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PAPER

Polyurethane nanomicelles: Novel eco-friendly and efficient polymeric ionic solvent for Cannizzaro reaction

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Anionic polyurethane dispersions (APUDs) are commodity synthetic polymers and have a broad range of well-known applications, nevertheless their possible use as a green catalyst or ionic solvent is yet unknown. Here, we demonstrate that how a polyurethane dispersion facilitates the progress of Cannizzaro reaction under very mild alkaline conditions. We introduce anionic polyurethane nanomicelles as an expeditious green polymer ionic solvent for Cannizzaro reaction. The reusable and novel eco-friendly polymer solvent, excellent yields of the products, low reaction times and low reaction temperatures are the main advantages of this reaction.

Introduction

Green chemistry is a rapidly developing and an interesting area in the chemical science. The design of a chemical agent and consideration of its influence on human life are the fundamental concepts of the green chemistry [1]. The design of safer chemicals, solvents and auxiliaries, maximize atom economy and energy efficiency, less hazardous chemical synthesis, use of renewable feedstocks and using natural and renewable catalysts are examples of green chemistry [2]. Among these concepts, using both safer solvents and natural catalysts have been extensively investigated due to their versatility and eco-friendly nature [3]. Ionic liquids, supercritical CO₂, supercritical water, biocatalysts and enzymes are the most widely used procedures in the green chemistry [4].

Aqueous polyurethane dispersion (APUD) is a rather new developing eco-friendly synthetic polymer [5]. The PUDs, a group of polymeric nanomicelles, have a variety of applications in different industries for example anti-scratch coatings, paints, adhesives, gloves, top coats and wood finishing [6]. Conventional polyurethanes are solvent-based synthetic polymers and have no extreme hydrophilic functional group for dispersing in aqueous media. Therefore, specific hydroxyl or amino terminated ionizable monomers are served to create the polyurethane ionomers [7]. Dimethylolpropionic acid (DMPA) and N-methyl diethanolamine (MDEA) are the most important diol emulsifiers which have a carboxylic acid and a tertiary amine functional group, respectively [8,9]. Thanks to the nanometer-sized particles, different functional groups in the main or side chain, ability to create Hydrogen bonding, and electrostatic or hydrophobic-hydrophilic interactions, PU nanomicelles could be considered as efficient nanoreactors or nanocatalysts to promote organic reactions. Furthermore, APUD

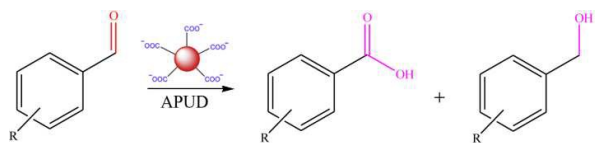
can be potentially used as the eco-friendly and efficient polymeric ionic solvent in a chemical process due to its water-based nature.

The redox disproportionation of non-enolizable aldehydes into their corresponding alcohols and carboxylic acids, known as Cannizzaro reaction, is one of the simplest well-known reactions in synthetic organic chemistry [10]. Harsh conditions of the reaction such as elevated temperatures and using strong bases necessitate the design of new methodologies to improve the conditions of Cannizzaro reaction [11]. Therefore, some procedures including using hydroxide ion catalysts for example NaOH in THF/HMPA (9:1), KOH aqueous solution (60%) and hydroxide ion in the gas-phase, salts of metal halides and famines for example LiBr and TEA, MgBr₂.OEt₂ and TEA, 1,1,3,3-tetramethylguanidine, phase-transfer catalysis and ultrasound have been reported for improvement of the reaction conditions [12]. In addition, there are different procedures for improving the conversion of aldehydes in well-known reactions such as the use of various Lewis acids [13], heterogeneous catalytic systems [14], supercritical solvents [15a], microwave irradiation [15b], ultrasound mediation [15c], solid-supported reagents [15d] and gas-phase process [15e]. However, most of these methods suffer from multi-sequential synthetic steps or the use of harsh reaction conditions. In a few cases that the reaction is performed at room temperature, strong basic media are still required [15f] or yields of the reactions are rather low [15g]. Therefore, the Cannizzaro reaction still requires more drastic modifications.

