in the early 1930s, a rich and varied chemistry and technology has developed around these interesting materials. There are literally thousands of publications and patents related to phthalocyanine and its analogs [5,6]. Phthalocyanines have found a wide range of application in the area of material science because of their distinct optical and electrical properties as well as their thermal stability [7], these compounds are prepared by reaction between metal salts, urea and phthalonitriles (phthalic anhydride, phthalimide or Phthalic acid)(Scheme 1). Typically, temperature around  $200^\circ C$  and reaction times of several hours and needed for such reaction. Phthalocyanine complexes of transition metals are attractive as potential oxidation catalysts because of their rather cheap and facile preparation in a large scale and their chemical and thermal stability. Their macro cyclic structure resembles that of porphyrins' complexes widely used by nature in the active sites of oxygenase enzymes [8]. Phthalocyanines constitute a remarkably versatile class of compound with divers' technological applications [9-10].

Sarah D'Souza *et al.* synthesised monoamino functionalized ZnPc derivatives for the first time. A monoamino functionalized ZnPc complex is attached to carboxylic acid functionalized quantum dots (QDs)[11]. It was reported that the metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from the *o*-phthalonitrile end-capped polymers. These polymers had high T<sub>g</sub> and were soluble in common organic solvents. Mohan Kumar and Achar synthesized lead tetranitro phthalocyanine and lead tetraamino phthalocyanine in pure state with very high yield (85–90%) for first[12].

Copper and iron were used as the metals in the above preparation. It is always advantageous to synthesize amorphous polymers having high glass transition temperatures and excellent thermo-oxidative stability, as they are soluble in common organic solvents, and allow for easy solution processing and chemical modification [13–15]. W. Wan *et al* synthesized metal containing end-capped copolymers from 1,2- dicyanobenzene containing bisphenol[16].

## MATERIALS AND METHODS

### General

IR spectra of the compounds were obtained on a Shimadzu IR-435 spectrometer using a KBr disk. The <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker AQS 300 Avance instrument at 300 MHz in dimethyl sulfoxide (DMSO-d<sub>6</sub>) using tetramethylsilane as an internal standard. The progress of reaction was followed with thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plates. All the products are known compounds and were characterized by comparing the IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopic data and their melting points with the literature values.

### General method of phthalocyanines synthesis

Ammonium molybdate (0.01 mmol, 0.012 g) was added to a solution of phthalic anhydride (10 mmol, 1.48 g), urea (50 mmol, 3.00 g), and metal salts (2.6 mmol) in nitrobenzene (15 mL). The mixture was stirred under N<sub>2</sub> at 185°C for 4 h. The reaction mixture was cooled to room temperature and diluted with toluene (80 mL). The resulting precipitate was collected by centrifugation. The solid was washed toluene, water, MeOH/ether (1:9), EtOAc/hexane (2:1), filtrated and dried it to afford a dark green solid (2.0 g, 98%) [18].

### Cobalt Tetranitrophthalocyanine(CoTNP) synthesis

Tetranitro-cobalt-phthalocyanine was prepared according to published procedures [18]; Ammonium molybdate (0.01 mmol, 0.012 g) was added to a solution of 3-nitrophthalic anhydride (10 mmol, 1.93 g), urea (50 mmol, 3.00 g), and metal salts (2.6 mmol) in nitrobenzene (15 mL). The mixture was stirred under N<sub>2</sub> at 185°C for 4 h. The reaction mixture was cooled and diluted with toluene (80 mL). The resulting precipitate was collected by centrifugation. The solid was washed with toluene, water, MeOH/ether (1:9), EtOAc/hexane (2:1), filtrated and dried it to afford a dark green solid (2.0 g, 98%).

