Improvement in the synthesis of metallophthalocyanines using microwave irradiation

Aleksandra Burczyk,[a] André Loupy,[b] Dariusz Bogdal[a],* and Alain Petit[b]

[a]*Department of Polymer Chemistry and Technology, Politechnika Krakowska, 31-155 Kraków, ul. Warszawska 24, Poland*
[b]*Laboratoire des Réactions Sélectives Sur Supports, ICMMO, Université Paris - Sud, bat. 410, 91 405 Orsay, France*

Abstract—A successful application of microwave irradiation, in which phthalocyanines were synthesized under solventless conditions from 1,2-phthalonitrile or phthalic anhydride and urea in the presence of metal templates is described. It was found that in comparison with conventional heating, the microwave process is a very useful alternative for cyclotetramerization processes because of reduction of the reaction time, better yield, and easy-to-perform procedure.
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1. Introduction

Phthalocyanines form nowadays an important group of organic compounds that belongs to the most studied subjects of organic functional materials.[1] However, although phthalocyanines have been not identified in the nature yet, they were one of the first macrocycles that were synthesized and used as model compounds to mimic the biologically important porphyrines.[2] The most important industrial application of phthalocyanines is the formation of color complexes with metal cations that are used as highly stable pigments and dyes.[3] In addition, they can find commercial applications as: photovoltaic materials in solar cells,[4–6] systems for fabrication of light emitting diodes (LED),[7,8] liquid crystalline[9] and non-linear optical materials,[10,11]

sensitizers for photodynamic (PDT) cancer therapy,[12,13] photoconductors in xerography,[14] dyes at recording layers for CD-R and DVD-R optical storage discs,[15] as well as diverse catalytic systems.[16,17] Recently, the synthesis, properties and potential application of phthalocyanine containing polymers were reviewed by McKeowon,[18] while an example of the preparation of nanoscale organic-inorganic composites containing rod-like phthalocyanine polymers was published by Kimura et al.[19]

Phthalocyanines are usually prepared by the high temperature cyclotetramerization processes of either phthalonitrile (**1**) or phthalic anhydride (**2**), in which the template effect afforded by a suitable metal cation is required (Scheme 1). The reactions can be carried out in a variety of solvents as

MX: CuCl$_2$ 2H$_2$O or CoCl$_2$ 6H$_2$O
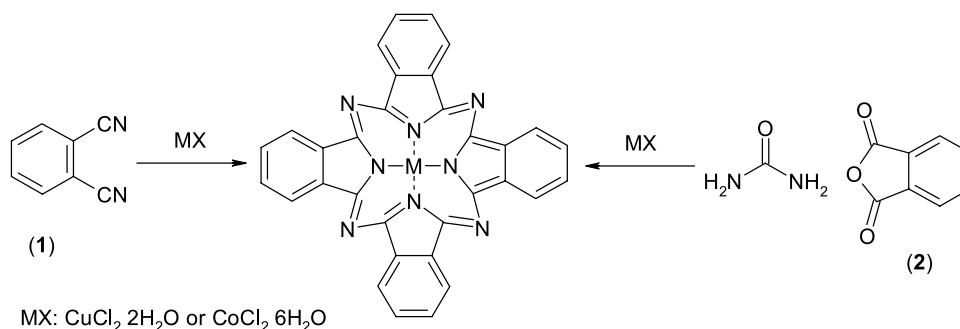
Scheme 1. Synthesis of phthalocyanines from phthalonitrile (**1**) or phthalic anhydride (**2**) and urea.

well as under solvent-free conditions, but both processes require temperature ca. 200 °C and long reaction times.[1] It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions.[20] On the other hand, the most successful examples of microwave applications are necessarily found to be related to the use of solvent-free systems, in which microwaves interact directly with reagents and, therefore, can more efficiently drive chemical reactions.[21,22] The possible accelerations of such reactions are expected to be optimal since they are not moderate or impeded by solvents. It was assumed and largely proven that specific (non-purely thermal) MW effects are related to mechanisms where the polarity is increased from the ground state to the transition state.[23] It is essentially the case of neutral reactants leading to a dipolar transition state. Thus, we have decided to apply microwave irradiation for the synthesis of phthalocyanine under solvent-less conditions in order to check whether such

non-classical method of chemical activation might influence yield, selectivity and time of reaction in comparison with a conventional thermal treatment under strictly similar sets of conditions.

2. Results

The synthesis of phthalocyanines under microwave irradiation has been previously investigated by Shaabani[24] and Villemin et al.[25] In the former case, the reactions were carried out applying a domestic oven without any temperature control, whereas in the latter case the syntheses were run in a modified domestic oven and microwave resonance cavity without temperature control as well. It was found that the results depend upon the quantity of products and were difficult to reproduce when the reactions were conducted with small samples less then 5 g.[25] To solve this problem and control reasonably well temperature during syntheses under MW conditions so that it was possible to compare their results with experiments under conventional

Table 1. The synthesis of phthalocyanine–Cu from phthalonitrile (**1**) and copper (II) chloride dihydrate under microwave and conventional conditions

