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Journal of Fluorine Chemistry 128 (2007) 608-611

www.elsevier.com/locate/fluor

# A polymer imidazole salt as phase-transfer catalyst in halex fluorination irradiated by microwave

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Available online 12 February 2007

#### Abstract

A new imidazole polymer salt was synthesized in order to develop a high efficiency phase-transfer catalyst for multi-phase reactions. The polymer salt was prepared easily by co-polymerization of 1-1'-(1,4-butamethylene)bis(imidazole) and 1,2-dibromoethane, and has the properties of excellent chemical and thermal stability and high ionic conductivity. It was applied as phase-transfer catalyst in the fluorination of chloronitrobenzenes under the irradiation of microwave and gave excellent yields of corresponding fluoronitrobenzenes. In addition, the enhanced mechanism of microwave was studied and found "non-thermal" effect was a great factor.

Keywords: Microwave chemistry; Polymer imidazole salt; Halogen-exchange fluorination; Fluoronitrobenzenes; Non-thermal effect

## 1. Introduction

Halogen-exchange (halex) fluorination is an important method to prepare fluorinated compounds. To accelerate the reaction between KF and substrates, phase transfer-catalyst (PTC) is often used. But quaternary ammonium salts containing  $\beta$ -H are prone to take place Hofmann Elimination during halex fluorination. At the same time, by-products derived from the decomposition would worsen the reaction greatly. To improve PTC's catalytic activity under the condition of high temperature, quaternary ammonium or phosphonium salts are grafted on polymer carrier and form a new kind of phase-transfer catalyst named polymer PTC. Yoshida grafted N-(2-ethylhexyl)-4-(N,N'-dimethyl)aminopyridinium bromide on polystyrene to get a polymer PTC (noted: Cat.A) [1]. Subsquently, he and his co-workers developed divinylbenzene across linked polystyrene supported tetraphenylphosphonium bromide and its modified analogue by replacing active hydrogen by methyl group (Note: Cat.B and Cat.C) [2]. The three polymers would not decompose obviously even over 210 °C. Luo and his coworkers also reported an effective and stable polydiallyldimethylammonium chloride (PDMDAAC) as PTC was used in

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hales fluorination [3]. Herein, we describe another stable and effective polyalkylimidazolimu bromide **1** (Scheme 1) acts as PTC in halex fluorination under the irradiation of microwave.

## 2. Results and discussion

As we know, efficient and stable PTC should have big relative molecular weight, stable structure and big polarity. As shown in Scheme 1, polymer 1 has a big density of catalytic component, so it should have high phase-transfer activity. In fact, polymer imidazole salts have received much attention because of their remarkable properties including catalytic activity, chemical and thermal stability and high ionic conductivity [4]. In addition, polymer imidazole salts have several beneficial features for phase transfer catalyst: (1) reactivity of the monomer molecule can be controlled easily by modification of the alkyl chain and reaction temperature, which makes it possible to control PTC's polymerization degree and density of catalytic active component, (2) addition of polymerization initiator is not required, which makes polymerization manageable. For the reasons above, polymer 1 is very suitable for halex fluorination on high temperature. Its decomposition temperature determined by TGA is about 340 °C. The TGA data of polymer 1 was demonstrated in Fig. 1. Catalytic capability of different polymer catalysts on preparation of 4-fluoronitrobenzene (PFNB) via halex fluorination



from 4-chloronitrobenzene (PCNB) with the conventional heating was tested. The results were shown in Table 1. From Table 1, it could be found that polymer 1 had excellent catalytic effect than the other polymer catalyst for the sake of its higher density of catalytic active center. [bmim]Br was unstable owing to elimination or substitution processes under the condition of high temperature and KF [5]. While polymer 1 was more stable due to its greater steric hindrance effect.

Reaction rate can be accelerated remarkably in some reactions under the irradiation of microwave, which was attributed to "thermal effect" and "non-thermal effect" of microwave [6]. The reason why "thermal effect" can accelerate reaction rate is known as overheat. So, it cannot change kinetics under the conditions of same reactant, catalyst and product when compared to conventional heating while "non-thermal effect" can change kinetic feature, reduce activation energy and even change reaction order [7]. The promoting effect of "non-thermal effect" is possibly attributed to an enhancement in the polarity of the system from the ground state towards the transition state [8]. It is consistent with the extension of anionic charge distributing in transition state.

Owing to the defect of our microwave equipment without temperature controller, we could not study "non-thermal effect" of microwave through comparing the activation energy  $(E_a)$  between microwave irradiation and conventional heating. But based on the theoretical premise that microwave can change kinetics feature, "non-thermal effect" can be revealed from the change of kinetics curve under microwave and convention heating conditions.



Fig. 1. TGA data of polymer 1.

The kinetics experiments were carried based on considerations below: (1) to eliminate the influence of diffusion, all reactions were carried at the same stirring speed. (2) To eliminate the influence of PTC's decomposition on fluorination reaction rate during the process of reaction, all reactions were carried without PTC. The kinetics curve on condition of microwave irradiation and conventional heating were shown in Figs. 2 and 3. From Fig. 2, we could find the reaction followed pseudo-first order kinetics based on the C(PCNB) under the conventional heating because the concentration of the  $F^-$  was



Fig. 2. First-order kinetic plot for fluorination of PCNB in  $Me_2SO$  under the irradiation of microwave.



Fig. 3. Second-order kinetic plot for fluorination of PCNB in Me<sub>2</sub>SO under the irradiation of microwave.

