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

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1. Experimental section

1.1. Materials

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), isophoronedisocyanate (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.

1.2. 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.

1.3. 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 MgSO₄ 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.

1.4. Measurements

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 (CDCl₃) 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.
Table S1. Important characteristic FTIR absorptions of the synthesized anionic polyurethane.

<table>
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<th>Bond</th>
<th>$v$(NH)</th>
<th>$v$ NCO</th>
<th>$v$(CH)$_{sym}$ str</th>
<th>$v$(C=O)$_{urethane}$</th>
<th>$v$(NH)$_{amide ~II}$</th>
<th>$v$(CH)$_{asym}$ str</th>
<th>$v$(OCO)$_{asym}$</th>
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</table>
Chemical characterization of benzoic acid (2b)

M.P. 120–121 °C, yield: 91%, $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ (ppm): d 8.12 (dd, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 1H).

Fig. S1. $^1$H NMR spectrum of benzoic acid.
Fig. S2. Expanded $^1$H NMR spectrum of benzoic acid.
Fig. S3. Expanded $^1$H NMR spectrum of benzoic acid.
Chemical characterization of 2-chlorobenzoic acid (3b)

M.P. 139–140 °C, yield: 90%, $^1$H NMR (250 MHz, CDCl$_3$): δ (ppm): 7.32–7.38 (m, 1H), 7.44–7.50 (m, 2H), 8.02 (d, J = 8 Hz, 1H).

Fig. S4. $^1$H NMR spectrum of 2-chlorobenzoic acid.
Fig. S5. Expanded $^1$H NMR spectrum of 2-chlorobenzoic acid.
Chemical characterization of 4-methoxybenzoic acid (8b)

M.P. 144–145 °C, yield: 91%, $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ (ppm): 7.96 (d, $J$=7.0 Hz, 2H), 6.86 (d, $J$=7.0 Hz, 2H), 3.81 (s, 3H).

Fig. S6. $^1$H NMR spectrum of 4-methoxybenzoic acid.
Fig. S7. Expanded $^1$H NMR spectrum of 4-methoxybenzoic acid.
Chemical characterization of 4-nitrobenzoic acid (10b)

M.P. 238–240 °C, yield: 90%, $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ (ppm): 8.11-8.21 (4H).

Fig. S8. $^1$H NMR spectrum of 4-nitrobenzoic acid.
**Fig. S9.** Expanded $^1$H NMR spectrum of 4-nitrobenzoic acid.
Chemical characterization of benzyl alcohol (1c)

Yield: 88%, $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ (ppm): 3.16 (s, 1H), 4.53 (s, 2H), 7.23-7.33 (m, 5H).

Fig. S10. $^1$H NMR spectrum of benzyl alcohol.
Fig. S11. Expanded $^1$H NMR spectrum of benzyl alcohol.