	Substrate	Quantity (mmol)	Conditions	Time (min)	Temp. (°C)	Conv.[a]/Yield (%)/(%)	CHN calc.	CHN found
1	**1**	8					C: 66.74	C: 66.01
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10	200–220	86/82	H: 2.5	H: 2.59
							N: 19.2	N: 18.51
2	**1**	12					C: 66.74	C: 62.35
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10	180–190	78/70	H: 2.5	H: 2.42
							N: 19.2	N: 18.35
3	**1**	12					C: 66.74	C: 17.49
	$CuCl_2 \cdot 2H_2O$	2.5	△	10	180	10/7	H: 2.5	H: 1.85
							N: 19.2	N: 4.84
4	**1**	12					C: 66.74	C: 66.21
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10	200–230	90/81	H: 2.5	H: 2.83
							N: 19.2	N: 19.76
5	**1**	12					C: 66.74	C: 66.42
	$CuCl_2 \cdot 2H_2O$	2.5	MW	15	190–210	94/88	H: 2.5	H: 2.38
							N: 19.2	N: 19.06
6	**1**	12					C: 66.74	C: 46.67
	$CuCl_2 \cdot 2H_2O$	2.5	△	15	200	20/10	H: 2.5	H: 2.91
							N: 19.2	N: 13.91
7	**1**	8					C: 66.74	C: 66.31
	$CuCl_2 \cdot 2H_2O$	2.5	MW	6	230–240	76/74	H: 2.5	H: 2.58
	H_2O	3 drops (75 mg)					N: 19.2	N: 18.73
8	**1**	12					C: 66.74	C: 57.19
	$CuCl_2 \cdot 2H_2O$	2.5	MW	6	200–230	85/76	H: 2.5	H: 2.33
	H_2O	3 drops (75 mg)					N: 19.2	N: 17.28
9	**1**	12					C: 66.74	C: 66.81
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10		90/86	H: 2.5	H: 2.85
	H_2O	3 drops (75 mg)					N: 19.2	N: 19.03
10	**1**	8					C: 66.74	C: 66.83
	$CuCl_2 \cdot 2H_2O$	2.5	MW	8	180	86/83	H: 2.5	H: 2.75
	DMF	3 drops (70 mg)					N: 19.2	N: 18.83
11	**1**	12					C: 66.74	C: 56.94
	$CuCl_2 \cdot 2H_2O$	2.5	MW	4	150–170	79/72	H: 2.5	H: 2.46
	DMF	3 drops (70 mg)					N: 19.2	N: 16.91
12	**1**	12					C: 66.74	C: 66.40
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10	210–220	88/82	H: 2.5	H: 2.75
	DMF	3 drops (70 mg)					N: 19.2	N: 18.83

[a] Conversion based on the consumption of **1**.

Table 2. The synthesis of phthalocyanine–Co from phthalonitrile (**1**) and cobalt (II) chloride hexahydrate under microwave and conventional conditions

	Substrate	Quantity (mmol)	Conditions	Time (min)	Temp. (°C)	Conv[a]/Yield (%)/(%)	CHN calc.	CHN found
1	**1**	12					C: 67.28	C: 63.71
	CoCl$_2$·6H$_2$O	2.5	MW	6	180	90/86	H: 2.80	H: 2.65
							N: 19.61	N: 17.89
2	**1**	12					C: 67.28	C: 67.30
	CoCl$_2$·6H$_2$O	2.5	MW	6	210–220	81/75	H: 2.80	H: 2.70
							N: 19.61	N: 19.50
3	**1**	12					C: 67.28	C: 28.42
	CoCl$_2$·6H$_2$O	2.5	△	6	210	10/5	H: 2.80	H: 2.41
							N: 19.61	N: 9.42
4	**1**	12					C: 67.28	C: 67.11
	CoCl$_2$·6H$_2$O	2.5	MW	10	190–200	86/80	H: 2.80	H: 2.70
							N: 19.61	N: 19.40
5	**1**	12					C: 67.28	C: 32.20
	CoCl$_2$·6H$_2$O	2.5	△	10	200	15/11	H: 2.80	H: 2.50
							N: 19.61	N: 10.45
6	**1**	12					C: 67.28	C: 61.78
	CoCl$_2$·6H$_2$O	2.5	MW	5	180–200	88/83	H: 2.80	H: 2.51
	H$_2$O	3 drops (75 mg)					N: 19.61	N: 18.20
7	**1**	12					C: 67.28	C: 63.31
	CoCl$_2$·6H$_2$O	2.5	MW	4	210–220	86/84	H: 2.80	H: 2.58
	H$_2$O	3 drops (75 mg)					N: 19.61	N: 18.73
8	**1**	12					C: 67.28	C: 67.20
	CoCl$_2$·6H$_2$O	2.5	MW	10	180–200	90/86	H: 2.80	H: 2.71
	H$_2$O	3 drops (75 mg)					N: 19.61	N: 19.56
9	**1**	12					C: 67.28	C: 61.46
	CoCl$_2$·6H$_2$O	2.5	MW	4	160	75/67	H: 2.80	H: 2.54
	DMF	3 drops (70 mg)					N: 19.61	N: 18.02
10	**1**	12					C: 67.28	C: 63.83
	CoCl$_2$·6H$_2$O	2.5	MW	4	180–190	78/65	H: 2.80	H: 2.75
	DMF	3 drops (70 mg)					N: 19.61	N: 18.83
11	**1**	12					C: 67.28	C: 67.10
	CoCl$_2$·6H$_2$O	2.5	MW	10	180	84/78	H: 2.80	H: 2.68
	DMF	3 drops (70 mg)					N: 19.61	N: 19.34