### Cobalt tetraaminophthalocyanine(CoTAP) synthesis

Sodium borohydride (7.4 g) was added to a solution of tetranitro-cobalt-phthalocyanine (2.5 mmol, 1.95 g) in DMF (50 mL). The reaction mixture was stirred under N<sub>2</sub> and heated at 60°C for 4 h. The mixture was cooled to room temperature and remove the solvent, then the solid stirring in 200 cc water for 1h and dried to afford a dark green solid (1.2 g, 75%)(Scheme 2, step 2).

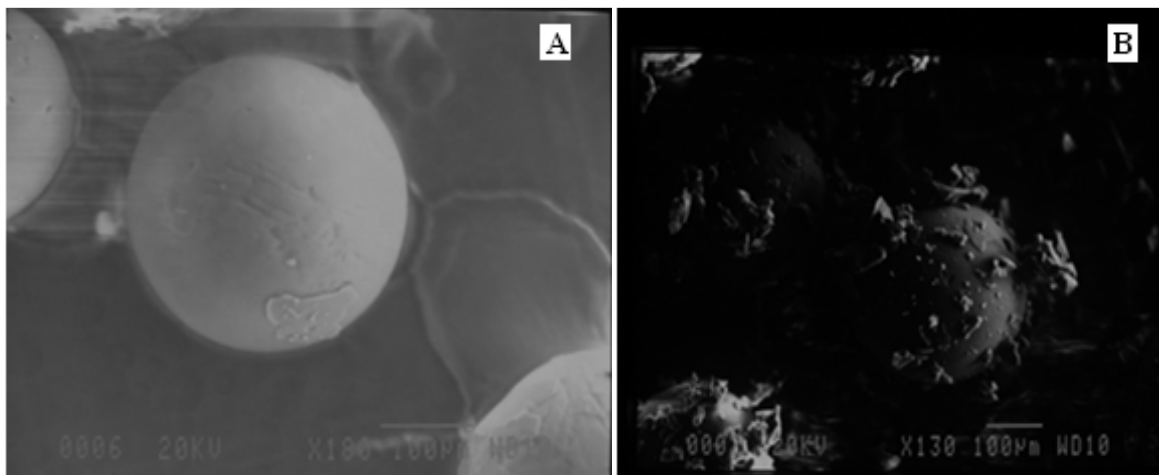
### CoTAP supported Chloromethylpolystyrene

A mixture of Tetraamino-cobalt-phthalocyanine (1 mmol, 0.69 g), polystyrene chloromethylated (2% vinyl benzene) (4 mmol, 1.4 g), and nitrobenzene or DMF (30 mL) was heated at 180°C (reflux). After 12 h, the mixture was cooled to room temperature and remove the solvent, then, the resulting precipitated was washed with water to remove excess tetraamino-cobalt-phthalocyanine, filtrated and dried it to afford a light green solid(Scheme 2, step 3).

