

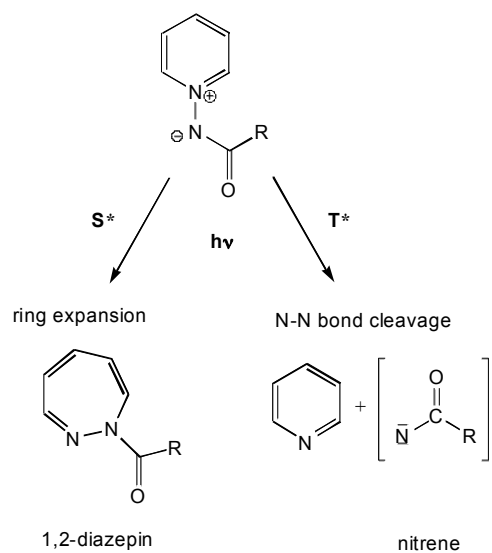
Synthesis of Photoreactive Block Copolymers based on 1- Iminopyridinium Ylides

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SUPPORTING INFORMATION



Scheme S1: Photoreactions of 1-imino pyridinium ylides.

Experimental Part

1-Aminopyridinium iodide (1API). The procedure of Meuwesen et al.^[38] was followed. Briefly, 3 equivalents of pyridine were added to a freshly prepared solution of one equivalent hydroxylamine-*O*-sulfonic acid in cold water. After heating the mixture to 90°C for 20 minutes and cooling it back down to room temperature, one equivalent of potassium carbonate was added. Water and excess pyridine were removed under reduced pressure and after the treatment of the residue with ethanol, the insoluble precipitate was removed by filtration. The reaction mixture was acidified with 57 % hydroiodic acid. By storing the resulting solution for 1 hour at -20°C, yellowish needles separated. Recrystallization from ethanol yielded 70 % of pure 1API as pink crystals. ¹H NMR (CDCl₃): δ = 8.73 (d, J = 6.6 Hz, 2H), 8.35 (t, J = 7.9 Hz, 1H), 7.99 (t, J = 7.4 Hz, 2H), 4.79 (br s, 2H).

{[2-(metacryloyloxy)ethoxy]carbonyl}(Pyridinium-1-yl)azanide (M1). A solution of hydroxyethyl methacrylate (HEMA) (2.60 g, 20.0 mmol) in THF (20 mL) was added dropwise to a stirred solution of carbonyldiimidazole (CDI) (3.36 g, 20.7 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred for 4 hours at room temperature and was added to a vigorously stirred suspension of 1API (5.00 g, 22.5 mmol) and potassium carbonate (25.00 g, 0.195 mol) in 50 mL of anhydrous THF. After stirring for additional 4 hours, the inorganic salts were separated by filtration and the solvent was removed under reduced pressure. The deep blue residue was purified by column chromatography over silica using CHCl₃/MeOH (20:1) as eluent and yielded 95 % of M1 (4.92 g, 19.7 mmol) as a yellow oil. ¹H NMR (CDCl₃): δ = 8.81 (d, J = 7.1 Hz, 2H), 7.79 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.2 Hz, 2H), 6.12 (s,

1H), 5.52 (s, 1H), 4.40 – 4.30 (m, 4H), 1.91 (s, 3H). FT-IR (cm^{-1}): 1717 (C=O), 1635 (C=O).

Pyridinium-1-yl-(4-vinylbenzoyl)azanide (M2). A solution of 4-vinylbenzoic acid (6.00 g, 40.0 mmol) in THF (30 mL) was added dropwise to a stirred solution of CDI (6.62 g, 41.0 mmol) in anhydrous THF (80 mL). After the addition of 5 drops of triethylamine, the reaction mixture was stirred for 5 hours at room temperature and was then added to a vigorously stirred suspension of 1API (9.83 g, 44.3 mmol) and potassium carbonate (48.00 g, 0.347 mol) in 50 mL of anhydrous THF. Stirring for additional 4 hours was followed by removing the solvent under reduced pressure and the addition of 250 mL of CHCl_3 to the deep blue residue. The inorganic salts were separated and the remaining solution was reduced on a rotary evaporator. Purification of the residue was first done by column chromatography over silica using $\text{CHCl}_3/\text{MeOH}$ (12:1) as an eluent and was followed by recrystallization of the obtained solid out of acetone. 74 % of M2 (6.67 g, 29.7 mmol) were obtained as yellow needles. ^1H NMR (CDCl_3): δ = 8.79 (d, J = 7.0 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H), 7.87 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 6.74 (dd, J_{trans} = 17.6 Hz, J_{cis} = 10.9 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H). FT-IR (cm^{-1}): 1580 (C=O)