[a] Conversion based on the consumption of **1**.

conditions, we have decided to use the dedicated monomode microwave reactor Synthewave 402 (Prolabo) with accurate measurement of temperature by an infrared detection (calibrated using an optical fiber) during the reaction course. Moreover, such a reactor allows also maintaining of temperature at a constant value by modulation of emitted MW power and an efficient mechanical stirring.[21]

First, we decided to use two metal salts as templates for the formation of phthalocyanines, that is, cobalt (II) chloride hexahydrate and copper (II) chloride dihydrate, because these phthalocyanines are usually applied and commercially available. Moreover, phthalocyanines containing cobalt and copper templates can be used as effective catalysts in oxygenation[17] and oxyhalogenation processes,[16] which are also of research interest in our labs.[26,27]

In a typical experiment, the reactions were carried out by simply mixing and grinding phthalonitrile (**1**) (1,2-dicyanobenzene) with copper or cobalt chloride, and the mixtures were then irradiated in open vessels in the microwave reactor. In the case of phthalic anhydride (**2**), additionally, an excess of urea was added to the reaction mixture before it was subjected to microwave irradiation in an open vessel as well. All the substrates used in the syntheses were solid,

and, in such a case, to initiate a chemical reaction under microwave conditions at least one of substrates need to be melting solid that absorbs relatively well microwaves.[28] These features can be ensured by phthalonitrile (**1**) or phthalic anhydride (**2**) that have melting points 139–141 °C and 131–134 °C,[29] respectively, provided that the reaction mixtures were irradiated strongly enough at the beginning of experiments. On the other hand, a small amount of a good microwave absorber added to substrates that do not absorb microwaves in solid state can initiate an increase of temperature and, in turn, a chemical reaction. Therefore, in the further stage of our investigations, we decided to check whether a small amount of water or DMF,[30] which are strong microwave absorbers, can influence reaction by faster increase of reaction temperature to level so high that is needed in the synthesis of phthalocyanines. Moreover, a small amount of solvent can provide better temperature homogeneity during the syntheses. The results and conditions of all the reactions are presented in Tables 1–3.

Regarding the reaction of phthalonitrile (**1**) (Tables 1 and 2), all the results under different reaction conditions (i.e., conventional and microwave) were compared on the basis of conversion of phthalonitrile (**1**), yield of the product after purification with water, acetone, methylene chloride, and

Table 3. The synthesis of phthalocyanine–Cu and Co from phthalic anhydride (**2**) and urea in the presence of ammonium molybdate under microwave and conventional conditions

	Substrate	Quantity (mmol)	Conditions	Time (min)	Temp. (°C)	Conv.[a]/Yield (%)/(%)	CHN calc.	CHN found
1	**2**	10					C: 66.74	C: 64.07
	Urea	20					H: 2.50	H: 2.82
	$CuCl_2 \cdot 2H_2O$	2.5	MW	10	200	88/80	N: 19.2	N: 19.04
	Ammonium molybdate	0.1						
2	**2**	15					C: 66.74	C: 66.81
	Urea	15					H: 2.50	H: 2.75
	$CuCl_2 \cdot 2H_2O$	2.5	MW	6	140–170	82/78	N: 19.2	N: 19.21
	Ammonium molybdate	2						
3	**2**	15					C: 66.74	C: 30.81
	Urea	15					H: 2.50	H: 2.05
	$CuCl_2 \cdot 2H_2O$	2.5	△	6	140–170	60/38	N: 19.2	N: 10.27
	Ammonium molybdate	2						
4	**2**	15					C: 67.28	C: 66.81
	Urea	15	MW	5	180	60/52	H: 2.80	H: 2.77
	$CoCl_2 \cdot 6H_2O$	2.5					N: 19.61	N: 19.48
	Ammonium molybdate	2						
5	**2**	15					C: 67.28	C: 19.68
	Urea	15	△	5	180	18/12	H: 2.80	H: 1.98
	$CoCl_2(6H_2O$	2.5					N: 19.61	N: 5.57
	Ammonium molybdate	2						

[a] Conversion based on the consumption of **2**.

concentrated sulfuric acid and final purity of the product (elemental analysis). For the reaction of phthalonitrile (**1**) and copper chloride, it was possible to optimize reaction conditions under microwave irradiation so that the phthalocyanine–Cu was obtained in a very good yield and high purity in a relatively short reaction time (Table 1, entries 1, 4, and 5). However, the reaction needed strong heating at the beginning and the final reaction temperature likely above 200 °C (for example, compare entries 1 and 2 in Table 1). A typical reaction temperature profile in which power of microwave irradiation and reaction temperature are shown is presented in Figure 1(a) (Table 1, entry 5). It can be seen that for the first half of the reaction, maximum MW power was applied to increase the reaction temperature from 20 to 100 °C, then when the reaction was initiated a fast temperature increase was observed together with a substantial reduction of MW power.