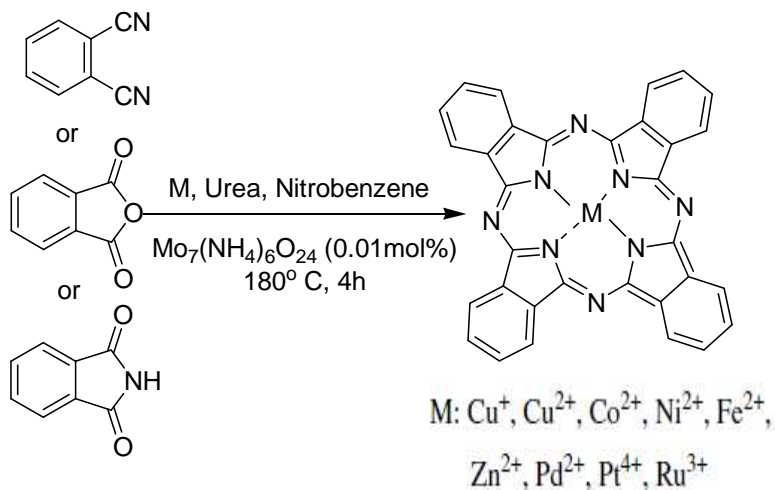
## RESULTS AND DISCUSSION

Firstly, tetraaminophthalocyanine synthesized and reacted with chloromethylpolystyrene to prepare our presented heterogenous catalyst. This catalyst was identified by the IR, XRD, SEM and solid UV. The structural information about the chloromethylpolystyrene (CMPS) and Cobalt-tetraaminophthalocyanine-bonded- chloromethylpolystyrene (CoTAP-bonded-CMPS) composites has been investigated by XRD and the corresponding results are shown in

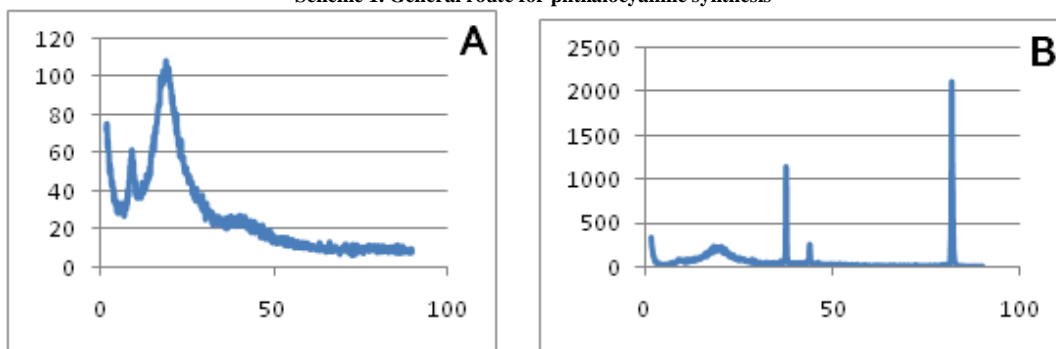
**Figure 2.** When we compare the XRD spectrum of polymer (CMPS) **Figure 2 (A)** with XRD spectrum of AMPCs-CMPs **Figure 2 (B)**, we see that tetraaminophthalocyanine joined with chromethylpolystyrene. Comparison the SEM image of polymer **Figure 1 (A)** with SEM image of CoTAP-bonded-polymer **Figure 1 (B)** shows that the novel phthalocyanine was formed.



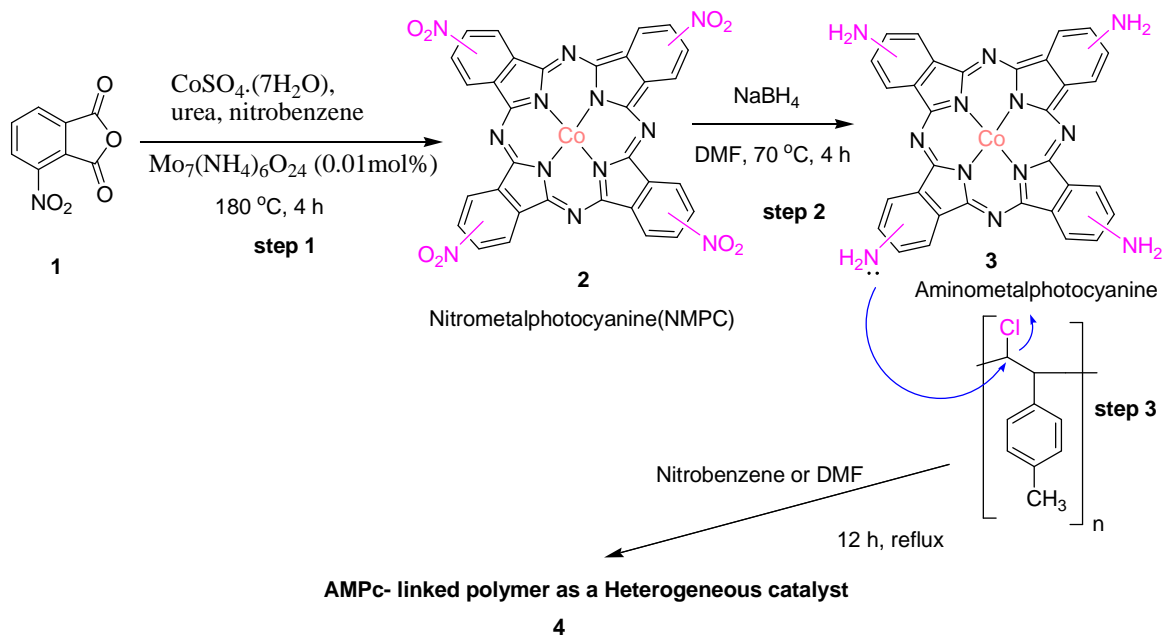
**Figure 1. A:** SEM image of (A) polymer, and CoTAP-bonded polymer (B)



