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1	Catalytic activity of aqueous cationic polyurethane dispersions:
2	A novel feature of polyurethanes
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10	
11	Abstract
12	Polyurethane ionomers are well-known and user-friendly polymers. Here, we introduce their
13	catalytic activity for organic reactions as a novel aspect of these polymers. We selected an
14	isocyanide-based multicomponent reaction for proving the catalytic activity of polyurethane
15	ionomers. Therefore, a convenient and very mild methodology is described for the preparation of
16	3-aminoimidazo[1,2-a]pyridines via a three component reaction between 2-aminopyridines,
17	aldehydes and isocyanides in the presence of a cationic polyurethane dispersion at low reaction
18	temperatures, in short reaction times and excellent yields.
19	Keywords
20	Imidazo[1,2-a]pyridines, Cationic polyurethane, Aqueous dispersion, Thermal properties,
21	Catalyst
22	

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#### 1 1. Introduction

2 Polyurethanes (PUs) have been gaining importance in a wide range of applications such as paints, textile, adhesives, gloves and wood finishing because of their good physical and 3 mechanical properties; or for use in heart valves, aortic grafts, dialysis membranes and intra-4 aortic balloons due to their biocompatibility characteristics [1-5]. Unfortunately, the 5 environmental regulations regarding the use of volatile organic chemicals (VOCs) has limited 6 traditional applications of the solvent-based PUs [6-8]. Aqueous polyurethane dispersions 7 8 (PUDs), however, have been more widely accepted because they are more environmentally 9 friendly with regards to solvent release into the atmosphere [9,10]. Conventional polyurethanes are insoluble in water and should contain hydrophilic groups in their structure to be dispersed or 10 dissolved in water. The hydrophilic groups, or emulsifiers, are either ionic or nonionic types 11 based on their structures. Nonionic types have hydrophilic soft segment pendant groups such as 12 polyethylene oxide [11], while ionic types contain pendant carboxylate or sulphonate groups, or 13 14 quaternary ammonium salts. Cationic aqueous polyurethane dispersions (CAPUs) are often used in coagulants, adhesives and membranes [12,13]. N-Methyl diethanolamine (N-MEDA) has been 15 reported to be used as an ionic dispersing agent in aqueous cationic polyurethane dispersions 16 17 [14–16].

Multi-component reactions (MCRs) have attracted much attention during recent years. These one-pot high-yielding procedures are interesting synthetic methods for attaining new and useful products. Imidazo[1,2-*a*]pyridines are an important class of fused heterocyclic compounds, as many compounds of this class possess antibacterial, antifungal, anthelmintic, antiviral, antiprotozoal and anticonvulsant properties. They have also been shown to act as glycosidase inhibitors and display gastrointestinal, anti-ulcer and immunomodulatory activities [17–19].

1 Several synthetic methods have been reported for the preparation of 2- or 3-substituted 2 imidazo[1,2-a]pyridines with the most common procedure being the condensation of 2-3 aminopyridine with  $\alpha$ -halocarbonyl compounds to form the five-membered ring [20, 21]. The preparation of imidazo [1,2-a] pyridines has been reported by different approaches including a) c 4 opper-catalyzed tandem coupling of 1,4-dihalo-1,3-dienes with azoles, b) the condensation of 5 ethyl bromopyruvate with 2-aminopyridine, c) the condensation of an 2- aminopyridine and 6 7 acetophenone, d) condensation of 2-aminopyridine with glyoxal trimer dihydrate, e) an intermolecular oxidative diamination of alkynes, f) the condensation of aldehydes, 2-8 9 aminopyridines and isonitriles, g) the condensation of aldehydes, 2-aminopyridines and alkynes, h) the reaction of 2-chloropyridine with 1,2,3-triazoles, i) the reaction of 2-aminopyridine and 10 11 ketones, j) the condensation of 2-aminopyridine and diketones, k) the reaction of 2aminopyridine with 1-nitro-1-alkenes, 1) the reaction of a pyridine, phenacyl bromide and 12 substituted N-hydroxyarylimidoyl chloride, m) direct intramolecular amination of N-aryl-2 13 14 aminopyridines, n) the reaction of  $\beta$ -lactam carbenes with 2-pyridyl isonitriles, o) the reaction of (arylacetyl)imidazoles with acetylenedicarboxylic esters and p) the cyclization of 1-(2-alkynyl)-15 16 2-aminomethylimidazoles (Scheme 1) [22]. However, most of these methods involve three or 17 more sequential synthetic steps or the use of harsh reaction conditions that afford low yield of the products [23–27]. A useful approach to imidazo[1,2-a]pyridines is a one-pot MCR between 2-18 19 aminopyridine, an aldehyde and an isocyanide [28]. We have reported a few alternative synthetic methods for the preparation of 3-imidazo[1,2-*a*]pyridines [29, 30]. 20