For those reactions under MW irradiation in which the best results were obtained, the experiments were run under conventional heating (△—oil bath) (Table 1, entries 2 vs. 3 and 5 vs. 6) with similar sets of conditions (for example, Fig. 1(a) and (b), respectively). In both cases, the yields of product under conventional conditions were much lower (7–10% instead of 70–88%), and, which is more important, purity of the product was unacceptable. Therefore, it was proven that the solvent-free procedure under microwave irradiation constitutes here an undeniable improvement for the reactions that were run with enhanced yields under MW conditions in comparison with conventional heating experiments.

The important specific MW effects observed here are consistent with the consideration of mechanisms and with the assumption that the MW effects are increased when the polarity of a system is enhanced. The rate-determining step consists of the addition of nitrile via its nitrogen site on the triple bond on the second nitrile group to form bipolar ions[31] that in turn can react with water molecules to produce 3-imino-2,3-dihydro-isoindol-1-one (**3**). The transition state is therefore more polar than ground state and consequently more prone to electrostatic interactions of dipole–dipole type with the electromagnetic field (Scheme 2). The stabilization of the transition state is therefore responsible of reactivity by a decrease of the activation energy.

It was found that molar ratios of the reagents (i.e., phthalonitrile (**1**) to the inorganic salt) influenced the conversion as well as yields, and the best results were obtained when **1** was used in an excess in comparison with copper chloride (Table 1, entries 4 and 5). However, in the opposite case (Table 1, entry 1), the purity of phthalocyanine–Cu was satisfactory, but it was obtained in lower yield.

As it can be seen in Figure 1(a) and (b), the increase of temperature at the beginning of phthtalonitrile reaction was relatively slow (as was mainly concerned with solid material), and, finally, lengthened the total reaction time under both microwave and conventional conditions. Therefore, we decided to add a small amount of a strong microwave absorber (water or DMF) to the reaction mixture in order to further reduce reaction time and improve temperature homogeneity (Table 1, entries 7–12). Applying water as a liquid microwave absorber, we obtained the best results when the reaction mixture was maintained for 10 min under microwave irradiation at 225 °C (Table 1, entry 9). Whereas the product, phthalocyanine–Cu, was prepared with lower yield when DMF was added to the reaction mixture under similar conditions (Table 1, entry 12).
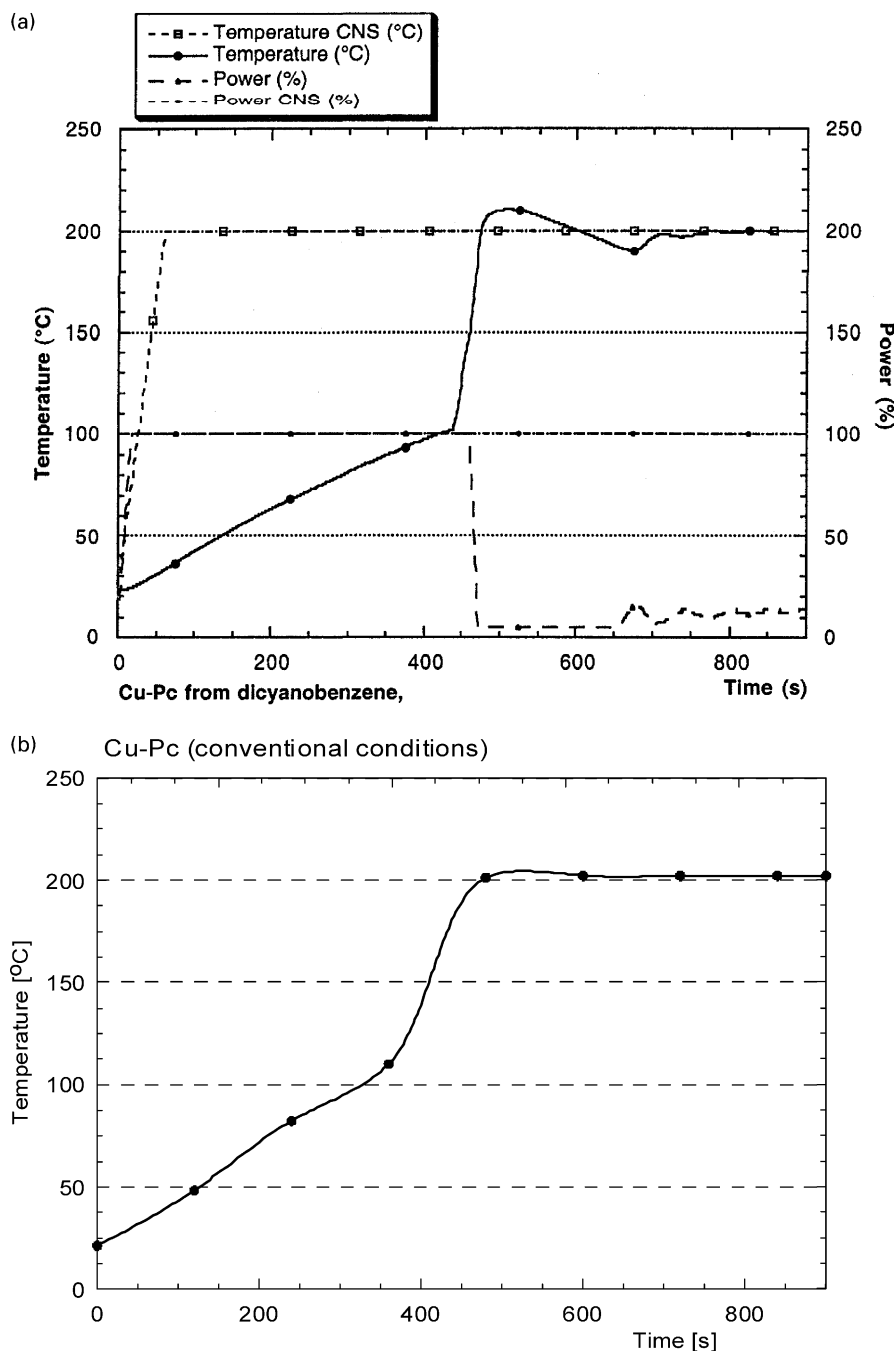
(a)