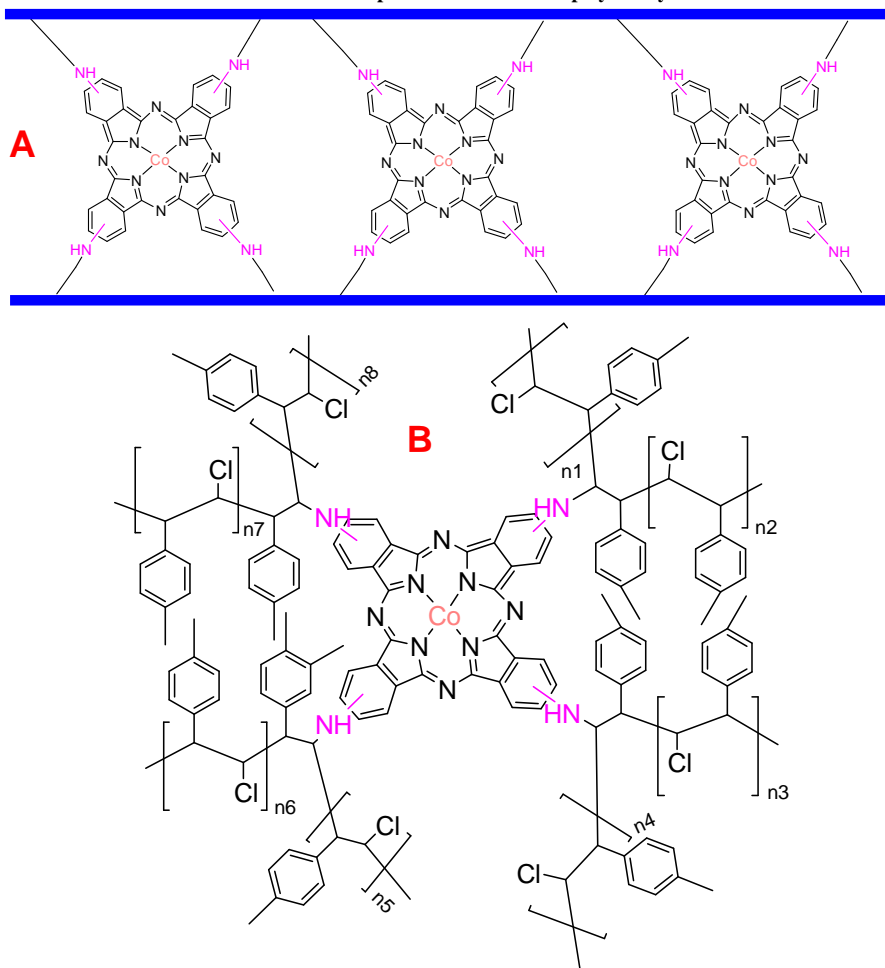
**Scheme 1.** General route for phthalocyanine synthesis