As part of our continuing efforts on the development of new applications of PUDs [31–37], we focused on the novel aspects of these ionomers, and examined their potential application as a polymer catalyst in organic reactions. In particular, we have selected an isocyanide-based three-

component reaction between 2-aminopyridines, aldehydes and isocyanides to assess the catalytic
 activity of these polymers (Scheme 2). To the best of our knowledge, there is no report in the
 open literature concerning the catalytic activity of polyurethane ionomers.

### 4 **2. Experimental**

### 5 2.1. Materials

Polytetramethylene glycol (PTMG) with a molecular weight 1000 was supplied by Arak Petrochemical Company (Iran) and dried at 50 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may interfere with the isocyanate reactions. N-Methyldiethanolamine (MDEA) (Merck) was dried at 100 °C for 4 h before use. N-Methylpyrrolidone (NMP), isophoronediisocyanate (IPDI) and acetic acid (HOAc) were purchased from Merck, Germany. All other chemical reagents were obtained from Merck and Aldrich chemical companies and were used without further purification.

13 2.2. Preparation of the aqueous cationic polyurethane dispersions

14 The CPUDs were synthesized via the following procedure [38]: Polytetramethylene glycol and isophorone diisocyanate were charged into the reaction vessel and the temperature of the oil bath 15 was increased to 90 °C. After 3 h, a solution of N-methyldiethanolamine (MDEA) in N-16 17 methylpyrrolidone (NMP) and 1,4-butanediol (1,4-BD) were added into the reactor. After that, acetic acid (HOAc) was added to the system in order to neutralize the amine groups at 65 °C. 18 Finally, required amount of deionized water was added dropwise into the system at room 19 20 temperature to obtain CPUDs with 30 wt % solid content (Schemes 3 and 4). The polyurethane 21 sample with mol ratio 1:3:1:1 showed the best physical and mechanical properties from the 22 different formulations of the CPUDs (Table 1), therefore, all of the catalysts were synthesized

and characterized based on this block ratio. In addition, all of the reactions were tested in the
presence of the CPUD with block ratio 1:3:1:1.

#### 3 2.3. Preparation of 3-Imidazo[1,2-a]pyridines

The procedure for the preparation of 3-cyclohexylamino-2-phenylimidazo[1,2-a]pyridine 4a 4 (entry 1, Table 2) is described as an example: A mixture of benzaldehyde (0.106 g, 1 mmol), 2-5 aminopyridine (0.094 g, 1 mmol) and cyclohexyl isocyanide (0.109 g, 1 mmol) in the presence 6 7 of cationic polyurethane dispersion (1 mL) was stirred at 20 °C for 3 h. Then, n-hexane as a nonsolvent was added  $(3 \times 3 \text{ mL})$  to the reaction mixture and the product and initial materials 8 9 were separated from CPUD and dried over MgSO<sub>4</sub>. The solvent was removed and the crude product was purified by crystallization from *n*-hexane-EtOAc (3:1) to give 4a. In addition, 10 following experiments were considered to assess the definite role of the polyurethane as catalyst 11 and/or solvent of the reaction. In the first experiment, the reaction was tested in ethanol (as a 12 13 standard solvent system) and the 0.05 ml CPUD (i.e. 0.015 mmol solid CPU) was added to the 14 reaction (entry 1, Table 3). The low conversion of the raw materials clarified that the catalytic activity of a CPUD is determined by its concentration. Then, the varying amounts of the CPUD 15 was tested in the reaction for the preparation of 3-cyclohexylamino-2-phenylimidazo[1,2-16 *a*]pyridine 4a at 25 °C and 3 h. The results of this experiment also confirmed the previous data 17 and showed that the CPUD probably acts as both catalyst and solvent of the reaction (Table 3). 18