(b)

Figure 1. (a) Thermal profile during microwave-assisted solvent-free reaction of **1** with CuCl$_2 \cdot$2H$_2$O (Table 1, entry 5); temperature CNS and power CNS are programmed temperature and power profiles, respectively. (b) Thermal profile for the solvent-free reaction of **1** with CuCl$_2 \cdot$2H$_2$O (Table 1, entry 6) under conventional conditions.

The temperature profiles for the reactions with the addition of a small amount of water and DMF are presented in Figures 2 and 3, respectively. In comparison with Figure 1(a), it can be observed that in both cases further reduction in reaction times from 15 to 10 min was mainly due to the reduction of initial time of the reactions from 5 to 1 min, that is, time in which the reaction mixture reached appropriate reaction temperature ca.200 °C.

Similarly to the reaction with copper chloride, the reaction of phthalonitrile (**1**) with cobalt chloride needed to be carried out at temperature above 200 °C. However, it was

possible to obtain the product, phthalocyanine–Co, with a good yield at temperature lower than 200 °C, but its purity was still unacceptable, which was proven by elemental analysis (for example: Table 2, entry 1).

Unlike in the synthesis with copper chloride, owing to the lack initial time in which the reaction temperature slowly increased from 20 to 100 °C (Fig. 1), the reaction time in the reaction with cobalt chloride was reduced to 10 min even in the absence of strong microwave absorbers (i.e., water or DMF). From the beginning, the reactions of cobalt chloride were characterized by a strong increase of reaction
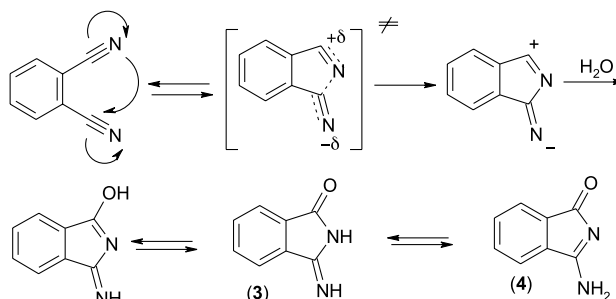
Scheme 2. Mechanism of the activation of 1,3-dicyanobenzene during the formation of phthalocyanines.

temperature (Fig. 4; Table 2, entry 4), which was likely due to higher content of water in hydrated cobalt chloride than copper chloride. Thus, after addition of small amount of water or DMF, in comparison with the reactions of copper chloride (Figs. 1 and 2), a further reduction of reaction time was not observed and yields were similar (Table 2, entries 8 and 11). However, in the case of DMF, it was possible to decrease the reaction temperature to 190 °C (Table 2, entry 11).

Temperature profiles for the reaction of cobalt chloride with addition of a small amount of water and DMF (Figs. 5 and 6) were similar to temperature profiles for the reaction of copper chloride (Figs. 2 and 3). As soon as microwave irradiation was applied to the reaction mixtures, the reaction temperature increased within ca. 60 s from the room temperature to 200 °C and higher, in which the synthesis of phthalocyanines can be carried out with good yield and purity (for example, Table 2, entries 8 and 11). As before, for those reactions under microwave irradiation in which the best results were obtained, the experiments were run under

conventional heating (oil bath) (Table 2, entries 3 and 5) with similar sets of conditions (time, temperature). In both cases, the yields of product under conventional conditions were much lower, and, which is more important, purity of the product was unacceptable. It was again shown that the solvent-free procedure under microwave irradiation in comparison with conventional heating experiments gives better results, which might be explained by a specific interaction of microwaves with substrates and an influence of non-thermal microwave effect[23] (i.e., increase of reaction rate that is non adequate to the reaction temperature) during microwave experiments.