**Figure 2.** Comparison of polymer XRD spectrum (A) and CoTAP-bonded-polymer XRD (B)



Scheme 2. Reaction steps of CoTAP-bonded-polymer synthesis



Scheme 3. Proposed structures(A and B) for {tetraaminophthalocyanine-bonded polymer} 4

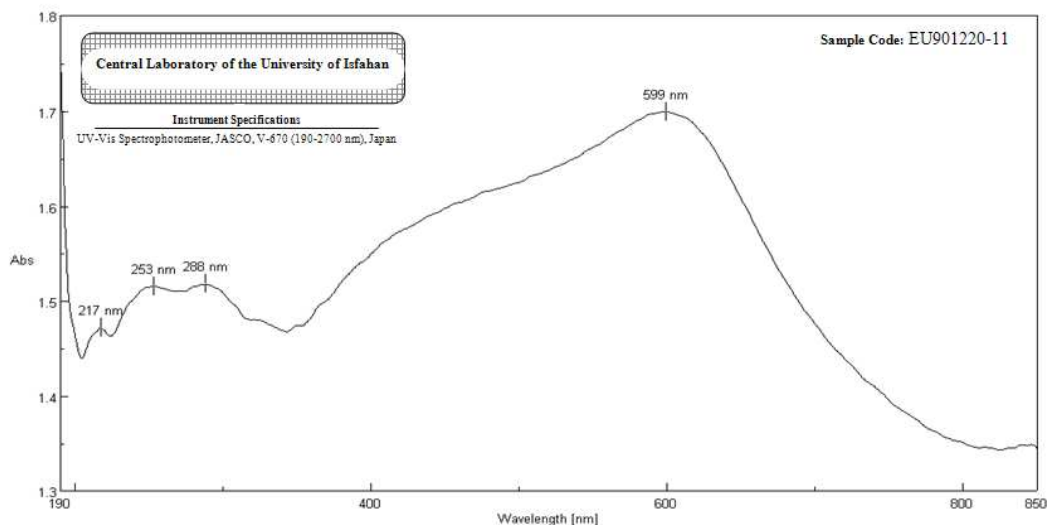


Figure 3. Solid UV-vis spectra of CoTAP-bonded-polymer

Formation of CoTAP supported polymer was confirmed with UV-vis (Figure 3). Figure 4 shows IR spectra of CoTNP (A) and CoTAP (B) so it confirms the formation of CoTAP. Figure 5 shows the IR spectrums polymer (A) and CoTAP supported polymer (B).

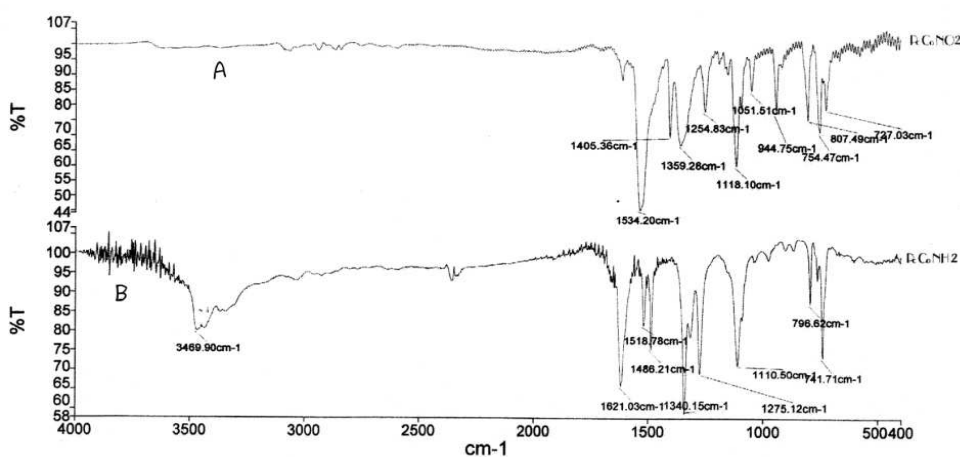


Figure 4. IR Comparison spectrum of CoTNP(A) and CoTAP(B)