### 19 **3. Results and discussion**

The chemical structure of the prepared cationic polyurethane with mol ratio 1:3:1:1 was characterized by Fourier transform infrared (FTIR) spectroscopy (Fig. 1) [37]. The synthesized polyurethane was characterized with the disappearance of the NCO vibration at 2265 cm<sup>-1</sup> and the presence of stretching vibrations of N–H at 3319 cm<sup>-1</sup>, C=O at 1714 cm<sup>-1</sup> and N–H for

Amide II band at 1538 cm<sup>-1</sup>. The asymmetric and symmetric stretching vibrations of aliphatic groups appeared at 2945, 2859 and 2795 cm<sup>-1</sup>. The absorption bands at 1463, 1365, and 1305 cm<sup>-1</sup> <sup>1</sup> were assigned to CH<sub>2</sub> bending vibration, C–H bending symmetric vibration and CH<sub>2</sub> wagging, respectively. C–O–C stretching vibrations of the polyol were observed over a range at 1000– 1150 cm<sup>-1</sup>.

6 In addition, some of the thermal, mechanical and physical properties of the synthesized7 polyurethane are shown in Table 4. Additional data is provided as supplementary information.

8 Differential scanning calorimetry (DSC) measurement was used to characterize the thermal 9 properties of the CPU. The DSC thermogram of the cationic PU extended with 1,4-butanediol is 10 shown in Fig. 2. The transition temperature of the cationic polyurethane appeared at 25 °C based 11 on the results of the DSC data.

Thermal mechanical properties of the synthesized polyurethane were studied by DMTA. Different types of transitions which are related to the morphology and structure of polymer sample can be detected by using DMTA measurements. The storage modulus (E') versus temperature curve of CPU catalyst is shown in Fig. 3. Based on this curve, the prepared polyurethane showed a transition at 26 °C and therefore, it is expected that dried films of polyurethanes could be used as hot-melt polymer catalysts for organic reactions carried out at elevated temperatures.

We assessed the catalytic activity of our CPUD in a multi-component coupling reaction used for the preparation of 3-aminoimidazo[1,2-a]pyridines. Thus, a mixture of an aldehyde 1, a 2aminopyridine 2 and an isocyanide 3 were treated with our prepared CPUD and the reaction progress monitored by TLC. Initially, it was observed that the CPUD gradually coagulated in the presence of the 2-aminopyridine. This may be attributed to the competition of the 2-

1 aminopyridine and surfactant of the polyurethane for bonding with protons of the catalyst. This 2 problem was eliminated by adding a trace amount of ethanol to the mixture to obtain a CPUD 3 with a 20 wt % solid content. As indicated in Table 2, all the reactions proceeded at 15-25 °C and went to completion within 1.5–2.5 h. TLC and NMR spectroscopic analysis of the reaction 4 mixtures confirmed the formation of the corresponding 3-aminoimidazo [1,2-a] pyridines **4a–l** in 5 excellent yields of 90-97%. Any product other than 4 could not be detected by NMR 6 7 spectroscopy. All the products were characterized by comparison of their melting points and 8 their spectral data with those of authentic samples.

9 The reusability of the CPUD as the catalyst was also investigated for the synthesis of compound 4h (entry 7, Table 2). After each run, n-hexane (3 × 3 mL) was added to the reaction mixture to separate the products and the unreacted starting materials. After washing, the recycled CPU was used for further runs. No decrease of activity was observed even after four runs (Fig. 4). This shows that the CPUD is an effective and recyclable catalyst for the synthesis of 3-alkylamino-2arylimidazo[1,2-*a*]pyridines.

The excellent yields and significantly lower temperatures of the reaction in the presence of 15 16 CPUD compared to previous reports were related to the specific structure of the polyurethane. 17 The chemical structure of the polyurethane is formed from two polar and non-polar segments: the urethane and polyol moieties, respectively. On the other hand, the reactants in this 3CR have 18 19 two polar functional groups and non-polar hydrocarbon parts. It seems the reactants escape from the polar solvent (water) to the surface of polyurethane because of their non-polar parts. The 20 21 presence of active protons in the structure of the polyurethane and their interactions with the 22 polar functional groups of the starting materials and reaction intermediates is another reason for

completion of the reaction under very mild conditions. Both quaternary ammonium carboxylate
 and urethane moieties may act as acid catalyst in this 3CR.