The reactions of phthalic anhydride (**2**) under microwave irradiation were compared with those run under conventional conditions (oil bath) for both copper and cobalt chlorides (Table 3, entry 3 and 5). Similarly to the experiments described for phthalonitrile (**1**), the yields of phthalocyanines under conventional conditions were significantly lower and the purity was unacceptable. Eventually, it was proven that the solvent-free procedure under microwave irradiation in
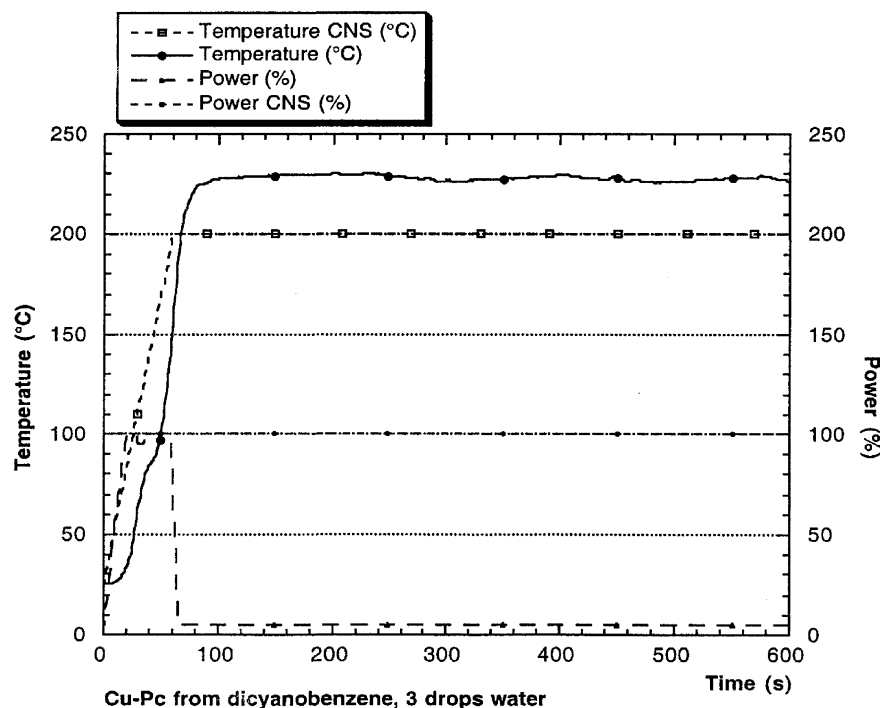

Figure 2. Thermal profile during microwave-assisted reaction of **1** with CuCl$_2$·2H$_2$O in the presence of 3 drops (75 mg) of water (Table 1, entry 9); temperature CNS and power CNS are programmed temperature and power profiles, respectively.
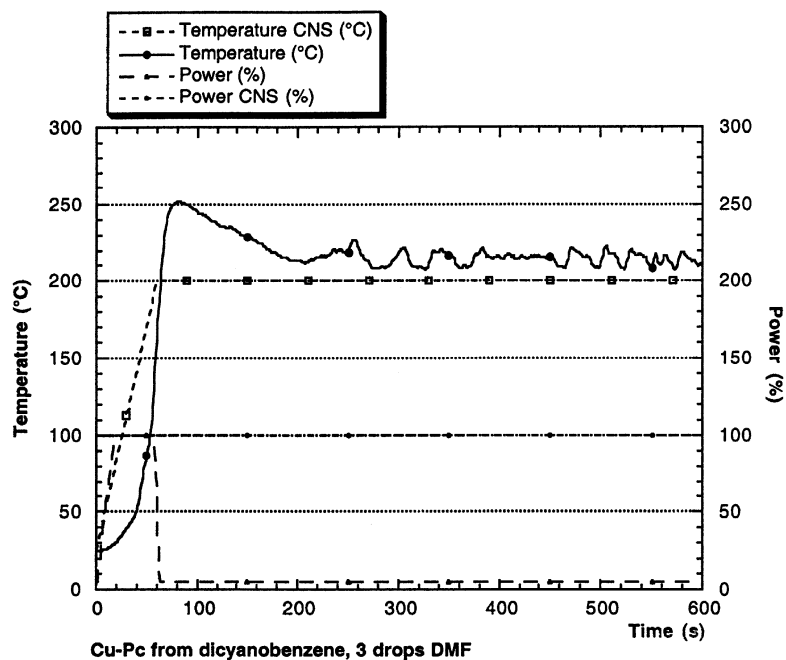
Figure 3. Thermal profile during microwave-assisted reaction of **1** with $CuCl_2 \cdot 2H_2O$ in the presence of 3 drops (70 mg) of DMF (Table 1, entry 12); temperature CNS and power CNS are programmed temperature and power profiles, respectively.

comparison with conventional heating experiments gave better results even as the substrate we used less reactive phthalic anhydride (**2**) in the presence of urea.