Table 4. The yield of oxidation benzhydrol in different solvent after 12 h, at 100°C

Number	Solvent	Yield %
1	Acetonitrile	Negligible
2	Xylene	Negligible
3	CH <sub>2</sub> Cl <sub>2</sub>	Negligible
4	DMF	80
5	DMSO	80
6	1,4-dioxane	68
7	Nitrobenzene	77
8	<b>Diethyleneglycol-dimethylether</b>	<b>82</b>
9	Water	Negligible
10	Solvent free	Negligible

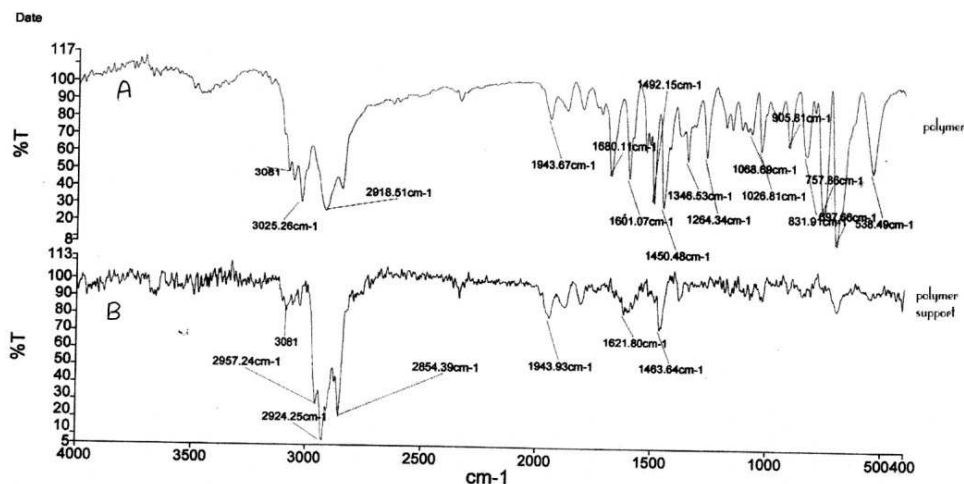


Figure 5. IR Comparison spectrum of polymer (A) and CoTAP-bonded-polymer (B). Spectra were taken in KBr plates.

Proposed Mechanism of the aerobic oxidation by using MPCs was in ref. [17]. To select the best solvent, the synthesis of CoTNP was examined in different solvents (Table 2). As Table 2 indicates, higher yields and shorter reaction times were obtained when the reaction was carried out in diethyleneglycoldimethylether. Thus, diethyleneglycoldimethylether was used as reaction media for all reactions.

Ease of recycling of the catalyst is one of the most advantages of our method. When the reaction was complete, the mixture was filtered, the residue was washed with warm ethanol and dried recycled catalyst was reused in the next reaction. For the reaction of oxidation of alcohol no significant loss of the product yield was observed when CoTAP-linked-polymer was used after four times recycling (Table 5).

Table 5. Recovery and Reusable of Catalyst

Number	Oxidation reaction	Yield%
1	First	81
2	Second	79
3	Third	80
4	Forth	78

The optimum yields of the products are obtained when 0.0059 g Co (10 mol% or 0.556 g catalyst) is used (Table 4).