A mechanistic rationalization for this reaction is provided, which involves a multistep sequence 3 of events including: condensation of the 2-aminopyridine 2 with the aldehyde 1 and formation of 4 5 the aminoalcohol intermediate 5, dehydration of aminoalcohol and formation of imine 6, 6 nucleophilic addition of the isocyanide 3 on imine 5 to give the isonitrilium intermediate 7 7 followed by cyclization into the 3-imino-2*H*-imidazo[1,2-a]pyridine intermediate 8, and finally 8 tautomerization of this imino intermediate under the reaction conditions to afford the 3-9 alkylamino-2-arylimidazo [1,2-a] pyridine 4. All these events may be facilitated by protonation-10 deprotonation sequences by the ammonium carboxylate and urethane moieties of the CPUD, as shown in scheme 5. 11

We are currently investigating the catalytic activity of the prepared CPUD system for other well-12 13 known organic reactions for example, Cannizarro reaction, Biginelli reaction, Ugi reaction, 14 Passerini reaction and Mannich reaction. As another model, we compared the catalytic efficiency of the CPUD to prepare the benzoic acid and benzyl alcohol through a redox disproportionation 15 of benzaldehyde (Cannizarro reaction) with the selected previously known catalysts (Table 5). 16 17 The significant roles of the CPUD as the catalyst and solvent for the Groebke reaction were also confirmed by the results of Cannizarro reaction. These results will be reported in future 18 19 publications.

#### 20 **4. Conclusions**

In summary, we introduced a new and straightforward polymer catalyst and solvent for the synthesis of 3-imidazo[1,2-*a*]pyridines via a one-pot, three-component condensation reaction

- 1 between 2-amino-pyridines, benzaldehydes and isocyanides. The very mild conditions of the
- 2 reaction and the reusability of the catalyst are the main advantages of this reaction.

### 3 Acknowledgment

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14	

### 1 **Figure captions**

- 2 Figure 1. FTIR spectrum of the aqueous cationic polyurethanes
- 3 Figure 2. DSC thermogram of the CPU catalyst extended with 1,4-butanediamine
- 4 Figure 3. DMTA measurements of CPU catalyst
- 5 Figure 4. The effect of reusability of CPUD catalyst on the product **4h** yield

### 1 Scheme captions

- 2 Scheme 1. The methods for the synthesis of imidazo[1,2-*a*]pyridines
- 3 Scheme 2. Schematic illustration of the one-pot synthesis of imidazo[1,2-*a*]pyridines
- 4 Scheme 3. Chemical procedure for synthesis of the aqueous cationic polyurethane dispersions
- 5 Scheme 4. Schematic procedure for micro-structure formation of CPUDs

- 6 Scheme 5. Plausible mechanism for preparation of imidazo[1,2-a]pyridines in the presence of
- 7 polymeric catalyst
- 8

### 1 Table captions

- 2 Table 1. Feed composition of cationic polyurethanes with variable block ratios.
- 3 Table 2. One-pot synthesis of imidazo[1,2-*a*]pyridines **4**.

- 4 Table 3. The effect of CPUD content on the yield of 3-cyclohexylamino-2-phenylimidazo[1,2-
- 5 a]pyridine.
- 6 Table 4. Thermal, mechanical and physical properties of the synthesized polyurethanes.
- 7 Table 5. CPUD-catalyzed Cannizzaro reaction.
- 8

Table 1 1

Sample no.	Block ratio	PTMG (g)	IPDI (g)	MDEA (g)	HOAc (g)	Film property
1	1:3:1:1	20	13.34	2.38	1.20	Excellent
2	1:4:1:2	20	17.78	2.38	1.20	Semi-brittle
3	1:4:2:1	20	17.78	4.77	2.40	Sticky

2

3

Sex.