In our continuing efforts on development of green polymeric catalysts and new applications for PUDs [16-18], we examine the ability of ionic PU nanomicelles as the eco-friendly ionic solvent for organic reactions. To the best of our knowledge, there is no report in open literature concerning the using PU nanomicelles as a green solvent for synthesis of organic chemicals. Herein, we report the first example of the APUD application as a novel, green, expeditious, very mild, recyclable, biocompatible and very remarkable polymeric ionic solvent for Cannizzaro reaction (Scheme 1). Furthermore, we show that the amount of NaOH used for catalysis of Cannizzaro reaction dramatically decrease from 100% down to 15%, compared to initial aldehyde.

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Scheme 1. Chemical illustration for redox disproportionation of non-enolizable aldehydes in the presence of the APUD.

Experimental

Materials and methods

Polytetramethylene ether glycol (PTMEG) with a molecular weight 950-1000 was obtained from Arak Petrochemical Company (Iran) and dried at 50 °C under vacuum for 24 h before use to ensure the removal of all impurities and water vapors that may interfere with the reactions of isocyanate functional groups. Dimethylolpropionic acid (DMPA), N-methylpyrrolidone (NMP), isophoronediiisocyanate (IPDI), 1,4-butanediol (1,4-BD) and triethylamine (TEA) were purchased from Merck, Germany. All other chemicals were obtained from Aldrich and Merck companies and used without further purification.

The synthesized APUD and the products of Cannizzaro reaction were characterized using the FTIR spectra from a Bruker-Equinox 55 IR spectrometer (Ettlingen, Germany). Melting points were determined using an Electrothermal apparatus. The silica gel 60 F-254 Al-plates (Merck) were used for analytical TLC. The ^1H NMR spectra were recorded in (CDCl_3) solution using a Bruker DPX-250 Spectrometer (250 MHz). A Polymer Lab TGA-1500 instrument (London) was served for evaluation of thermal stability of the APUD films under a nitrogen atmosphere with a heating rate of 10 °C/min. Stress-strain measurements of APUDs were carried out on an Instron Mechanical Testing instrument tensile tester. Young's modulus, also known as the tensile modulus, was evaluated using a tensile tester model 10/M (MTS System Corporation, Eden Prairie, MN) at a strain rate of 50 mm/min. Scanning electronic microscopy (SEM) (Model Vega, Tescan Co., Czech Republic) was used to probe the morphological aspects of polyurethane surface. The morphology of the APU nanomicelles was observed on a transmission electron microscope (JEOL 1200EX). The PU dispersions were diluted to about 0.05 wt % with distilled water. Some drops of the diluted dispersion were inserted on the coated side of a 200-mesh nickel and analyzed after drying.

General procedure for synthesis of anionic polyurethane nanomicelles

The APUD was synthesized by using a simple prepolymer mixing process. As a summary, both PTMEG and IPDI were placed into the reaction vessel and the temperature of the reactor was increased to 90 °C. After the formation of NCO-terminated prepolymer, a solution of DMPA in NMP and 1,4-butanediol were added into the reactor, respectively. After that, an equivalent of TEA was added into the polymer mixture to neutralize the acid functional groups. Finally, a polyurethane dispersion with a 30 wt% solid content was prepared by addition the required amount of deionized water into the reactor at room temperature.

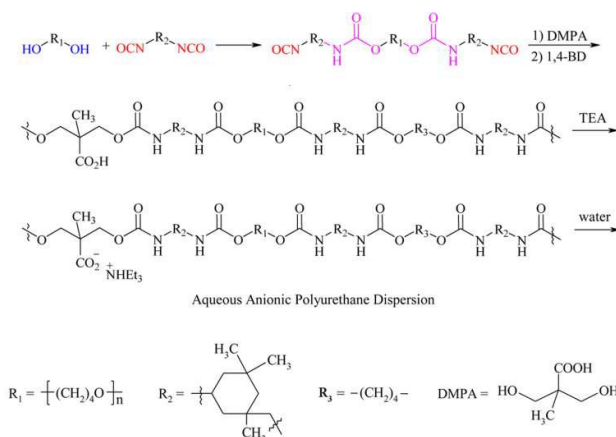
General recipe for Cannizzaro reaction of aromatic aldehydes

The conversion of benzaldehyde to benzyl alcohol and benzylic

acid (entry 1, Table 1) is described as an example: A mixture of benzaldehyde (**1a**, 1 mmol) and sodium hydroxide solution (40 mg of 20% w/w, 0.15 mmol) were stirred in the presence of 1 mL of APUD (30% w/w, 0.03 mmol) at room temperature for 3 h. Progress of the reaction was monitored by TLC analysis to observe no aldehyde in the mixture. The product and uncreated materials were separated from APUD by using the n-hexane as a convenient nonsolvent (2×2 mL). The polymeric solvent was used for further reactions after washing. After that, the mixture was neutralized with cold HCl solution (2 M), and the precipitate, aryl acid, was obtained by filtration (**1b**). Then, the filtrate was extracted and dried with ethyl acetate and MgSO_4 to obtain the aryl alcohol (**1c**). The melting points, FTIR and NMR spectrometric data of isolated products were compared with the literature and/or authentic samples.