The specific non-thermal MW effects observed in this case are also clearly consistent with the more polar species generated during the course of the reaction. The reaction rate of the formation of phthalocyanine form urea and phthalic anhydride is proportional to the first power of the concentration of urea.[32] The urea molecule can be represented by one of the three tautomeric forms (Scheme 3). The polarized form could exist as transient or intermediate species in an excited state that decompose into ammonia and isocyanic acid in the presence of a catalyst (for example, ammonium molybdate). Ammonia react with phthalic anhydride to produce phthalimide, which in turn can react with isocyanic acid to give 3-imino-2,3-dihydro-isoindol-1-one (**3**). The reaction can proceed by passing through a concerted four center mechanism to form carbon dioxide.[32]
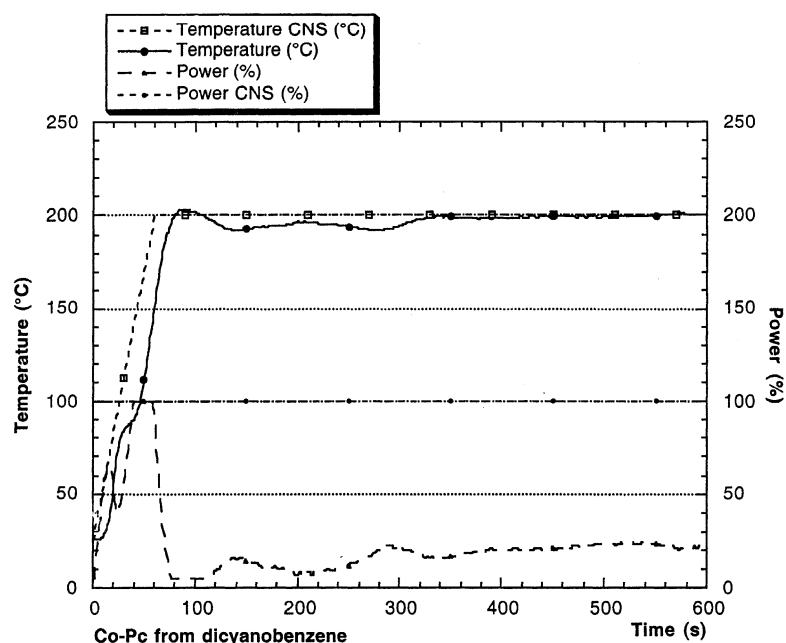

Figure 4. Thermal profile during microwave-assisted solvent-free reaction of **1** with $CoCl_2 \cdot 6H_2O$ (Table 2, entry 4); temperature CNS and power CNS are programmed temperature and power profiles, respectively.
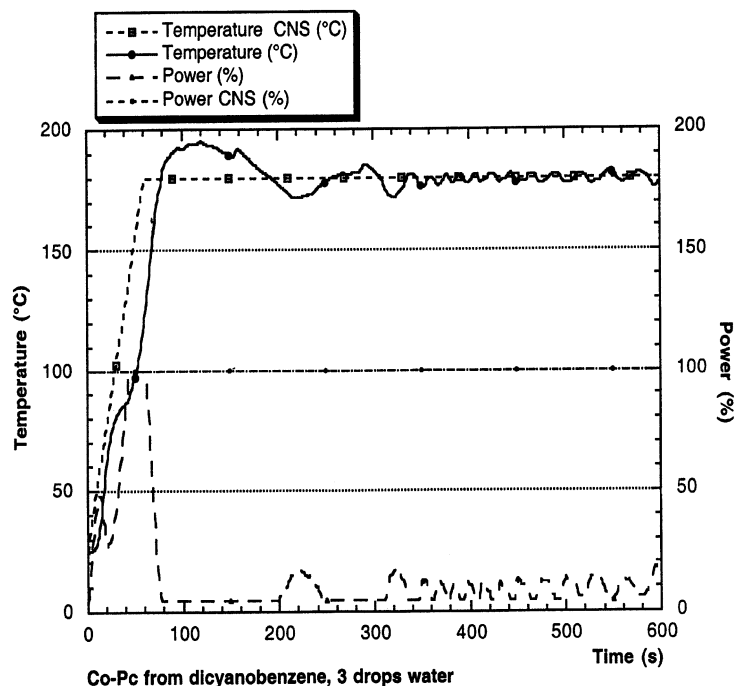
Figure 5. Thermal profile during microwave-assisted reaction of **1** with CoCl2·6H$_2$O in the presence of 3 drops (75 mg) of water (Table 2, entry 8); temperature CNS and power CNS are programmed temperature and power profiles, respectively.

Recently, the microwave-assisted procedure for the synthesis of phthalocyanine–Cu from phthalic anhydride (**2**) and urea in a solution of alkylbenzene was published by Park et al.[33] They found that under microwave irradiation phthalocyanine–Cu could be prepared at lower temperature and shorter time than those required under conventional conditions. Moreover, the samples synthesized under microwave conditions had smaller average size and narrower size distribution.