1 Table 2

		Ar H +	$+ R - N^+$	ēc - <sup>CPUD</sup> ≁	X N	<sup>™</sup> N ={	
		1 2	3		H 4	Ar	
Entry	ArCHO 1	2-Aminopyridine 2	R	Time (h)	t (°C)	4, %Yield <sup>a</sup>	mp (°C)
1	СНО	N NH <sub>2</sub>	$\bigcirc \downarrow \downarrow$	2.5	20	<b>4a</b> , 94	199–200 <sup>39</sup>
2	Н <sub>3</sub> С-СНО	N NH <sub>2</sub>	$\bigcirc +$	1.5	15	<b>4f</b> , 96	168–169 <sup>21</sup>
3	СІСНО	N NH <sub>2</sub>	$\rightarrow \vdash$	2.5	20	<b>4i</b> , 95	149–150 <sup>26</sup>
4	СНО	H <sub>3</sub> C NNH <sub>2</sub>	$\rightarrow \vdash$	2	25	<b>4c</b> , 95	216–217 40
5	СНО	Br	$\rightarrow \vdash$	2.5	25	<b>4e</b> , 91	205–206 <sup>40</sup>
6	СНО	H <sub>3</sub> C N NH <sub>2</sub>	$\bigcirc +$	1.5	15	<b>4b</b> , 96	201–203 40
7	Н <sub>3</sub> С-СНО	H <sub>3</sub> C N NH <sub>2</sub>	$\bigcirc +$	1.5	15	<b>4h</b> , 97,96,95,94	218–220 40
8	Н <sub>3</sub> С-СНО	H <sub>3</sub> C NNH <sub>2</sub>	$\rightarrow$	2	15	<b>4</b> g, 95	212–213 <sup>40</sup>
9	СНО	Br	∕_+	2	20	<b>4d</b> , 92	208–211 40
10	сі—	N NH2	XX	2	20	<b>4j</b> , 92	200–202 <sup>41</sup>
11	сі—	Br N NH <sub>2</sub>	$\rightarrow \downarrow$	2.5	25	<b>41</b> , 92	175–176 <sup>41</sup>
12	Cl—CHO	H <sub>3</sub> C N NH <sub>2</sub>		2	25	<b>4k</b> , 95	208–210 41

<sup>a</sup> Isolated yield.

2

### 1 Table 3

Entry	CPUD amount (ml)	<b>4a</b> , %Yield <sup>a</sup>				
1	0.05	15				
2	0.1	24				
3	0.2	38				
4	0.5	70				
5	1	94				
<sup>a</sup> Isolated yield.						

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1 Table 4

Thermal decomposition <sup>1</sup> $(T_{10})$	Glass Transition temperature <sup>2</sup> $(T_g)$	Elongation at Break <sup>3</sup> (%)	Tensile Strength <sup>3</sup> (MPa)	Contact angle <sup>4</sup> (°)
260	26	1300	23.3	75

2  $^{1}$  T<sub>10</sub> = temperature of 10% weight loss (from TGA measurements)

<sup>2</sup> The central point of the maximum of the tan  $\delta$  peak (from DMTA measurements)

<sup>3</sup> The date were obtained based on stress–strain measurements by Instron Mechanical Testing instrument (MTS System Corporation, Eden Prairie, MN) tensile tester model 10/M at a strain

6 rate of 50 mm/min.

<sup>7</sup><sup>4</sup> Contact angle measurements were performed at room temperature by a G10 (Kruss, Hamburg,

8 Germany) instrument via the sessile drop method.

### 1 Table 5

	A	und H -		→ Ar OF	+ OH H Ar		
		1		2	3		
Entry	Catalyst	mol %	Solvent	Temp (°C)	Time (min)	Yield (%)	Reference
1	NaOH	100	_	unknown	10	96	42a
2	TMG	100	$\mathrm{H}_{2}\mathrm{O}$	100	1200	2	42b
3	NaOH	100	toluene	40	40	63 <sup>a</sup>	42c
4	NaOH:Al <sub>2</sub> O <sub>3</sub>	600:3 g	_	unknown	0.25	97 <sup>b</sup>	42d
5	MgBr <sub>2</sub> .OEt <sub>2</sub> :TEA	50:200	$CH_2Cl_2 \\$	rt	180	90°	42e
6	LiBr:TEA	50:150	_	rt	2 days	98 <sup>d</sup>	42f
7	NaOH:CPUD	50:1.00 <sup>e</sup>	$\mathrm{H}_{2}\mathrm{O}$	rt	150	96	This work

- <sup>a</sup> Cannizzaro reaction with sonication. The frequency of ultrasound: 20 kHz.
- <sup>b</sup> Microwave-assisted Cannizzaro reaction
- 4 <sup>c</sup> Based on the alcohol
- 5 <sup>d</sup> Based on the alcohol
  - <sup>e</sup> The MW of synthesized CPUD is approximately 30000 g.mol<sup>-1</sup>

6 7

### 1 Highlights

- Catalytic activity of a polyurethane dispersion was examined for the first time.
- CPUD (cationic polyurethane dispersion) was considered as a green catalyst.

- CPUD was shown to be an effective and reusable catalyst in the Groebke reaction.
- 5 3-Imidazo[1,2-*a*]pyridines were synthesized under mild condition by using PUD catalyst.



Figure(2)

