Results and discussion

The APUD was synthesized through a simple prepolymer mixing process. We used DMPA to donate the hydrophilicity to the PU structure and prepare PU nanomicelles (Scheme 2) [18]. The chemical structure of the synthesized APUD was characterized by the Fourier transform infrared (FTIR) spectroscopy. The synthesized APUD was characterized with the appearance of the stretching vibrations of N–H at 3319 cm^{-1} , C=O at 1714 cm^{-1} and N–H for amide II band at 1538 cm^{-1} (Fig. 1a). The most important deterministic bands are shown in Table S1. As shown in Fig. 1b, it demonstrates a well defined spherical morphology with an average particle size of ~ 38 nm diameter for APU dispersion. Furthermore, the results of dynamic light scattering (DLS) showed that the particle size of synthesized PU is roughly in the range of 15-95 nm with the maximum intensity in 37 nm. This clearly exhibits that the synthesized APUD can potentially facilitate the progress of organic reactions as a green nanometer-sized polymeric ionic solvent.



Scheme 2. Chemical procedure for the synthesis of the APUD. The urethane linkages (purple bonds) are formed from the reaction of hydroxyl (blue atoms) and isocyanate (red atoms) functional groups.

After characterization of the anionic PU nanomicelles, we selected Cannizzaro reaction for confirming the possible promoting role of our APUD. All of the reactions were condensed in APUD as ionic solvent and catalyzed by an extreme mild alkaline medium to produce the corresponding alcohol and carboxylic acid in 80–91%

yields under very mild conditions. The melting points, FTIR and NMR spectrometric data of isolated products were compared with the literature and/or authentic samples. 2-Chlorobenzoic acid (**3b**), as a typical example, was characterized by following data: mp 139–140 °C, yield: 90%, ^1H NMR δ (ppm): 8.02 (d, $J = 8$ Hz, 1H), 7.44–7.50 (m, 2H), 7.32–7.38 (m, 1H). As indicated in Table 1, all the reactions were carried out at 15–25 °C and completed within 2–5 h.

The prepared APUD was found as a reusable ionic solvent for the intermolecular Cannizzaro reaction. For proving this aim, n-hexane (2×2 mL) was added to the reaction mixture after each run to separate the products and the unreacted starting materials. The recycled APUD was used for further runs after washing. It is important noting that a negligible decrease of activity was observed after 11 runs (Fig. 2).

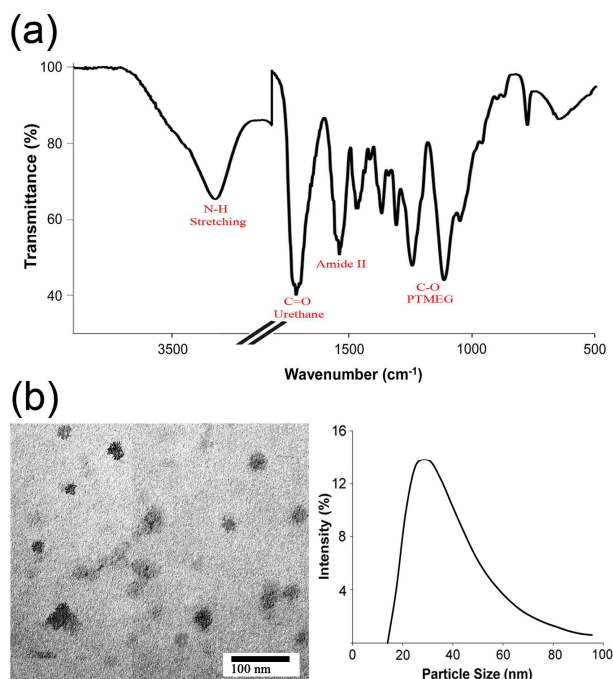


Fig. 1. Chemical and physical characteristics of APU nanomicelles: (a) FTIR spectrum of APU film, (b) Spherical morphology of PU nanomicelles in their dispersion obtained by TEM (Left), and size distribution of nanomicelles using DLS (Right).