3. Conclusions
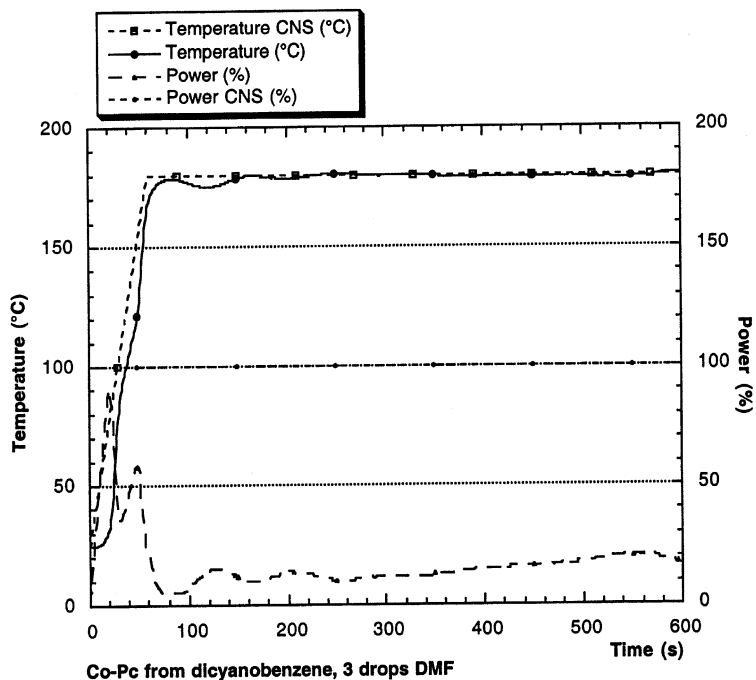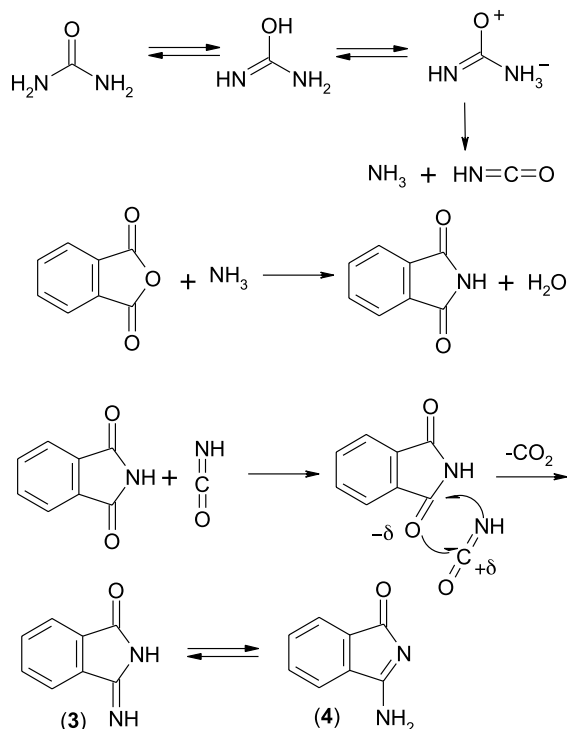
In summary, the synthesis of phthtalocyanines under

Figure 6. Thermal profile during microwave-assisted reaction of **1** with CoCl$_2$·6H$_2$O in the presence of 3 drops (70 mg) of DMF (Table 2, entry 11); temperature CNS and power CNS are programmed temperature and power profiles, respectively.

Scheme 3. Mechanism for condensation of urea with phthalic anhydride.

microwave irradiation can be performed easily in a reduced time scale applying phthalonitrile (**1**) or phthalic anhydride (**2**) as a substrate. Solvent-free conditions lead by far to the best results and to easy-to-perform procedures with considerable improvements over classical methods. More-over, the application of the dedicated monomode micro-wave reactor (Prolabo 402) with temperature monitoring allowed directly comparing two activation modes (i.e., con-ventional heating and microwave irradiation) and showed that non-thermal microwave effects might be very favour-able during microwave experiments. This can be explained when one considers the enhancement in the polarity of the system when the reaction is in progress thanks to a well-fitted mechanism. Eventually, the reactions under conven-tional conditions that were carried out in the same time scale gave products in much lower yields of unacceptable purity.

4. Experimental

4.1. Materials

1,2-Dicyanobenzene, phthalic anhydride, urea, copper (II) chloride dihydrate and cobalt (II) hexahydrate were purchased from the Aldrich Chemical and were used without further purification.

Infrared spectra were recorded on the BIORAD spectro-photometer model FTS-165 as KBr pastille. The elemental analyses were realized in CNRS (Centre National de la Recherche Scientifique in Gif sur Yvette) 91198, France). The microwave reactor was Synthewave 402 from Prolabo.

The preparation of copper phthalocyanine is representative of the general procedures.

4.1.1. Procedure A. Phthalodinitrile (**1**) (12 mmol, 1.54 g) and copper chloride dihydrate (2.5 mmol, 0.425 g) were ground together and placed in a tube. The mixture was then irradiated in the microwave reactor for time given in Tables 1 and 2. The crude product was washed successively with hot water, acetone, dichloromethane and then was dried. Next the product was twice dissolved in the concentrated H_2SO_4, precipitated from distilled water, filtrated off and washed with water to pH neutral. After drying under reduced pressure, the phthalocyanine–Cu was analysed.

4.1.2. Procedure B. Phthalic anhydride (**2**) (10 mmol, 1.49 g), urea (20 mmol, 1.2 g), copper chloride dihydrate (2.5 mmol, 0.425 g) and ammonium molybdate as a catalyst (2.0 mmol, 0.47 g) were ground together, placed in a tube and irradiated in the microwave reactor at high power for time reported in Table 3. After completion of the reaction, the product was washed hot water, acetone and dichloro-methane. Finally, the product was twice dissolved in the concentrated H_2SO_4, precipitated from distilled water, filtrated off and washed with water to pH neutral. After drying under reduced pressure, the phthalocyanine–Cu was analysed.

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