Supplementary Material

A novel use of cross-linked poly(N-isopropylacrylamide) gel for organic reactions in aqueous media

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Materials. N-Isopropylacrylamide (NIPAAm) was obtained from Aldrich and recrystallized from a hexane-toluene mixture (90:10, v/v) before use. N-[3-(Dimethylamino)propyl]acrylamide (NDMAPAAm) was purified over alumina. The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol.

Experimental procedure for synthesis of cross-linked PNIPAAm gel (2a) and characterization data. A solution of NDMAPAAm (0.64 ml; 4.0 mmol), 1-bromododecane (0.91 ml, 3.8 mmol), 1,12-dibromododecane (32.8 mg, 0.10 mmol), and N-isopropylacrylamide (5.43 g; 48 mmol) in t-BuOH (40 ml) was degassed by ultrasonication for 30 min under an argon atmosphere and AIBN (16.4 mg; 0.10 mmol) was added. Then the solution was degassed in three freeze/thaw cycles and heated at 75 °C for 48 h under an argon atmosphere. After evaporation of the solvent, the polymer gel (1a) was washed with dichloromethane (100 ml × 2), methanol (100 ml × 2), acetone (100 ml × 2), and diethyl ether (100 ml × 2). The resulting polymer gel (1a) was suspended in aqueous sodium hydroxide (10%, 100 ml) and stirred at 25 °C for 6 h. The solid was filtered and washed with water to obtain 5.93 g (81 %) of cross-linked PNIPAAm gel in hydroxide form (2a). The polymers were crushed in a mortar. Completion of the anion exchange and subsequent washing were monitored in the negative Beilstein test of the polymer and neutral pH value of the washings, respectively.

PNIPAAm gel in hydroxide form (2a): IR (KBr, cm⁻¹): 3300, 3070, 2970, 1650; gel-phase ¹H NMR (400 MHz, CDCl₃)δ 0.8–2.6 (m, 135 H), 3.2–4.2 (m, 24 H), gel-phase ¹³C NMR (100 MHz, CDCl₃)δ 14.2, 22.6, 22.7, 29.4, 29.6, 29.7, 31.9, 41.3, 42.4, 50.8, 174.3; elemental anal. Calcd for C₉₁H₁₈₉N₁₄O₂₂·8nH₂O: C 59.9 H 10.4 N 10.6; found: C 59.9 H 10.4 N 10.5.
A typical experimental procedure for the 2a-catalyzed reaction in aqueous media is as follows: A mixture of benzaldehyde (2 mmol), acetophenone (2 mmol), and 2a (0.17 g, 0.1 mmol) in 10% aq. NaOH (2 ml) was stirred for 2 h. After removal of the aqueous phase and washing with distilled water (2 ml x 3), diethyl ether (4 mL) was added to the gel and stirred for 20 min. Recovered 2a, which was filtered and washed with diethyl ether (2 ml x 3), was reused for subsequent catalytic experiments. The combined ethereal phase was dried over MgSO4. The products were purified by column chromatography with silica gel and isolated yields were determined.

1,3-Diphenyl-2-propen-1-one (chalcon, 6)\(^2\)

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\text{CAS registry Number [94-41-7]}
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\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.42-7.43 (m, 3 H), 7.50-7.67 (m, 6 H), 7.82 (d, J = 15.6 Hz, 1 H), 8.02-8.04 (m, 2 H)

1,3-Diphenyl-3-hydroxy-1-propanone (7)\(^3\)

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\text{CAS registry Number [42052-51-7]}
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\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 3.38-3.91 (m, 2 H), 3.59 (d, J = 2.8 Hz, 2 H), 6.0 Hz, 1 H), 7.29-7.61 (m, 8 H), 7.95-7.97 (m, 2 H)

2,3-Diphenylacrylonitrile (9)\(^4\), 2a

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\text{CAS registry Number [2510-95-4]}
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\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.40-7.50 (m, 6 H), 7.55 (s, 1 H), 7.68-7.70 (m, 2 H), 7.89-7.91 (m, 2 H).

1,3-Diphenyl-2,3-epoxy-1-propanone (10)\(^5\)

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\text{CAS registry Number [5411-12-1]}
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\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 4.08 (d, J = 2.0 Hz, 1 H), 4.30 (d, J = 2.0 Hz, 1 H), 7.37-7.64 (m, 8 H), 8.01-8.03 (m, 2 H).

References

Cross-linked PNIPAAm gel in hydroxide form (2a).
1,3-diphenylpropenone (chalcon, 6)

1,3-Diphenyl-3-hydroxy-1-propanone (7)
2. 3-Diphenylacrylonitrile (9)

3. 1,3-Diphenyl-2,3-epoxy-1-propanone (10)