Table 1	
Comparison of different polymer catal	lysts in halogen-exchange fluorination

Catalyst	$M_{ m w}$	PCNB (mmol)	KF (mmol)	Solvent	Temperature (°C)	Time (h)	Yield of PFNB (%)	Reference
Polymer 1 (0.5 g)	28,400 <sup>a</sup>	50	75	Me <sub>2</sub> SO (10 mL)	192	2	92.8	
Cat.A (2.43 g)	970	25	37.5	TMSO <sub>2</sub> (15 g)	180	5	87.0	[1]
Cat.B (4.5 g)	892	50	75	TMSO <sub>2</sub> (30 g)	180	4	72.0	[2]
Cat.C (4.2 g)	840	50	75	TMSO <sub>2</sub> (30 g)	180	5	83.0	[2]
PDMDAAC (0.33 g)	200,000	25	37.5	Me <sub>2</sub> SO (20 mL)	185	3	90.1	[3]
[bmim]Br (0.5 g)	219	50	75	Me <sub>2</sub> SO (10 mL)	192	2	78.4	

<sup>a</sup>  $M_{\rm w} = 28,400; M_{\rm n} = 24,483, D = 1.160.$ 

Table 2

Fluorination of different substrates in Me<sub>2</sub>SO under irradiation of microwave

Entry	Reactant ( <b>2a–2f</b> ) (substance $C_6H_5 NO_2$ )	KF (equiv.)	Power (W)	Temperature $(^{\circ}C)^{a}$	Time (h)	Product ( <b>3a–3f</b> ) (substance $C_6H_5 NO_2$ )	Yield (%) <sup>b</sup>
1	4-C1	1.5	300	202	1.5	4-F	94.2
2	2-Cl	1.5	300	203	2	2-F	87.8
3	$2,4-Cl_2$	3	250	203	2	2,4-F <sub>2</sub>	70.2
4	3,4-Cl <sub>2</sub>	1.5	250	206	0.5	3-Cl, 4-F	87.4
5	2,5-Cl <sub>2</sub>	1.5	250	204	1	5-Cl, 2F	84.4
6 <sup>c</sup>	4-Cl, 3-NO <sub>2</sub>	1.5	200	90	4	4-F, 3-NO <sub>2</sub>	88.3

<sup>a</sup> Determined by Reytek infrared thermometer.

<sup>b</sup> Determined by GC.

<sup>c</sup> Reacted in 15 mL CH<sub>3</sub>CN.

essentially constant due to the excess of insoluble KF present throughout the reaction. To our surprise, the relationship of ln C(PCNB) and reaction time was not linear any more on condition of microwave irradiation (Fig. 2). The reaction followed pseudo-second order kinetics based on the  $C^2(PCNB)$  (see Fig. 3).

Different substrates were halex fluorinated in Me<sub>2</sub>SO under the irradiation of microwave. The results were shown in Table 2. From Table 2, it could be found that all reactions were performed well under the irradiation of microwave. The reason why 3,4-dichloronitrobenzene could be promoted best is that the "non-thermal effect" of microwave was most significant in the fluorination. To our surprise, the fluorination reaction rate of 2,4-dichloronitrobenzene could be accelerated slightly. The reason may be the limitation of mass transfer between inorganic solid phase and organic liquid phase besides of reaction activity of substrate, which is also the reason why more and more scientists devoted themselves to research and development of high efficiency phase-transfer catalyst.

## 3. Conclusion

Polymer 1 is a new kind of polymer phase transfer catalyst, which has the superiority of convenience for preparation, good thermal stability and high catalytic activity. So it is very suitable for halogen-exchange fluorination at high temperature. Some fluorinitrobenzene derivatives were prepared via halogen-exchange fluorination catalyzed by polymer 1 from corresponding chloronitrobenzene derivatives under the irradiation of microwave. The yields of products under the optimum reaction conditions were in the range of 70.2–94.2%,

and the reaction time can be shortened more or less when compared with conventional heating. The catalytic effect is better than other kind of polymer phase transfer catalysts. In addition, "non-thermal effect" of microwave was found in fluorination through comparing macroscopic kinetics between conventional heating and microwave heating.

#### 4. Experimental

Thermal gravimetric analyses data were obtained by SHIMADZU DTA-50 thermal analyzer. Molecule weight was recorded on AGILENT 1100 gel permeation chromatograph. Reactions were carried in Sanle WHL07S-1 chemistryoriented microwave oven made in Nanjing Sanle Microwave Technology and Development Co. Ltd. Yields were determined by Agilent 4890 gas chromatograph.

## 4.1. Synthesis of polyalkylimidazolium bromide

1-1'-(1,4-Butamethylene)bis(imidazole) was prepared by a coupling reaction of 1 mol 1,4-dibromobutane with 2 mol imidazole potassium salt in THF according to procedures described in reference [9].

A 0.1 mol 1,2-dibromoethane was added dropwise to a stirred mixture of 0.1 mol 1-1'-(1,4-butamethylene)bis(imidazole) and 50 mL toluene, then the mixture was heated and maintained at 110 °C for 24 h. Cooled to room temperature and filtered, yellow crude product could be obtained. The crude product was wished several times with acetic ether and chloroform successively and dried in vacuum at 100 °C for 36 h before use.

#### 4.2. Preparation of fluorinated nitrobenzene derivates

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Seventy-five millimole or 150 mmol of KF, 0.5 g of polyalkylimidazolium bromide 1, 10 mL of Me<sub>2</sub>SO and 50 mmol of substrate were placed in an open vessel equipped with a mechanical stirrer and water condenser, then heated by microwave with violently stirred and maintained at reflux temperature for certain time. After cooled down to temperature and filtered, a sample of crude product mixture was analyzed by gas chromatography. Conversion and yield were determined by the internal standard method.

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