Table 6. Result of reaction with different quantities of catalyst

Number	Cat (mol%)	M <sub>Co</sub> (gr) M <sub>Cat</sub> (gr)	Time (h)	Yield (%)
1	0	0 0	6	negligible
2	5	0.00063 0.273	3	72
3	10	0.0059 0.556	6	87
4	15	0.0089 0.0830	6	86

ICP result: 11.49 ppm for 0.05 gr Cat, V=0.05 L  
 $\frac{11.49(\text{ppm}) \times 0.05(\text{lit})}{59(\text{gr/mol})} = 0.0097\text{mmolCo}$

### CONCLUSION

In summary, we have developed an efficient method for the synthesis of MPCs-polymer via the condensation of amino metallophthalocyanine with chloromethylpolystyrene. CoTAP-linked polymer don't solve in any solvent. This new strategy has several advantages, such as excellent yield, more high recovery of catalyst, simple

experimental as well as isolation procedures, and finally, it is in agreement with the green chemistry protocols. In this reaction the catalyst can be recovered by filtration and reused. We hope that we reported the synthesis of novel metalphthalocyanine was linked with chloromethylpolystyrene, so we developed its efficiency, more easily its application of MPCs-polymer and high recovery.

#### **Acknowledgments**

The authors gratefully acknowledge partial support of this work by the Research Affairs Office of Bu-Ali Sina University (Grant number 32-1716 Iranian National Elites entitled development of chemical methods, reagent and molecules.), and Center of Excellence in Development of Chemical Method (CEDCM) Hamedan, I.R Iran

#### **REFERENCES**

- [1] B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **1965**, 7, 27.
- [2] (a) F. H. Moser and A. L. Thomas, *The Phthalocyanines*, CRC Press, Boca Raton, FL, **1983**; (b) K. Venkataraman, *Synthetic Dyes*, Academic Press, **1952**, vol. 2, 1118-1142.
- [3] Synthesis and photocatalytic properties of new water-soluble phthalocyanines and related compounds; Zur Erlangung des Doktorgrades der Naturwissenschaften, Dr. rer. Net., Bremen **2006**.
- [4] Singh R., Hay A. S. *Macromolecules* **1992**, 25, 1017.
- [5] Singh R., Hay A. S. *Macromolecules* **1992**, 25, 1025.
- [6] Yang H, Hay AS. *J Polym Sci, Polym Chem Ed* **1996**, 34, 2621.
- [7] Kadish KM, Smith KM and Guilarnd R (Eds.) *The Porphyrin Handbook*, Academic Press: san Diego, **2003**, Vol. 15-20.
- [8] Hitoshi Uchida, Masanari Mitsui, Paidi Yella Reddy, Shuichi Nakamura, and tekeshi Toru, *ARKIVOC* **2005** (xi) 17-23.
- [9] Ahmet Bilgin, Cigdem Yagci, Aysegul Mendi, Ufuk Yildiz, *Polyhedron* **2007**, 26, 617-625.
- [10] A. Munoz\_Castro, D. Mac\_Leod Carey, R. Arratia\_Perez, *Polyhedron* **2010**, 29, 451-455.
- [11] (a) Sarah D'Souza, Edith Antunes, Christian Litwinski, Tebello Nyokong, *Journal of Photochemistry and Photobiology A: Chemistry* 220 (**2011**) 11-19. (b) T.M. Mohan Kumar; B.N. Achar; *Journal of Organometallic Chemistry* 691 (**2006**) 331-336.
- [12] Mandal H, Hay AS. *JMS Pure Appl Chem* **1998**, A35(11), 1797-808.
- [13] Meng YZ, Abu-Yousef IA, Hlil AR, Hay AS. *Macromolecules* **2000**, 33, 9185-9191.
- [14] Meng YZ, Hlil AR, Hay AS. *Polym Adv Technol* **2001**, 12, 206-14.
- [15] W. Wan, Y.Z. Meng, Q. Zhu, S.C. Tjong, A.S. Hay, *Polymer* **2003**, 44, 575-582.
- [16] Shaabani Ahmad, Farhangi Elham, Rahmati Abbas, *Applied catalysis A: General* **2008**, 338, 14-19.
- [17] Shaabani Ahmad, Farhangi Elham, *Applied catalysis A: General* **2009**, 371, 148-152.