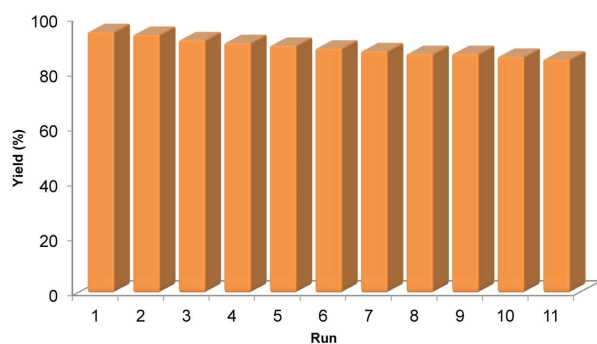


Fig. 2. The effect of APUD reusability on the yield of 2-chlorobenzoic acid.

In this context, the extreme polar functional groups of hard domains and the non-polar parts of the soft segments of the APUD create unique sites for the migration of the starting aldehyde onto the surface of polyurethane. In addition, both carboxylate groups and urethane moieties may activate the carbonyl functional group of starting aldehyde for the attack of hydroxide ions. Therefore, the redox disproportionation of non-enolizable aldehydes was performed under significantly mild conditions and excellent yields compared to the previous reports (Table 2). It is important to note that the time of Cannizzaro reaction increases up to 1 day without using the APUD as the ionic solvent, while the yield of the reaction drops to 71% (Table 2, Entries 7 and 8).

Conclusions

In summary, we examined the role of the APUD as an ionic solvent for Cannizzaro reaction. The APUD promoted and facilitated the mentioned reaction because of its polar functional groups and effective hydrogen bonding. The redox disproportionation of non-enolizable aldehydes was performed under very mild reaction conditions and low reaction times. The APUD was found as an eco-friendly, reusable and effective polymeric ionic solvent for Cannizzaro reaction. The Cannizzaro reaction could be progressed under very mild alkaline medium when APUD used as ionic solvent.

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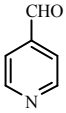
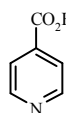
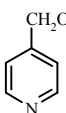
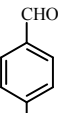
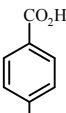
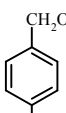
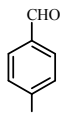
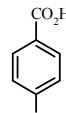
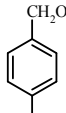
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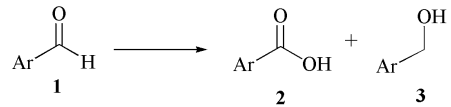
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9				4	25	91	316–318 [19g]
	9a	9b	9c				
10				5	30	90	238–240 [19g]
	10a	10b	10c				
11				3.5	25	86	183–184 [19f]
	11a	11b	11c				

^a Reaction conditions: Aryl aldehydes (1 mmol), NaOH aqueous solution (0.15 mmol), APUD (0.01 mmol). ^b Alcohols were not purified except for 3a.

^c Isolated yield of acids.

Table 2. Comparison of APUD catalyzed Cannizzaro reaction with the selected previously known catalysts.

									
Entry	Catalyst	Co-catalyst	Catalyst loading (mol%) ^a	Co-catalyst loading (mol%) ^a	Solvent	Temp (°C)	Time (min)	Yield (%)	Reference
1	TMG	–	100	–	H ₂ O	100	20 h	2	[12e]
2	NaOH	–	100	–	toluene	40	40	63 ^b	[15c]
3	NaOH	–	100	–	–	unknown	10	96	[20a]
4	NaOH	Al ₂ O ₃	600	3	–	unknown	0.25	97 ^c	[20b]
5	LiBr	TEA	50	150	–	rt	2 days	98 ^d	[12c]
6	MgBr ₂ ·OEt ₂	TEA	50	200	CH ₂ Cl ₂	rt	180	90 ^e	[12d]
7	NaOH	–	15	–	H₂O	rt	1 day	71	This work
8	NaOH	–	15	–	APUD^f	rt	150	91	This work

^a Catalyst loading compared to initial mmol of aldehyde

^b Cannizzaro reaction with sonication. The frequency of ultrasound: 20 kHz

^c Microwave-assisted Cannizzaro reaction

^d Based on the alcohol

^e Based on the alcohol

^f The MW of synthesized CPUD is approximately 30000 g·mol^{–1}

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Cannizzaro reaction is performed under very mild alkaline conditions using anionic polyurethane nanomicelles as a novel reusable polymeric ionic solvent.

